



UNIT  
PROCESSES  
OF  
EXTRACTIVE  
METALLURGY

## CONTENTS

|                                                                       |      |
|-----------------------------------------------------------------------|------|
| Preface.....                                                          | xiii |
| Chapter 1 <i>Introduction</i>                                         |      |
| 1-1. Source of Metals.....                                            | 1    |
| Iron.....                                                             | 1    |
| Copper.....                                                           | 2    |
| Aluminum.....                                                         | 2    |
| Lead.....                                                             | 2    |
| Tin.....                                                              | 2    |
| Titanium and Manganese.....                                           | 4    |
| 1-2. Mineral Engineering.....                                         | 4    |
| 1-3. Extractive Metallurgy.....                                       | 4    |
| 1-4. Chemical Metallurgy in the Extraction of Metals.....             | 5    |
| Chapter 2 <i>Pyrometallurgy I. Roasting—Agglomeration—Calcination</i> |      |
| 2-1. Roasting of Sulfide Ores.....                                    | 7    |
| Thermodynamics of Roasting Reactions.....                             | 7    |
| Volatilization During Roasting.....                                   | 12   |
| 2-2. Industrial Roasting Processes.....                               | 12   |
| Mechanical or Hearth Roasting.....                                    | 12   |
| Flash Roasting.....                                                   | 13   |
| Fluid Bed Roasting.....                                               | 15   |
| Sinter-Roast.....                                                     | 16   |
| 2-3. Sintering.....                                                   | 16   |
| Fuel Requirement.....                                                 | 18   |
| Engineering Relationships for Design of Sintering Operations.....     | 19   |
| Control.....                                                          | 19   |
| 2-4. Pelletizing.....                                                 | 19   |
| 2-5. Calcination.....                                                 | 22   |
| Thermodynamics of Calcination.....                                    | 22   |
| Kinetics—Mechanism of Calcination.....                                | 23   |
| Chapter 3 <i>Pyrometallurgy II. Oxidation—Reduction Reactions</i>     |      |
| 3-1. Thermodynamic Stability of Mineral Compounds.....                | 27   |
| Thermodynamic Stability of Oxides.....                                | 27   |
| Carbon-Oxygen Equilibria—The Boudouard Reaction.....                  | 32   |
| Thermodynamic Stability of Sulfides.....                              | 33   |
| Reducibility of Chlorides.....                                        | 35   |
| Stability of Carbides and Nitrides.....                               | 38   |

## Contents

|                                                                             |    |
|-----------------------------------------------------------------------------|----|
| 3-2. Oxidation—Reduction Reactions Involving Liquid Metallic Solutions..... | 38 |
| Thermodynamics of Metallic Solutions.....                                   | 39 |
| Free Energy and Activity.....                                               | 39 |
| Nonideal Solutions.....                                                     | 39 |
| Dilute Solution Behavior.....                                               | 40 |
| Conversion from One Standard State to Another.....                          | 43 |
| Solute Interactions in Dilute Solutions.....                                | 46 |
| 3-3. Industrial Application of Reduction Reactions.....                     | 47 |
| Kroll Process.....                                                          | 47 |
| Production of Tungsten.....                                                 | 48 |
| Pidgeon Process.....                                                        | 49 |
| Carbothermic Reduction of Magnesia and Alumina.....                         | 50 |
| Extraction of Zinc.....                                                     | 51 |
| Cadmium Production.....                                                     | 55 |
| Mercury Production.....                                                     | 55 |
| The Mond (Carbonyl) Nickel Process.....                                     | 55 |
| Direct Reduction of Iron Ore.....                                           | 56 |
| Several Commercial Processes for Direct Reduction of Iron Ores.....         | 60 |

### Chapter 4 *Pyrometallurgy III. Smelting and Converting*

|                                              |    |
|----------------------------------------------|----|
| 4-1. Reverberatory Smelting.....             | 67 |
| Tin Smelting.....                            | 70 |
| Copper Smelting.....                         | 70 |
| 4-2. Blast Furnace Smelting.....             | 71 |
| The Lead Blast Furnace.....                  | 71 |
| The Iron Blast Furnace.....                  | 72 |
| Chemistry of the Iron Blast Furnace.....     | 74 |
| Blast Furnace Stoichiometry.....             | 78 |
| Energy Balance.....                          | 79 |
| Improvements in Blast Furnace Operation..... | 79 |
| 4-3. Autogenous Smelting.....                | 82 |
| 4-4. Copper Converting.....                  | 82 |
| 4-5. Steelmaking.....                        | 87 |
| Bessemer Converter Processes.....            | 89 |
| Open Hearth Process.....                     | 91 |
| Oxygen Steelmaking.....                      | 91 |
| Oxygen Converter Gas Recovery Processes..... | 95 |
| Kaldo and Rotor Processes.....               | 95 |
| Spray Steelmaking.....                       | 98 |
| Electric Furnace Steelmaking.....            | 98 |

### Chapter 5 *Pyrometallurgy IV. Refining Processes*

|                                                   |     |
|---------------------------------------------------|-----|
| 5-1. Liquid Phase Refining.....                   | 105 |
| Deoxidation Equilibria.....                       | 105 |
| Aluminum Deoxidation of Steel.....                | 106 |
| Summary of Deoxidation Data.....                  | 108 |
| Precipitation Stoichiometry.....                  | 108 |
| Desulfurization of Molten Pig Iron.....           | 109 |
| Parkes Process.....                               | 111 |
| Kinetics of Nucleation of a Separating Phase..... | 113 |
| Growth and Flotation of a Separating Phase.....   | 115 |

## Contents

|                                                    |     |
|----------------------------------------------------|-----|
| Liquid Phase Separation.....                       | 116 |
| Processing Operations—Lead-Silver System.....      | 116 |
| Lead-Copper System.....                            | 116 |
| Zinc Recovery by Liquid Phase Separation.....      | 116 |
| Engineering Design.....                            | 117 |
| Process Yield.....                                 | 117 |
| Purity of Product.....                             | 121 |
| Thermal Requirements.....                          | 122 |
| Process Kinetics.....                              | 122 |
| Refining by Oxidation.....                         | 122 |
| Zone Refining.....                                 | 124 |
| Secondary Metal Refining.....                      | 130 |
| 5-2. Distillation Processes.....                   | 130 |
| Clausius-Clapeyron Equation.....                   | 131 |
| Relative Volatility.....                           | 133 |
| Equilibrium Distillation.....                      | 135 |
| Molecular Distillation.....                        | 137 |
| Vacuum Dezincing of Desilverized Lead Bullion..... | 140 |
| Observations on Liquid Iron Alloys.....            | 140 |
| 5-3. Degassing Operations.....                     | 141 |
| Fundamentals of Gas-Metal Reactions.....           | 141 |
| Diatomic Gases.....                                | 141 |
| Compound Gases.....                                | 146 |
| Inert Flush Degassing.....                         | 148 |
| An Equilibrium Process.....                        | 148 |
| Boundary Layer Model.....                          | 151 |
| Calculation of Residence Time.....                 | 152 |
| Vacuum Degassing.....                              | 155 |
| Other Degassing Processes.....                     | 163 |
| Temperature Drop of the Melt During Degassing..... | 167 |

### Chapter 6 *Hydrometallurgy*

|                                                          |     |
|----------------------------------------------------------|-----|
| 6-1. Hydrometallurgical Processes.....                   | 176 |
| Leaching.....                                            | 176 |
| Leaching Techniques.....                                 | 177 |
| Recovery of Metal from Solution.....                     | 179 |
| Thermodynamics of Reduction of Metals from Solution..... | 179 |
| Electrode Potentials.....                                | 180 |
| The Hydrogen Electrode.....                              | 180 |
| Metal-Metal Ion Electrode Potentials.....                | 181 |
| Hydrogen Reduction of Metal Ions.....                    | 182 |
| Kinetics of Gaseous Reduction in Aqueous Solutions.....  | 185 |
| Other Recovery Methods.....                              | 187 |
| 6-2. Industrial Hydrometallurgical Operations.....       | 191 |
| Hydrometallurgy of Copper.....                           | 191 |
| Gold and Silver Hydrometallurgy.....                     | 191 |
| Uranium Hydrometallurgy.....                             | 193 |
| Zinc Hydrometallurgy.....                                | 194 |
| Hydrometallurgy of Nickel and Cobalt.....                | 195 |
| Hydrometallurgy of Aluminum-Bayer Process.....           | 195 |

### Chapter 7 *Electrometallurgy*

|                                      |     |
|--------------------------------------|-----|
| 7-1. Principles of Electrolysis..... | 201 |
| Half-Cell Reactions.....             | 201 |

## Contents

|                                                     |     |
|-----------------------------------------------------|-----|
| Faraday's Laws.....                                 | 202 |
| Reversible Cell Potential.....                      | 203 |
| Cell Voltages.....                                  | 204 |
| Ohmic Resistance.....                               | 205 |
| Reversible Cell Potential.....                      | 205 |
| Polarization.....                                   | 205 |
| Over-Voltage.....                                   | 207 |
| 7-2. Electrolysis of Fused Salts.....               | 207 |
| Aluminum.....                                       | 208 |
| Hall (Heroult) Process.....                         | 208 |
| Cell Potential.....                                 | 209 |
| Magnesium.....                                      | 211 |
| Sodium.....                                         | 214 |
| 7-3. Electrolytic Refining.....                     | 214 |
| Copper Refining.....                                | 215 |
| Anode Preparation.....                              | 215 |
| Refining Systems.....                               | 215 |
| Tank House Practice.....                            | 218 |
| Treatment of Insolubles.....                        | 221 |
| Refining of Copper Cathodes.....                    | 223 |
| Nickel and Lead Refining.....                       | 224 |
| Electro-Winning Metals from Leaching Solutions..... | 224 |

## Chapter 8 *Melting, Pouring, and Solidification*

|                                                        |     |
|--------------------------------------------------------|-----|
| 8-1. Melting Practice.....                             | 229 |
| Thermal Requirements for Melting.....                  | 229 |
| Melting Units.....                                     | 229 |
| Sensible Heat of the Metal.....                        | 236 |
| Sensible Heat of the Melting Unit.....                 | 236 |
| Heat Losses.....                                       | 236 |
| Mass and Energy Balance on Melting Unit.....           | 237 |
| 8-2. Pouring Operations.....                           | 242 |
| Rate of Pouring.....                                   | 242 |
| Temperature Drop.....                                  | 243 |
| 8-3. Casting and Solidification.....                   | 244 |
| Rate of Solidification.....                            | 244 |
| Ingot Structure.....                                   | 246 |
| Effect of Rate of Heat Removal on Ingot Structure..... | 246 |
| Influence of Metal Composition.....                    | 247 |
| Influence of Shrinkage.....                            | 249 |
| Effect of Dissolved Gases.....                         | 250 |
| Defects in Ingots.....                                 | 253 |
| 8-4. Continuous Casting.....                           | 254 |
| 8-5. Other Casting Procedures.....                     | 256 |

## Chapter 9 *Computer Applications in Extractive Metallurgy*

|                                                          |     |
|----------------------------------------------------------|-----|
| 9-1. General Nature of Digital and Analog Computers..... | 261 |
| The Digital Computer.....                                | 261 |
| The Analog Computer.....                                 | 265 |
| 9-2. Applications of Electronic Computers.....           | 265 |
| Comparison of Analog and Digital Machines.....           | 266 |
| Extractive Metallurgy and System Engineering.....        | 266 |

## Contents

|                                                        |     |
|--------------------------------------------------------|-----|
| 9-3. Material Handling—A Queueing Theory Approach..... | 268 |
| Queueing Theory.....                                   | 269 |
| Single Station Queueing Problem.....                   | 269 |
| Example of Single Station Queueing Problem.....        | 270 |
| Multistation Queueing Problem.....                     | 271 |
| Example of Multistation Model.....                     | 272 |
| Other Approaches to Queueing Problems.....             | 273 |
| 9-4. Linear Programming.....                           | 274 |
| Applications of Linear Programming.....                | 276 |
| 9-5. Process Simulation.....                           | 278 |

## Appendix A

|                                                                                               |     |
|-----------------------------------------------------------------------------------------------|-----|
| Table A-I. Summary of Free-Energy Equations for Sulfation Reactions.....                      | 287 |
| Table A-II. Standard Free Energies of Formation of Compounds at Steelmaking Temperatures..... | 288 |
| Table A-III. Activity Coefficients at Infinite Dilution in Liquid Metals.....                 | 292 |
| Table A-IV. Standard Free Energy of Solution of Various Elements in Liquid Iron.....          | 296 |
| Table A-V. Interaction Coefficients for Elements Dissolved in Liquid Iron at 1600°C.....      | 297 |
| Table A-VI. Nonferrous Interaction Parameters.....                                            | 298 |
| Table A-VII. Vapor Pressures of Liquid Metals.....                                            | 302 |
| Table A-VIII. Standard Electrode Potentials at 25°C for Oxidation Reactions.....              | 303 |
| Table A-IX. Heat Content of Several Metals.....                                               | 304 |
| Table A-X. The Error Function.....                                                            | 305 |

## Appendix B *Example Problems and Computer-Facilitated Solutions*

|                                                                                                                                  |     |
|----------------------------------------------------------------------------------------------------------------------------------|-----|
| Example Problem No. 1: Thermochemical Data Calculation—Enthalpy Increments.....                                                  | 307 |
| Example Problem No. 2: Calculation of Adiabatic Flame Temperatures at the Tuyeres of a Coke-Fueled Shaft Furnace.....            | 314 |
| Example Problem No. 3: Cooling of Pig Iron in a Transfer Ladle.....                                                              | 328 |
| Example Problem No. 4: Predicting the Scrap Requirement for the Oxygen Steelmaking Process.....                                  | 335 |
| Example Problem No. 5: Digital Computer Analysis of Heat Flow and Temperature Distribution Around a Copper Converter Tuyere..... | 345 |
| Example Problem No. 6: Heat Loss Through a Furnace Roof.....                                                                     | 354 |
| Example Problem No. 7: Digital Computer Simulation of a Bottom-Pouring Ladle.....                                                | 358 |
| Example Problem No. 8: Unsteady State Heat Flow—Cooling of a Slab.....                                                           | 366 |
| Example Problem No. 9: Linear Regression Analysis—BOF Steel Chemistry.....                                                       | 374 |
| Example Problem No. 10: Linear Programming—Optimization of Cupola Charge.....                                                    | 381 |

|            |     |
|------------|-----|
| Index..... | 391 |
|------------|-----|

## Preface

For over a decade the need has existed for a college textbook on extractive metallurgy which reflects developments in the technology and science of this engineering area. In particular, the use of chemical thermodynamics to describe the behavior of metallurgical processes has developed extensively and is now an integral part of the engineering approach to process analysis. During this same time interval, the use of computers has become increasingly important in engineering practice. This text places strong emphasis on the use of both engineering tools as applied to extractive metallurgy.

Most educators in the field of extractive metallurgy have recognized that a unit process treatment of the subject has much more to offer than a descriptive presentation of current practice on a metal-by-metal basis. This text is based on the unit process concept and emphasis is placed on basic principles rather than detailed practice. Nevertheless, some descriptive material has been included to provide a background and engineering context for the student. The instructor can utilize lectures and assigned reading to extend the description of industrial practice while emphasizing fundamental principles as presented in the text. An attempt has been made to extend the unit process concept to consideration of the design of entire extractive processing systems.

The future of metallurgical process engineering undoubtedly will involve, in addition to the advances in metallurgical science, techniques which are adapted from chemical engineering, instrumentation, computing science, economics, operations research, and other allied fields. The metallurgical engineer should be acquainted with these areas, at least to the point of being able to evaluate possible contributions to metallurgical processing operations by specialists from these related fields. Ideally, the trained metallurgist should be prepared to assume a position of leadership in the engineering team which handles the multi-faceted problems of metallurgical process design and operation. This book reflects an effort to expand the teaching emphasis in extractive metallurgy, and includes an introduction to some of the fields which are important in metallurgical processing systems. In addition to an analytical approach to the engineering of metallurgical unit processes, the text includes introductory material on the use of computers in process engineering, operations research procedures which treat system behavior in terms of queueing theory or linear programming models, and mathematical simulation of processing systems.

The objective of providing a textbook on extractive metallurgy for the junior, senior or beginning graduate student placed constraints on the text. These constraints prevented extensive development of each subject area in the broad field encompassed by extractive metallurgy. On the other hand, a detailed development of several subjects is included to emphasize the rigor and thoroughness characteristic of sound engineering.

The text is developed on the basis of three alternative approaches to metal extraction and refining: pyrometallurgy, hydrometallurgy, and electrometallurgy. These production alternatives have their roots in physical chemistry but draw upon many related fields. Furthermore, these three stems of extractive metallurgy are not independent, but often are combined in many extraction and refining systems. Pyrometallurgical unit processes are developed in considerable detail in the first several chapters, followed by hydrometallurgical, and electrometallurgical processes. A chapter on melting, pouring and solidification then follows which involves topics on pyrometallurgy but is focused toward the semi-finished product. The text concludes with a chapter covering the principles and techniques for computer-oriented analysis of extraction and refining systems.

Traditionally the teaching of metallurgical engineering has been problem-oriented. Some engineering problems have specific solutions. Other problems have a range of solutions, some of which are more optimal than others. Both types are encountered in engineering practice, and therefore both have been included in the text. In all cases an effort is made to emphasize the underlying basic principles.

Example problems are a useful supplement in the study of the text material. The text contains a number of such problems as worked examples. Problems and discussion questions are provided with each chapter. The text and problem sets are self-contained. However, the discussion questions, while based on material introduced in the text, suggest avenues for further study.

An appendix of problems with documented computer solutions is included to illustrate the application of this modern technological tool. The problems and approaches to solving them illustrate a variety of numerical methods which can be implemented on the digital computer. The problems have been selected on the basis of their pertinence to engineering practice and hopefully they will have applications beyond the college classroom.

I wish to thank all those who have helped in the preparation of this book. The development of this text has involved several years of teaching a senior course at The University of Michigan entitled Metallurgical Process Design. The students in those classes as well as many interested graduate students contributed immensely to the text material as it developed. Many colleagues and peers, both in industry and in academe, have generously contributed suggestions, comments and encouragement. Special recognition goes to Ralph D. Higgins who reviewed the early manuscripts, to Elaine Galoit who typed the final manuscript, and to Robert E. Marrone who assisted in preparing the computer appendix, to name only a few of the many who contributed. I am grateful to my students for their inspiration and to my family for their help, encouragement, and understanding.

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## CHAPTER 1

### Introduction

Within the broad field of metal sciences and technology, the initial processing steps are extraction and refining. These extractive and purification processes, the subject of this text, are built upon the principles of chemical metallurgy. Chemical metallurgy (as contrasted with physical metallurgy, the study of the solid state and the structure and properties of metallic materials) utilizes physical chemistry, draws upon inorganic chemistry and electrochemistry, and depends upon some areas of organic chemistry to describe metallurgical systems. The unit processes of extractive metallurgy are presented in this text with emphasis on the underlying chemical metallurgical principles.

#### 1-1 Source of Metals

The original source of all metals is the earth's crust, which contains metallic deposits usually in the form of their oxides or sulfides called ores, from which metals can be extracted. In some instances, noble metals, such as gold, silver, and sometimes copper, are found in *native* or free elemental form. Ores are seldom composed of one metallic compound but usually are made up of several, including the mineral of the desired metal as well as other impurity compounds referred to as *gangue*. The important minerals of the most common metals are listed by name and chemical formula in Table 1-1.

Ores are found in a wide variety of locations and at various depths in the crust of the earth. Ores are mined by underground methods or by surface mining techniques, such as open pit or strip mining. Magnesium is obtained primarily from sea water.

The virtually inexhaustible supply of many common metallic elements is reflected by the large amounts of iron, aluminum, silicon, calcium, sodium, and potassium in the earth's crust. In the case of magnesium, a vast supply exists since each cubic mile of sea water contains several million tons of magnesium.

A very important metallic element is *iron*, which accounts for the largest part of the metal industry. The primary source of iron is from the minerals magnetite ( $\text{Fe}_3\text{O}_4$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), and limonite ( $\text{Fe}_2\text{O}_3$  plus some combined water); the concentration of iron in high-grade, direct smelting ores may range as high as 60%, but ores containing only 25% iron have been smelted. The principal source of high-grade ore within the United States is the Lake Superior district in Upper Michigan and Minnesota. Other important deposits still exist in the Lorraine Basin of France, the English Midlands, the Donetz Basin and the Ural Mountains of Russia, and in northern Sweden. Important deposits which are being mined include those in

northern Quebec, Labrador, Brazil, and Venezuela. Until recently, the readily available, iron-bearing minerals were of sufficiently high grade that little attention was paid to methods for concentrating them, but depletion of high-grade deposits has led to development of techniques for concentrating low grade ores, one of which is taconite, a plentiful low-grade iron ore containing approximately 30% iron, in which the iron oxide is finely dispersed throughout a silica matrix. The upgrading of taconite is accomplished by grinding and concentration, followed by agglomeration into pellets for charging to the iron blast furnace.

*Copper* is found in nature in forms ranging from the pure metal to sulfide, oxide, and carbonate. The pure metal is found in appreciable amounts only in the Upper Peninsula of Michigan, but these "lake copper" deposits are nearly depleted and do not now represent an important source of copper. Copper is most commonly found as a sulfide, either chalcocite, chalcopyrite, or covellite. The action of surface waters on sulfide minerals of copper leads to oxidation, and the upper portions of copper ore deposits are usually high in copper oxides. Copper ores are usually low in copper content, containing less than 5% copper, but ores containing as little as  $\frac{1}{2}$  wt % copper can usually be processed at a profit. Shipping costs for these low-grade ores dictate that concentration facilities be located at the mine. The principal sources of copper are the Cordillera of the western United States and South America, the Central African Plateau in northern Rhodesia and Katanga province of the Belgian Congo, and the Canadian Shield. The largest and richest copper mine in the world is at Chuquibambilla, Chile, and the second largest mine is in Bingham Canyon, Utah.

*Aluminum* is one of the most abundant metallic elements and represents approximately 8% of the earth's crust, occurring as the oxide. Although several minerals contain appreciable amounts of aluminum, the only ore utilized commercially is bauxite, a rock containing hydrated oxides of aluminum, principally gibbsite and diaspore. These ores are usually found in tropical or subtropical climates, the most important sources of commercial bauxite being in Surinam, British Guiana, Jamaica, and Indonesia. Other deposits are being mined in southern United States and at several locations in southern Europe.

*Lead* is found in nature as the sulfide galena, although surface waters have often converted upper portions of lead deposits to the sulfate anglesite or the carbonate cerussite. The ores of lead usually contain, in addition to zinc blende (see below), recoverable amounts of copper, silver, gold, antimony, and bismuth. The largest producers of lead include the United States, Australia, Russia, Canada, and Mexico. Appreciable quantities of lead are also produced in South America, the principal sources being Peru, Bolivia, and Argentina.

The most important *zinc* mineral is the sulfide sphalerite, often referred to as zinc blende. The minerals sphalerite (ZnS) and galena (PbS) nearly always occur together, and a listing of the principal zinc-producing regions would be essentially the same as those for lead. The only exception where zinc deposits do not also contain appreciable amounts of lead is at Franklin Furnace, New Jersey, where the deposits are a mixture of zincite and the iron- and manganese-bearing mineral franklinite.

*Tin* is a relatively rare metal, accounting for less than 0.001 wt % of the earth's

TABLE 1-1  
Minerals of Common Metals

| Metal      | Mineral       | Formula                                                                                      |
|------------|---------------|----------------------------------------------------------------------------------------------|
| Iron       | Magnetite     | $\text{Fe}_3\text{O}_4$                                                                      |
|            | Hematite      | $\text{Fe}_2\text{O}_3$                                                                      |
|            | Limonite      | $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$                                           |
|            | Siderite      | $\text{FeCO}_3$                                                                              |
| Copper     | Native Copper | Cu                                                                                           |
|            | Chalcocite    | $\text{Cu}_2\text{S}$                                                                        |
|            | Covellite     | CuS                                                                                          |
|            | Chalcopyrite  | $\text{CuFeS}_2$                                                                             |
|            | Cuprite       | $\text{Cu}_2\text{O}$                                                                        |
|            | Diaspore      | $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$                                             |
| Aluminum   | Gibbsite      | $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$                                            |
|            | Kaolinite     | $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$                        |
|            | Galena        | PbS                                                                                          |
| Lead       | Cerussite     | $\text{PbCO}_3$                                                                              |
|            | Anglesite     | $\text{PbSO}_4$                                                                              |
|            | Sphalerite    | ZnS (Zinc blende)                                                                            |
| Zinc       | Zincite       | ZnO                                                                                          |
|            | Franklinite   | (Fe, Zn, Mn) O                                                                               |
|            | Magnesite     | MgO                                                                                          |
| Magnesium  | Dolomite      | $\text{MgCO}_3 \cdot \text{CaCO}_3$                                                          |
|            | Cassiterite   | $\text{SnO}_2$                                                                               |
|            | Stannite      | $(\text{Cu}_2\text{S} \cdot \text{FeS} \cdot \text{SnS}_2)$                                  |
| Nickel     | Millerite     | NiS                                                                                          |
|            | Garnierite    | Hydrosilicate of<br>Ni and Mg                                                                |
|            | Pentlandite   | $(\text{FeNi}) \text{S}$                                                                     |
| Manganese  | Pyrolusite    | $\text{MnO}_2$                                                                               |
|            | Rhodochrosite | $\text{MnCO}_3$                                                                              |
|            | Rhodonite     | $\text{MnSiO}_3$                                                                             |
|            | Chromite      | $\text{FeCr}_2\text{O}_4$                                                                    |
| Chromium   | Ilmenite      | $\text{FeO} \cdot \text{TiO}_2$                                                              |
| Titanium   | Rutile        | $\text{TiO}_2$                                                                               |
| Zirconium  | Baddeleyite   | $\text{ZrO}_2$                                                                               |
| Vanadium   | Zircon        | $\text{ZrSiO}_4$                                                                             |
|            | Patronite     | $\text{V}_2\text{S}_5$ + sulfur                                                              |
|            | Carnotite     | $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ |
|            | Vanadinite    | $3\text{Pb}_3(\text{VO}_4)_2\text{PbCl}_2$                                                   |
| Molybdenum | Molybdenite   | $\text{MoS}_2$                                                                               |
|            | Molybdate     | $\text{MoO}_3$                                                                               |
|            | Wolframite    | $\text{FeWO}_4$                                                                              |
| Tungsten   | Scheelite     | $\text{CaWO}_4$                                                                              |
| Silver     | Native silver |                                                                                              |
|            | Argentite     | $\text{Ag}_2\text{S}$                                                                        |
|            | Cerargyrite   | $\text{AgCl}$                                                                                |
| Gold       | Native gold   | Au                                                                                           |
|            | Calaverite    | $\text{AuTe}_2$                                                                              |
|            | Sylvanite     | $(\text{AuAg})\text{Te}_2$                                                                   |

TABLE 1-1 (Continued)

| Metal     | Mineral     | Formula                                                       |
|-----------|-------------|---------------------------------------------------------------|
| Beryllium | Beryl       | $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ |
| Mercury   | Cinnabar    | $\text{HgS}$                                                  |
| Uranium   | Pitchblende | Complex oxide                                                 |
| Cadmium   | Greenockite | $\text{CdS}$                                                  |
| Antimony  | Stibnite    | $\text{Sb}_2\text{S}_3$                                       |
| Cobalt    | Cobaltite   | $\text{CoAsS}$                                                |

crust. The most important mineral of tin is the oxide cassiterite. As a heavy mineral, tin oxide is often concentrated into a placer deposit by the action of water breaking down igneous rock both by physical and chemical means and thus concentrating the heavier minerals. These placer deposits are located principally in Malaya and Indonesia, where the tin is recovered by hydraulic mining techniques, often employing dredges with self-contained equipment for concentrating the ore. Bolivia has substantial tin deposits. The tin is mined there by open cut methods where it occurs in vein deposits as the mineral stannite.

*Titanium and manganese* are relatively common metals, accounting for 0.1–1.0% of the earth's crust. Titanium occurs as ilmenite or rutile, and these deposits are located in the United States, Canada, India, Australia, and Brazil. Manganese occurs primarily as the oxide pyrolusite; the primary producer is the U.S.S.R., accounting for about one-half of the world output. Other important producers of manganese include India, Ghana, South Africa, Brazil, and Morocco.

Other metals such as gold, silver, cadmium, bismuth, arsenic, etc., are the by-products of copper and lead production. Most other metals are found in relatively small, low-grade deposits in the form of minerals listed in Table 1-1.

## 1-2 Mineral Engineering

Mineral engineering, the first major step in the extraction of metals, involves the separation and concentration of ores. These concentration techniques, which are primarily physical or mechanical separations, are referred to as mineral dressing. It is outside the scope of this text to discuss these concentration techniques in any detail. However, it should be noted that the economics with which the extractive metallurgist must work in optimizing his processes for smelting and refining of metals depend very much on the raw materials with which he is working. These raw materials are the product of the ore-dressing step.

## 1-3 Extractive Metallurgy

Following ore dressing, the removal of any remaining gangue, decomposition of the metallic mineral to produce a metal, and subsequent refining of the metal are the functions of extractive metallurgy. Extractive metallurgy can be divided into three

TABLE 1-2

1969 World and United States Production of Principal Metals<sup>a</sup>

| Metal                    | World production (thousands of short tons) | U.S.A. production (thousands of short tons) | Percentage of world |
|--------------------------|--------------------------------------------|---------------------------------------------|---------------------|
| Iron                     |                                            |                                             |                     |
| Pig iron and ferroalloys | 459,697                                    | 97,593                                      | 21                  |
| Steel ingots and casting | 633,431                                    | 141,262                                     | 22                  |
| Aluminum                 | 10,019                                     | 3,793                                       | 38                  |
| Copper                   | 7,304                                      | 1,585                                       | 21                  |
| Zinc                     | 5,586                                      | 1,041                                       | 19                  |
| Lead                     | 3,671                                      | 639                                         | 17                  |
| Tin                      | 252                                        | <0.5                                        | —                   |
| Magnesium                | 222                                        | 100                                         | 45                  |

<sup>a</sup> From *Minerals Yearbook*, Vol. I and II, *Metals, Minerals and Fuels*, U.S. Dept. of the Interior, Bureau of Mines; U.S. Government Printing Office, 1971.

principal areas or types of processes:

1. Pyrometallurgy, which employs high temperatures to carry out smelting and refining reactions and melting operations.
2. Hydrometallurgy, which employs liquid solvents, usually aqueous, to separate the desired metal.
3. Electrometallurgy, which employs electrical energy, principally for carrying out electrolysis to extract and refine metals.

The type of process or sequence of processes used depends to a great extent upon the starting material, i.e., the mineral concentrate, and the desired product. Selection of the particular process also depends upon the local economics, including the facilities available, power and fuel costs, and other factors such as the accessibility of water, shipping costs, availability of the market, etc. These considerations, along with the demand for various products and the availability and costs of ores, have determined the makeup of today's world metallurgical industry. A general picture of that industry is provided by Table 1-2, which lists the world and United States production of principal metals for the year 1969.

## 1-4 Chemical Metallurgy in the Extraction of Metals

Following the mining and concentration of minerals, their extraction is accomplished by application of chemical metallurgy in one of the three areas of extractive metallurgy: pyrometallurgy, hydrometallurgy, or electrometallurgy. In the following chapters these topics are treated in detail. Pyrometallurgy is discussed in terms of the roasting of ores to convert sulfides to the more easily processed oxides. The physical chemistry of roasting and calcining reactions is presented and agglomerating techniques are discussed. The principles of oxidation and reduction reactions are

presented in terms of application to smelting of minerals by reduction to the metallic state or to a fused sulfide (matte), and conversion to a semi-refined metal. Subsequent pyrometallurgical refining processes, distillation, liquid phase refining and degassing operations are quantitatively discussed in terms of thermodynamic and kinetic limitations. Hydrometallurgical and electrometallurgical processes are reviewed. Then the pyrometallurgical processes of melting, pouring, casting, and solidification are described. Finally, computer applications in the field of extractive metallurgy are developed, along with the presentation of example programs.

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### Discussion Questions

1. Develop a correlation between the current market price of the more common metals and their level of production or use. What are the major factors in establishing these relationships?
2. What are the current price levels for scrap as contrasted with ingot or primary material for common engineering metals? Discuss the role of secondary metal in each metal market.
3. At what concentrations of mineral are the principal mining operations being worked to recover the major metals?
4. In extracting and refining aluminum, copper, zinc, lead, mercury, nickel, tungsten and magnesium, a key unit process is used. Considering the chemical and physical properties of the metal and its most common mineral, state which process is applicable to each metal and why the particular process is used.

## CHAPTER 2

### Pyrometallurgy I: Roasting—Agglomeration—Calcination

Minerals recovered from ores are not always in the optimum chemical or physical state for conversion to metals. Oxides are more conveniently reduced to metals than sulfides, or the metal might be more readily leached from the ore if it were present as a sulfate, a chloride, or an oxide. Chemical conversion to the desired species often is an integral segment of the extractive process. Sulfide ores, for example, usually are heated in an oxidizing atmosphere (roasted) to convert them to an oxide or sulfate.

The physical state of an ore may be too fine for charging to a process. Fine ores often are agglomerated by sintering prior to charging to a blast furnace, the principal smelting unit for lead and iron. In the case of iron ore, pelletizing, another very important agglomeration process, recently has achieved commercial adaptation in the iron and steel industry. Pelletizing is a process in which iron oxides fines first are agglomerated into small pellets that are then fired to produce a small oxide briquet suitable for charging to the iron blast furnace.

In the following sections, several commercial techniques for roasting and agglomerating ores are discussed. In addition, the thermodynamics of sulfate roasting is considered, and the thermodynamics and kinetics of calcination are presented.

#### 2-1 Roasting of Sulfide Ores

Many important metals, including copper, lead, and zinc, occur in nature as sulfides. In early civilizations it was discovered that heating sulfide ores in air converted them to a form whereby they could easily be reduced by charcoal to a metallic form. In modern industrial practice, with a considerable amount of fine material being produced in various concentration operations on low-grade ores, several types of roasting equipment have been developed. Roasting is carried out by rabbling over a tier of hearths in a multihearth roaster, by exposing the sulfide ore to oxidizing gases in a shower roaster where the ore falls through hot gases, in fluidized beds, or by exposing the ore in a packed bed to a controlled flow of gas, as on the Dwight-Lloyd sintering machine. The conditions of roasting determine whether or not the sulfide ore is partially roasted to a sulfate or completely roasted to an oxide.

#### Thermodynamics of Roasting Reactions

A number of reactions take place during the roasting of sulfides. Overall reactions using the roasting of galena (PbS) as an example are given in the following equations. In addition, several other intermediate reactions can occur involving the oxysulfate of lead.

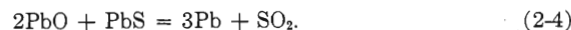
Most roasting is carried to completion (so-called "dead" or "sweet" roast) with elimination of most of the sulfur by the overall reactions



Similar reactions can be written for zinc, copper, and iron. At lower temperatures, sulfates can be formed:



At higher temperatures, the oxide can be reduced by the sulfide to produce the free metal,



Control of temperature and oxygen potential (pressure) can be employed to produce the desired oxidation state. In the case of concentrated zinc ores that later are going to be reduced with carbon, an oxidizing roast with elimination of as much sulfur as possible is desired. In the case of a copper ore which is to be leached, the objective is the formation of as much water-soluble sulfate as possible.

In considering the thermodynamics of roasting, it should be noted that sulfur trioxide is formed in the gas phase according to the reaction,



This reaction is favored at lower temperatures. Oxide-sulfate equilibria can be considered in the form,



where M represents a metal ion. These equilibria could also have been treated in a form obtained by combination of Eqs. (2-5) and (2-6), as for example, in Eq. (2-3), where the equilibrium constant\* would be expressed as

$$K_3 = \frac{a_{\text{PbSO}_4}^2}{a_{\text{PbO}}^2 P_{\text{SO}_2}^2 P_{\text{O}_2}} \quad (2-7)$$

Standard free energy relationships for several sulfation equilibria of this form are summarized in Table A-I (see Appendix A).

The metal-sulfide equilibria can also be presented as oxygen-sulfur dioxide equilibria with the chemical reaction written:



The equilibrium constant can be written in the form,

$$K_3 = \frac{a_{\text{M}} P_{\text{SO}_2}}{a_{\text{MS}} P_{\text{O}_2}} \quad (2-9)$$

\* An understanding of physical chemistry has been presumed, including thermodynamics, phase equilibria, and elementary kinetics.

Then for pure solids in their standard state at unit activity:

$$\log P_{\text{SO}_2} = \log K_3 + \log P_{\text{O}_2} \quad (2-10)$$

The thermodynamics of sulfate systems then can be presented conveniently in terms of predominance area ( $\log P_{\text{SO}_2}$  versus  $\log P_{\text{O}_2}$ ) diagrams. Free energy data for oxide and sulfide systems are required to determine relations of the form shown in Eq. (2-10), or for Eq. (2-7), where for unit activity of the solids

$$\log P_{\text{SO}_2} = -\frac{1}{2} \log K_3 - \frac{1}{2} \log P_{\text{O}_2} \quad (2-11)$$

A predominance area diagram for the nickel-oxygen-sulfur system is presented in Fig. 2-1 for a temperature of 1000°K. The small square in Fig. 2-1 encloses an area where the oxygen and sulfur dioxide pressures range from  $10^{-1}$ – $10^{-2}$  atm. In operations at 1 atm total pressure, gas compositions from 3–10% oxygen and 3–10% sulfur dioxide would yield nickel sulfate as the stable solid phase. At a gas phase

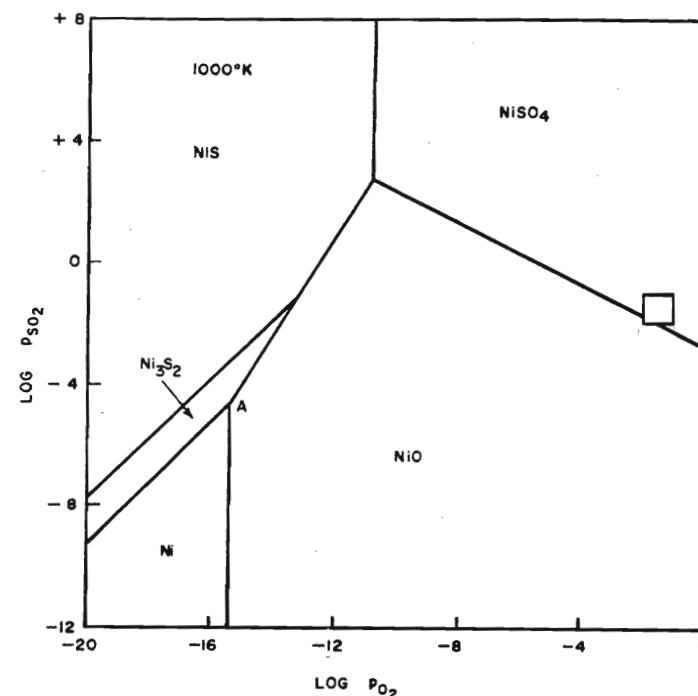


Fig. 2-1. Predominance Area Diagram for the Ni-S-O System at 1000°K

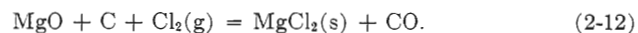
Source: T. R. Ingraham, "Sulphate Stability and Thermodynamic Phase Diagrams with Particular Reference to Roasting" *Applications of Fundamental Thermodynamics to Metallurgical Processes*, Gordon and Breach Science Publishers Inc., New York, 1967, p. 187.



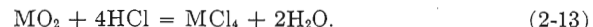
### Volatilization During Roasting

The roasting of sulfide ores permits, in addition to the conversion of sulfide to oxide or sulfate, the vaporization of volatile compounds. In particular, antimony and arsenic are found in appreciable concentrations in flue dusts from the roasting of charge materials that contain only traces of these metals. The trioxides of antimony and arsenic, formed by heating the sulfides in air at temperatures as low as 400°C are sublimed in the later stages of roasting. Zinc and cadmium when heated under reducing conditions are vaporized (see Pyrometallurgy II).

A chloridizing roast in which salt (sodium chloride) is mixed with the sulfide ore charged to the roasting operation can result in a conversion of iron, silver, lead, and copper to chlorides that are readily dissolved in water. Such a conversion to chloride is facilitated by the presence of carbon. For example, tin and tungsten are partially separated by roasting in an atmosphere of chlorine and hydrochloric acid. At 600°C the tin and some of the tungsten are volatilized, and at higher temperatures the remainder of the tungsten, and iron and manganese, come off as chlorides. The presence of a reducing agent such as carbon can markedly lower the temperature required for this type of reaction. For example, chlorination of magnesium oxide is carried out at 1000°C in the presence of coke according to the reaction



HCl gas also can be used to convert some metallic oxides to chlorides by a reaction of the form



## 2-2 Industrial Roasting Processes

As mentioned previously, roasting is carried out not only to render the material chemically suitable for a subsequent processing operation, but also to provide a suitable physical state of the material. In the case of copper and other metals that are smelted in reverberatory furnaces, the roasted material (calcine) should be finely divided, whereas in blast furnace operations for materials such as iron and lead, the calcine must be in a reasonably large agglomerated form. Several processes are available for providing these conditions. The important industrial techniques for roasting are mechanical roasting, flash roasting, fluidized bed roasting, and blast or sinter roasting.

*Mechanical or hearth roasting* is carried out in a vertical multihearth system in which 8–12 hearths are enclosed in a large cylindrical shell 20–25 ft in diameter and 30 ft high. A sectioned view of this type of roaster is shown in Fig. 2-3. The ore enters at the top and drops from hearth to hearth while the sulfide ore particles are roasted as they come in contact with the rising gases. The vessel is lined with fire brick and is equipped with a rotating rabble attached to a central shaft that serves to move, or rabble, the ore across each disc-shaped hearth. The ore is plowed toward an opening on the outer or inner edge of the hearth where, in turn, it falls to the hearth below. The rotating rabble arms are cooled, and openings are provided in the shell for ease of maintenance. This type of equipment can roast from 100–200 tons

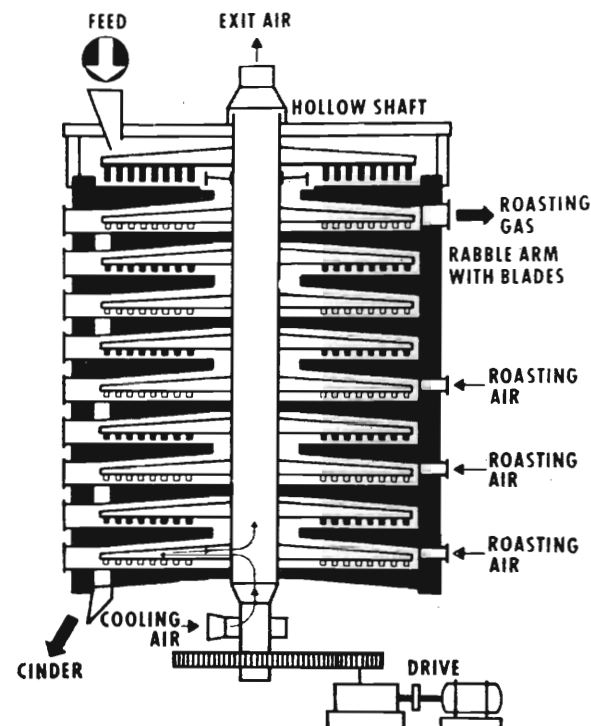


Fig. 2-3. Multiple Hearth Roasting Furnace

Source: *Lurgi Manual*, Lurgi Gesellschaften Frankfurt (Main) Germany, June 1961, p. 192.

of material per day. Heat can be supplied by combustion of fuel, but usually the process is autogenous, that is the oxidation of the material is sufficient to supply thermal energy to the system.

*Flash roasting* is a modification of the multihearth roaster. After it was observed that the oxidation occurred on the surface of ore exposed to the roasting gases and, in particular during the period of fall from hearth to hearth, flash roasting was developed. This process is carried out in a unit similar to a hearth roaster except that several intermediate hearths are removed. The concentrate which often is wet is dried on the first upper hearth or two and then falls through a combustion chamber. After settling on the lower hearths, the calcine is collected and discharged from the unit. In the case where combustion is not autogenous, auxiliary fuel is burned in the unit to maintain the process temperature. To provide for conversion to sulfate in the case of zinc roasting, additional amounts of  $\text{SO}_2$  are often added to control the atmosphere on the lower hearths. A cross-sectional view of a flash roaster for processing zinc concentrates is shown in Fig. 2-4.

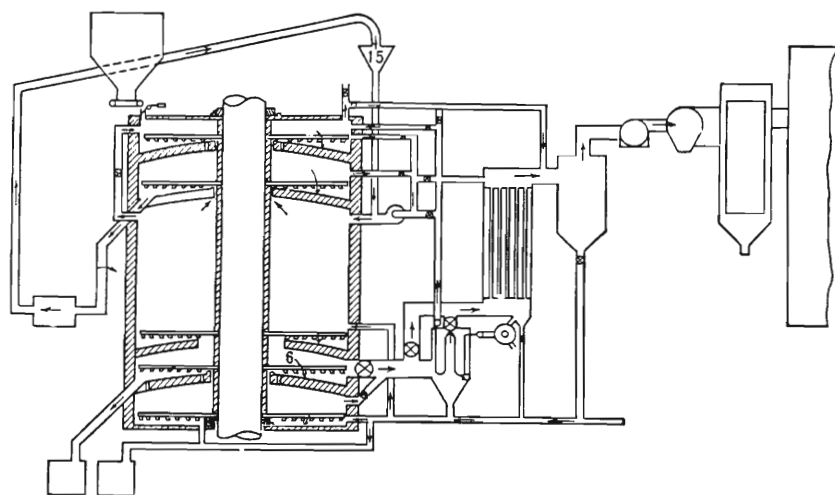


Fig. 2-4. Suspension Roaster for Roasting Zinc Concentrates, Trail, British Columbia

Source: Stimmel, et al., *AIME Trans.*, 1936, Vol. 121, p. 542.

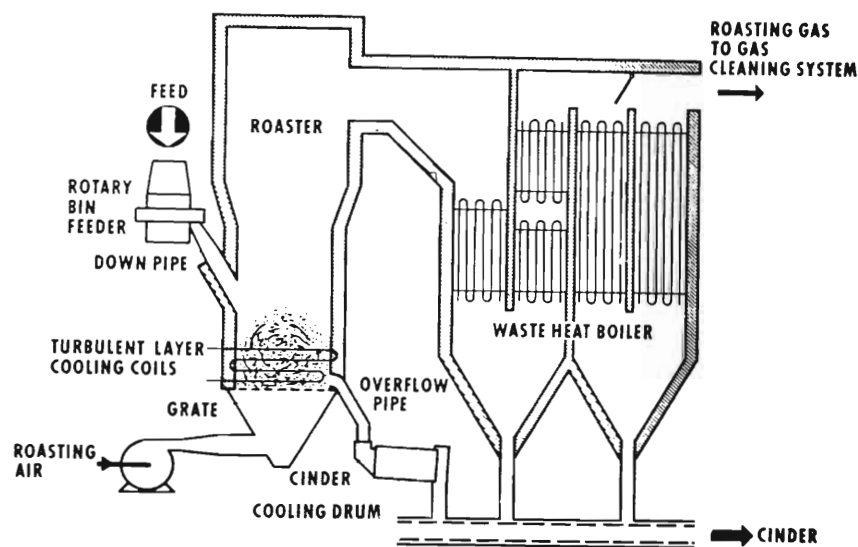


Fig. 2-5. Fluidized Bed Roaster

Source: *Lurgi Manual*, Lurgi Gesellschaften, Frankfurt (Main) Germany, June 1961, p. 195.

*Fluid bed roasting* has been developed since World War II and is now widely used for roasting iron sulfide, and in several instances the sulfides of copper, cobalt and nickel. A schematic diagram of a fluidized bed system for roasting sulfide concentrates is shown in Fig. 2-5.

The most important variables in the fluidized bed are the particle diameter, or average diameter, and the superficial gas velocity. Figure 2-6 shows the relationship between particle diameter and superficial gas velocity for fluidization at 900°C. It should be noted that because of interaction between the solid particles in a fluidized bed, particles which are fine enough to be carried out of the bed and particles which are coarse enough to sink through the bed may exist in the fluidized state. Consequently, within a reasonable range of particle size, the average diameter may be used to characterize the behavior of the bed.

Temperatures in the fluidized bed can be controlled by proportioning the relative amounts of feed and air. Once initiated, combustion in the bed is self-sustaining and a continuous supply of air and feed is provided to the roaster.

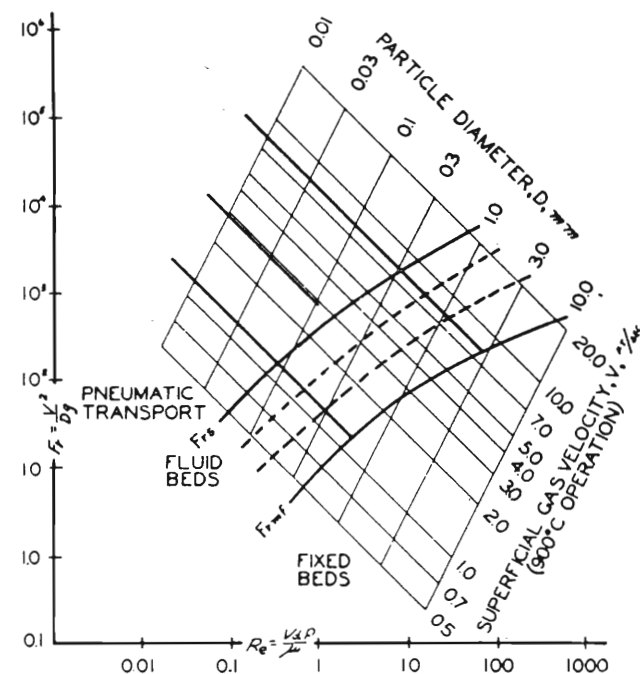


Fig. 2-6. Gas Velocity—Particle Diameter Relationship for Fluidization at 900°C

Source: R. B. Thompson and G. Roesner, *Extractive Metallurgy of Copper, Nickel and Cobalt*, AIME Symposium, New York, Interscience Publishers, Inc., 1961, p. 4.

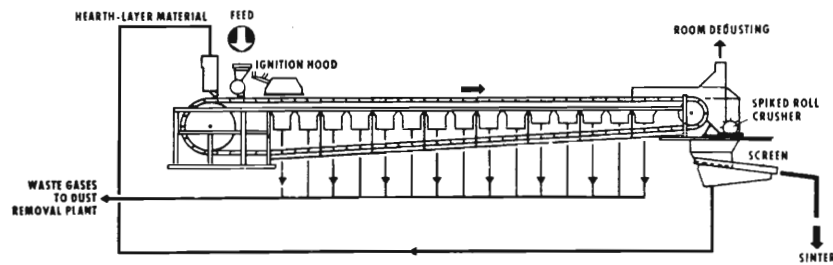


Fig. 2-7. Dwight-Lloyd Sintering Machine

Source: *Lurgi Manual*, Lurgi Gesellschaften, Frankfurt (Main) Germany, June 1961, p. 150.

*Sinter-roast* offers an advantage over the previously described roasting processes in that agglomeration of the roasted material is accomplished. The blast furnace requires a suitably large particle size, and hence iron and lead sulfide ores are sinter-roasted. This process is usually carried out on a Dwight-Lloyd sintering machine, as shown in Fig. 2-7. Roasting is accompanied by incipient fusion, which produces a porous cinder-like material called sinter.

The Dwight-Lloyd sintering machine, which was developed more than 50 years ago, consists of a series of pallets or grates mounted on an endless track. The concentrate is charged to a depth of about 6–20 in. on the pallets, which move over wind boxes at 2–3 ft/min. Combustion of the bed is initiated on its surface by a burner, and the combustion is maintained and carried through the mass of the charge by the air drawn through the concentrate to the wind box below, which is connected to a suction fan. Relatively high temperatures (900–1200°C) are developed in the material, causing it to fuse into a compact mass. After the sinter has reached the end of the machine it is discharged, cooled, and sized to provide a uniform product. Fines from the sizing operation are returned as charge material.

In sinter-roasting, the sulfur in the ore acts as a fuel. The relatively high temperatures and oxidizing conditions usually provide low sulfur contents, particularly for the roasting of pyrite ( $\text{FeS}_2$ ) or pyrrhotite ( $\text{FeS}$ ). In the case of low sulfur or oxide ores, fuel is added. The latter case is referred to simply as sintering and is used in particular for preparation of charge material to the iron blast furnace.

### 2-3 Sintering

The requirement for coarse charge material for the blast furnace necessitates agglomeration of fine ores. One method for agglomerating fines is by sintering. Sintering is the process of heating fine materials to an elevated temperature without complete fusion such that the small, solid particles in contact with one another adhere and agglomerate into larger, more useful particles. The predominant mechanisms in the action of sintering are surface diffusion and incipient fusion, and both occur in the commercial sintering of ore.

The sintering of large quantities of material is often necessary in the operation

of a metallurgical plant. This process provides an opportunity to use fine material, and often makes a particular process feasible by converting available fine materials to an agglomerated form for use as a charge material. Sintering is sometimes carried out in rotary kilns or by batch processing on sinter pans or hearths. Flow of air through the charge may be by updraft or downdraft methods, but the predominant industrial technique for sintering ore is on a moving hearth, as with the Dwight-Lloyd continuous sintering machine. As originally designed for processing copper ores, the sulfide fines were distributed in a thin layer along a traveling belt made up of grates. The charge was ignited and the sulfur burned out of the ore as air was drawn through the charge by large fans. The fines fused together, forming a strong sinter cake that was desirable for charging to a blast furnace. The basic difference between the processing of sulfide ores and the sintering of oxide-ferrous ores is the self-contained fuel of the sulfide material. In the processing of hematite or magnetite fines, carbon in the form of coal or coke has to be added to provide fuel for the sintering process.

The utilization of the Dwight-Lloyd machine (Fig. 2-7) in the processing of iron ores is essentially the same as for nonferrous sulfide ores. A schematic diagram of an iron ore sintering plant is shown in Fig. 2-8. It is evident that an important part of the sinter plant is the mixing system that blends the fine ores, limestone, coke, plus the fines returned from the sinter strand. The charge mix is loaded onto the moving grates of the sintering machine, where it passes under a burner that ignites the bed. Air is drawn through the burning bed by the suction system below,

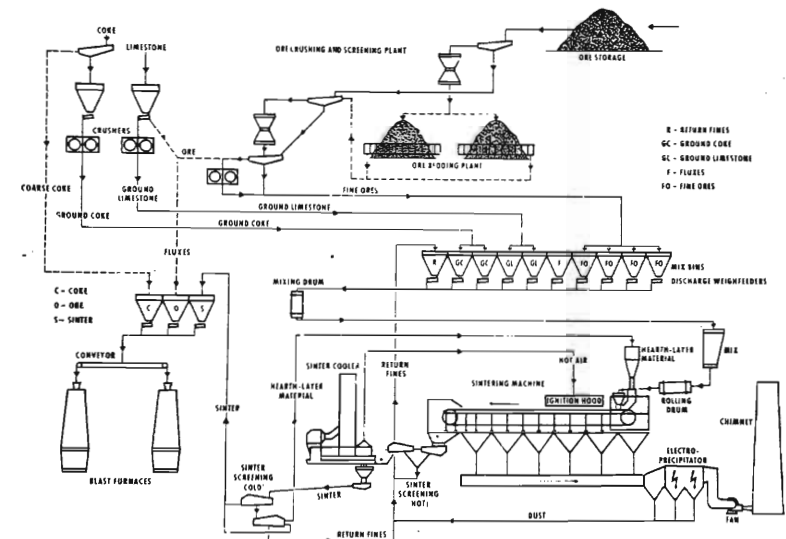


Fig. 2-8. Iron Ore Sintering Plant for Preparation of Self-fluxing Sinter

Source: *Lurgi Manual*, Lurgi Gesellschaften, Frankfurt (Main) Germany, June 1961, p. 151.

and at the end of the strand the sinter drops off the pallets, where it is cooled and screened. The undersize particles are then returned to the sintering process as recycle.

The fuel requirement for the sintering of iron oxide ores ranges from 5–8% coal or coke, and is relatively independent of the material to be sintered. The optimum for the fuel requirement varies slightly and depends upon whether or not chemical reactions are involved in the sintering process. The presence of appreciable amounts of limestone or water will require additional fuel, and may depress the maximum temperature achieved. Variation in the carbonate or moisture content of the sinter mix will give a variation in the width of the hot zone that moves down through the ore bed. In normal downdraft sintering, the combustion of the fuel in the sinter mix is initiated in the upper levels of the sinter bed. The hot combustion gases are pulled downward through the bed and preheat the sinter charge.<sup>2</sup> The presence of water in the sinter mix will limit the increase in temperature of the sinter bed until the water is vaporized. The presence of carbonate, such as limestone that is charged to self-fluxing sinter (see Pyrometallurgy III), will result in a broadening of the combustion front that follows the heat front down through the bed.

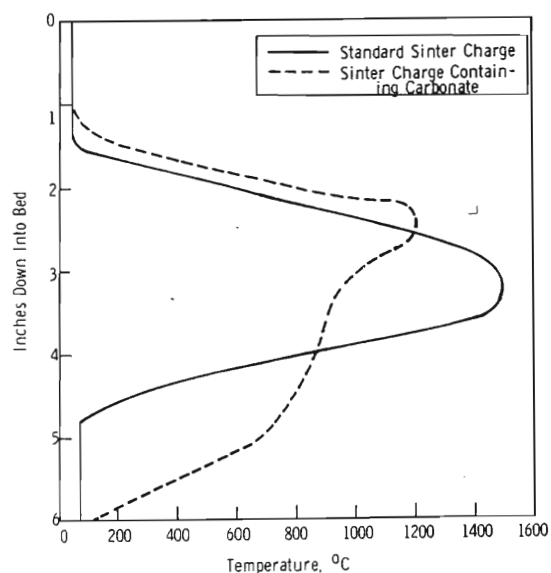


Fig. 2-9. Temperature Distribution for Two Sinter Mixes.

(Combustion is occurring approximately at the midpoint of the bed)

<sup>2</sup> S. Eketorp, *STEELMAKING, The Chipman Conference*, p. 180, MIT Press, Cambridge, Mass., 1965.

Figure 2-9 shows the influence of the presence of a large amount of calcium carbonate in the charge. The peak temperature of the bed is decreased and the width of the hot zone is increased. A well-defined planar front should occur in sintering, as illustrated by the solid line in Fig. 2-9.

The engineering relationships for design of sintering operations are based on flow of air through porous beds. Of particular importance is the bed permeability, which often can be determined by laboratory sintering tests.<sup>3,4</sup> In commercial operations, 1 to 3½ tons of material can be sintered per square foot of hearth area per day on a Dwight–Lloyd sintering machine. A decrease in fuel requirements could be achieved through the use of preheated air supplied from a closed hood over the sinter strand. Up to 40% of the thermal energy required for sintering can be supplied by fuels such as flue gas, natural gas, or fuel oil burned in a hood above the sinter machine. With this “mixed firing process,” the mechanical and chemical properties of the sinter can be improved.<sup>5</sup>

Control of the sintering of iron ores by the Dwight–Lloyd process is of particular importance as the productivity of the iron blast furnace increases. The control of material flow and suitable proportioning of raw materials to provide a chemically uniform sinter mix is of prime importance. Maximum utilization of the sinter strand requires control of the “burn through” point such that combustion is completed just as the sinter reaches the discharge end of the strand. The temperature in the wind box often can be used to monitor this “burn through” point.<sup>6</sup>

## 2-4 Pelletizing

Pelletizing is a recently developed agglomerating process for iron ores that has made possible the economic utilization of low-grade taconite ores. The use of pellets as a blast furnace charge has resulted in marked increases in blast furnace productivity (see Pyrometallurgy III). Taconite is an intimate physical mixture of magnetite or hematite with gangue materials. Successful separation of the iron oxide from the gangue material requires crushing and grinding to extremely fine particle sizes. The agglomeration of this material has been successfully accomplished by balling the ore in various rotating devices such as discs, drums, cones, etc., and once the fine material is balled, it is hardened by heating, generally referred to as *induration*. A schematic diagram of a pelletizing plant is shown in Fig. 2-10. During induration, several chemical reactions occur, including vaporization of free water, vaporization of combined water, calcination of any limestone present, and in the case of a magnetite ( $\text{Fe}_3\text{O}_4$ ) concentrate, the oxidization of the magnetite to hematite ( $\text{Fe}_2\text{O}_3$ ). Laboratory tests are usually employed to determine the optimum time–temperature pattern for induration. The final temperatures during induration reach 2300–2400°F, depending upon the concentrate being pelletized. Shaft furnaces, kilns, and traveling grates with updraft or downdraft techniques are used to

<sup>3</sup> E. W. Voice, S. H. Brooks, and P. K. Gledhill, *J.I.S.I.* 174, 136 (1953).

<sup>4</sup> E. W. Voice and R. Wild, *J. Metals* 10, 105 (1958).

<sup>5</sup> *Lurgi Manual*, p. 150, Lurgi Gesellschaften Frankfurt (Main), Germany, June, 1961.

<sup>6</sup> A. Bragard, *J. Metals* 19, 49–57 (1967).

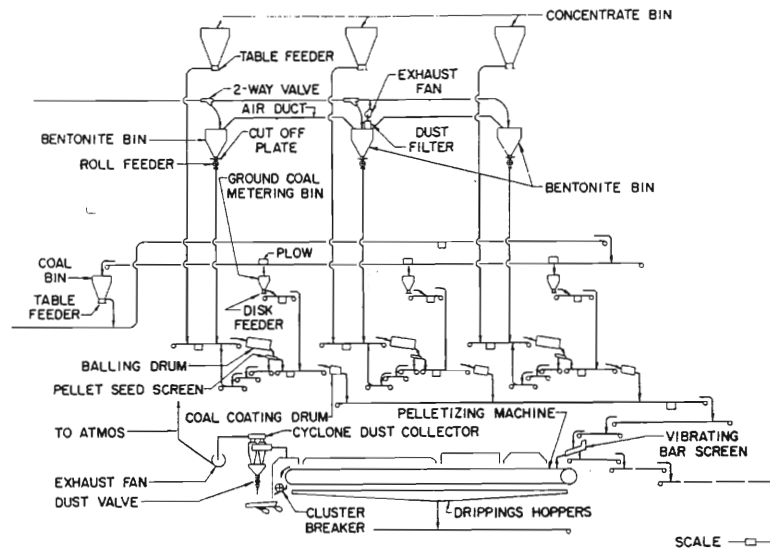


Fig. 2-10. Pelletizing Plant Flow Diagram

Source: M. J. Greaves and A. English, *Agglomeration*, New York, Interscience Publishers, 1962 p. 442.

fire the pellets. Pelletizing machines are designed for producing between 2500–3000 tons of pellets per day and designs are being prepared for machines capable of producing 5000 tons per day.

A typical balling drum circuit, in conjunction with shaft furnaces for indurating the pellets, is shown in Fig. 2-11. With a suitable amount of moisture and a binding agent, usually a clay such as bentonite, the finely divided material is rolled on an inclined drum, disc, etc., causing the ore particles to cling together and roll up into small spheres. The material discharged from the balling unit is sized, and the undersized pellets are recycled. Limestone often is added to provide a fluxing agent during subsequent smelting in the blast furnace.

Other techniques are available for indurating the pellets, including the horizontal grate shown in Fig. 2-12. A recently designed pelletizing process employs a traveling conveyor for drying and initiating induration, a rotary hearth furnace for raising the temperature of the pellets to 1200°F, and an indurating stove or shaft furnace where the reaction from magnetite to hematite is accomplished by a controlled flow of air through the packed bed. The stove includes both a heating and cooling section. The system is shown schematically in Fig. 2-13. Automatic control of the pelletizing plant, utilizing bed-level control, temperature controls, pressure

controls, and flow instruments in conjunction with a digital computer, is being installed in several locations.

The rapid development of pelletizing plants on the North American continent stemmed from the need for treating fine size magnetite concentrates produced from taconites of the Massabi range, which could not be sintered successfully because of their extreme fineness. The advantage of this process is such that the bulk of the iron ore produced in North America is now being pelletized. High-grade ores mined underground are also being directly pelletized, and consideration is being given to partial reduction of the pellets during induration, which could lead to even higher productivities for the blast furnace. Fully reduced pellets are being prepared for direct charging to steelmaking furnaces.

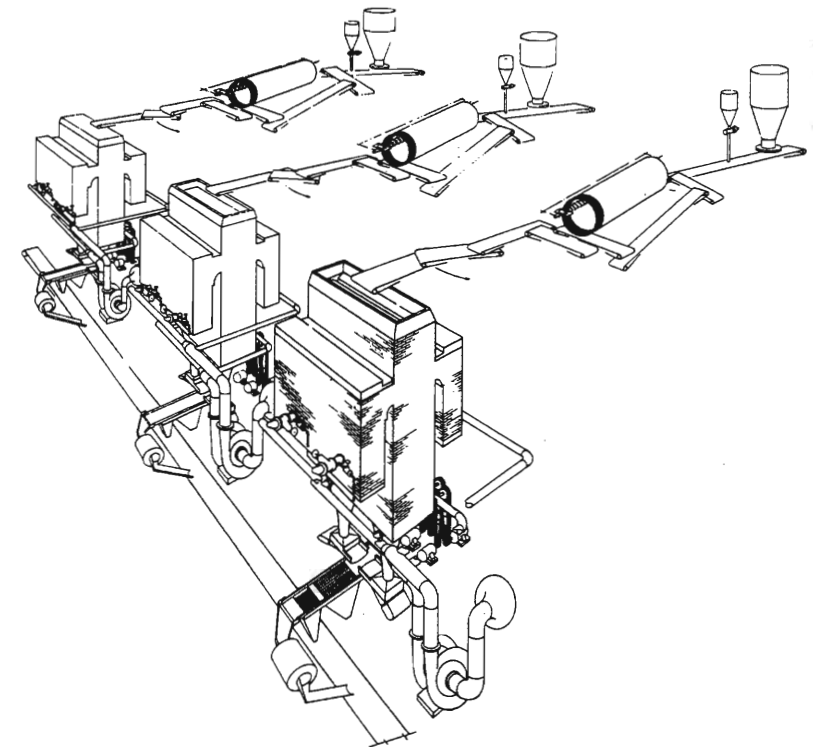


Fig. 2-11. Typical Shaft Furnace Pelletizing Plant

Source: A. English and M. J. Greaves, *Soc. Mining Engineering Transactions*, September 1963, p. 308.

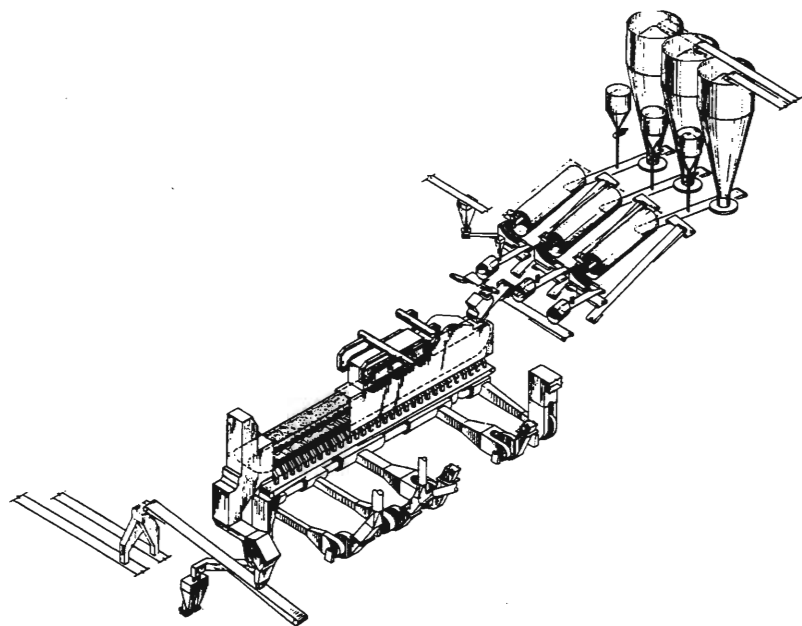


Fig. 2-12. Horizontal Grate Pelletizing Plant of Reserve Mining Co. with Million ton per Year Capacity, Magnetite Concentrate

Source: A. English and M. J. Greaves, *Soc. Mining Engineers Transactions*, September 1963, p. 309.

## 2-5 Calcination

Calcination of natural carbonates yields lime and magnesia which have long been important materials in the metallurgical industries. The major tonnage outlet for magnesia is as the refractory "dead-burned grain magnesite." Lime is also a refractory material, but cannot be used in commercial service. Exposure to the atmosphere after calcination will result in reaction (slaking) with the water vapor in the air, thus rendering the lime useless. The use of lime as a neutralizing agent for acid pickling and leaching solutions is well known. The use of lime as a flux for oxygen steelmaking has markedly increased the lime consumption in the steel industry, replacing the limestone previously used in the open hearth process. Calcination of limestone is carried out in many types of kilns, including rotary, shaft, and rotary hearth.

### Thermodynamics of Calcination

The reaction that occurs in calcining a chemically pure limestone may be expressed as

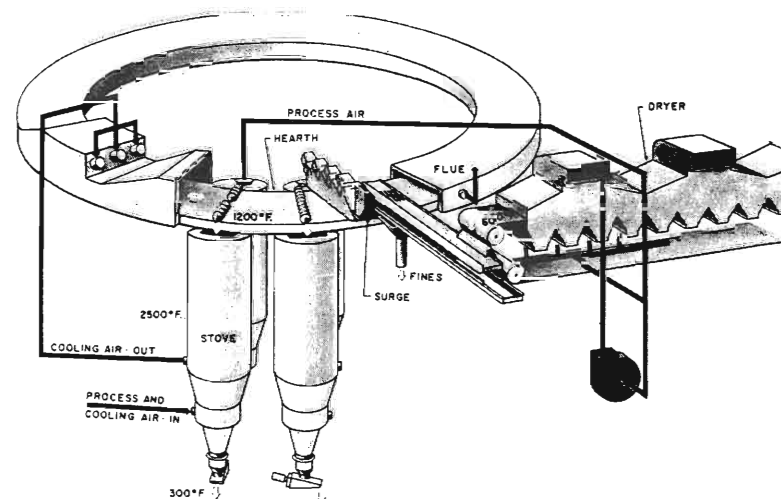


Fig. 2-13. Heat process equipment (in which green balls of magnetite ore are loaded onto a steel dryer conveyor and dried and preheated at temperatures up to 600°F in air.)

Source: L. W. Smith, D. Beggs, and F. G. Rinker, *J. of Metals*, 1966 Vol. 18, No. 9, p. 1022.

The equilibrium constant for Eq. (2-14) is

$$K_{14} = P_{\text{CO}_2} \quad (2-15)$$

The free energy of decomposition may be expressed<sup>7</sup> as a function of temperature as

$$\Delta G^\circ = 42,490 - 37.7 T = -4.575 T \log (P_{\text{CO}_2}) \quad (2-16)$$

Equations (2-15) and (2-16) can be utilized to calculate the equilibrium pressure of  $\text{CO}_2$  in contact with heated limestone.

### Kinetics—Mechanism of Calcination

In addition to predicting the temperatures at which decomposition of the limestone can take place, it is necessary as well to consider the kinetics of the reaction. Although several experimental investigations have been made to elucidate the exact manner in which the decomposition takes place, little success has been obtained in defining a mechanism for calcination. It has been found, however, that calcination of limestone takes place at a definite boundary plane, i.e., the boundary of two solid phases, one of lime ( $\text{CaO}$ ) and the other of limestone ( $\text{CaCO}_3$ ). This plane progresses from the surface of the piece of limestone being calcined toward

<sup>7</sup> O. Kubaschewski and E. L. Evans, *Metallurgical Thermochemistry*, John Wiley, New York, 1956.

the center at a definite rate and is maintained in about the same shape as the external surface of the stone.

Based upon calcination data, Furnas<sup>8</sup> derived the following equation, which can be used to determine the progressive penetration of the zone of calcination:

$$\log R = 0.003145 T - 3.3085, \quad (2-17)$$

where

$R$  = rate of advance of calcination interface, cm/hr,

$T$  = temperature of surroundings, °C.

Assuming that the heat absorbed by the limestone is proportional to the surface area of the receding interface, a constant rate of advance of the interface is predicted. If the rate of movement of the interface is dependent only upon temperature and available area and is independent of size and shape of the particle, the time required to calcine is directly proportional to the size of the piece. Conley,<sup>9</sup> Pehlke and Kim,<sup>10</sup> and others have demonstrated the validity of a constant rate of advance of the calcination interface, although the rate equations vary with the particular stone under study. Thus, in operating practice, it is necessary to evaluate the calcination behavior of a material before specifying operating conditions for a calcination process.

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## Discussion Questions

1. The sinter-roasting of fine nickel sulfide (-200 mesh) has several inherent disadvantages. Its low melting point favors fusion on oxidation, producing a

<sup>8</sup> C. C. Furnas, *Ind. Eng. Chem.* 23, 534 (1931).

<sup>9</sup> J. E. Conley, Technical Publication Number 1037, *Mining Tech.* 3 (1939).

<sup>10</sup> R. D. Pehlke and Y. U. Kim, Private communication, The University of Michigan, 1965.

relatively dense product which is insufficiently active for certain subsequent processing operations. Suggest a process which will result in a more acceptable product.

2. Discuss the economic factors which determine the optimum length for a sinter strand.
3. Summarize the preliminary processing steps for the principal ores of the common metals.
4. Contrast the advantages and disadvantages of sintering and pelletizing of iron oxide fines.
5. What are the relative merits of the shaft kiln, rotary kiln, and rotary hearth furnace for calcining lime?
6. Diagram the steps involved in concentrating and agglomerating taconite ores.
7. Describe various gas treating systems employed to control the sulfur-bearing gases from roasting operations.

## Problems

1. Nickel sulfide roasting is carried out at 1 atm total pressure and 1000°K with gas phase compositions in the ranges 3-10% O<sub>2</sub> and 3-10% SO<sub>2</sub>. Over what portion of these composition ranges is nickel sulfate the stable phase?
2. Sulfide concentrates of copper and cobalt are sulfated in a fluidized bed operation at 950°K and near 1 atm pressure to produce 97% soluble copper and 94% soluble cobalt. Roaster gases are reported to analyze 8% SO<sub>2</sub> and 4% O<sub>2</sub>. Was gas-solid equilibrium reached in this system?
3. Copper and cobalt are to be separated by roasting at 1 atm and 950°K to produce water soluble cobaltous sulfate and water insoluble cupric oxide. Recommend a control point for roaster gas composition.
4. Roasting of sphalerite is being carried out at 1520°F and at an average roaster gas composition of 10% SO<sub>2</sub> and 4% O<sub>2</sub>. The resulting calcine is basic sulfate (ZnO·2 ZnSO<sub>4</sub>). How would you change the gas composition and/or temperature to produce a calcine of:
  - (a) ZnO
  - (b) ZnSO<sub>4</sub>
5. Evaluate the thermodynamic feasibility of roasting to a sulfate and to an oxide for separation in a subsequent leaching operation for sulfide ores containing:
  - (a) iron and copper
  - (b) iron and zinc
  - (c) zinc and cobalt
  - (d) nickel and copper

Specify roaster gas compositions if separation can be accomplished.

6. Calculate the maximum pressure of  $\text{SO}_2$  at which Pb and  $\text{PbO}$  can coexist at  $1100^\circ\text{K}$  under equilibrium conditions (i.e., without forming the lower sulfate  $\text{PbSO}_4 \cdot 4\text{PbO}$ ).
7. Consider the fluidized bed roasting of nickel sulfide at  $2000^\circ\text{F}$  and a rate of 1 ton/hr.

Given: 136  $\text{ft}^3$  (STP) of roaster gas ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{SO}_2$ ) per pound of sulfide. The product contains 0.5% S. Heat losses equal 850,000 Btu/hr. Sensible heat of product equals 400 Btu/lb Ni.

Compute: (a) The heat evolved by oxidation of the nickel sulfide.  
(b) The excess air which is required to fluidize the bed.  
(c) The percentage of thermal energy which is retained in the exiting roaster gas.

8. It is desired to produce a feed for electro-winning of copper from a sulfide ore using a fluidized bed roaster. Specify the required operating temperature of the reactor and the composition of the exiting gas stream.

| Ore Component                            | Composition (wt %) |
|------------------------------------------|--------------------|
| Copper (as sulfide)                      | 48                 |
| Iron (as sulfide)                        | 11                 |
| Sulfur (as sulfide)                      | 21                 |
| $\text{H}_2\text{O}$ , free and combined | 5                  |
| $\text{CO}_2$ , as carbonate             | 3                  |
| Inerts, $\text{SiO}_2$ , etc.            | 12                 |

The oxidizing gas is 10 moles of air/mole of copper supplied to the roaster.

9. One hundred pounds of calcium carbonate is stored in a sealed cannister with a volume of 5  $\text{ft}^3$ . The cannister is heated to  $800^\circ\text{C}$ .
- (a) What is the pressure of  $\text{CO}_2$  at equilibrium?  
(b) How much  $\text{CaO}$  would be formed at equilibrium?
10. Specify operating conditions for a large rotary kiln calcining 1-in. pieces of limestone.

## CHAPTER 3

### Pyrometallurgy II: Oxidation-Reduction Reactions

#### 3-1 Thermodynamic Stability of Mineral Compounds

Less reactive metals, including gold, silver, copper, and the platinum metals, are sometimes found in nature in the metallic state. Most metals, however, are usually found as mineral compounds such as oxides, sulfides, carbonates, or silicates; the mineral may be a single compound or it may be a physical mixture of a number of compounds. As outlined in Chapter 1, a combination of several separation or concentration processes are employed in the extraction of metals from their ores. When further concentration cannot be carried out by physical means, chemical separations must be employed. The conversion of sulfides to oxides by roasting or conversion of carbonates to oxides by calcination are typical pyrometallurgical processes designed to modify the minerals of useful metals to a more easily separable form. The ease with which a metal can be recovered from its mineral form can be evaluated quantitatively in terms of the thermodynamic stability of the mineral compound; consequently, some attention should be given here to the nature of various mineral compounds.

#### Thermodynamic Stability of Oxides

The practicality of chemical processing for the extraction of metals can be assessed on the basis of free energy changes for the reactions involved, a negative free energy change indicating that the reaction will tend to occur. The first step in evaluating the free energy change is to determine standard free energy changes. A convenient means for comparing free energy changes occurring in various chemical reactions is to display them graphically. One useful chart, first proposed by Ellingham,<sup>1</sup> is a plot of the standard free energy of formation versus temperature for a group of compounds of a given type, e.g., oxides of various chemical elements. This chart indicates the relative tendency toward oxidation for these elements and shows directly conditions under which reactions occur, thus providing a basis for evaluating the possibility of chemical separation by an oxidation-reduction reaction. The Ellingham diagram showing the standard free energies of formation of oxides as a function of temperature is presented in Fig. 3-1.

The free energy-temperature relationship shown in Fig. 3-1 is nearly linear. The apparent linearity is the result of heat capacities of reactants and products being essentially equal. The slopes of the plots on the Ellingham diagram are

<sup>1</sup> H. J. T. Ellingham, *J. Soc. Chem. Ind.* **63**, 125 (1944).

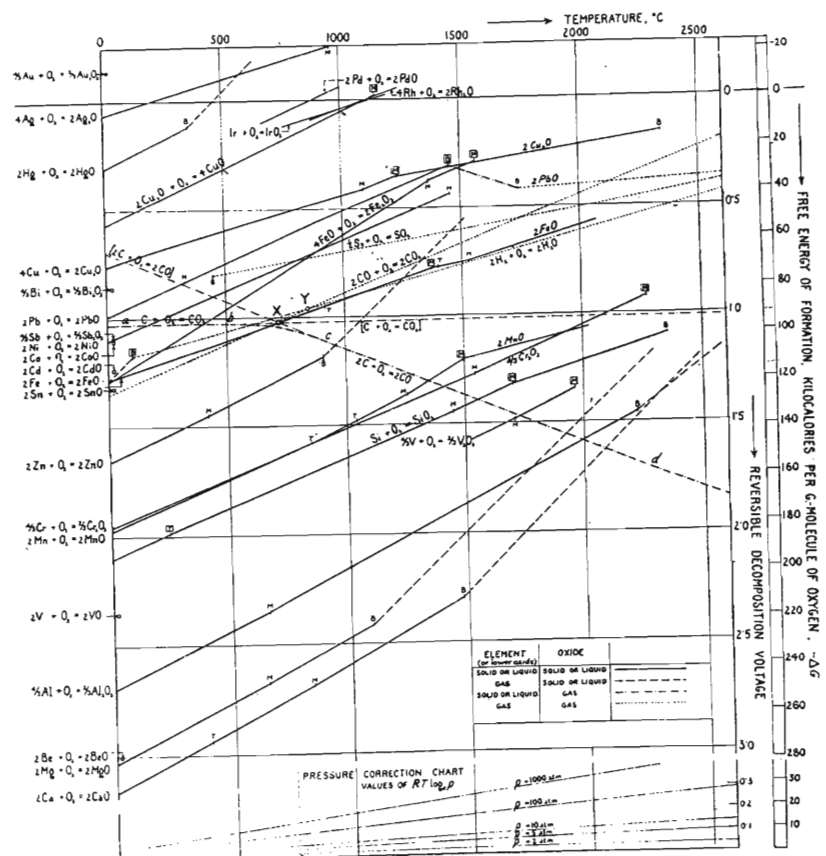


Fig. 3-1. Free Energy of Formation of Oxides

Source: H. J. T. Ellingham, *J. Soc. Chem. Ind.*, 1944, Vol. 63, p. 127, Society of Chemical Industry.

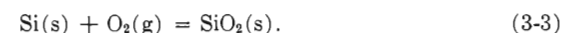
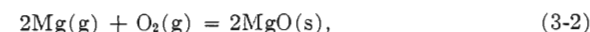
defined by the well-known thermodynamic relationship

$$\left(\frac{\partial \Delta G^0}{\partial T}\right)_P = -\Delta S^0. \quad (3-1)$$

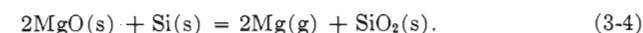
The positive slope for most cases shown in Fig. 3-1 indicates that the entropy change is negative, or that a decrease in entropy occurs for these reactions as written. This is consistent with the fact that a mole of oxygen disappears on reaction, yielding an entropy decrease. The free energy-temperature relationships consist of straight line segments with break points in the lines denoting a phase

change. If the entropy change occurs in the reactants, the increase in entropy by a phase change, e.g., solid to liquid or liquid to gas, increases the entropy of the reactants and results in a more negative entropy change for the reaction. In cases where the product shows a phase change, with an accompanying increase in entropy, the slope of the line decreases in a corresponding manner. Standard free energies of formation at high temperatures for several reactions of metallurgical interest are summarized in Table A-II in the form of equations that are linear with temperature.

The standard free energy change for an overall reduction process can be calculated by combining free energy changes for the individual oxidation-reduction reactions involved. Consider the two reactions,

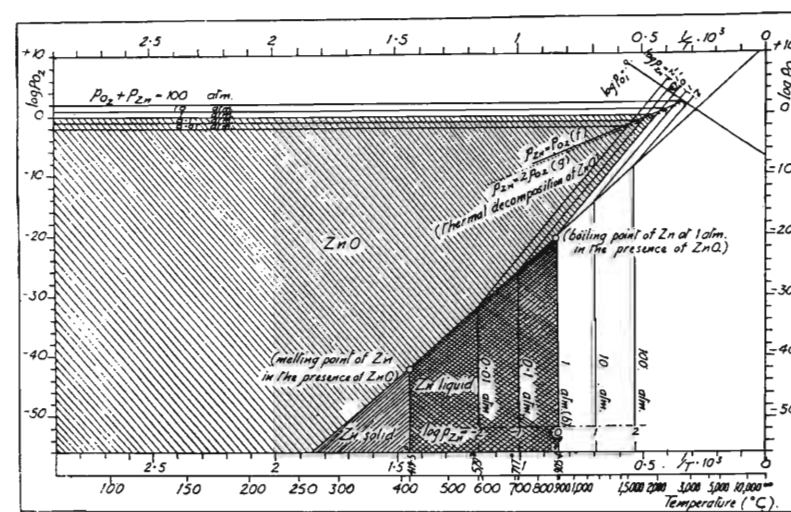


The standard free energy change for the reduction of magnesium oxide by silicon can be determined by subtracting Eq. (3-2) from Eq. (3-3) to obtain



The standard free energy change is given by the difference between the standard free energy changes for Eq. (3-3) and Eq. (3-2), i.e.,

$$\Delta G_4^0 = \Delta G_3^0 - \Delta G_2^0 \quad (3-5)$$



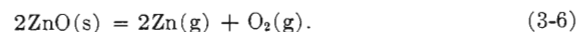
Equilibrium of the System Zn-O

Fig. 3-2. Equilibrium in the System Zn-O

Source: M. J. N. Pourbaix and C. M. Rorive-Boute, *Disc. Faraday Soc.*, 1948, Vol. 4, p. 142, Butterworth and Company (Publ.) Ltd.

This reaction forms the basis for the Pidgeon process<sup>2</sup> for the production of magnesium.

Pourbaix<sup>3</sup> proposed another form of diagram for treating phase equilibria in oxide systems in which he plotted the logarithm of the equilibrium oxygen pressure against reciprocal temperature. An example of a Pourbaix diagram for the zinc-oxygen system is shown in Fig. 3-2. The lines on Fig. 3-2 represent phase equilibria between zinc oxide and zinc in solid, liquid, or gaseous form. The phase equilibria are shifted by pressure, and this is indicated by the vertical lines, which show increasing zinc vapor pressure with increasing temperature. Figure 3-2 shows that heating zinc oxide to high temperatures will result in thermal dissociation, depending upon the partial pressure of oxygen and zinc, according to the reaction,



If zinc oxide decomposes under high vacuum conditions wherein the pressure of zinc is twice the pressure of oxygen in the atmosphere as shown by curve (g) of Fig. 3-2,

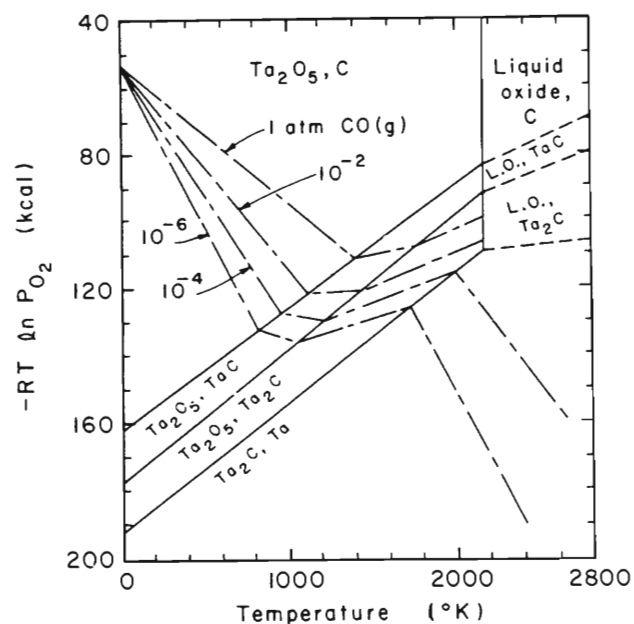


Fig. 3-3. Pourbaix-Ellingham Diagram for the Ta-C-O System

Source: W. L. Worrell and J. Chipman, *Trans. Met. Soc. AIME*, 1964, Vol. 230, p. 1684.

<sup>2</sup> L. M. Pidgeon, *Trans. Canad. Mm. Inst.* **49**, 621 (1946).

<sup>3</sup> M. J. N. Pourbaix, *Bull. Soc. Chim. Belg.* **53**, 145 (1944).

the decomposition pressure or total pressure in the system reaches 0.01 atm at about 1477°C and 1 atm at about 1962°C.<sup>4</sup>

A very useful equilibrium phase diagram can be derived by combining the concepts of the Ellingham and Pourbaix diagrams. This is illustrated in Fig. 3-3, a Pourbaix-Ellingham diagram for the tantalum-carbon-oxygen system. In Fig. 3-3, the near linearity of the Ellingham diagram and the description of phase equilibria of the Pourbaix diagram have been combined by plotting versus temperature the standard free energy of decomposition of the phases in equilibrium to form oxygen gas at 1 atm pressure.

At 1500°K and 1 atm carbon monoxide pressure, tantalum oxide,  $\text{Ta}_2\text{O}_5$ , is in equilibrium with tantalum carbide,  $\text{TaC}$ . If the temperature is increased to 1800°K, the carbide  $\text{Ta}_2\text{C}$  will form, or if at 1500°K the carbon monoxide pressure were increased to several atmospheres, the tantalum carbide would decompose, forming graphite; a decrease in pressure would result in the formation of the dicarbide  $\text{Ta}_2\text{C}$ .

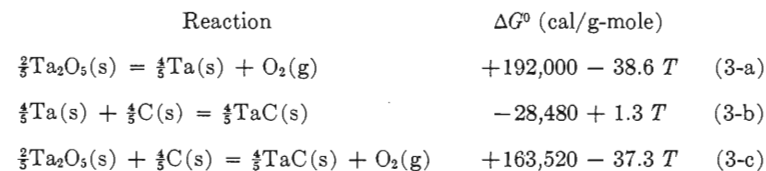
*Example Problem 3-1.* Figure 3-3 is a Pourbaix-Ellingham diagram for the Ta-C-O system. Using the data (averaged for the range 298–2000°K) below,<sup>5</sup> calculate the equation for the line representing the gas-solid equilibrium between carbon,  $\text{Ta}_2\text{O}_5$ , and  $\text{TaC}$  as shown on the diagram. Also calculate the “ $10^{-4}$  atm  $\text{CO(g)}$ ” line shown in the tantalum oxide-graphite field of Fig. 3-3.

| Compound                 | $\Delta G_f^\circ$ (cal/mole) | Melting point (°K) |
|--------------------------|-------------------------------|--------------------|
| $\text{Ta}_2\text{O}_5$  | $-480,000 + 96.5 T$           | 2145               |
| Ta                       | —                             | 3273               |
| $\text{Ta}_2\text{C(s)}$ | $-47,000 + 0.5 T$             | 3773               |
| $\text{TaC(s)}^a$        | $-31,000 + 1.6 T$             | 3983               |
| $\text{TaC(s)}^b$        | $-35,600 + 1.6 T$             | —                  |
| $\text{CO(g)}$           | $-26,760 - 21.0 T$            | —                  |
| $\text{CO}_2\text{(g)}$  | $-94,260 - 0.3 T$             | —                  |

<sup>a</sup> Metal rich carbide.

<sup>b</sup> Carbon rich carbide.

*Solution.* Expressing the reaction for the gas-solid equilibrium in terms of one mole of oxygen:



<sup>4</sup> M. J. N. Pourbaix and C. M. Rorive-Boute, *Disc. Faraday Soc.* **4**, 139 (1948).

<sup>5</sup> W. L. Worrell and J. Chipman, *Trans. Met. Soc. AIME* **230**, 1682 (1964).

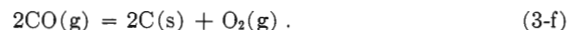
The equilibrium constant for reaction (3-c) can be expressed as

$$K_c = P_{O_2} \quad (3-d)$$

since the solids are at unit activity. Then the line representing the equilibrium between  $Ta_2O_5$ ,  $TaC$ , and  $C$  is

$$-RT \ln P_{O_2} = \Delta G^0 = 163,520 - 37.3 T \text{ cal.} \quad (3-e)$$

Considering a carbon monoxide potential fixed at  $10^{-4}$  atm in the  $Ta_2O_5$ - $C$  field: the equilibrium between carbon, oxygen, and carbon monoxide is



The equilibrium constant for Eq. (3-f) is

$$K_f = \frac{P_{O_2} a_c^2}{P_{CO}^2} \quad (3-g)$$

at unit carbon activity and  $10^{-4}$  atm CO pressure.

$$K_f = P_{O_2}(10)^2 \quad (3-h)$$

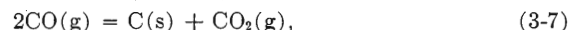
Then the line representing  $10^{-4}$  atm of CO pressure is

$$-RT \ln P_{O_2} = 53,520 + 42.0 T + (8)(2.303)(1.987) T, \quad (3-i)$$

$$-RT \ln P_{O_2} = 53,520 + 78.6 T. \quad (3-j)$$

#### Carbon-Oxygen Equilibria—The Boudouard Reaction

The Boudouard reaction,



is composed of the reactions for the oxidation of carbon to carbon dioxide and carbon monoxide:



The corresponding standard free energies of formation for carbon monoxide and carbon dioxide can be represented in the temperature range 1500–2000°K by the relationships,

$$\Delta G_8^0 = -94,755 + 0.02 T, \quad (3-10)$$

$$\Delta G_9^0 = -28,200 - 20.16 T. \quad (3-11)$$

The corresponding free energy change in the same temperature range for the Boudouard reaction Eq. (3-7) is

$$\Delta G_7^0 = -38,355 + 40.34 T. \quad (3-12)$$

The Boudouard reaction forms the basis for carbothermic reduction of metals and is extremely important in smelting processes involving carbon as a reducing agent, e.g., the iron or lead blast furnace process or the smelting of tin or zinc. From Fig.

3-1, it can be seen that at 1 atm the standard free energy for the oxidation of carbon to form carbon monoxide and the standard free energy of reaction for the formation of carbon dioxide are the same at a temperature of approximately 710°C. Below this temperature, carbon monoxide is a more active reducing agent, whereas above it, solid graphite is the more active reducing agent. The oxidation of carbon will produce a mixture of carbon monoxide and carbon dioxide, but at low temperatures carbon dioxide will be the predominant component of the gas phase in equilibrium with solid carbon, whereas at higher temperatures carbon monoxide is the predominant gaseous component.

**Example Problem 3-2.** The standard free energies of formation for  $CO$  and  $CO_2$  are equal at 710°C. In a system consisting of only carbon and oxygen with excess solid carbon present, what would the gas phase composition be at 1 atm total pressure? At  $10^{-4}$  atm?

**Solution.** Since the  $\Delta G^0$  for the reactions,



is equal at 710°C, their difference is zero, and  $\log K = 0$  for the reaction,



Then at 710°C

$$K = 1 = \frac{P_{CO_2}}{P_{CO}^2} \quad (3-d)$$

but

$$P_{CO} = 1 - P_{CO_2}. \quad (3-e)$$

Substitution of Eq. (3-e) into (3-d) and rearranging,

$$(P_{CO_2})^2 - 3P_{CO_2} + 1 = 0, \quad P_{CO_2} = 0.382 \text{ atm.} \quad (3-f)$$

Then

$$X_{CO_2} = 0.382,$$

$$X_{CO} = 0.618.$$

At  $10^{-4}$  atm, a similar calculation yields  $X_{CO_2} = 0.0001$ . The reduction in pressure, following LeChatelier's Principle, drives Eq. (3-c) to the left.

#### Thermodynamic Stability of Sulfides

The standard free energies of formation of common metallic sulfides are presented on an Ellingham diagram (Fig. 3-4). The position of the curve for the reaction,



shows that oxygen will displace sulfur from the sulfides of all of the metals except the alkaline earths, i.e., an oxidizing roast can be employed to convert sulfides to oxides, as discussed in the previous chapter. In contrast, the position for the curve

for the reaction,



shows that hydrogen is not suitable for reducing sulfides, and, similarly, neither is carbon.

The possibility of desulfurizing steels with calcium is clearly shown by the position of the line for the reaction,

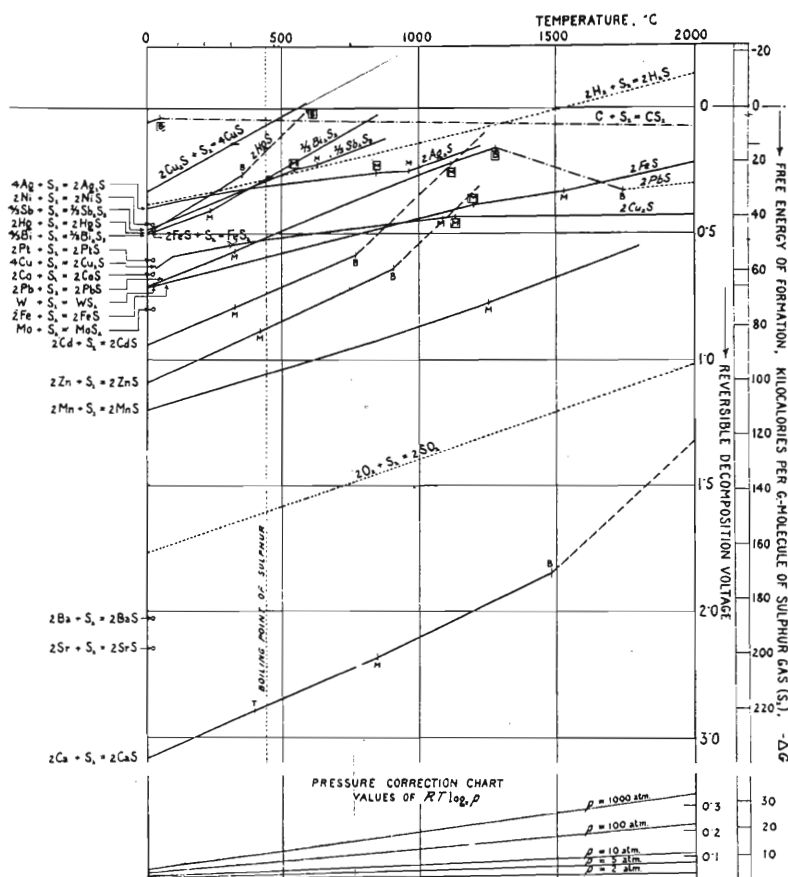


Fig. 3-4. Free Energy of Formation of Sulfides

Source: H. J. T. Ellingham, *J. Soc. Chem. Ind.*, 1944, Vol. 63, p. 128, Society of Chemical Industry.

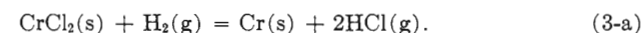
The ability of manganese to form manganese sulfide in steels during hot rolling is suggested by the position of the line for the formation of manganese sulfide relative to iron sulfide, or the sulfides of other elements commonly present in steels.

### Reducibility of Chlorides

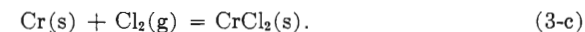
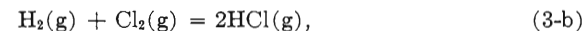
The Ellingham diagram giving the standard free energy of formation of chlorides versus temperature is presented in Fig. 3-5. The position of the curve for the formation of carbon tetrachloride clearly shows that carbon is not a suitable reducing agent for chlorides.

The position of the curve for the formation of hydrogen chloride indicates that hydrogen is a potential reducing agent for several of the metallic chlorides. If the curve for the standard free energy of formation for a metallic chloride lies above that for the formation of hydrogen chloride at a given temperature, the metallic chloride will be reduced to the metal by hydrogen, provided the substances are in their standard states. Conversely, a metal whose chloride lies below the hydrogen chloride curve at a given temperature would, under standard conditions, be converted to the chloride by treatment with HCl gas. The hydrogen chloride curve decreases slightly with increasing temperature, whereas the curves for most of the other chlorides increase with temperature, thus providing a more favorable condition for hydrogen reduction at higher temperatures. The hydrogen reduction of chromium chloride is illustrated in the following example problem.

**Example Problem 3-3.** The reduction of chromium chloride by hydrogen gas has been proposed as a method for producing pure chromium. Calculate the purity of hydrogen gas that must be maintained in a reaction chamber at 800°C to carry out the reduction,



**Solution.** Equation (3-a) can be expressed as the difference between the reactions,



From Fig. 3-5, the standard free energy change for Eq. (3-a) is

$$\Delta G^\circ_a = \Delta G^\circ_b - \Delta G^\circ_c = -48,500 - (-63,300) = +14,800 \text{ cal.} \quad (3-d)$$

Thus it can be seen that the reaction is not spontaneous at standard conditions. At equilibrium at 800°C, with the solid phases at unit activity

$$\Delta G^\circ_a = -RT \ln \left[ \frac{P_{\text{HCl}}^2 a_{\text{Cr}}}{P_{\text{H}_2} a_{\text{CrCl}_2}} \right] = -RT \ln \left[ \frac{P_{\text{HCl}}^2}{P_{\text{H}_2}} \right] = 14,800, \quad (3-e)$$

$$\log \left[ \frac{P_{\text{HCl}}^2}{P_{\text{H}_2}} \right] = -3.017. \quad (3-f)$$

Assuming a total pressure of 1 atm in the system,

$$P_{\text{HCl}} + P_{\text{H}_2} = 1. \quad (3-g)$$

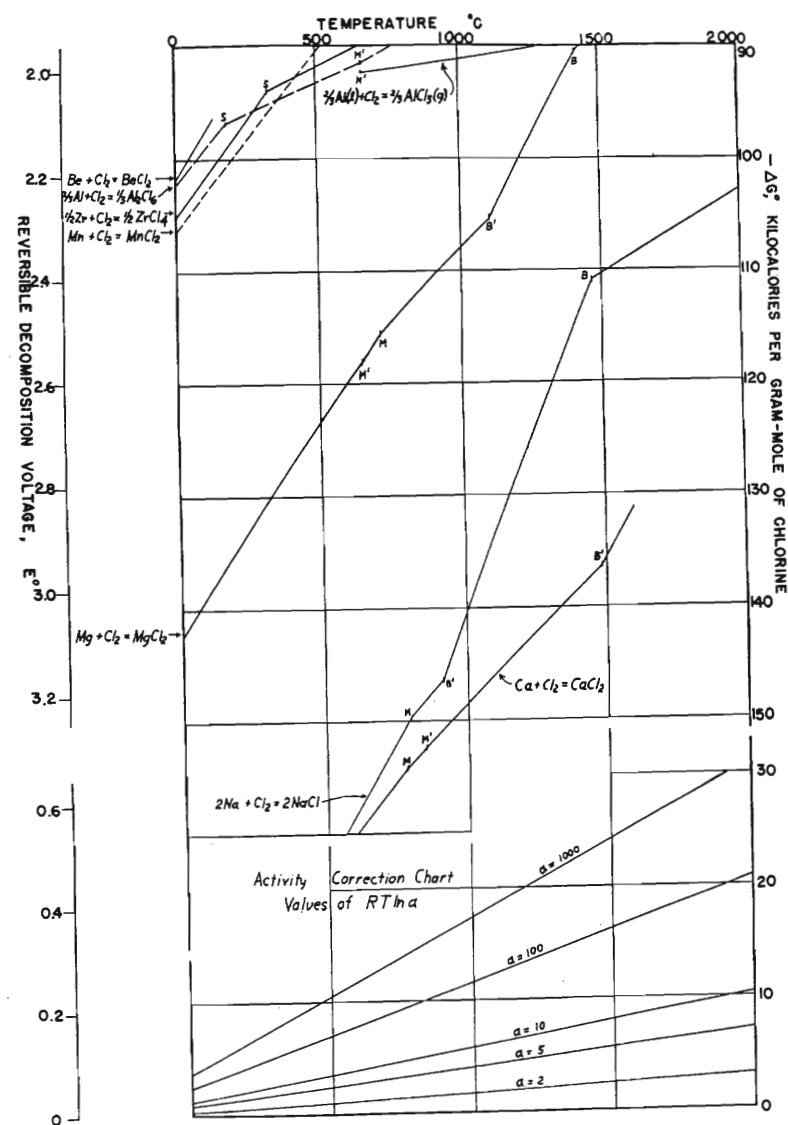
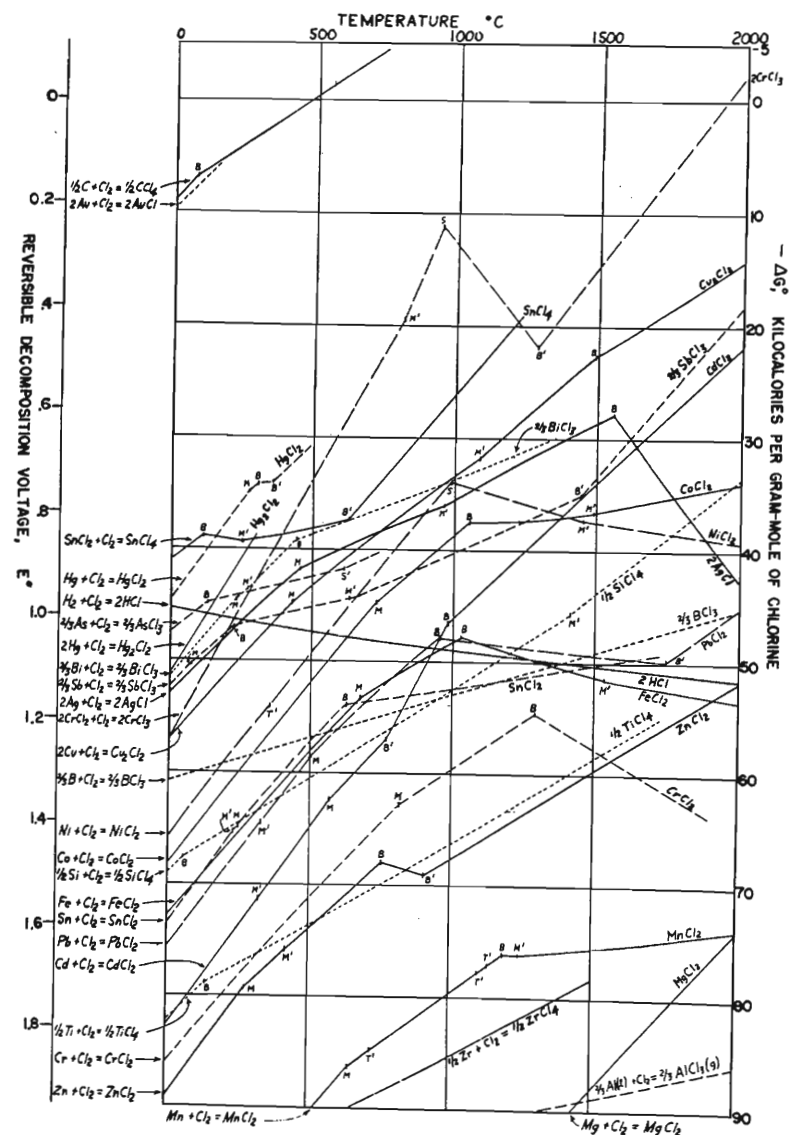


Fig. 3-5. Standard Free Energies of Formation for Metal Chlorides as a Function of Temperature,  $\Delta G^\circ$  between +5,000 and -160,000 cal.

Source: H. H. Kellogg, *Trans. AIME*, 1950, Vol. 188, p. 864.

Then

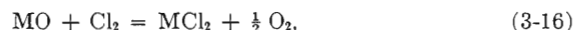
$$P_{\text{HCl}} = 0.031 \text{ atm,}$$

$$P_{\text{H}_2} = 0.969 \text{ atm.}$$

In order to cause the reaction to occur as written, the concentration of HCl must be maintained below 3.1 vol% (at 1 atm), e.g., by removing HCl and adding dry hydrogen to the system.

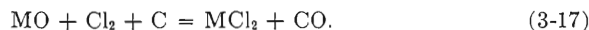
Magnesium chloride is the most stable chloride shown in Fig. 3-5, with the exception of the chlorides of sodium and calcium. The high stability of magnesium chloride forms the basis of the Kroll process for the production of titanium sponge by magnesium reduction of titanium tetrachloride.

The chlorination of metallic oxides can be accomplished for several metals by heating the oxide in chlorine gas, to allow a reaction of the general form,



to occur. A comparison of the standard free energies of formation of the oxides and chlorides show that this reaction can readily be carried out at 1000°C for lead, copper, manganese, nickel, zinc, tin, and iron.

Metals with more stable oxides, such as magnesium, chromium, titanium, aluminum, and silicon, can be chlorinated directly in the presence of a reducing agent such as carbon, carbon monoxide, or sulfur. For example,



Anhydrous magnesium chloride has been produced commercially from MgO using coke and chlorine gas. Titanium tetrachloride can be produced similarly by the chlorination of ilmenite, the most common titanium mineral (nominal composition,  $\text{FeTiO}_3$ ).

#### Stability of Carbides and Nitrides

The standard free energies of formation for several metallic carbides and nitrides also are presented in Table A-II. A comparison made between standard free energies of formation of carbides or nitrides in temperature ranges typical of pyrometallurgical operations will show that titanium and zirconium carbides and nitrides are highly stable. This precludes the possibility of carbothermic reduction of zirconium or titanium oxides except at extremely high temperatures. On the other hand, iron nitride is one of the least stable metallic nitrides, whereas nitrides of chromium, vanadium, and aluminum are much more stable, and as such are often found as inclusions in steel.

### 3-2 Oxidation-Reduction Reactions Involving Liquid Metallic Solutions

The foregoing discussion has considered standard free energy changes in which the reactants and products were present in the most commonly defined state, i.e., as pure materials. In practical metallurgical operating situations, reactions are often

carried out in the presence of a liquid metallic phase that may have an appreciable solubility for many of the reactants and products present. It is necessary under these circumstances to consider the resulting change in the activities of the various components. In some circumstances an advantage in thermodynamic calculation is realized by changing the standard state.

#### Thermodynamics of Metallic Solutions

The chemical activity,  $a$ , (the tendency of a component of a phase to react), is dependent upon the concentration of the component in that phase, as well as temperature (see Eq. 3-22). In a solution, the chemical activity of a component is related in some fashion to the amount of the component present. As an example, if liquid metal A and liquid metal B are mixed in equal molar proportion, component A might have about one-half the chemical activity of pure liquid A. If the solution were more dilute in A, its activity would be less. A component whose activity is directly proportional to its concentration expressed as mole fraction is said to be ideal and to obey Raoult's law:

$$a_A = \frac{\text{moles A}}{\text{total moles}} = \frac{n_A}{n} = X_A. \quad (3-18)$$

At  $n_A = n$  in Eq. (3-18),  $a = 1$ . Thus, the pure phase is the reference concentration or the *standard state*. The reference concentration could also have been chosen at some other point. For example, a 1 mol % solution could be used as the standard state and the activities indexed from that point. Then, in an ideal solution, the component activities are equal to molar percentages, i.e., a 1 mol % solution would have an activity equal to 1, whereas a pure solution of a component would have an activity (index) of 100.

Other standard states often are used as well. For a gas, the standard state is taken usually as 1 atm pressure of that particular gas component. An ideal gas with a partial pressure of 1 torr (1 mm of mercury) would have an activity of 1/760. If, however, 1 torr had been chosen as the standard state, the activity would be equal to 1 if the gas component were at a pressure of 1 torr and equal to 760 at 1 standard atm. In metallic solutions, a standard state often is chosen such that the activity at infinite dilution is equal to the concentration in weight percent. This standard state, referred to as the hypothetical 1 wt% solution, often is convenient since compositions in industrial practice generally are expressed in weight percent.

*Free Energy and Activity.* The free energy of a component,  $i$ , is related to the chemical activity of the component by the relationship

$$\bar{G}_i - \bar{G}_i^0 = RT \ln (a_i) = 4.575 T \log_{10} (a_i), \quad (3-19)$$

where  $\bar{G}_i$  is the free energy of component  $i$  within the phase and  $\bar{G}_i^0$  is the free energy of the component in its standard state in which  $a_i^0 = 1$ .

*Nonideal Solutions.* Most real solutions are not ideal. In order that a solution be ideal, the atomic species of the component must interact with those of the other components in the same manner that they do with their own.

The activity of silicon in molten iron is shown in Fig. 3-6. Silicon does not

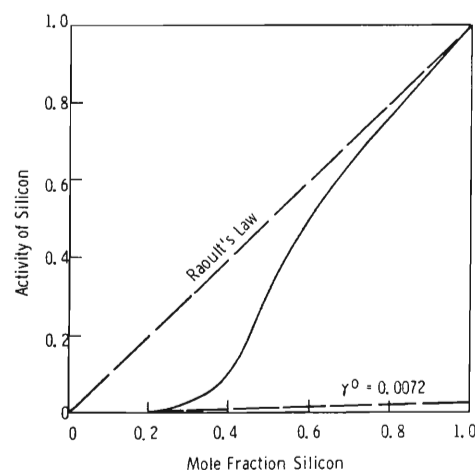


Fig. 3-6. Activity of Silicon in Liquid Iron at 1600°C (2912°F)

Based on *Basic Open Hearth Steelmaking*, 3rd Edition, edited by G. Derge, AIME, New York, 1964, p. 674.

behave ideally. The silicon atoms are more strongly associated with the iron atoms than with other silicon atoms, thus lowering the chemical activity of silicon below the ideal behavior prediction. The strong association between silicon and iron atoms is indicated by the facts that (1) energy is given off (exothermic heat of solution) when silicon is added to iron, and (2) intermetallic compounds of iron and silicon are readily formed in the solid phase.

Figure 3-7 shows the activity of copper in iron. Unlike silicon, copper atoms do not associate as readily with iron atoms as with other copper atoms. Therefore, the chemical activity of copper is increased above that predicted on the basis of ideal behavior. This is also shown by (1) endothermic heat of solution of copper, and (2) the tendency to form two immiscible liquids.

Since few solutions are ideal, it is necessary to account for this when calculating activities from concentrations. This is done by means of an activity coefficient, defined by the ratio of activity to mole fraction:

$$\gamma_i = \frac{a_i}{X_i} \quad (3-20)$$

**Dilute Solution Behavior.** In considering copper and silicon solutions with liquid iron, it can be noted from Figs. 3-6 and 3-7 that although solutions of copper and silicon in iron do not behave ideally, their activities in *dilute solution* are *proportional* to concentration. Such behavior is described by *Henry's law*. The activity coefficient for the Henry's law region is defined by

$$\gamma_i^0 = \lim (\gamma_i)_{X_i \rightarrow 0} = \lim \left[ \frac{a_i}{X_i} \right]_{X_i \rightarrow 0} \quad (3-21)$$

A summary of activity coefficients at infinite dilution for a number of metallic solutions is presented in Table A-III.

From the definition of the activity coefficient in Eq. (3-20) and the defining expression for free energy it can be shown that

$$\frac{d(\ln \gamma_i)}{d(1/T)} = \frac{\Delta H_i}{R} \quad (3-22)$$

where  $\Delta H_i$  is the partial molar enthalpy of solution for component  $i$ . This result suggests that a straight line extrapolation of  $\ln \gamma_i$  versus the inverse of the absolute temperature may be used over a short temperature range to obtain values of  $\gamma_i$  at temperatures other than those for which data are available.

For cases where the solutions of interest are dilute, as in most refining operations, it often is convenient to refer activities to the Henry's law behavior of the dilute solution, expressed in weight percent. The *Henrian activity*,  $h$ , then is defined

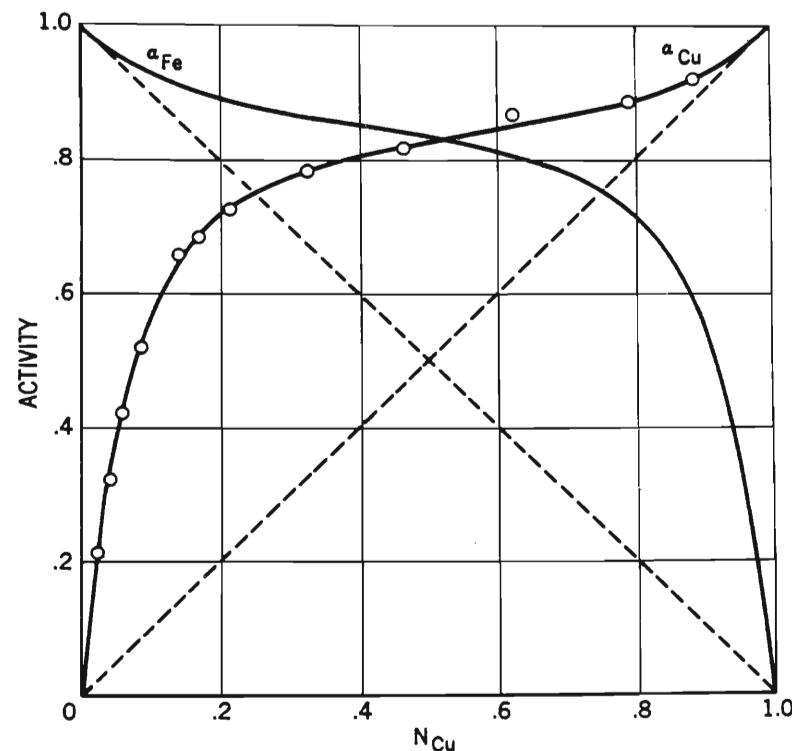


Fig. 3-7. Activities of Copper and Iron in Fe-Cu Alloys at 1550°C. (Standard State: Pure Liquid)

Source: J. P. Morris and G. R. Zellers, *Met. Soc. Trans. AIME*, 206, (1956), p. 1089.

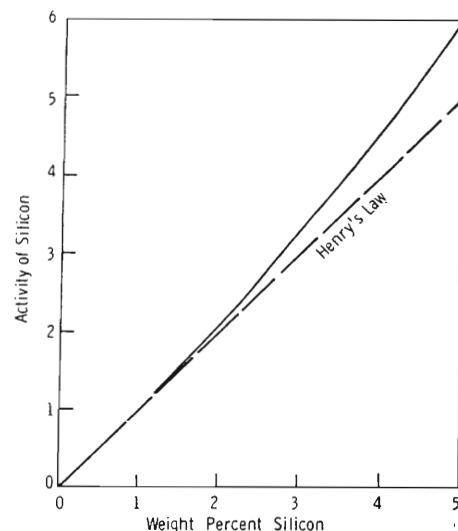


Fig. 3-8. Activity of Silicon in Liquid Iron at 1600°C (Standard State: Infinite Dilution Referred to One Weight Percent Solution)

Based on *Basic Open Hearth Steelmaking*, 3rd Edition, edited by G. Derge, AIME, New York, 1964, p. 674.

by the expression,

$$h_i = \left[ \frac{a_i}{(a_i/\text{wt}\% i)} \right]_{\text{wt}\% i \rightarrow 0} \quad (3-23)^*$$

and on the limiting slope portion of the activity curve, the concentration in weight percent can be substituted directly for the activity.

At concentrations beyond the Henry's law range, a *Henrian activity coefficient*,  $f$ , is used to define the activity relative to the concentration. The Henrian activity coefficient is defined by the relationship,

$$f_i = \left( \frac{h_i}{\text{wt}\% i} \right), \quad (3-24)$$

whereby

$$h_i = f_i(\text{wt}\% i). \quad (3-25)$$

In accordance with Eq. 3-23 the activity coefficient approaches unity as the concentration of the solute approaches zero. Figures 3-8 and 3-9 show the dilute solution behavior in molten iron for silicon and copper, respectively.

\* Note: In deriving these dilute solution relationships, the symbol,  $h$ , has been used for Henrian activity. However, the reader should be aware that the symbol,  $a$ , often is used for activity, regardless of standard state; even in this book, e.g., Fig. 3-9:

### Conversion from One Standard State to Another

It is frequently necessary to convert from one standard state to another in order to make use of data which may give  $\Delta G^0$  as a function of temperature relative to a reference state which differs from the desired one. For example, the free energy

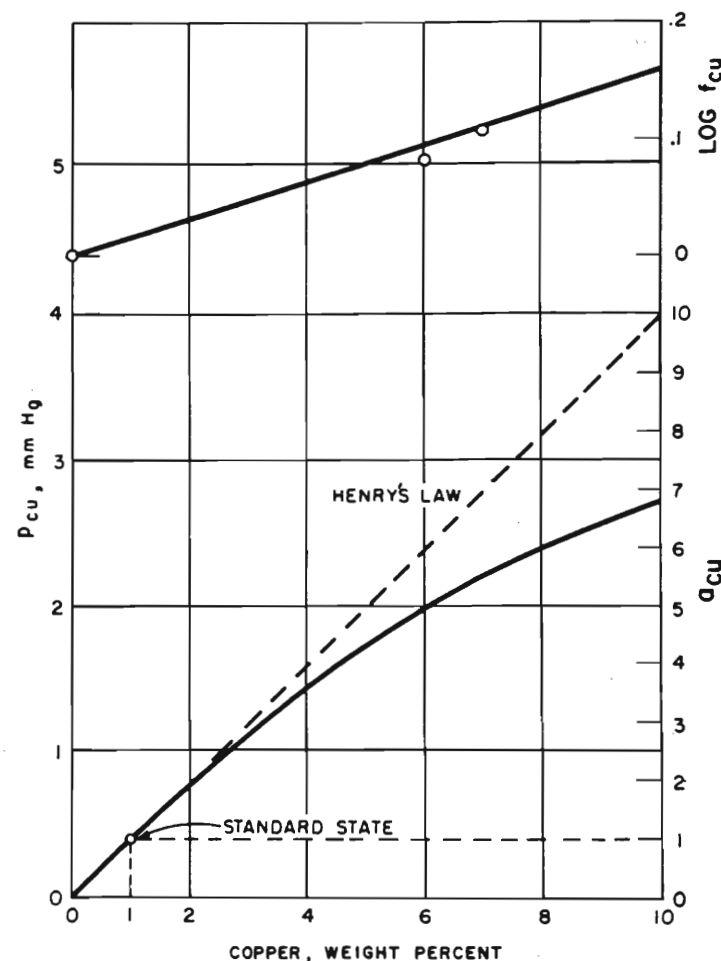


Fig. 3-9. Vapor Pressure and Activity of Copper Dissolved in Liquid Iron at 1540°C (Standard State: Infinite Dilution Referred to One Weight Percent Solution)

Source: *Basic Open Hearth Steelmaking*, 3rd Edition, edited by G. Derge, AIME, New York, 1964, p. 652.

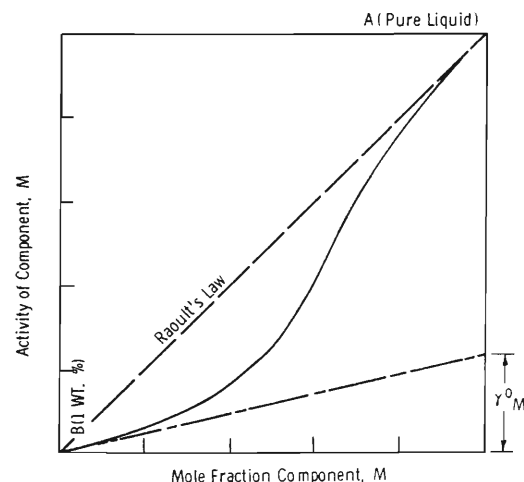
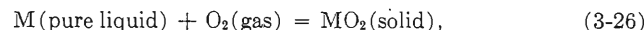


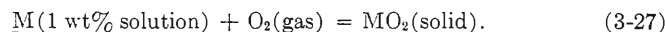
Fig. 3-10. Activity-Composition Diagram Showing Factors Involved in Converting Activities from One Standard State to Another

of formation of a metal oxide may be known for the reaction,

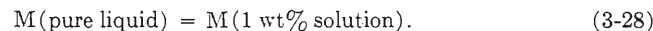


but the oxidation of interest may occur from solution in a liquid metal solvent, say liquid iron. The activity of the metal must be expressed in terms of its concentration in solution in liquid iron. Figure 3-10 shows the assumed activity of a given metal,  $M$ , in solution in iron as a function of mole fraction,  $X_M$ .

If the reaction of interest involves a dilute solution of  $M$  in iron such that the activity could be closely represented by Henry's law behavior, a standard state of infinite dilution referred to weight percent (State  $B$  of Fig. 3-10) would be more convenient. The reaction of interest then would be\*



Subtraction of Eq. 3-27 from Eq. 3-26 yields



Equation 3-28 represents the conversion of standard states, i.e., from State  $A$  to State  $B$  on Fig. 3-10. This conversion is usually not given in thermodynamic data references and will be developed, using an iron-base solution as an example. A parallel development could be applied to other solvents, or to other standard states.

The difference in standard free energy changes for the two reactions is

$$\Delta G_{26}^0 - \Delta G_{27}^0 = \Delta G_{28} = -RT \ln \frac{K_{26}}{K_{27}} = +RT \ln \frac{a_M}{h_M}, \quad (3-29)$$

\* The underline notation refers to the element in metallic solution.

where  $K_{26}$  and  $K_{27}$  are the equilibrium constants for the reactions of Eqs. 3-26 and 3-27, respectively.  $a_M$  is the activity of  $M$  in solution relative to liquid pure  $M$  and  $h_M$  is the Henrian activity as defined by Eq. 3-23. The activity of solute  $M$ , relative to State  $A$ , is  $a_M$ . The activity of solute  $M$ , relative to State  $B$ , is

$$h_M = f_M(\text{wt}\% M).$$

The Henrian activity coefficient defines the deviation from Henry's law behavior, and referring to Fig. 3-10

$$f_M = \frac{h_M}{(\text{wt}\% M)} = \frac{a_M}{(\gamma_M^0 X_M)}.$$

Rearranging,

$$a_M = \frac{h_M \gamma_M^0 X_M}{\text{wt}\% M}. \quad (3-30)$$

The relationship between mole fraction and weight percent is

$$X_M = \frac{\text{wt}\% M}{(AW)_M} \left/ \left[ \frac{\text{wt}\% M}{(AW)_M} + \frac{100 - \text{wt}\% M}{(AW)_S} \right] \right., \quad (3-31)$$

where  $(AW)_M$  is the atomic weight of  $M$  and  $(AW)_S$  is the atomic weight of the solvent, in this case 55.85 for iron. Application of Eq. 3-31 to a dilute iron solution

$$X_M = \text{wt}\% M \left[ \frac{0.5585}{(AW)_M} \right]. \quad (3-32)$$

Noting that the standard state solution follows infinite dilution behavior, Eq. 3-32 may be substituted into 3-30 and Eq. 3-29 yields

$$\Delta G_{28} = RT \ln \left[ \frac{0.5585 \gamma_M^0}{(AW)_M} \right]. \quad (3-33)$$

Equation 3-33 represents the free energy change for conversion of standard states according to Eq. 3-28. Thus the standard free energy change for Eq. 3-27 is

$$\Delta G_{27}^0 = \Delta G_{26}^0 - RT \ln \left[ \frac{0.5585 \gamma_M^0}{(AW)_M} \right] = -RT \ln \left[ \frac{a_{MO_2}}{h_M P_{O_2}} \right]. \quad (3-34)$$

The Henrian activity may be taken as the concentration in weight percent, i.e.,  $h_M \simeq \text{wt}\% M$ , in the dilute solution region.† This convenience represents a substantial advantage in most calculations involving dilute solutions.

Free energy changes for conversion of the standard state from the pure component to the infinitely dilute solution referred to 1 wt% are presented in Table A-IV for common alloying elements in liquid iron.

† It should be noted that the extent of the dilute solution region depends upon experimental accuracy.

## Solute Interactions in Dilute Solutions

The thermodynamic properties of a solute in dilute solution can be influenced by the presence of other alloying elements. The prediction of these influences ultimately may be accomplished entirely from statistical mechanical considerations. However, at present, liquid solution models that are simple enough for analytical treatment are inadequate for this purpose. As a means for expressing experimental data on dilute solutions, Wagner<sup>6</sup> devised the concept of the *interaction parameter*. The interaction parameter is a coefficient in a Taylor series expansion of the logarithm of the activity coefficient taken at infinite dilution and expressed in terms of the concentration of alloying elements:

$$\ln \gamma_i = \ln \gamma_i^0 + \left[ x_i \left( \frac{\partial \ln \gamma_i}{\partial x_i} \right)_{x_{\text{solvent}} \rightarrow 1} + x_j \left( \frac{\partial \ln \gamma_i}{\partial x_j} \right)_{x_{\text{solvent}} \rightarrow 1} + \dots \right] + \left[ \frac{1}{2} x_i^2 \left( \frac{\partial^2 \ln \gamma_i}{\partial x_i^2} \right)_{x_{\text{solvent}} \rightarrow 1} + x_i x_j \left( \frac{\partial^2 \ln \gamma_i}{\partial x_i \partial x_j} \right)_{x_{\text{solvent}} \rightarrow 1} + \dots + \dots \right] \quad (3-35)$$

If all except the first-order terms are neglected, the expression for the logarithm of the activity coefficient becomes linear with respect to the mole fractions of the solutes present in the dilute alloy.

$$\ln \gamma_i = \ln \gamma_i^0 + x_i \epsilon_i^i + x_j \epsilon_i^j + x_k \epsilon_i^k + \dots \quad (3-36)$$

The interaction parameters are thus defined as

$$\epsilon_i^i = \left( \frac{\partial \ln \gamma_i}{\partial x_i} \right)_{x_{\text{solvent}} \rightarrow 1}, \quad \text{self-interaction parameter,} \\ \text{i.e., deviation from Henry's law;} \\ \epsilon_i^j = \left( \frac{\partial \ln \gamma_i}{\partial x_j} \right)_{x_{\text{solvent}} \rightarrow 1}, \quad \text{ternary interaction parameter.}$$

The experimental determination of the parameter  $\epsilon_i^i$ , which represents the influence of alloying element  $i$  on its own activity coefficient in dilute solution, can be accomplished from thermodynamic studies of the dilute binary alloy. The parameter  $\epsilon_i^j$  represents the effect of additions of component  $j$  on the activity coefficient of component  $i$  when both are very dilute. Thermodynamic data on the dilute ternary alloy are required to compute this parameter.

The inclusion of second-order terms would seem to permit a better representation of the data since a binomial expression could be fitted to the activity data rather than a linear one. Indeed, such a representation can be extended validly to compositions further away from the infinitely dilute solution than can the linear form!

<sup>6</sup> C. Wagner, *Thermodynamics of Alloys*, p. 52, Addison-Wesley, Reading, Mass., 1952.

<sup>7</sup> P. H. Turnock and R. D. Pehlke, *Trans. Met. Soc. AIME* **236**, 1540 (1966).

It can be demonstrated from the Gibbs-Duhem equation that

$$\epsilon_i^j = \epsilon_j^i.$$

This reciprocity relationship is an important advantage of the Wagner representation.

A slight modification of this representation has been proposed<sup>8</sup> that involves the use of weight percent as a concentration variable rather than mole fraction, and also common logarithms rather than natural ones:

$$\log f_i = \log f_i^0 + e_i^i (\% i) + e_i^j (\% j) + \dots, \quad (3-37)$$

where

$$f_i = \frac{h_i}{\% i} \quad \text{and} \quad e_i^j = \left[ \frac{\log f_i}{\% j} \right]_{\% \text{solvent} \rightarrow 100} \quad (3-38)$$

The reciprocal relationship for this parameter is

$$e_j^i = e_i^j \frac{M_j}{M_i} + 0.434 \times 10^{-2} \left[ \frac{M_i - M_j}{M_i} \right], \quad (3-39)$$

where  $M$  is the atomic weight of the subscripted specie. The relationship between the two parameters is

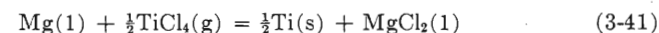
$$\epsilon_i^j = \frac{(2.303)(100)M_j}{M_{\text{solvent}}} e_i^j + \frac{M_{\text{solvent}} - M_j}{M_{\text{solvent}}}. \quad (3-40)$$

It can be shown that the interaction parameter will vary linearly with reciprocal absolute temperature, providing the partial molar enthalpy is essentially independent of temperature. A summary of interaction parameters in ferrous and non-ferrous systems is presented in Tables A-V and A-VI.

## 3-3 Industrial Application of Reduction Reactions

The thermodynamics of reduction reactions plays a role in several commercial processes. Examples are presented for reduction by hydrogen, carbon, and metallic elements such as magnesium and silicon.

The *Kroll process*<sup>9</sup> is employed to reduce the tetrachlorides of titanium or zirconium with magnesium metal. The high stability of magnesium chloride (as shown in Fig. 3-5) indicates that the reduction reaction



is favorable for production of titanium. A flow diagram for this process is shown in Figure 3-11. The anhydrous magnesium chloride byproduct is recycled to produce magnesium metal and chlorine gas.

The titanium tetrachloride used in the Kroll Process is prepared by heating titania and carbon in an electric furnace to form titanium carbide which in turn is

<sup>8</sup> J. Chipman, *J. Iron Steel Inst.* **180**, 97 (1955).

<sup>9</sup> W. J. Kroll, *Trans. Electrochem. Soc.* **78**, 35 (1940).

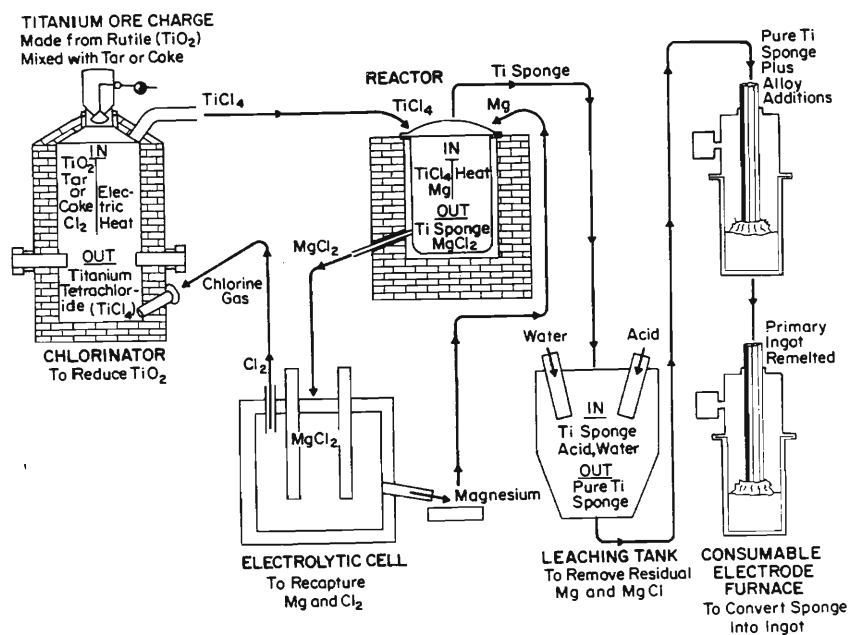


Fig. 3-11. Flow Diagram for Kroll Process

Based on S. C. Williams, *Report on Titanium*, Brundage, Story and Rose, New York, 1965.

reacted with chlorine gas. The titanium tetrachloride is vaporized by the exothermic reaction and condensed as a liquid. Redistillation of the tetrachloride will improve the purity of the titanium produced from it.

The Kroll process is conducted in a heated steel chamber that is maintained at a temperature of about 750°C. Magnesium bars are placed in the bottom of the chamber, which is evacuated and filled with helium; hydrogen flushing at temperature is sometimes used to remove oxygen from the chamber surfaces. The  $\text{TiCl}_4$  is allowed to drip on the molten magnesium, where it reacts exothermically to form titanium sponge and magnesium chloride.

Sodium reduction of  $\text{TiCl}_4$  also is used to produce titanium. The chloride processing avoids contamination with carbon, nitrogen, or oxygen which render titanium brittle.

Zirconium sponge is produced in the same manner.  $\text{ZrCl}_4$  is a solid at ambient temperatures and is vaporized by heating in the upper zone of a closed chamber. The  $\text{ZrCl}_4$  vapor diffuses to the lower zone where it reacts with liquid magnesium at about 800°C. Zirconium also has been produced by calcium or calcium hydride reduction of zirconia.

*Production of Tungsten*—The principal minerals of tungsten are wolframite

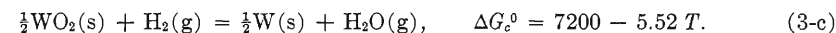
( $\text{FeWO}_4$ ) and scheelite ( $\text{CaWO}_4$ ). By suitable chemical processing, tungsten is separated from these minerals and converted to sodium tungstate, from which the pure oxide is precipitated. The oxide is then reduced to metallic tungsten by reaction with dry hydrogen at a temperature between 1200 and 1400°C.

*Example Problem 3-4.* In reducing tungsten trioxide with hydrogen at 1400°C, the thermodynamically limiting step is the final reduction of  $\text{WO}_2$  to metallic tungsten. What is the maximum concentration of water vapor which could be allowed in the reducing atmosphere?

*Solution.* From Table A-II



Combining Eqs. (3-a) and (3-b)



The equilibrium constant for Eq. (3-c) at 1400°C is

$$K = \frac{a_{\text{W}^{1/2}} P_{\text{H}_2\text{O}}}{a_{\text{WO}_2^{1/2}} P_{\text{H}_2}} \quad (3-d)$$

$$\log K = \frac{-7200}{4.575(1673)} + \frac{5.52}{4.575}$$

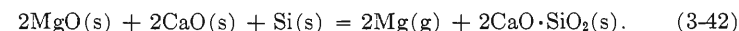
$$\log K = -0.941 + 1.207 = 0.266.$$

For this case, the activities of tungsten and tungsten oxide are unity and

$$K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = 1.84.$$

At 1400°C and any total pressure of hydrogen and water vapor, the reducing gas must be less than about 65% water vapor to effect the conversion to metallic tungsten.

The *Pidgeon process* is employed to produce magnesium from calcined dolomite by the reaction,



The magnesium is evolved from the lime as a vapor and the free energy change for the reaction is reduced by operating at a low partial pressure in the reaction vessel. Furthermore, the free energy change for the reaction is lowered because the calcium oxide reacts with the silica to form a silicate.

*Example Problem 3-5.* What is the minimum temperature at which the Pidgeon process (Eq. 3-42) can be carried out with a partial pressure of magnesium over the solid reactants of 1 mm Hg?

*Solution.* The standard free energy for Eq. (3-42) can be expressed<sup>10</sup> as

$$\Delta G^\circ = 122,400 + 11.74 T \log T - 100.38 T. \quad (3-a)$$

The equilibrium constant, assuming unit activity for the solid reactants, is

$$K = \frac{P_{Mg}^2 a_{CaO} \cdot SiO_2^2}{a_{MgO}^2 a_{CaO}^2 a_{Si}} = (P_{Mg}(\text{atm}))^2. \quad (3-b)$$

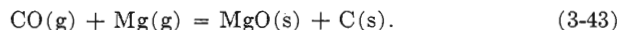
The equilibrium partial pressure of magnesium, expressed in millimeters of mercury (torr), is given by the relationship

$$\log P_{Mg} = \frac{-\Delta G_a^\circ}{2(4.575)T} + 2.88. \quad (3-c)$$

where the latter term converts from atmospheres to millimeters of mercury. A trial and error solution of Eq. (3-c) for  $T$  at the specified partial pressure of 1 mm yields a temperature of 1250°C.

#### Carbothermic Reduction of Magnesia and Alumina

Magnesium oxide can be reduced by carbon at high temperatures. However, as the gases containing carbon monoxide and magnesium vapor cool, the reaction reverses itself to reform the reactants:



In an effort to prevent the reversion reaction, Hansgirg<sup>11</sup> developed a process in which the magnesium vapor is rapidly chilled, retaining most of it in the metallic state. This "shock cooling" process is accomplished by withdrawing the product gases from a retort furnace and chilling them in a rapidly flowing stream of natural gas or hydrogen. The product usually contains over 50% magnesium metal, with the remainder being MgO and carbon. Although the process was operated in Wales and in California during World War II, both plants were closed following the war because of operating difficulties and failure to achieve projected production output.

Reduction of alumina with carbon will take place to some extent at temperatures in the vicinity of 2000°C. However, the primary reaction products are the carbide and oxy-carbide. The possibility of operating at reduced pressures exists, but thermodynamic calculations indicate that the primary reaction product probably will not be aluminum vapor, but Al<sub>2</sub>O. Although considerable research has been carried out on this process, pure metallic aluminum has not been produced commercially by carbothermic reduction.

<sup>10</sup> O. Kubaschewski and E. LL. Evans, *Metallurgical Thermochemistry*, p. 375, 3rd ed., Pergamon Press, New York, 1958.

<sup>11</sup> Dungan, *Trans. AIME* 159, 308 (1944).

#### Extraction of Zinc

The extraction of zinc is accomplished by a variety of processes with about half of the production by electrolysis<sup>12</sup> (see Zinc Hydrometallurgy and Electro-Winning

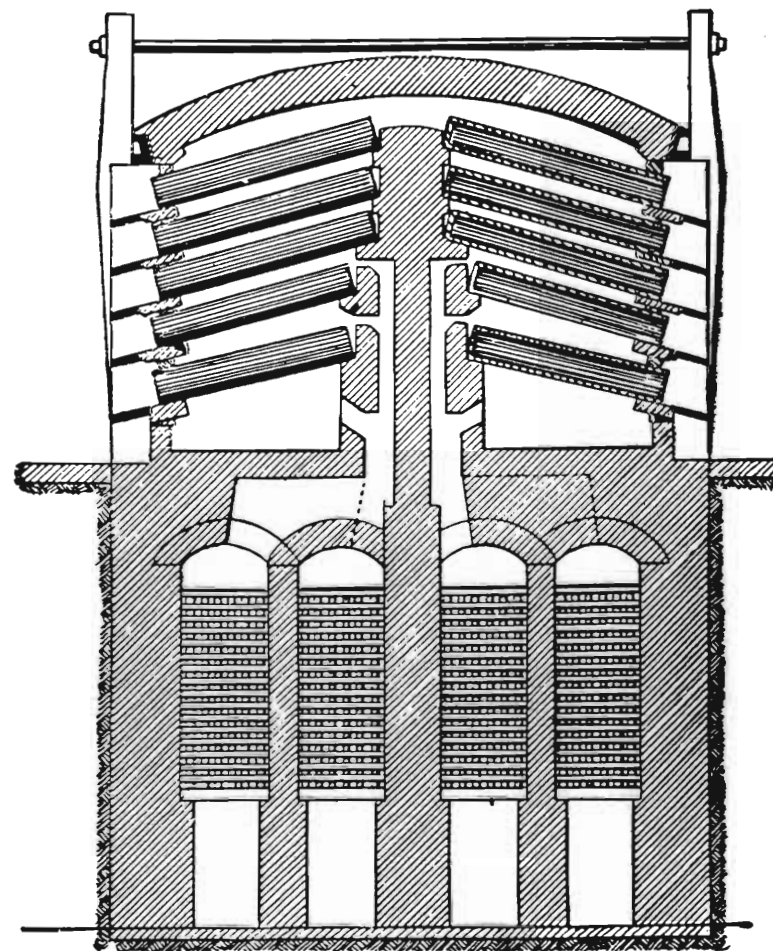


Fig. 3-12. Zinc Retort Furnace (Diagram shows regenerative chambers and gas flow openings. Working floor is shown on upper level)

Source: C. R. Hayward, *Outline of Metallurgical Practice*, 3rd edition, D. Van Nostrand, New York, 1952, p. 226.

<sup>12</sup> S. W. K. Morgan and D. A. Temple, *J. Metals* 19, 23-29 (1967).

Metals from Leaching Solutions). The remainder is produced primarily by reduction of oxide ores or roasted sulfides with carbon. Lead-zinc ores can be processed advantageously in a modified blast furnace (Imperial Smelting Process).

The reduction of the oxide by carbon usually is carried out in a closed retort. The retorts are of several designs, the classic type being horizontal in a gas-fired regenerative furnace as shown schematically in Fig. 3-12. The retorts are clay tubes about 7–9 ft long. The retorts are charged with zinc oxide and fine coal or coke breeze, and then placed in the furnace which holds several hundred retorts. The walls of the retort are about an inch thick and the refractory material used (usually a mixture of silicon carbide and clay) and the charge itself have a relatively low thermal conductivity. This condition and the endothermic reaction of the process require that the diameter of the retort be small. Since zinc oxide reduction is carried out at temperatures above the boiling point of zinc, a condenser is inserted in the open end of the retort. Zinc vapor condenses to liquid zinc and is collected in the condenser. CO gas is evolved from the condenser and burns in the air as shown in Fig. 3-13.

Roasting of the ore for charging to the retort is critical since any sulfur present

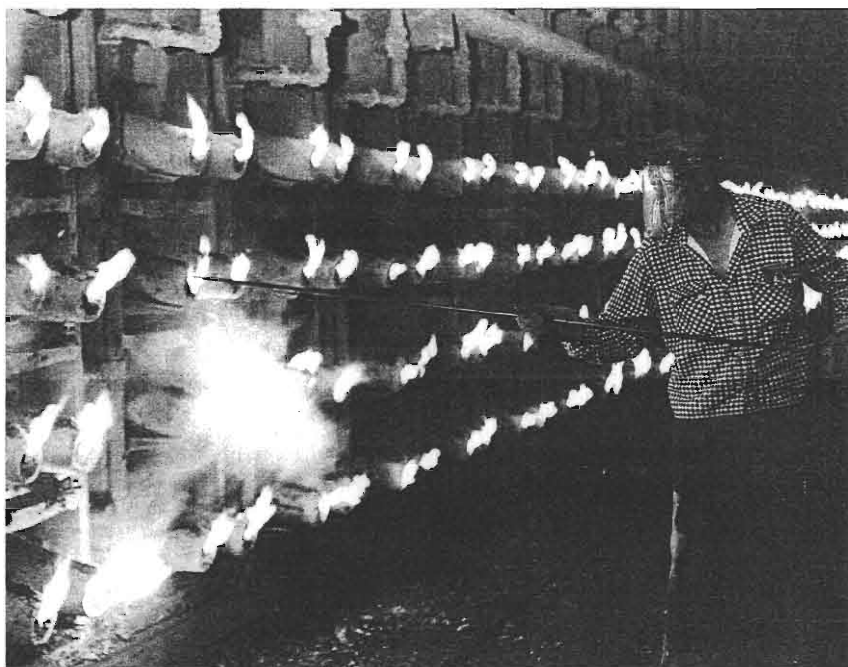


Fig. 3-13. Zinc Retort Process (CO Flame is shown coming from condensers)  
Courtesy of American Smelting and Refining Company.

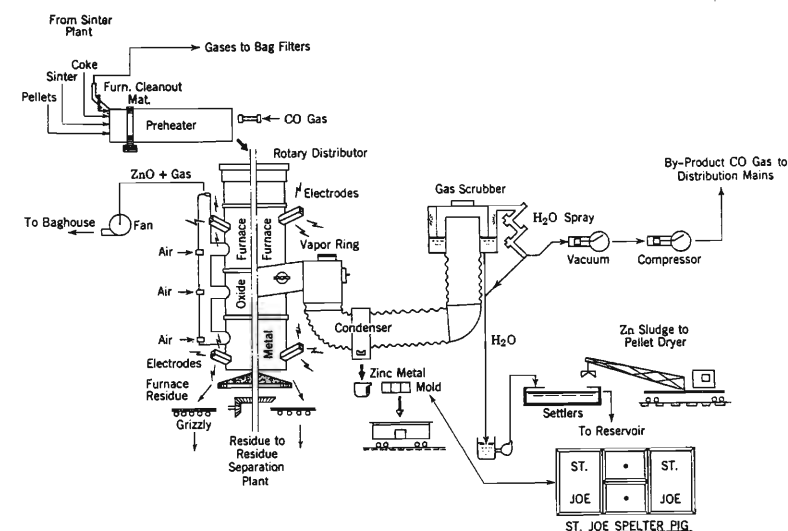


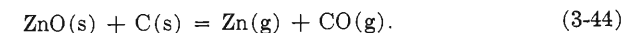
Fig. 3-14. Electrothermic Zinc Process

Source: Weaton, et al. *Trans. AIME*, 159, 1944, p. 155.

as sulfate or unroasted sulfide will not be removed and will retain zinc equal to twice its own weight. If iron oxide is present in the charge, it may be reduced to Fe and react with the sulfur present to release additional zinc. However, slag forming oxides, such as the oxides of iron, will attack the refractory and decrease retort life.

The retorts are charged and discharged every 24–48 hr. Efficient reduction is accomplished with less than 20% reducing agent in the charge. However, the size of the charge is only on the order of 100–150 lb. Consequently, this process is not highly efficient from a material handling viewpoint. St. Joseph Lead Company has developed an electrothermic process which operates continuously and also avoids the use of individual retorts.<sup>13</sup> The flow sheet for this process is presented in Fig. 3-14.

A comparison of the standard free energies of formation of zinc oxide and carbon monoxide in Fig. 3-1 indicates that they are equal at a temperature of about 935°C. The standard free energy change at 935°C is then zero for the reaction,

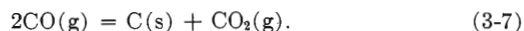
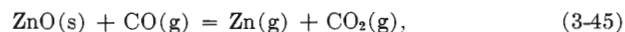


Since the standard states for the gaseous components are taken at 1 atm pressure, the equilibrium total pressure with reactants and products in their standard states would be 2 atm. If the total pressure on the system is reduced to 1 atm, and the partial pressures of zinc and carbon monoxide are fixed at 0.5 atm, the equilibrium

<sup>13</sup> C. C. Long, *J. Metals* 17, 1351, 1352 (1965).

temperature falls just below 900°C, but correspondingly, the boiling point of zinc at 0.5 atm is only 840°C. Any further reduction of the pressure only serves to increase the difference between the two temperatures. Thus, it is necessary that the reduction be carried out with zinc vapor as a reaction product.

Alternatively, the pressure on the system could be increased such that zinc is produced as a liquid phase. However, a complication arises in that the reduction process is not fully represented by Eq. (3-44) but consists of a combination of the Boudouard reaction and a reaction representing gaseous reduction of zinc oxide:



As the pressure on the system is increased, the Boudouard reaction, Eq. (3-7), is forced to the right, increasing the relative concentration of carbon dioxide in the gas phase, and shifting the equilibrium for Eq. (3-45) to the left. However, production of liquid zinc in a carbothermic reduction process carried out at several atmospheres pressure is feasible at temperatures above 1040°C.

The increased oxidizing potential (corresponding equilibrium oxygen pressure) of CO<sub>2</sub> at decreasing temperatures can result in a reversion of Eq. (3-45) on condensation of zinc with attendant formation of "blue powder" (partially oxidized zinc). This reaction increases the zinc losses, and several attempts have been made to use a graphite "eliminator,"<sup>14</sup> wherein the Boudouard reaction, Eq. (3-7), is shifted to the left to markedly decrease the concentration of CO<sub>2</sub> in the effluent gases.

Several attempts have been made to extract zinc by reduction in a blast furnace. Because of the large volumes of nitrogen and carbon monoxide present, the difficulties in condensing the metal have prevented development of this process. An alternative has been developed in the Imperial Smelting Process (see Pyrometallurgy III), wherein the zinc is condensed by absorption in liquid lead.

**Example Problem 3-6.** The reactions in the zinc retort can be represented by Eq. 3-44. The reaction products enter the condenser at 950°C and leave at 450°C. Assuming equilibrium condensation, estimate the efficiency of zinc recovery in the condenser.

**Solution.** The equilibrium partial pressure of zinc over liquid pure zinc is given by the relationship (Table A-VII),

$$\log P_{\text{mm Hg}} = -\frac{6670}{T} + 12.00 - 1.126 \log T.$$

At 450°C,  $P_{\text{Zn}} = 0.36$  mm Hg. The gases escape at one atmosphere so the moles of zinc per mole of CO would be

$$\frac{0.36}{760 - .36} = 4.75 \times 10^{-4}.$$

<sup>14</sup> S. W. K. Morgan, Proc. Fourth Empire Min. Met. Cong., Paper HI.2., 1949.

One mole of zinc is released per mole of CO (Eq. 3-44), so the zinc loss is 0.0475%, i.e., the efficiency of recovery under these conditions would be 99.95%.

Another technique for recovering zinc from other oxides is by zinc fuming. If a mixture of oxides containing zinc is heated with a reducing agent at a high temperature, the zinc will vaporize and then oxidize in vapor form, creating a finely divided fume. The zinc oxide, *per se*, is not volatile, but vaporization of the metal and subsequent oxidation is the mechanism by which the fume is formed. Zinc oxide has a number of commercial applications, including use in skin medications. Fuming operations are employed to produce both zinc oxide and as a means for recovering zinc from low-grade materials such as slags. Treatment of lead blast furnace slag with a mixture of air and pulverized coal to fume the zinc is a practice carried out at most lead smelters. The zinc fume is usually collected in filters. Specific processes designed for this purpose include the Weatheril process, where zinc fume is produced from calcined material mixed with coal or some other solid reducing agent, and the Waelz process, which employs a rotary kiln for heating a reducing agent and the zinc-bearing material.

#### Cadmium Production

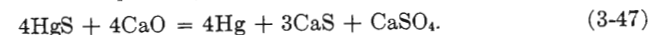
Cadmium is usually associated with zinc, and being the more volatile constituent, is distilled during the first stages of the carbothermic reduction. The first fraction of zinc to be condensed can be collected and redistilled to recover the cadmium. Thus, cadmium is usually obtained as a by-product of zinc production, e.g., by recovery from lead blast furnace dust and from the residues of electrolytic zinc plants.

#### Mercury Production

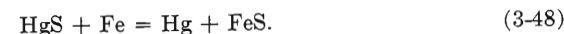
Mercury occurs in nature principally as cinnabar (HgS), and since mercury is not easily oxidized, the roasting of the sulfide mineral results directly in formation of the metal according to the reaction,



The sulfide may also be decomposed by lime according to the reaction



Alternatively, iron can be used to reduce the sulfide according to the reaction,

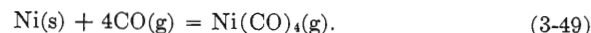


These reactions are carried out at temperatures above the boiling point of mercury, 357°C, and means must be provided for condensation of the vapor. Shaft furnaces, small rotary kilns, and multiple hearth furnaces have been used for processing mercury-bearing ores.

#### The Mond (Carbonyl) Nickel Process

Nickel combines with carbon monoxide at low temperatures to form a volatile nickel carbonyl, Ni(CO)<sub>4</sub>. The process can be used on ores and roasted calcines that

contain nickel in the form of free oxide. The nickel oxide is reduced to nickel by heating at 350–400°C in a reducing atmosphere containing hydrogen and carbon monoxide. If carbon monoxide gas is circulated over the nickel at about 60°C, the nickel is converted to nickel carbonyl according to the reaction,



The volatile carbonyl gas then can be passed over nickel pellets at about 180°C to reverse the reaction, decomposing the carbonyl and depositing nickel on the pellets. The process is very efficient; on the order of 95% of the nickel is recovered and the product is very pure.

#### Direct Reduction of Iron Ore

The term "direct reduction" refers to the reduction of oxides to metals at temperatures below the melting point of the metal or any associated impurities. However, in the development of direct reduction processes, some techniques have been developed that do involve some melting of the charge constituents; with regard to iron oxides, the term direct reduction is commonly used to describe any process other than the iron blast furnace. Solid carbonaceous fuels are used for many processes, and in those instances where the reduction is effected by a gaseous reactant such as hydrogen or carbon monoxide, the reaction is often termed "gaseous reduction." One of the advantages of direct reduction processes is that the product

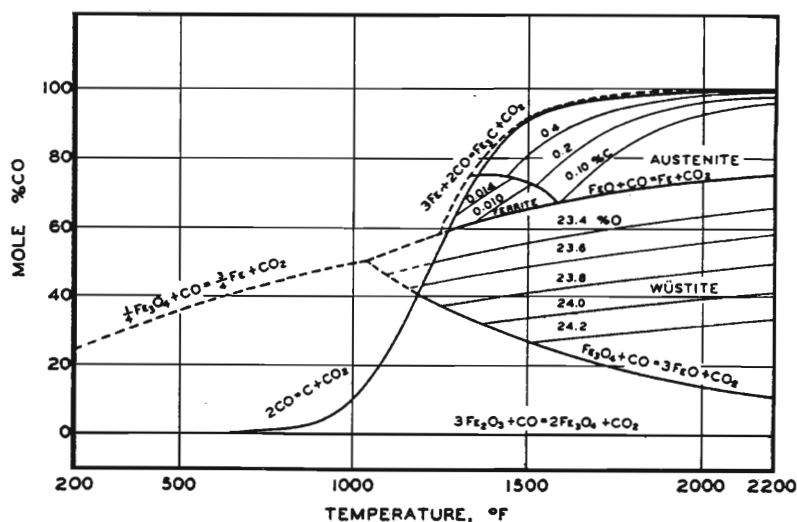


Fig. 3-15. Equilibrium of Iron-oxygen-carbon System at 1 atm

Source: Kun Li, *Proc. Blast Furn. Conf. AIME*, 1960, Vol. 19, p. 162.

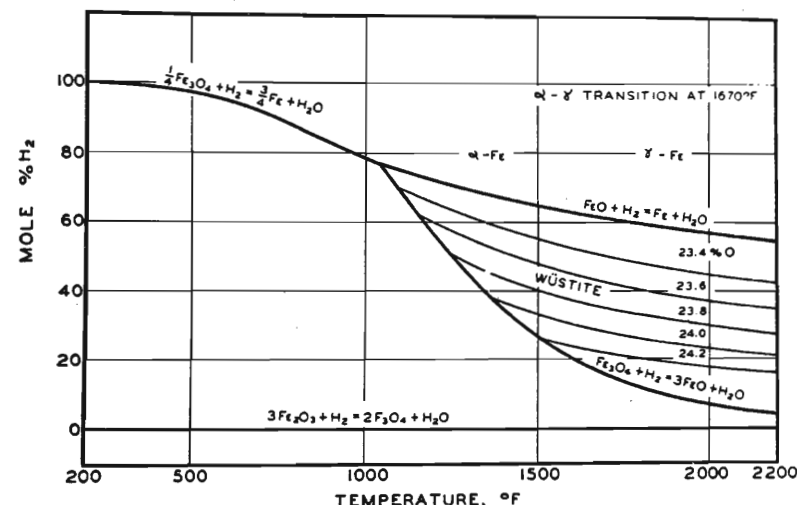


Fig. 3-16. Equilibrium of Iron-oxygen-hydrogen System at 1 atm

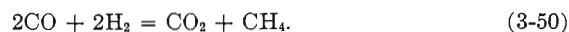
Source: Kun Li, *Proc. Blast Furn. Conf. AIME*, 1960, Vol. 19, p. 163.

can be made in relatively small quantities with a capital investment much below that of a blast furnace plant.

Direct reduction processes consume energy. This energy is usually provided by additional fuel, or by electrical energy in the case of the electric furnace smelting processes. The endothermic or exothermic nature of the reduction reactions do not have much effect on the total energy requirements. The net heat effects, however, are of importance since the reduction of iron oxide, e.g., proceeds in stages from hematite ( $\text{Fe}_2\text{O}_3$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ) to wüstite ( $\text{Fe}_x\text{O}$ ) to iron. Each reaction involves a different heat effect and thus the heat requirement in a process will vary from point to point.

Several materials could be used as reducing agents for iron oxide, but in practice only hydrogen, carbon monoxide, and/or carbon have been used. The equilibrium relationships in the iron-oxygen-carbon system at 1 atm pressure are shown in Fig. 3-15, and the iron-oxygen-hydrogen system is shown in Fig. 3-16. From Figs. 3-15 and 3-16 it can be observed that wüstite (a nonstoichiometric compound usually written as  $\text{Fe}_x\text{O}$ , where  $x$  varies between 0.8 and 0.95) is unstable below 1040°F. Thus it is possible to reduce magnetite directly to iron without producing the wüstite phase at temperatures below 1040°F. In the carbon monoxide reduction process, Fig. 3-15, the decomposition of carbon monoxide to carbon and carbon dioxide does not permit magnetite reduction directly to iron at temperatures below 1275°F. Hematite is easily reduced to magnetite at all temperatures with gases of relatively high oxidation potential. As the temperature increases, the ratio of hydrogen to water vapor required to achieve a given degree of reduction decreases,

whereas the effect is reversed with carbon monoxide; here, the higher the temperature, the higher is the ratio of carbon monoxide to carbon dioxide required to establish a given oxygen potential. In mixtures of hydrogen and carbon monoxide used as reducing gases, gas phase reactions occur with the formation of methane, according to the reaction,



The kinetics of reduction reactions are made complex by the diverse nature of iron-bearing minerals. As one might expect, reduction rates are influenced by temperature, pressure, composition of reducing agent, gas flow rates, the nature of the iron-bearing material, particle size, state of oxidation, presence of impurities, etc. The reducing reaction may be controlled by diffusion in the gas phase or in the solid, or by the rate of chemical reaction. The controlling mechanism is determined by the specific system and the temperature of the process. The reduction interfaces move parallel to the outside surface of the iron-bearing material. Porous oxide minerals usually show a single interface, since the magnetite is fully reduced before a wüstite phase appears. McKewan<sup>15,16</sup> showed that the rate of reduction per unit area was constant with time, and in the case of the reduction of iron oxide by hydrogen, was directly proportional to the partial pressure of hydrogen. In this case the reaction was controlled at the oxide-metal interface rather than by diffusion through the reaction product layer.

In view of the foregoing considerations, a rate equation can be derived to fit the reported data. Consider a sphere of iron oxide of initial radius,  $r_0$ , and initial density,  $\rho_0$ . Assume that the rate of formation of a uniform reaction product layer is proportional to the receding surface area of the remaining oxide. If  $W$  is the weight of that part of the original material that has reacted, then

$$\frac{dW}{dt} = kA, \quad (3-51)$$

where  $k$  is a proportionality constant having the dimensions  $m^{-2}t^{-1}$  and is a function of temperature, pressure, and gas composition. From this it follows that

$$r_0 \rho_0 f = kt, \quad (3-52)$$

where  $f$  is the ratio of the thickness of the reduced layer to the initial radius. Equation (3-51) states that at the oxide metal interface the amount of oxide reacting per unit area per unit time is constant, or that the reaction interface advances at a constant rate.

The fractional reduction,  $R$ , is defined as the weight of oxygen removed divided by the total weight of oxygen originally present as iron oxide. The fractional reduction,  $R$ , bears the following geometrical relationship to the fraction thickness,  $f$ ,

$$f = 1 - (1 - R)^{1/3}. \quad (3-53)$$

<sup>15</sup> W. M. McKewan, *Trans. Met. Soc. AIME* **212**, 791 (1958).

<sup>16</sup> W. M. McKewan, *Trans. Met. Soc. AIME* **218**, 2 (1960).

Substituting this value for  $f$  into Eq. (3-52),

$$r_0 \rho_0 (1 - (1 - R)^{1/3}) = kt. \quad (3-54)$$

The same equation would apply to a cube whose side equals  $2r_0$ . The reduction rate for any particle whose shape is similar to a sphere or cube can be approximated by Eq. (3-54). Equations also can be derived to fit other geometrical shapes.

The kinetics of reduction reactions vary with temperature. The rate constant which increases with temperature can be treated in terms of the theory of absolute reaction rates where the specific rate constant,  $k'$ , is defined<sup>17</sup> as

$$k' = \kappa \frac{kT}{h} e^{-\Delta H^*/RT} e^{\Delta S^*/R}, \quad (3-55)$$

where

$\kappa$  = transmission coefficient initially taken to be unity,

$k$  = Boltzmann constant,

$h$  = Planck constant,

$\Delta H^*$  = enthalpy of activation,

$\Delta S^*$  = entropy of activation.

An alternative approach to the kinetics of reduction of a granular bed of iron ore is to assume that the reduction of iron ore in a gas stream tends to follow a first-order reaction rate according to the expression,

$$-\frac{dc}{dt} = k_r c, \quad (3-56)$$

where

$$-\frac{dc}{dt} = \text{rate at which oxygen is removed from ore, lb O}_2/\text{lb of Fe/hr,}$$

$c$  = concentration of oxygen in the material, lb O<sub>2</sub>/lb of Fe,

$k_r$  = reduction rate constant, hr<sup>-1</sup>.

Collecting terms and integrating between  $c_0$  at  $t = 0$  and  $c$  at time  $t$ ,

$$\ln \left[ \frac{c_0}{c} \right] = k_r t \quad (3-57)$$

and the fraction of oxygen remaining at time  $t$  is

$$f_0 = \frac{c}{c_0} e^{-k_r t}. \quad (3-58)$$

As a first approximation it may be assumed that the overall reduction rate of ore particles proceeds according to this type of equation. The actual value of the reaction constant,  $k_r$ , could be determined in a small scale reduction bed in which

<sup>17</sup> Ibid., p. 2.

conditions are typical of those in the larger unit that is being designed. It should be noted that with small particles, the mass flow rate at which reactant can be supplied may be a critical design factor.

#### Several Commercial Processes for Direct Reduction of Iron Ores

One of the earliest commercial processes was the Hoeganaes process, which is used in the United States and has been in use in Southern Sweden for over 50 years. The process involves a relatively pure iron ore charged to a kiln with coal and limestone.

The Wiberg process involves reduction of iron ore with carbon monoxide and hydrogen in a shaft furnace. Recovery of metallic iron averages 85–90%.

The Krupp–Renn process is carried out in a rotary kiln and involves some melting of the slag phase and production of small iron nodules. This process is particularly effective in that it permits separation of the gangue materials and does not require a high purity iron oxide, as do the Hoeganaes and Wiberg processes.

The use of natural gas to directly reduce iron has been put into practice at Monterrey, Mexico, and is called the HyL process. This process requires a high purity ore as a charge material, and its product in turn is charged to a steelmaking furnace. In this operation all gangue present in the ore is concentrated in the sponge iron product. Phosphorus is not eliminated, but about 85% of the sulfur is removed as hydrogen sulfide.

The H-Iron process employs a pressurized fluidized bed operating at 450–550 lb/in.<sup>2</sup> at a temperature of 1000°F to produce powdered iron. The reducing agent is nearly pure hydrogen gas and the off gas is regenerated and recirculated.

There are other iron ore reduction processes that have received considerable commercial attention. The R-N process uses solid carbonaceous fuels as reducing agents. No fusion takes place in this kiln operation, and the product can be externally beneficiated by magnetic separation to produce a concentrate of 90–95% metallic iron. Electric furnace reduction of iron ores can be carried out in the Strategic-Udy process. Ore, coke, and fluxes are preheated, and the ore is partially reduced in a rotary kiln. This hot charge is moved to an electric furnace where controlled conditions of temperature, reducing potential, and slag composition are used to produce a pig iron or semisteel. The FIOR (fluid-iron-ore reduction) process of Esso Research and the Nu-Iron Process of U. S. Steel Corporation involve fluidization of iron ore in a reducing gas made from natural gas or liquid petroleum components. The product is a briquetted iron consisting of 90–95% metal.

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#### Discussion Questions

- Outline the steps and data required to develop a Pourbaix–Ellingham diagram for the Cr–O–C system. Describe a process which might be employed for carbothermic reduction of chromium oxide.
- Discuss the advantages of using various standard states.
- A gas–solid direct reduction process has been proposed to produce a metal “X” from its oxide “XO<sub>2</sub>”. What information is required to determine the feasibility of the process and required operating conditions? Describe any laboratory experiments which would be required to determine this information.
- It is desired to recover tin from cassiterite concentrate containing several other oxide minerals (Fe, Ti, Ta, Nb, Pb, and W). Describe a process in terms of equipment and operating conditions which would selectively reduce the tin oxide to an impure metal.
- Describe procedures which might be used to improve recoveries of metallics in the CaCl<sub>2</sub> roasting of low-grade oxide concentrates.
- Compare the gas cleaning systems required for recovery of particulate material in various reduction processes.

#### Problems

- Calculate the equilibrium oxygen pressure over pure calcium oxide in contact with calcium gas at a total pressure of 0.10 mm Hg at 1600°C.
- Calculate the equilibrium oxygen pressure over tantalum oxide in contact with solid pure tantalum at 1600°C.
- Calculate the H<sub>2</sub>/H<sub>2</sub>O ratio required to reduce titanium oxide at 1400°C.
- Calculate the H<sub>2</sub>/H<sub>2</sub>O ratio required to reduce tungsten oxide at 1400°C.
- Calculate the equilibrium CO/CO<sub>2</sub> ratio in contact with graphite at 1600°C at 1 atm total pressure.
- Air containing 5% (by volume) water vapor is allowed to contact graphite in a closed system. The system comes to equilibrium at 0.5 atm total pressure and 1600°C. What is the composition of the gas phase?
- Calculate the reduced pressure required to decompose the following nitrides:
  - AlN
  - BN
  - Si<sub>3</sub>N<sub>4</sub>
  - VN

at 1600°C. (Assume presence of pure metal in liquid or solid form.)

8.  $\text{MoO}_2$  is to be reduced by dry  $\text{H}_2$  at 1400°C to metallic molybdenum. The reaction is to be carried out at 1 atm total pressure.
  - (a) What fraction of the dry hydrogen introduced into the reduction chamber will be utilized if we may assume that equilibrium is achieved?
  - (b) What would be the effect of pressurizing the system to 10 atm?
  - (c) Can dry hydrogen reduce  $\text{MoO}_2$  at 1 atm total pressure and 800°C?
9. Specify the minimum operating temperature for carbothermic reduction of molybdenum at  $10^{-2}$  atm.
10. A mixture of carbon monoxide and carbon dioxide at 1 atm pressure is slowly passed through a bed of graphite chips maintained at a temperature of 1000°C in the upper portion of a two zone furnace. The gas is then directly brought into contact with an iron sample at 1500°C in the lower zone of the furnace. If a heating element failure allows the upper zone of the furnace to slowly cool, at what temperature will oxide appear on the iron sample in the lower portion of the furnace?
11. Electromotive force measurements in the cadmium-lead system were taken relative to a liquid pure cadmium electrode at 500°C yielding the following results:

| $N_{\text{Cd}}$ | Wt % Cd | Activity <sub>Cd</sub> |
|-----------------|---------|------------------------|
| 0.00            | 0.00    | 0.00                   |
| 0.05            | 2.78    | 0.15                   |
| 0.10            | 5.70    | 0.27                   |
| 0.15            | 8.70    | 0.375                  |
| 0.30            | 18.90   | 0.57                   |
| 1.00            | 100.00  | 1.00                   |

- (a) Based on the standard state of liquid pure cadmium at 500°C (reference state  $N_{\text{Cd}} = 1$ ), compute an activity coefficient for each of the compositions given above.
- (b) Based on the standard state of an infinitely dilute solution at 500°C (reference state: 1 wt% solution), compute an activity coefficient for each of the compositions given above.
12. The equilibrium conditions for the reduction of metal M from its oxides by CO are given below at four different temperatures. The reactions are:

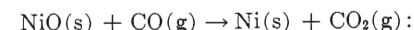


| Temp °C                                     | 400  | 700  | 900  | 1100 |
|---------------------------------------------|------|------|------|------|
| $\frac{\text{CO}}{\text{CO} + \text{CO}_2}$ | 0.55 | 0.32 | 0.26 | 0.20 |



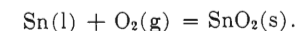
| Temp °C                                     | 400  | 700  | 900  | 1100 |
|---------------------------------------------|------|------|------|------|
| $\frac{\text{CO}}{\text{CO} + \text{CO}_2}$ | 0.20 | 0.70 | 0.83 | 0.90 |

- (a) Which of these reactions absorbs and which evolves heat? Outline the method by which you would find the numerical value of heat absorbed and evolved at a given temperature for either reaction. Compute a standard free energy change for each equation, expressed as a function of temperature.
- (b) Calculate the actual free energy change if 1 mole of MO and 1 mole of CO are mixed and the mixture is allowed to reach equilibrium, the temperature and total pressure being held constant at 700°C and 1 atm, respectively, for the process.
13. The following equilibrium data have been determined for the reaction,



| Temp °C            | 663   | 716   | 754   | 793   | 852   |
|--------------------|-------|-------|-------|-------|-------|
| $K \times 10^{-1}$ | 4.535 | 3.323 | 2.554 | 2.037 | 1.577 |

- (a) Determine  $\Delta H^\circ$  and  $\Delta G^\circ$  at 1000°K
- (b) Would an atmosphere of 30%  $\text{CO}_2$ , 5% CO and 65%  $\text{N}_2$  oxidize nickel at 1000°K?
14. Dry air is injected into a hot coke bed and converted to a gaseous fuel. If the temperature is 1400°C and the total pressure is 3 atm:
  - (a) Calculate the equilibrium gas composition.
  - (b) Is there any advantage in raising the temperature to 1600°C or in increasing the pressure to 5 atm.
15. The formation of tin oxide from the pure elements is given by the reaction,



What is the standard free energy for the above reaction when the standard state for tin is the infinitely dilute solution in thallium, referred to a 1 wt% solution?

16. Derive the reciprocity relationship,  $\epsilon_i^j = \epsilon_j^i$  (Eq. 3-36).
17. Derive the relationship between  $\epsilon_i^j$  and  $e_i^j$  (Eq. 3-40).
18. Show that the interaction parameter will vary linearly with reciprocal absolute temperature, provided that the partial molar enthalpy is essentially independent of temperature.
19. Estimate the concentration of sulfur at 1600°C in the following liquid iron

alloy in equilibrium with an  $\text{H}_2\text{S}/\text{H}_2$  mixture where the partial pressure ratio,  $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$  is  $1.68 \times 10^{-3}$ .

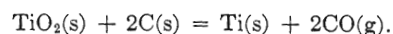
| Element | Wt % |
|---------|------|
| C       | 1.01 |
| Al      | 0.31 |
| P       | 1.52 |
| Si      | 3.95 |
| Mn      | 2.17 |

20. Estimate the activity of cadmium in the following alloy at  $700^\circ\text{C}$ .

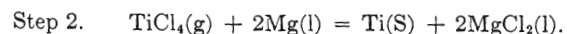
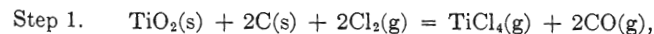
| Element | Mole fraction |
|---------|---------------|
| Sn      | 0.75          |
| Cd      | 0.10          |
| Pb      | 0.05          |
| Zn      | 0.10          |

21. Two processes have been proposed for the production of titanium at 1 atm pressure from rutile sands.

*Process I*—Direct carbothermic reduction at  $1200^\circ\text{C}$ :



*Process II*—Chlorination under reducing conditions at  $1200^\circ\text{C}$  followed by magnesium reduction of  $\text{TiCl}_4$  at  $750^\circ\text{C}$ :



Evaluate the feasibility of the two processes.

22. Sodium reduction of titanium tetrachloride is used to produce sponge titanium and sodium chloride. Compare the material balance and free energy change for this process with those for the Kroll process.
23. A vacuum reduction system for the production of zinc has been proposed. The system which operates at or below 1 mm Hg consists of two chambers: a high temperature retort ( $750^\circ\text{C}$ ) to which zinc oxide and coke breeze are charged, and a water-cooled condensing chamber where zinc is rapidly condensed as a solid to avoid blue powder formation. Assess the thermodynamic feasibility of this process.
24. Quantitatively assess the effectiveness of a graphite "eliminator" in preventing reversion of the zinc reduction reaction to form blue powder. The eliminator would be a graphite packed bed held at about  $1000^\circ\text{C}$  to reduce the

$\text{CO}_2$  content of the gases evolved from the retort. The gases leaving the eliminator then would be cooled, condensing the zinc as a liquid.

25. A zinc retort is charged with  $\text{ZnO}$  and  $\text{C}$  at  $1000^\circ\text{C}$  and the gases  $\text{Zn}$ ,  $\text{CO}$  and  $\text{CO}_2$  are generated at 1 atm total pressure.

- Compute the theoretical minimum charge ratio of  $\text{ZnO}$  to  $\text{C}$ .
- If the process were operated at low pressure, e.g.,  $10^{-4}$  atm, how would the charge ratio change?

26. In the "H-Iron" process for direct reduction of iron oxide, dry pure hydrogen is reacted with magnetite at a relatively low temperature and high pressure. The wet hydrogen is recirculated after drying and metallic iron is intermittently removed from the reactor. If the mean temperature in the reactor is  $950^\circ\text{F}$  and the pressure is 250 psig, estimate the  $\text{H}_2\text{O}$  content of the exiting gas stream.

27. Direct reduction of magnetite with carbon monoxide at  $900^\circ\text{C}$  in the presence of lime has been proposed according to the reaction,



Calculate the minimum  $\text{CO}$  pressure to cause this reaction to go to completion.

28. Derive a relationship of the same general form as Eq. (3-54) for the hydrogen reduction of hematite when the particle is:

- A cube of initial edge length  $S_0$ , where  $f = (S_0 - S)/S_0$ ;
- A long cylinder of initial radius  $r_0$ , where  $f = (r_0 - r)/r_0$ ;
- A large thin plate of initial thickness  $X_0$ , where  $f = (X_0 - X)/X_0$ .

## CHAPTER 4

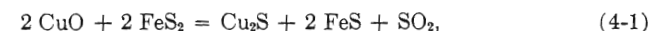
### Pyrometallurgy III: Smelting and Converting

The most extensive industrial applications of oxidation and reduction processes occur in the smelting of metals, i.e., recovering the metallic elements from an oxide or sulfide by heating with fusion while in the presence of a reducing agent. The smelting operation may produce an impure matte (liquid metallic sulfide) or a metal, such as the iron blast furnace which produces liquid pig iron, containing up to 5% carbon as well as appreciable amounts of manganese, silicon, phosphorus, sulfur, etc. Further refining to produce a purer metallic product, such as metallic copper or steel, is accomplished in an oxidizing process referred to as conversion or converting.

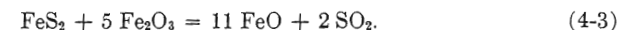
#### 4-1 Reverberatory Smelting

Smelting, essentially a melting operation wherein the charge is melted down into two layers consisting of metal or matte, and slag, is often carried out in a reverberatory furnace in which the thermal energy is supplied to the charge primarily by radiation from the furnace roof. These immiscible liquids form two layers on the furnace hearth. In a matting operation, such as that used in copper smelting, the sulfides collect as a molten matte and the slag-forming oxides fuse into a slag layer that floats on the matte. A flow diagram for a reverberatory copper smelting furnace is shown in Fig. 4-1.

In copper smelting, the copper in the charge, in the form of oxide, sulfide, or possibly sulfate, is converted to cuprous sulfide,  $\text{Cu}_2\text{S}$ . The affinity of oxygen for iron and sulfur and of sulfur for copper results in the reverberatory smelting reactions,



Some of the iron sulfides present may be oxidized to ferrous oxide according to the reaction,



Magnetite ( $\text{Fe}_3\text{O}_4$ ) is usually present in the charge either in the calcines or recycled converter slag (see Copper Converting). Magnetite also can be formed by oxidation of  $\text{FeO}$  or partial reduction of  $\text{Fe}_2\text{O}_3$ . The magnetite often settles out to form accretions on the bottom or may form a "false bottom" or layer between the slag and matte and hinder matte separation.

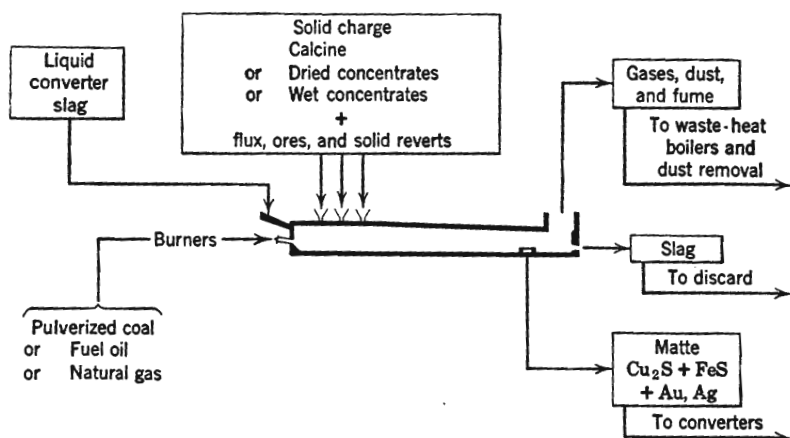


Fig. 4-1. Flow Diagram for Reverberatory Copper Smelting Furnace

Source: J. Newton, *Extractive Metallurgy*, John Wiley and Sons, Inc., 1959, New York, p. 340.

Matte copper content varies between 20 and 70%. The sulfur is in the range of 20–25%. The remainder is iron and minor constituents. The matte can be assumed to be a mixture of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ , although the sulfur is usually slightly less than the concentration required to account for stoichiometric formation of these compounds.

The slag is a complex silicate, primarily  $2\text{FeO} \cdot \text{SiO}_2$ , although substantial quantities of other oxides may be present. The slag contains some sulfur and some copper resulting in a copper loss. The concentration of copper is usually a few tenths of a percent and may be present both as dissolved copper or copper sulfide, and as entrained matte.

A schematic diagram of a reverberatory smelting furnace is shown in Fig. 4-2. The roof is usually arched and is 20–30 ft. wide. The length of the reverberatory furnace may range from 40 ft to as much as 100 ft in large smelting furnaces such as those used in the copper industry. In the past the refractory lining was usually of silica brick, although in modern furnaces, where the charges are now more basic than formerly, the use of magnesite brick has markedly increased. The reverberatory furnace is equipped with charging facilities, often feed hoppers set in the roof, and it is heated by burners, usually located in the end wall of the furnace. The flame extends across the charge, which is heated by radiation from the flame and the hot interior refractories. Natural gas, fuel oil, or pulverized coal is used as fuel.

The metal, or matte, in the case of oxide-sulfide smelting, and slag collect in layers on the furnace hearth. Tap holes and doors are provided in the front wall for additional charging or slag skimming. The hot combustion gases from the furnace often are directed to waste heat boilers to recover their sensible heat.

The charge to the smelting furnace usually consists of calcines from a roasting operation or concentrates directly from a beneficiation process. In addition, molten

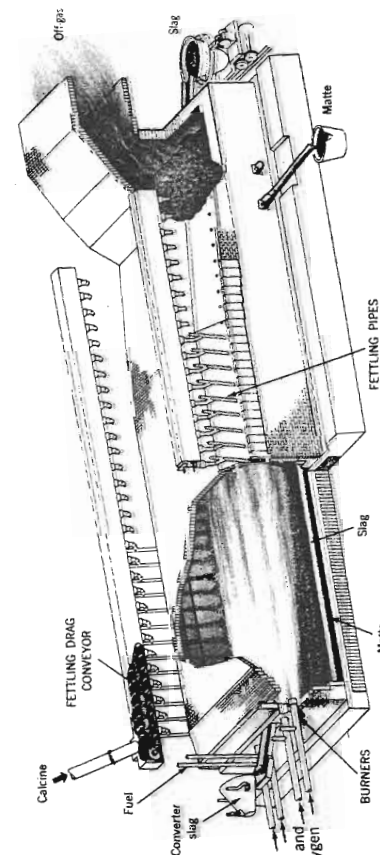


Fig. 4-2. Cutaway View of Reverberatory Smelting Furnace  
Source: J. R. Boldt, Jr., *The Winning of Nickel*, D. Van Nostrand Company, Princeton, New Jersey, 1967, p. 242.

slag from converters often is returned as charge to the preceding smelting operation. Flux is added to provide a liquid slag; silica is commonly used in copper smelting, whereas in smelting operations in which a basic slag is desired lime or burnt dolomite are common flux materials.

*Tin Smelting* is carried out in a reverberatory furnace wherein a reducing agent, such as powdered coal or coke, is charged directly with tin concentrates to produce metallic tin. One of the primary contaminants of tin is iron, and there is a tendency for tin to enter the oxide slag and for iron to be reduced into the metallic tin. The smelting process, therefore, is carried out in two stages, the first with moderate reducing conditions to minimize the simultaneous reduction of iron, followed by a second stage in which the slag is remelted at higher temperatures with additions of reducing agent to recover as much tin as possible. Subsequent purification of the tin is primarily by fire-refining techniques (see Pyrometallurgy IV) using liquation and drossing. Electrolytic refining also has been practiced to produce tin of even higher purity.

*Copper Smelting* usually is carried out in a reverberatory furnace, although blast furnaces have been used to produce copper or copper-nickel matte. Calcines from a roasting operation and liquid slag from the subsequent copper converting operation are charged to the furnace. These materials contain copper, iron, sulfur, and oxygen, along with gangue oxides such as silica, alumina, and magnesia. The mixture is heated to temperatures above  $1200^{\circ}\text{C}$  so that the entire charge is molten. Two liquid phases result: (1) a copper matte consisting of copper, iron and sulfur, and (2) a slag that is a solution of iron oxide, silica, alumina, magnesia, and other oxides but with a low copper content. Any precious metals present are soluble in the matte and collect in it. The two phases separate under the influence of gravity, the heavier matte accumulating in the bottom of the furnace. The two liquid phases are tapped separately from the furnace and are the principal products of the process. In addition, some reactions yield sulfur dioxide along with other gases from the burning of the fuel; these gases pass out through the flue.

The composition of the matte produced influences the energy balance for the subsequent converting operation. The most satisfactory grade of matte is one that contains from 40–50% copper. Low-grade concentrates that are rich in iron may yield matte with about 20% copper, whereas some of the rich African ores yield a matte that is nearly pure  $\text{Cu}_2\text{S}$ .

The processing of *copper-nickel sulfide ores* was carried out until recently primarily by the Orford process. This process was based on the mutual solubility of copper, nickel, and sodium sulfides at high temperatures, and the insolubility of  $\text{Ni}_3\text{S}_2$  in the sodium-copper matte at lower temperatures. By smelting to produce a sodium-copper-nickel matte and slowly cooling, the more dense  $\text{Ni}_3\text{S}_2$  separated out. The upper portion of the solidified charge would contain most of the copper with a small amount of nickel whereas the lower portion or "bottoms" would contain most of the nickel and only a small amount of copper. The copper-sodium matte was then treated in a copper converter. The nickel sulfide was sintered and then reduced in a reverberatory smelting operation to impure liquid nickel, which was cast as anodes for final purification by electrolytic refining.

More recently the separation of copper and nickel sulfides has been carried out

directly by reverberatory smelting to produce a copper-nickel matte free of iron sulfide. The matte is slowly cooled in large cakes, which results in the separation of crystals of  $\text{Cu}_2\text{S}$  and  $\text{Ni}_3\text{S}_2$ . The frozen matte is crushed and ground to mechanically break up the copper sulfide and nickel sulfide crystals, which in turn are separated by standard mineral dressing techniques.

## 4-2 Blast Furnace Smelting

The *lead blast furnace*, much smaller than the iron blast furnace, is typical of non-ferrous blast furnaces. A cross-sectional view of a lead blast furnace is shown in Fig. 4-3. The walls of the furnace in the bosh (melting zone) are water-cooled steel plates, and the crucible below the bosh zone of the furnace is lined with refractory material. Whereas the iron blast furnace is circular in cross section, the lead blast furnace is rectangular, with tuyeres (nozzles through which the blast is supplied) located along the sides of the furnace but not on the ends. The lead oxide is easily reduced and since it is not necessary to operate the furnace at a high temperature or under strong reducing conditions as in the iron blast furnace, the blast is not preheated. The charge to the lead blast furnace includes lead oxide, usually the product of the Dwight-Lloyd sintering machine, plus about 10% coke and a small amount of scrap iron, which serves to reduce lead sulfide and to minimize the lead content of the slag. Operating the furnace at low temperatures minimizes volatilization of lead, but requires that a fluid slag be provided at a relatively low temperature. Lead blast furnace slags usually contain 30–40%  $\text{SiO}_2$ , 25–45% iron oxides, with the balance being  $\text{CaO}$  and  $\text{ZnO}$ . The lead content of the slags is

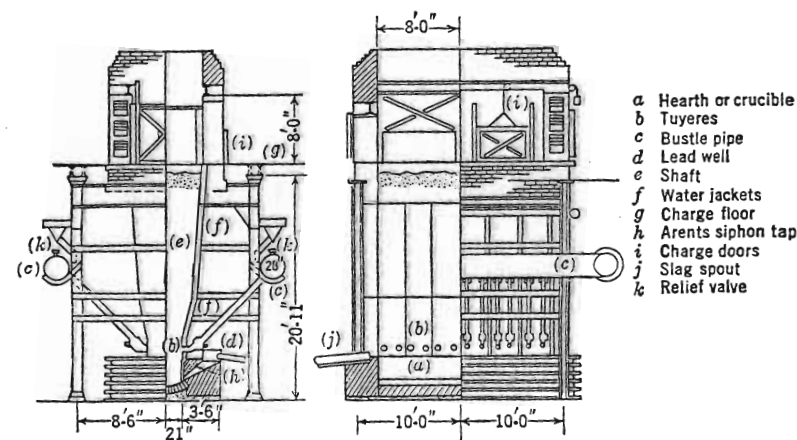


Fig. 4-3. Lead Blast Furnace

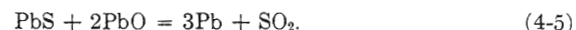
Source: J. L. Bray, *Non-Ferrous Production Metallurgy*, 2nd Ed., John Wiley and Sons, Inc., New York, 1947, p. 292.

usually about 1%. Zinc is concentrated in the slag, sometimes in concentrations as high as 20 wt%. A separate operation, such as that conducted in a fuming furnace (see Pyrometallurgy II), is usually employed to recover the zinc. The smelted lead is alloyed with small amounts of easily reduced metals such as copper, antimony, tin, arsenic, and any previous metals present. Matte or speiss (arsenides or antimonides, as contrasted with matte which is sulfide) may form if there is excess sulfur, arsenic, or antimony in the charge. The matte or speiss will collect as a liquid layer between the lead and the slag, and facilities are provided outside the furnace to separate matte or speiss from the slag. If there is an appreciable amount of copper in the charge, it is customary to charge sinter with a sufficient amount of sulfur to form a copper matte and thus minimize the solution of copper in the molten lead.

Nearly all lead is smelted in lead blast furnaces, although it is possible to carry out the smelting operation in a reverberatory furnace. High galena (PbS) ores can be smelted on an oxidizing hearth with coke and a blast of air that oxidizes the galena according to the reaction,



The lead oxide reacts with additional galena to produce metallic lead according to the reaction,



The molten lead collects on the hearth. This procedure is not efficient, particularly with respect to recovery of precious metals, and is now obsolete.

The smelting of lead-zinc ores in the blast furnace for recovery of *both* lead and zinc was considered to be an impossibility for many years. A recent development, the Imperial Smelting Process (see Pyrometallurgy IV), which is carried out in a blast furnace resembling the lead blast furnace in size and appearance, reduces the lead in the standard manner and volatilizes the zinc in the stack gases. The zinc is subsequently condensed from these gases by absorption in liquid lead. This process for treating ores containing both lead and zinc has effected a considerable economic advantage in the processing of this type of ore.

Recent development work<sup>1</sup> has shown that oxygen enrichment of the blast can increase the rate of smelting in a lead blast furnace as well as provide a savings in coke. The oxygen enrichment levels proposed are on the order of 3% for normal operation. A marked improvement in furnace performance during start-up has been noted especially with oxygen enrichment.

The *iron blast furnace* process consists of charging ore, fuel and flux into the top of a shaft furnace and blowing heated air or blast into the bottom. This process is the backbone of the steel industry, producing a high-carbon, silicon- and manganese-containing iron that is converted to steel in steelmaking furnaces. A cross-sectional view of a modern blast furnace is shown in Fig. 4-4. In the case of the iron blast furnace, the approximate relations between the reactants and products is such that for each ton of iron produced, approximately 1.6 tons of ore, 0.5 tons of

<sup>1</sup> R. W. Ruddle, *The Physical Chemistry of Copper Smelting*, Institution of Mining and Metallurgy, London, 1953.

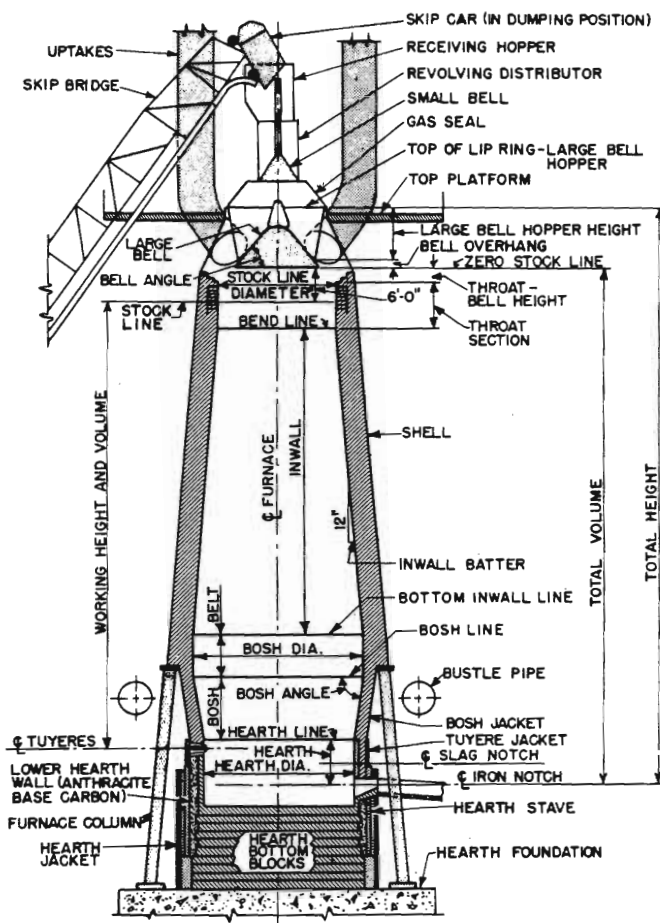


Fig. 4-4. Identification of Principal Dimensions and Components of a Blast Furnace

Source: *The Making, Shaping and Treating of Steel*, edited by Harold E. McGannon, Pittsburgh, United States Steel Corporation, 9th edition, 1971, p. 429.

coke, 0.2 tons of a mixture of limestone and dolomite, and 1.7 tons of air are charged into the furnace. From these materials there is produced 1.0 tons of iron, 0.3 tons of slag, <0.05 tons of flue dust, and 2.7 tons of blast furnace gas. This rough statement relates to the production of pig iron in relatively modern furnaces in north-central United States, accounting for about 75% of the production in the United States.



where the underline notation refers to the element in metallic solution.

The water vapor in the blast also plays a role in the process:



The hydrogen liberated by the above reaction may react with iron oxide, reducing it:



The water so formed is again decomposed. It should be noted that relatively few of the reactions involved furnish the heat required for the process; it is the oxidation of carbon and some of the reduction reactions involving carbon monoxide that furnish the heat to dry the raw materials, decompose the limestone, melt the iron and slag, and replace the heat losses.

The distribution of the alloying elements manganese, silicon and sulfur is controlled principally by slag composition and temperature of the hearth since the liquid metal is saturated with carbon and the gas composition in the vicinity of the tuyeres is controlled primarily by the blast temperature and is not subject to great variation. Between 70–80% of the total amount of manganese charged, principally in the ore, is found in the pig iron. Higher manganese contents are obtained with higher hearth temperatures and basic<sup>2</sup> slags. All of the phosphorus is reduced into the iron. Sulfur that is carried into the furnace primarily in the coke, and often in the ore, may be largely retained in a basic slag at high temperatures in the presence of carbon-saturated iron. The silicon content of the pig iron is controlled by temperature and the thermodynamic activity of silica in the slag. High temperatures and acid slags favor high silicon contents. In view of the extremely important role played by slag composition in the blast furnace process, considerable research effort has been expended on studies of blast furnace slags.<sup>3</sup>

In addition to the role played by slag composition, the interactions between dissolved elements in liquid iron also are important with respect to blast furnace metal composition. A principal interaction that occurs in blast furnace metal is between carbon and silicon in solution. The solubility of carbon in liquid iron is greatly reduced by the presence of silicon, as shown in Fig. 4-6. Since the liquid pig iron leaving the blast furnace hearth is essentially saturated with carbon, i.e., at equilibrium with pure carbon at the temperature of the hearth, the activity of silica in the slag (which is a function of silica content, slag composition, and temperature) controls the silicon content of the metal. The silicon content, assuming favorable reaction kinetics, in turn controls the carbon content. The influence of temperature on the solubility of carbon in iron-silicon alloys also is shown in Fig. 4-6.

The control of reactions occurring in iron and steelmaking primarily involves

<sup>2</sup> The terms basic and acid follow from the classical scientific definitions. In metallurgical processes, basic refers to oxides such as CaO and MgO which are available for dephosphorization or desulfurization. Basic oxides are contrasted with acid oxides, such as SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>. These two types of oxides react to form fairly stable compounds such as Ca<sub>2</sub>SiO<sub>4</sub> or Ca<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.

<sup>3</sup> J. Chipman, *Thermodynamic Properties of Blast Furnace Slags*, Proceedings of International Symposium on the Physical Chemistry of Process Metallurgy, Part I (G. R. St. Pierre, Ed.), Interscience Publishers, New York, 1961.

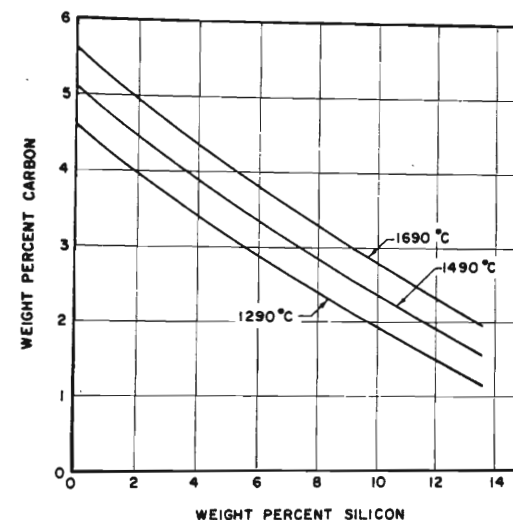


Fig. 4-6. Solubility of Carbon in Iron-Silicon Alloys

Based on "The Solubility of Carbon in Molten Iron and in Iron-Silicon and Iron-Manganese Alloys", J. Chipman, Robert M. Alred, et al., *Transactions ASM*, Vol. 44, 1952, p. 1221.

adjustment of the oxygen potential first to a level to reduce the iron ore to an impure pig iron and then later to increase the oxygen potential to oxidize impurities from that iron in the steelmaking operation. In the iron blast furnace the oxygen potential is extremely low in the hearth zone and continually increases as the reducing gases move up the furnace, reacting with iron oxide and coke according to Eqs. (4-6) and (4-7). The temperature profile of the furnace shows a continually decreasing temperature from about 3000°F in the bosh zone just above the tuyeres down to 400°F at the top of the furnace. The range of oxygen potentials in the furnace is illustrated in the following example problem.

**Example Problem 4-1.** Compare the oxygen potentials in the blast furnace hearth with those in the blast furnace stack.

**Solution.** Preheated air is blown into the furnace where the oxygen reacts immediately with hot coke to form carbon monoxide. The pressure is approximately 2 atm and the gas composition would be approximately  $\frac{1}{3}\text{CO}$  and  $\frac{2}{3}\text{N}_2$ . Assuming a temperature of 1550°C and equilibrium for the reaction,



$$K_a = \frac{a_{\text{C}}^2 P_{\text{O}_2}}{P_{\text{CO}}^2} = \frac{P_{\text{O}_2}}{(0.67)^2} \quad (4-b)$$

From Table A-II,

$$-RT \ln K_a = -RT \ln \frac{P_{O_2}}{(0.67)^2} = 56,400 + 40.32 T, \quad (4-c)$$

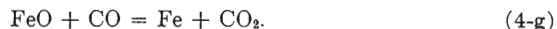
$$\log K_a = -\frac{56,400}{4.575(1823)} - \frac{40.32}{4.575}, \quad (4-d)$$

$$\log \frac{P_{O_2}}{(0.67)^2} = -6.75 - 8.81, \quad (4-e)$$

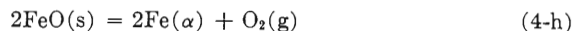
$$P_{O_2} = 0.67^2(10)^{-15.56} = 1.24 \times 10^{-16} \text{ atm.} \quad (4-f)$$

The oxygen potential in the hearth, the lowest oxidation level in the furnace, is on the order of  $10^{-16}$  atm.

Up in the furnace stack, the gases become less reducing. Consider the point at which wüstite is reduced to iron, at a temperature on the order of  $750^\circ\text{C}$  according to the reaction,



The maximum oxygen potential at which this reduction can occur is given by the reaction,



Approximating the standard free energy change of Eq. (4-h) by extrapolating the linear temperature relationship for delta iron (Table A-II) to lower temperatures, and noting that the solid phases are at unit activity,

$$\log K_a = \log P_{O_2} = -\frac{125,200}{4.575(1023)} + \frac{30.36}{4.575}, \quad P_{O_2} = 10^{-20}. \quad (4-i)$$

The oxygen potential is then  $10^{-20}$  atm, but at a temperature of  $750^\circ\text{C}$ . If the oxygen potentials of the gas phases in the hearth and in the stack are compared at the same temperature, e.g.,  $1550^\circ\text{C}$ , the effective oxygen potential of the gas in the furnace stack would be only  $2.5 \times 10^{-8}$  atm.

#### Blast Furnace Stoichiometry

A material balance around the blast furnace (or any extractive metallurgical process) not only describes in detail the mass flow of the streams going to and from the system and permits an energy balance to be written based on it, but is also very helpful in performing charge calculations. The material balance for the blast furnace requires a knowledge of the composition and amounts of each stream going to and from the blast furnace system. Often this information is known with limited accuracy and one must, therefore, estimate or make assumptions concerning the disposition of given materials between various streams. The slag volume and theoretical slag composition may be calculated from lime, magnesia, silica, and alumina balances; an iron balance is used to calculate the mass of the metal stream while

carbon, oxygen, and hydrogen balances are used to determine the exit gas volume and composition. Several examples of this type of calculation have been presented.<sup>4-6</sup>

#### Energy Balance

The total enthalpy balance for a blast furnace operation during a given reference period may be written in the form,

$$H_{\text{blast}} + H_{\text{burden}} + H_{\text{stone}} + H_{\text{coke}} = H_{\text{hot metal}} + H_{\text{slag}} + H_{\text{top gas}} + H_{\text{heat loss}} \quad (4-13)$$

where the enthalpy terms include heats of formation as well as sensible heats. It is necessary to solve the equation for the term  $H_{\text{heat loss}}$ . In doing so, the sensible heat of the burden, stone, and coke are taken as zero, since these components may be assumed to enter at  $77^\circ\text{F}$ , the usual base temperature for such calculations. The sensible heats of the blast and hot metal may be computed directly. The sensible heat of the top gas may be computed using the reported  $\text{CO}/\text{CO}_2$  ratio and assuming the ratio  $\text{H}_2/\text{H}_2\text{O} = 4$ . For normal operation, i.e., without high blast moisture or hydrocarbon injection at the tuyeres, the latter assumption has little or no effect on the overall enthalpy balance. It is usually necessary to assume a temperature for the exit gases, and  $400^\circ\text{F}$  is often selected. In calculating the sensible heat of the slag, the stream can be assumed to be a mixture of  $2\text{CaO} \cdot \text{SiO}_2$ ;  $2\text{CaO} \cdot \text{Al}_2\text{O}_3$ ;  $\text{SiO}_2$ ;  $\text{CaO} \cdot \text{SiO}_2$ ;  $2\text{MgO} \cdot \text{SiO}_2$ ; and  $\text{CaS}$ . Heats of formation for these compounds and their specific heats may be used to compute the sensible heat of the slag. It is a reasonable assumption to neglect the heats of mixing of these slag components. The heat loss term of Eq. (4-13) then can be computed.

The variation in hot metal cost resulting from the use of different blends of available raw materials can be assessed using linear programming techniques (see Computer Applications). This approach was first used by Bailey,<sup>7</sup> who incorporated into his linear program the statistical information developed by Flint.<sup>8</sup> A linear program involving a mass-energy balance, restrictions on the quality requirements for input and output streams, together with the economics of operating and freight costs can be used to optimize the blast furnace burden at different geographic locations with regard to cost and production rate.

#### Improvements in Blast Furnace Operation

In addition to design improvements, the principal advancements in blast furnace technology during the past two decades have been control of the blast humidity, oxygen enrichment of the blast, natural gas or other fuel injection, pressurized operation, and the increased use of beneficiated materials.

<sup>4</sup> W. K. Lewis, A. H. Radasch, and H. C. Lewis, *Industrial Stoichiometry*, Chemical Engineering Series, Chapter 10, McGraw-Hill, New York, 1954.

<sup>5</sup> H. N. Lander, H. W. Meyer, and F. D. Delve, *AIIME Trans.* **221**, 485 (1961).

<sup>6</sup> H. N. Lander, H. W. Meyer, and F. D. Delve, *AIIME Blast Furnace Proc.* **19**, 219 (1960).

<sup>7</sup> D. R. Bailey, *AIIME Proc. Blast Furnace, Coke Oven and Raw Materials Conf.* **16**, 15 (1956).

<sup>8</sup> R. V. Flint, *AIIME Proc. Blast Furnace, Coke Oven and Raw Materials Conf.* **11**, 49-73 (1952).

Almost one-half of the material entering the blast furnace is air. Consequently, relatively small changes in humidity are important with regard to the amount of water carried into the furnace. Indeed, controlled humidity has been proposed as a means of regulating the blast furnace.<sup>9</sup> The endothermic decomposition of the water vapor in the hot zone adjacent to the tuyeres absorbs considerable heat. This additional heat absorbed in the hearth of the furnace increases the amount of fuel required in the form of coke. Some fuel savings can be accomplished by drying the blast stream either by a refrigeration cycle or by passing the air through suitable drying columns.

Oxygen enrichment of the blast as a means of increasing furnace output has been proposed for some time, and the availability of large supplies of low-cost oxygen as the result of developments in air separation processes has made this proposal even more feasible. A 6% oxygen enrichment of the blast should increase production rates from 20–25%. Since the effect of oxygen enrichment would be to decrease the nitrogen content of the blast, this should result in less heat being carried away from the furnaces by the top gas, a decreased volume and velocity of the reacting gas with a corresponding reduction in flue dust, and an increased efficiency of combustion of the coke with higher hearth temperatures.

The amount of oxygen passing through the furnace for a given gas velocity may be increased if the furnace is operated under pressure. Modifications to several existing blast furnaces were made at the time of World War II and showed a 15% increase in production with a decrease in coke rate of about 12½% and in flue dust of about 33%. Top pressures of about 1-atm gauge (2 atm absolute pressure) are maintained on some furnaces and attempts to increase this pressure have been made, although there is often considerable mechanical difficulty connected with the operation of a blast furnace under high pressure.

Enrichment of the blast with natural gas also results in a lower coke rate.

The use of pelletized concentrates has markedly increased blast furnace productivity. The first commercial test of taconite pellets was made on the Bellefonte Furnace of Armco Steel Corporation at Middletown, Ohio, in the summer of 1960. During a 30-day test, the furnace, which was rated at 1500 tons per day using a conventional burden, achieved daily production records of 2700–2800 tons of pig iron.<sup>10</sup>

The beneficiation of materials improves burden properties by concentration and enrichment, and also may improve the physical form of the burden as well. The washing and sizing of the burden is a very important aspect in obtaining optimum furnace performance. Considerable economy also is obtained with regard to transportation of charge materials to the furnace site if they are beneficiated at the mine. In addition, sizing of material prevents channeling of the gases, with resulting improvement in mass and heat transfer in the furnace shaft, and also promotes a more uniform movement of the burden down through the furnace.

<sup>9</sup> A. L. Hodge, AISI Meeting, New York, May 25, 1960; Also *Iron Age*, June 2, 1961.

<sup>10</sup> E. W. Davis, *Pioneering with Taconite*, p. 191, Minnesota Historical Society, St. Paul, Minn., 1961.

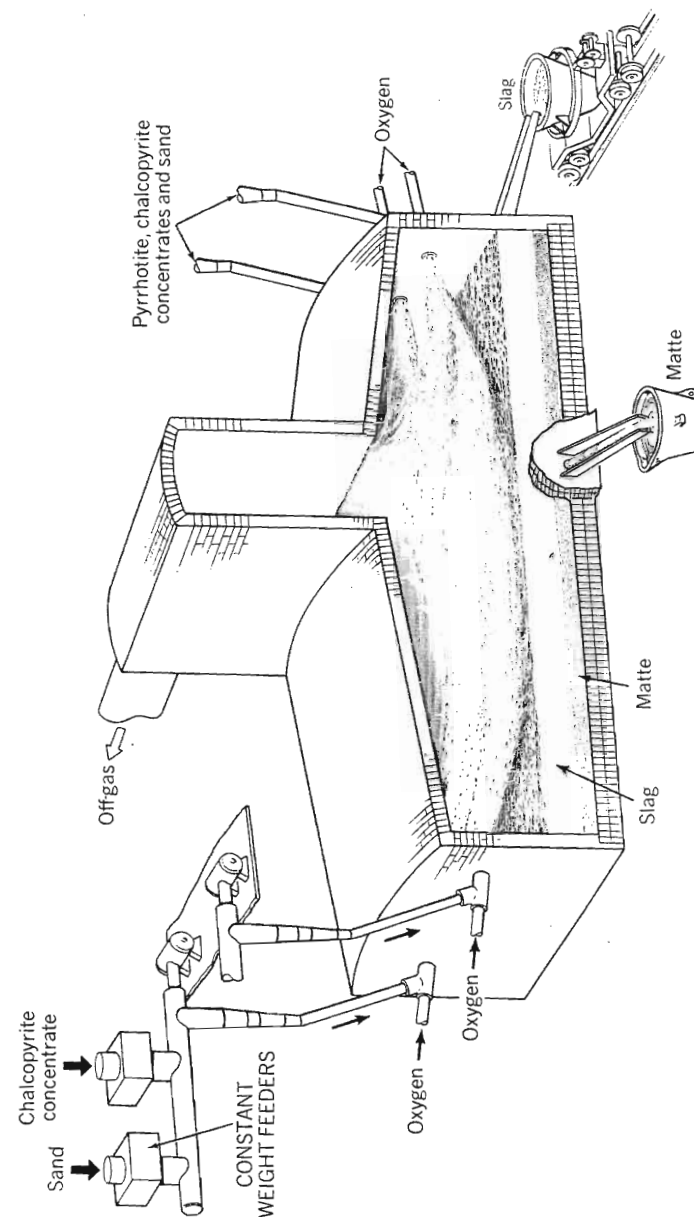


Fig. 4-7. Oxygen Flash Smelting Furnace

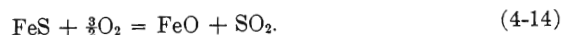
Source: J. R. Boldt, Jr., *The Winning of Nickel*, D. Van Nostrand Company, Princeton, New Jersey, 1967, p. 245.

### 4-3 Autogenous Smelting

Utilization of the heat of combustion of sulfides for smelting to matte and slag has been the objective of considerable development work. The flash roasting of sulfides has been extended into development of an oxygen flash-smelting process. An oxygen flash smelting furnace is shown in Fig. 4-7. Flash smelting takes place without additional fuel when a concentrate is suspended in a stream of oxidizing gases, such as oxygen-enriched air or pure oxygen, wherein the heat of oxidation brings the suspended particles to a temperature that permits melting to occur. Thermal balances for oxidation of sulfides show that it is necessary to preheat the air, enrich it with oxygen, or supply additional fuel to achieve temperatures sufficient to carry out a smelting operation. In flash smelting, a fine, high-grade sulfide ore falls through an oxidizing gas and the slag and matte are collected on a hearth. Mixing of preheated air and dried concentrate in a burner at the top of the reaction shaft spreads a shower of particles over the entire shaft area, permitting smelting to take place as the particles fall through the upwardly rising gases. Control of the furnace is accomplished by altering the preheat temperature of the air, or the fuel rate. The hot gases are cleaned and then cooled by passing them through a waste heat boiler. The concept of flash smelting is to carry out simultaneously the roasting, smelting, and conversion of sulfide ores. The roasting and converting operations are exothermic processes, whereas smelting is endothermic and the heat consuming portion of the process. By combining the three steps, considerable fuel savings can be realized, but it is necessary to carry out this process on relatively low-grade concentrates with sufficient sulfur to serve as fuel.

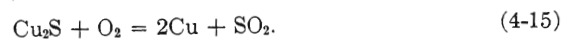
### 4-4 Copper Converting

The conversion of copper matte to metallic copper is accomplished by blowing air through the matte to oxidize the iron and sulfur. The conversion takes place in two stages. In the first stage iron sulfide is oxidized to iron oxide according to the reaction,



The iron oxide then combines with the silica flux to form a slag. After the first stage of blowing, the matte consists of essentially pure  $\text{Cu}_2\text{S}$ , which is called "white metal." A very small concentration of  $\text{Cu}_2\text{O}$ , on the order of 1%, is built up in the slag during the first stage of blowing. Copper that is oxidized into the slag tends to be reduced by iron sulfide in the matte until the FeS concentration becomes very small. The oxidation of iron is highly exothermic, and with low grade mattes, i.e., those containing high iron contents, copper scrap is often added to maintain the temperature of the charge being oxidized in the converter.

The second stage of blowing consists of oxidation of the "white metal" according to the reaction,



In operating practice the converter is charged with molten matte and silica flux. The air is turned on and the converter rotated to the position shown sche-

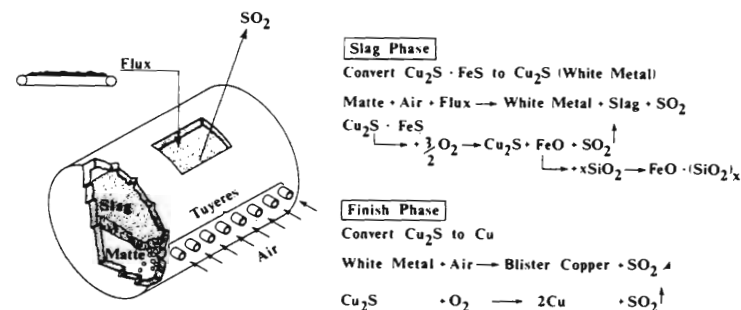


Fig. 4-8. Schematic Illustration of Copper Converter

Source: "Mathematical Model for Copper Converter Control," James H. Foreman, *Quarterly of the Colorado School of Mines*, 1964, Vol. 59, No. 4—Part A, p. 435.

matically in Fig. 4-8. As the iron is oxidized and slag builds up, the slag is run off and more matte and silica are added. This cyclic operation continues until the charge consists of essentially white metal. In the conversion of white metal, the copper sinks to the bottom of the vessel, leaving a layer of  $\text{Cu}_2\text{S}$  above it. Application of the Bessemer converter (see next section) in the copper industry was unsuccessful until the tuyeres were located at the sides of the vessel instead of the bottom. The failure of bottom blowing has been ascribed to separation of the copper-rich and copper sulfide-rich layers in the vessel. Bottom blowing would oxidize the copper and require mixing of the two immiscible liquids to react the copper oxide and copper sulfide according to the reaction,



whereas side blowing permits direct exposure of the  $\text{Cu}_2\text{S}$  to the oxidizing air bubbles.

Two general styles of converter have been used, the Great Falls converter, which was a pear-shaped vessel similar to a Bessemer converter (see following section), and the Pierce-Smith converter, which is a longitudinally oriented cylinder. An operating Pierce-Smith converter is shown in Fig. 4-9.

The product of the copper converter is termed "blister copper" because of the formation of gas by combination of dissolved sulfur and oxygen during solidification. The blister copper which is approximately 99% pure, contains the precious

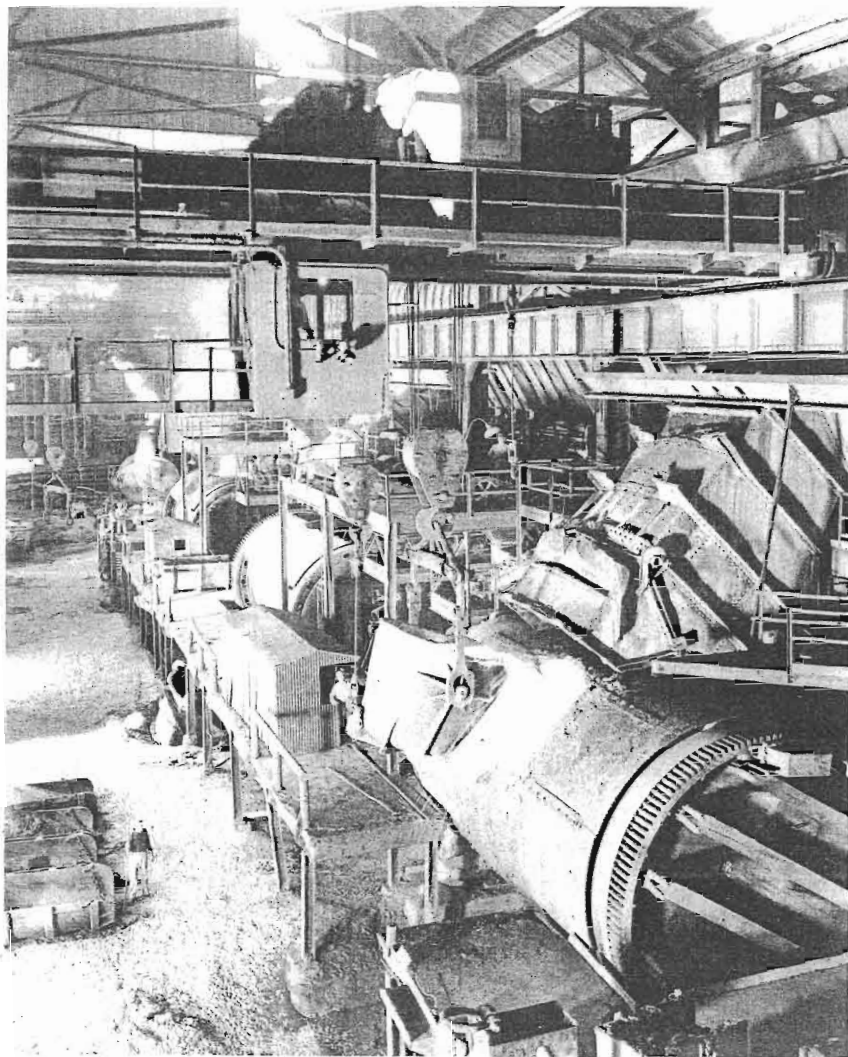


Fig. 4-9a. Charging Matte to Copper Converter at Utah Plant,  
Courtesy of Kennecott Copper Corporation

metals present in the matte and is subjected to further refining. Material flow in the smelting and converting of copper is illustrated in Fig. 4-10.

During operation, the tuyeres of the copper converter must be repeatedly opened by punching. One of the mechanisms leading to plugging of the tuyeres is the formation of magnetite in the slag during the first stage of blowing (see Appendix

B, Example Problem 5). Each converter is equipped with automatic tuyere punching devices.

Overall copper smelter efficiency is highly dependent upon the converter operation. The converter slag, which contains 2-5% copper, is returned to the reverberatory furnace and thus the smelting rates are influenced by the silica and

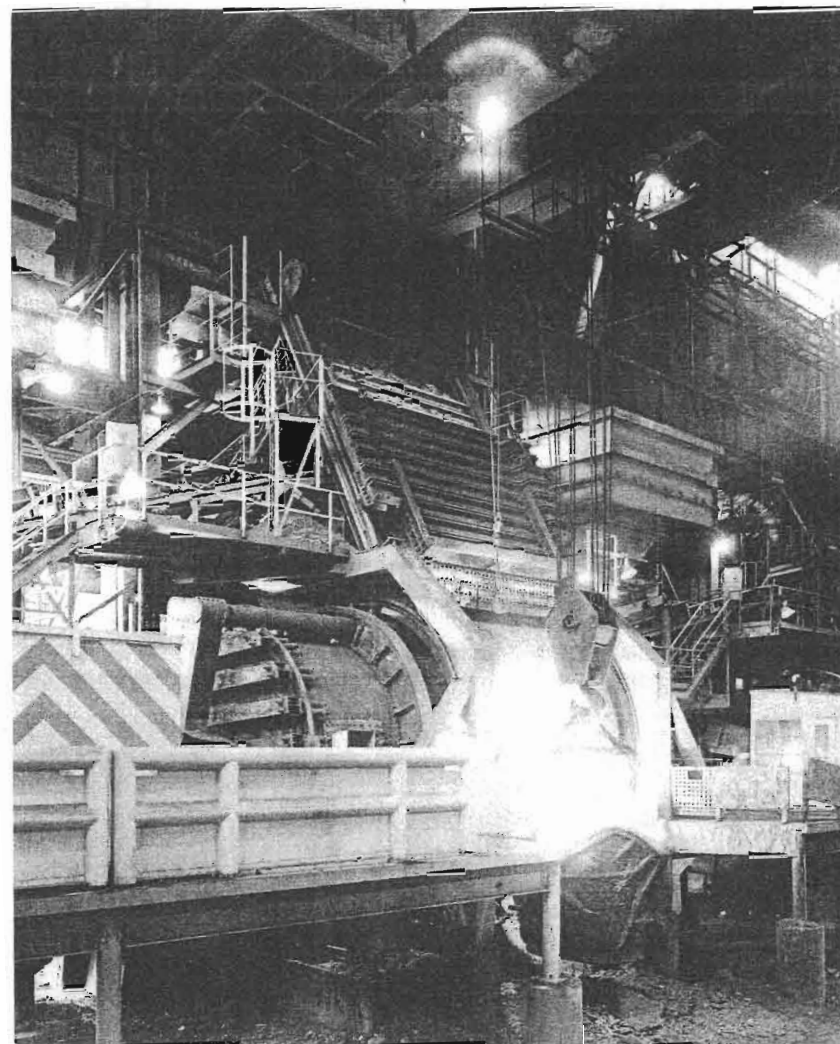


Fig. 4-9b. Pouring Copper from Converter at Utah Plant,  
Courtesy of Kennecott Copper Corporation

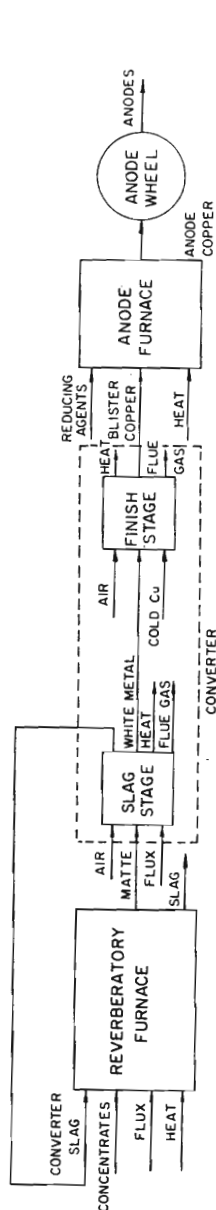


Fig. 4-10. Flow of Materials in Copper Processing

Source: E. H. Dudgeon, L. K. Nenonen, A. G. Balogh, and P. L. Fowler, "Measurements for Control of a Copper Converter," *Continuous Processing and Process Control*, Gordon and Breach Science Publishers Inc., New York, in press.

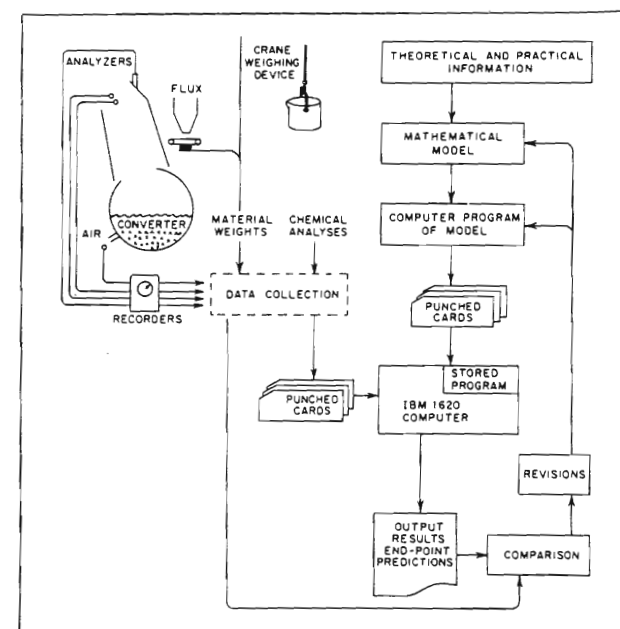


Fig. 4-11. Schematic Diagram of a Simulation Development Procedure for a Copper Converter

Source: J. Foreman, *J. Metals*, 1965, Vol. 17, p. 617.

magnetite concentrations in the returned converter slag. Lining life in both the reverberatory and converter operations is determined by temperature and slag control. Most operations are manually controlled at present, but with suitable instrumentation, computer control could be realized.<sup>11,12</sup> A thermochemical model describing copper converter operation in terms of a mass and energy balance has been described.<sup>13</sup> A schematic diagram showing development of a control model is shown in Fig. 4-11. Application of the concept of oxygen top blowing has been applied to the copper converter, and preliminary experimental work has shown promise for producing blister of high quality. Oxygen-enriched air has also been considered for the conversion of copper matte.

#### 4-5 Steelmaking

From an economic viewpoint, the production of steel is the most important process in extractive metallurgy because of the large tonnages involved. Steel has been

<sup>11</sup> E. H. Dudgeon, L. K. Nenonen, A. G. Balogh, and P. L. Fowler, *Measurements for Control of a Copper Converter*, presented at 2nd Operating Met. Conf., Philadelphia, December 1966.

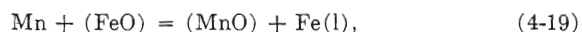
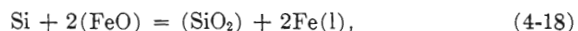
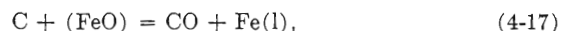
<sup>12</sup> J. Foreman, *J. Metals* 17, 616 (1965).

<sup>13</sup> Ibid.

known and used for over 5000 years, although until about 1700 A.D. it was not produced in the liquid state. The reduction of iron ores by carbonaceous fuel directly to a steel composition was practiced in ancient times, but liquid processing was unknown until development of the crucible process, wherein iron sponge or cemented wrought iron, coal, and flux materials were melted in a crucible to produce small quantities of liquid steel. Modern steelmaking processes came into being with the invention of the air-blown converter by Bessemer in 1856. In 1878, the Thomas process, a modified Bessemer process was developed to permit treatment of high phosphorous pig iron. The Siemens-Martin process, commonly referred to as the open hearth process, was developed at about the same time as the Thomas process. The open hearth process utilizes regenerative heat transfer to preheat air used in a burner, and is able to generate sufficient heat to refine solid steel scrap and pig iron in a reverberatory furnace. The availability of high tonnage oxygen at reasonable costs following World War II led to the development of various oxygen steelmaking processes, including the top-blown oxygen process, the Kaldo process, and the rotor process.

Steelmaking is a refining process in which impurity elements are oxidized from pig iron and scrap steel that are charged to the process. Steelmaking processes are classified as acid or basic, depending upon whether the slag is high in silica (acid) or high in lime (basic). The furnace lining in contact with the slag must be of a compatible material; a silica or siliceous material is used in acid processes and a basic material, such as burned dolomite or magnesite, is used in basic processes. Carbon, manganese, and silicon, the principal impurity elements in pig iron, are easily oxidized and separate as oxides, the manganese and silicon oxides going into the slag and carbon being removed primarily as carbon monoxide in the off-gases. Phosphorus also is oxidized but does not separate from the metal unless the slag is basic. Removal of sulfur occurs to some extent by absorption in a basic slag. Thus the basic steelmaking processes are more versatile in the raw materials they can handle, and consequently have become the predominant steelmaking methods.

The pig iron charge to the steelmaking process contains on the order of 4% carbon, 1% manganese, and 1% silicon. The phosphorus and sulfur levels in the pig iron vary, depending upon the steelmaking process, the basic Bessemer using phosphorus levels from 1.5–2%, whereas in other processes it is desirable to have the phosphorus as low as possible. Steel as tapped from the steelmaking furnace generally falls in the composition range 0.04–0.80% carbon, 0.06–0.30 manganese, 0.01–0.05 phosphorus, 0.01–0.05 sulfur, and negligible silicon. The reactions occurring in steelmaking can be represented as\*



\* As noted in Chapter 3, the underline notation refers to the element in metallic solution. The bracket notation refers to the compound in solution in the slag phase.

The equations above are treated in terms of oxidation by liquid iron oxide in the slag. Several alternative mechanisms are considered possible, such as direct oxidation by gaseous oxygen, as illustrated by the reaction,



or alternatively, the oxygen may dissolve in the liquid iron and react according to the relationship,



The removal of phosphorus from the bath requires a basic oxidizing slag as illustrated by Eq. (4-20). The actual form of the phosphorus in the slag is thought to be tricalcium or tetracalcium phosphate, although the evidence is not entirely clear in this regard. Sulfur is absorbed by a basic slag, although it may or may not form a calcium sulfide molecule as indicated by Eq. (4-21).

#### Bessemer Converter Processes

The original Bessemer converter employed an acid lining, but this acid process is not used too extensively at present. The process requires a very low phosphorus and low sulfur-bearing pig iron since these elements are not removed in the process. A cross section of a Bessemer converter is shown in Fig. 4-12. Oxidation of the charge is accomplished by blowing air through a wind box on the bottom of the vessel. Elements are eliminated essentially in the same order as the stability of the oxide, i.e., silicon is eliminated first, along with manganese, and finally carbon as shown in Fig. 4-13. The Bessemer process is autogenous, i.e., no additional heat is

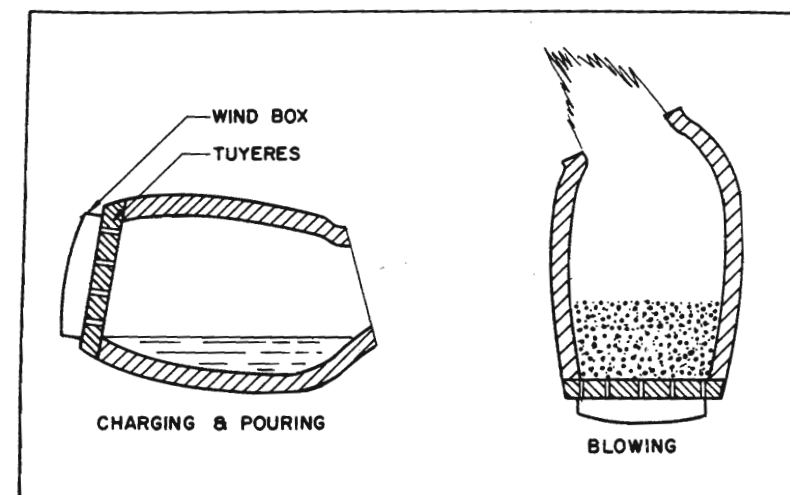


Fig. 4-12. Operating Positions of Bessemer Converter

supplied to the process, and the oxidation of the metalloids, particularly silicon, is sufficient to keep the charge molten and raise the temperature as purification proceeds such that a low carbon steel at a temperature near 2900°F is produced at the end of the process.

The Thomas or Basic Bessemer process, which is used extensively in Europe, is carried out in a basic-lined vessel and utilizes lime or limestone as a charge material to form a basic slag. Pig iron charged to this process contains up to 2 wt% phosphorus, which is oxidized from the bath after most of the carbon has been removed in a so-called "after blow." The oxidation of the phosphorus is exothermic and adds considerable thermal energy to the process.

One of the disadvantages of Bessemer steelmaking is the resulting high phosphorus and nitrogen contents in the steel. The nitrogen content of Bessemer steel is on the order of 0.015 wt%, although lower nitrogen levels can be achieved by careful control of temperature, and by carrying out the final oxidation of the bath with iron ore additions.

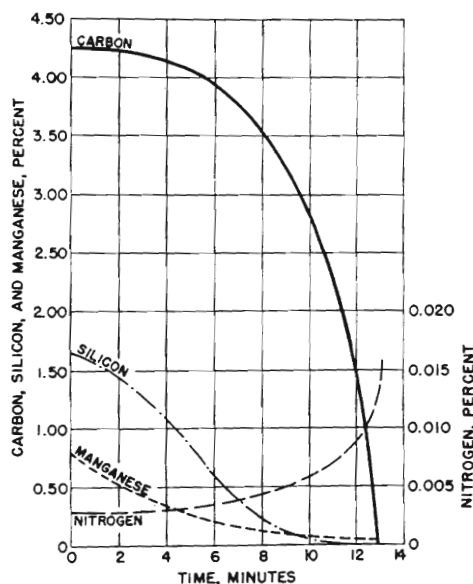


Fig. 4-13. Changes in Metal Bath Composition During Blowing Period of 25 Ton Bessemer Converter

Source: *The Making, Shaping and Treating of Steel*, edited by Harold E. McGannon, Pittsburgh, United States Steel Corporation, 9th edition, 1971, p. 479.

An important aspect of converter steelmaking is control, not only because of the rapidity with which the end point of the process is approached, but because of the necessity for providing a careful thermal balance for the autogenous process. End point control has been greatly enhanced by the use of photocells to observe the character of the flame and emission from the vessel toward the end of the blow.

### Open Hearth Process

Starting at the turn of the century up through the late 1950s, the basic open hearth process was the workhorse of the American industry, accounting for approximately 85% of the steel produced in the United States in 1955. The basic open hearth process (see chapter on Melting, Pouring and Solidification), because of its melting capabilities, can handle a wide range of pig iron to scrap ratios, the optimum operation being 40–60% pig iron with the balance of the metallic charge as steel scrap. Furthermore, in a basic operation a wide range of raw materials can be treated and the phosphorus and sulfur concentrations kept under suitable control. An advantage of the open hearth over the Bessemer process is that the steels produced contain less than 0.005 wt% nitrogen which is low enough to provide good properties in deep-drawing sheet material.

The solid constituents, steel scrap, limestone, and iron ore, are charged to the furnace, and the burner turned on. Burners are built into both ends of the furnace and the direction of the flame is changed from time to time to take advantage of the regenerative heat transfer system for the air, which is located on either side of the furnace at a lower level. As soon as the charge starts to melt down, pig iron is added and the iron oxide reacts with the molten pig iron to produce carbon monoxide in the so-called "ore boil." As the temperature increases, the decomposition of limestone proceeds at the bottom of the furnace, and a "lime boil" occurs, CO<sub>2</sub> being evolved at a relatively rapid rate. As the calcined lime floats up through the charge, phosphorus is removed as well as some sulfur.

The productivity of the open hearth furnace has been limited by both charging time and the extensive melting and refining periods, requiring on the order of 6–8 hr for melting and refining alone. The availability of low-cost oxygen has made it feasible to insert lances in the open hearth as illustrated in Fig. 4-14. Oxygen blowing in the open hearth has decreased the time required from 12–14 hr per heat down to approximately 6 hr. Oxygen blowing, however, creates fume and has necessitated gas cleaning equipment. This limitation on productivity and the added expense of gas cleaning equipment on an older installation has led to a relatively rapid displacement of the open hearth furnace by the oxygen top-blowing process.

### Oxygen Steelmaking

The high dissolved nitrogen content in Bessemer steel, which limits its application, has made apparent the necessity for finding a nitrogen-free gas for blowing in the converter. The use of pure oxygen in a bottom blown vessel will result in ex-

Typical Roof Lance For Open Hearth Furnace

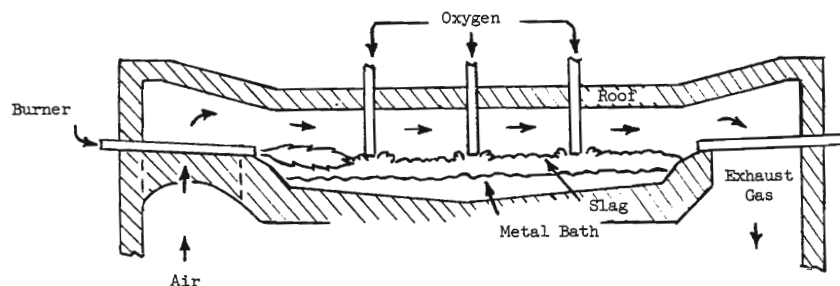
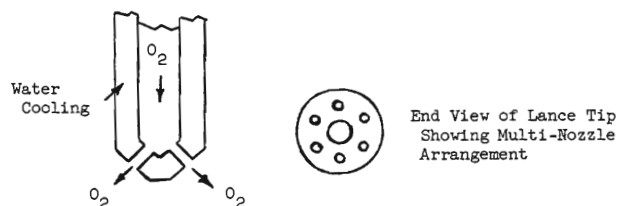


Fig. 4-14. Oxygen Lancing of an Open Hearth Heat

tremely severe erosion of the bottom lining and tuyere area. An alternative is to blow a Bessemer converter with oxygen and steam to produce low nitrogen steel. This process has received considerable attention in Europe.

In the early 1950s commercial development of the oxygen steelmaking process was brought to fruition at Linz, Austria. Austrian ores are low in phosphorus and could not thermally support the basic Bessemer process, and furthermore a shortage of scrap in Austria following World War II eliminated economic application of the open hearth. These factors, together with availability of low-cost tonnage oxygen, led to development of the top-blown oxygen process, based on previous experience with a small vessel at Gerlafingen, Switzerland. The first large-scale oxygen steelmaking converters were 30-ton vessels. Further development of the process, particularly in the United States, has increased the size of the vessel until most oxygen steelmaking shops employ 250-ton vessels, with vessels as large as 300 tons in operation. The top-blown process is referred to as the BOF, BOP, OP, or L-D process.

Figure 4-15 shows an oxygen steelmaking vessel in which a 250–300 ton heat is being blown. The process is autogenous and uses on the order of 25–35% scrap, the remainder being basic pig iron that is relatively low in sulfur. Burned lime is used

as a flux and a sufficient amount is added to produce a lime-silica ratio in the final slag on the order of 3 to 1. Oxygen is blown vertically down into the bath through a Laval nozzle, which produces supersonic flow. With larger vessels the use of a 3-hole lance has improved operation. The flow rate of oxygen gas in standard cubic feet per minute is given by the relationship,

$$Q_{\text{SCFM}} = 17.46 P_d A^*, \quad (4-24)$$

where

$P_d$  = nozzle driving pressure, psia,

$A^*$  = throat area of nozzle, sq in.

This relationship assumes that the oxygen temperature ahead of the nozzle is 60°F. The calculated flow rate can be corrected for oxygen supply temperature by the

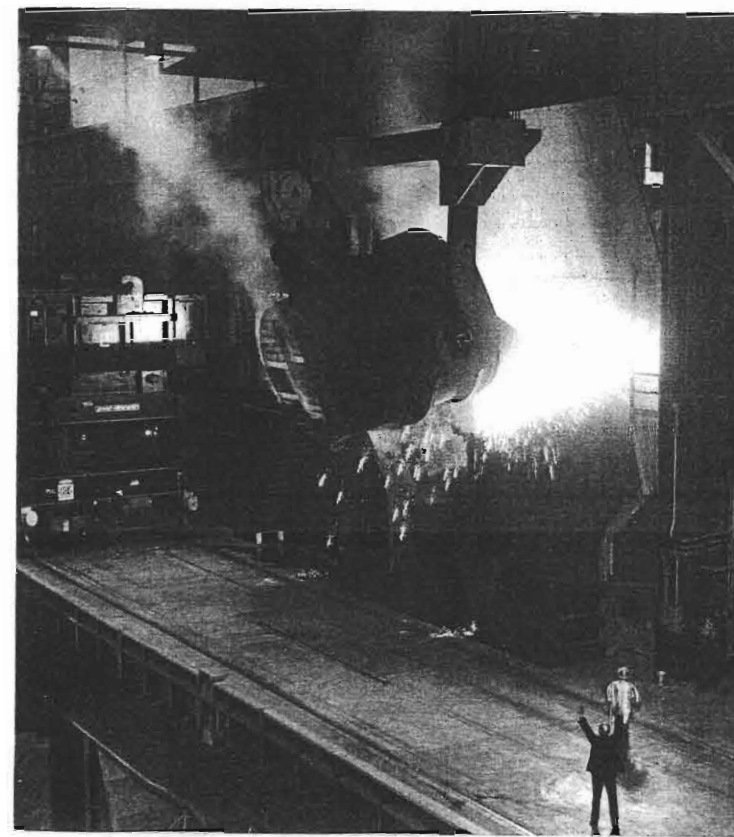


Fig. 4-15. A Large Oxygen Steelmaking Furnace in Operation  
Courtesy of Bethlehem Steel Corporation, Bethlehem, Pennsylvania.

relationship,

$$Q(\text{actual}) = Q(\text{Eq. 4-24}) \left[ \frac{(60 + 460)}{[T_{O_2}(\text{°F}) + 460]} \right]^{1/2} \quad (4-25)$$

Copious fume in the form of micron-sized particles of iron oxide is evolved during the oxygen blow. This fume loss amounts to 2–3% of the metallic charge and a large portion of the capital expenditure of a Basic Oxygen Furnace plant is for gas-cleaning equipment. Significant operating variables include the lance height and oxygen flow rate. The required blowing time for a heat, including those approaching 250 tons, is on the order of 20 min. By suitable adjustment of the lance height, some iron can be oxidized early in the blow to dissolve the lime and produce an early basic oxidizing slag to assist in phosphorus removal. Later in the heat, lowering the lance or increasing the oxygen flow rate provides the deep penetration necessary to agitate metal and slag and provide for relatively low iron losses in the slag.

Control of the oxygen steelmaking process requires that the bath temperature at the end of the heat be within  $\pm 20^\circ\text{F}$  of a given temperature, usually  $2920^\circ\text{F}$  for production of low carbon (below 0.10 wt%) steels. Since the process is autogenous (no external fuel) and the final temperature requires a balanced charge to achieve the desired end-point temperature at the end of the heat, the use of a thermally balanced charge as a control means has met with some success. However, this approach is limited in its performance because of the difficulty in making measurements on the charge materials which are sufficiently accurate, as illustrated in the following example problem.

**Example Problem 4-2.** Control of the oxygen steelmaking process is based initially on a thermally balanced charge. The calculation of the proper scrap charge (see Appendix B, Example Problem 4) requires accurate knowledge of the charge composition, in particular the hot metal analysis, and the hot metal temperature.

Estimate the influence on end point temperature of a variation of 0.05 in the wt% silicon in the hot metal. (A variation of 0.03–0.05 is the typical standard deviation in silicon analysis of hot metal encountered in operating practice.) Base the calculation on 240,000 lb of hot metal and a heat size of 300,000 lb.

**Solution.** The assumed value of 0.05 wt% error would yield an error of

$$\frac{0.05}{100} (240,000 \text{ lb hot metal}) \frac{1}{28.06} = 4.27 \text{ moles of Si.}$$

The thermal balance for silicon involves

|                                                  |                       |
|--------------------------------------------------|-----------------------|
| Heat to hot metal temperature                    | +19700 Btu/lb mole Si |
| Solution in hot metal                            | –34150                |
| Heat to slag temperature                         | –55800                |
| Reaction with oxygen to form $\text{SiO}_2$      | +369700               |
| Reaction of $\text{SiO}_2$ with CaO              | +53640                |
| Energy available to raise steel bath temperature | 353,090               |

$(353090)(4.27) = \text{Btu from error in silicon analysis.}$

$(300000)(0.184)\Delta T = \text{change in steel bath energy in Btu} = (\text{wt})(C_p)(\Delta T).$

Equating these energies and solving for  $\Delta T$ ,

$$\Delta T = 27.3^\circ\text{F.}$$

Even a deviation of only 0.03 in the wt% silicon would change the predicted turn-down temperature by

$$\frac{0.03}{0.05} (27.3) = 16.3^\circ\text{F.}$$

Thus the analysis for silicon in the hot metal is very important in making a proper charge balance. The desired accuracy of the end point temperature,  $\pm 20^\circ\text{F}$ , cannot be reached with present sampling and analysis techniques and instrumentation. (Hot metal temperature is also a very significant variable). Techniques are being developed for “in process” temperature measurements, stack gas analysis, and flow measurements (dynamic control). Temperature can be used as a basis for adjusting the blowing practice and making additions of exothermic or cooling materials. The gas analysis is indicative of proper blowing practice as well as providing a measure of the carbon content, either by determining the carbon lost in the stack from measured  $\text{CO}/\text{CO}_2$  ratios and stack gas flow rates, or by correlating the  $\text{CO}/\text{CO}_2$  ratio with bath carbon.

A detailed material and energy balance for the oxygen steelmaking process in the form of a thermochemical model that shows the influence of hot metal silicon on scrap melting is presented as Example Problem 4 in Appendix B.

The processing of high phosphorus irons in the top-blown oxygen steelmaking process is possible by injecting powdered lime into the oxygen stream. This technique is known as the LD-AC process and is used in Europe to process pig iron containing more than 0.5 wt% phosphorus.

**Oxygen Converter Gas Recovery Process.** The recovery of carbon monoxide evolved from the oxygen steelmaking process is referred to as the O-G Process (oxygen converter gas recovery process). Many oxygen steelmaking vessels have open hoods into which air is ingested to burn the hot evolved converter gases, which are about 90% carbon monoxide during much of the oxygen blowing period. Considerable effort has been carried out, particularly in Japan, to recover the converter gas that averages over 80% carbon monoxide for use as a fuel in the steel plant. The use of a closed hood and special precautions to prevent explosion of the carbon monoxide has resulted in a process which is economic in recovering the thermal energy in the carbon monoxide. In most hoods, a waste heat boiler is employed to recover the sensible heat of the stack gas, but a marked improvement in thermal efficiency is achieved by collecting the carbon monoxide gas for use as a supplementary fuel in the steel plant. Furthermore, the gas cleaning problems are made less difficult because the volume of gas is only approximately  $\frac{1}{3}$  as great as when air is ingested in an open hood system. A general view of a gas recovery system is shown in Fig. 4-16.

**Kaldo and Rotor Processes.** Other oxygen blowing processes have been developed that employ rotating converters. The rotation of the vessel mixes the slag and metal, and also provides for heat transfer from the hot lining to the charge of

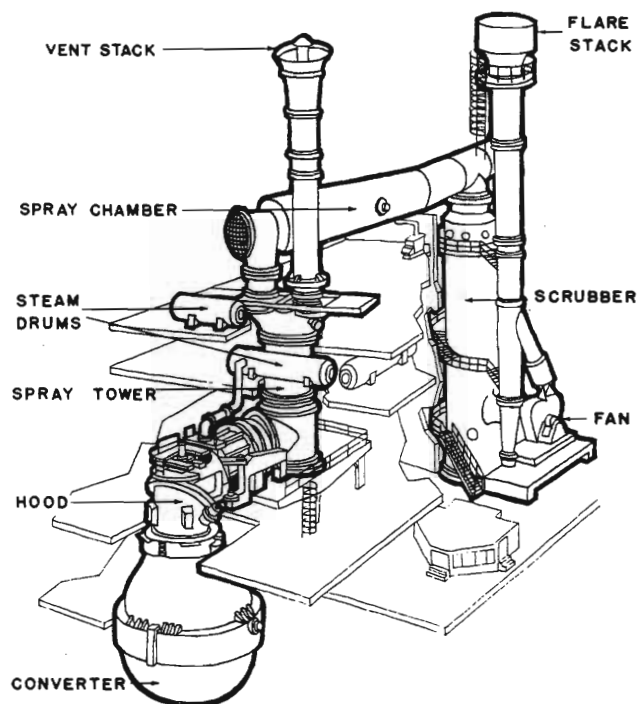


Fig. 4-16. Schematic View of a Gas Cleaning System for an Oxygen Converter  
Courtesy of Swindell-Dressler, Division of Pullman Inc.

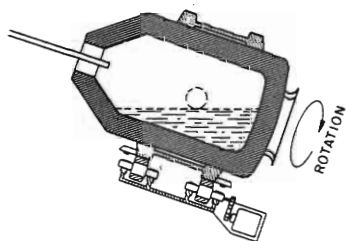


Fig. 4-17. Stora Kaldor Process

Source: *The Making, Shaping and Treating of Steel*, edited by Harold E. McGannon, Pittsburgh, United States Steel Corporation, 9th edition, 1971, p. 474.

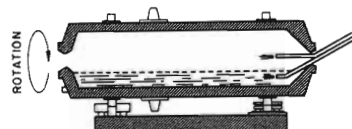


Fig. 4-18. Rotor Process

Source: *The Making, Shaping and Treating of Steel*, edited by Harold McGannon, Pittsburgh, United States Steel Corporation, 9th edition, 1971, p. 474.

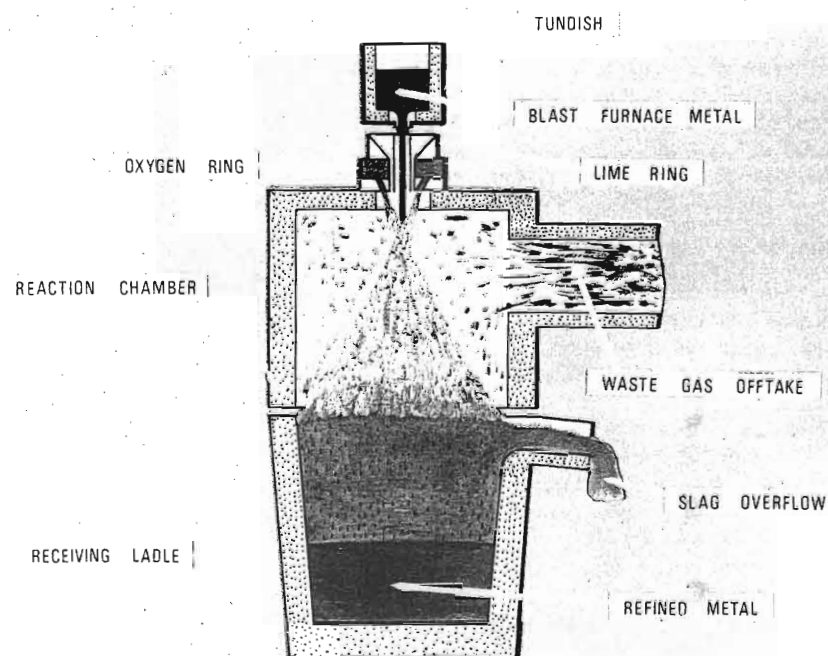


Fig. 4-19. Spray Steelmaking Process

Courtesy of British Iron and Steel Research Association.

the vessel. Schematic diagrams of these two processes are shown in Figs. 4-17 and 4-18. Adjustment of the oxygen lance to provide for limited penetration of the  $O_2$  jet into the bath permits combustion of the carbon monoxide formed by oxidation of carbon in the iron bath to carbon dioxide within the furnace. This release of heat permits the melting of relatively large quantities of steel scrap, which is an economic advantage.

The Kaldor converter is a cylindrical, refractory-lined vessel that rotates on an inclined axis at speeds up to 35 rpm. A single oxygen jet is blown onto the surface of the metal. Oxygen consumption is approximately 2000 ft<sup>3</sup> per ton of steel, whereas in the top-blown vessel it averages 1700 to 1800 ft<sup>3</sup> per ton of steel produced, depending upon the composition of the charge.

The Rotor vessel is of cylindrical shape and rotates in a horizontal plane at speeds on the order of 1-5 rpm. Oxygen is blown into the vessel through two nozzles, one below and one above the bath surface. This type of oxygen injection provides for combustion of the carbon monoxide with a relatively high thermal efficiency. A two-slag rotor process in which high phosphorus irons are processed has been employed in England.

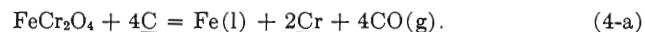
**Spray Steelmaking.** The spray steelmaking process offers the possibility of higher processing rates. This method utilizes a stream of oxygen to break up liquid blast furnace iron as it flows from the nozzle of a ladle or tundish (large pouring basin). The stream of oxygen together with powdered lime reacts with the resulting spray of fine droplets removing carbon, silicon, sulfur and phosphorus. The refined metal droplets and slag are collected in a ladle below as shown schematically in Fig. 4-19.

### Electric Furnace Steelmaking

Direct arc furnaces ranging in size up to 120 tons are used to produce steel. The electric furnace may be either acid or basic-lined and has some advantage over the open hearth and oxygen converter processes in that very high temperatures can be produced (see Melting, Pouring and Solidification). The high temperature and the flexibility of using either a 100% solid charge, or up to 40 or 50% hot metal, provides considerable versatility for this melting unit. The very high temperatures are particularly useful in producing alloy steels. If large amounts of alloying elements are added to the ladle of steel from an oxygen converter or an open hearth furnace, the steel often is cooled to an extent that good quality ingots cannot be poured, or if the alloying elements are added in the furnace, they may be oxidized into the slag. This is particularly true for elements such as columbium, vanadium, and chromium. Furthermore, the requirement in certain types of stainless steel to provide for very low carbon contents requires that the carbon be removed without excessive chromium losses. This is possible only at high temperatures, as shown in the following problem.

**Example Problem 4-3.** The decarburization limit of stainless steels is enhanced by increased temperature; hence the electric furnace has been the primary unit for producing stainless steel. To illustrate this aspect of stainless steel production, calculate the minimum carbon content attainable at 1600°C (2912°F) and 1700°C (3092°F) for a steel bath containing 5% Cr, assuming chromite ( $\text{FeCr}_2\text{O}_4$ ) saturation of the slag.

**Solution.** The slag-metal reaction limiting decarburization is



The standard free energy change for Reaction (4-a)<sup>14</sup> is

$$\Delta G^\circ = 198,200 - 129.2 T \quad (4-b)$$

Assuming an effective CO pressure of 1 atm and unit activity of chromite in the slag,

$$\log K_b = \log \frac{(\% \text{Cr})^2 (a_{\text{Fe}})}{a_{\text{C}}^4} \quad (4-c)$$

<sup>14</sup> C. E. Sims, Ed., *Electric Furnace Steelmaking*, Vol. 2, p. 172, Interscience Publishers, New York, 1963.

Rearranging Eq. (4-c) for a steel bath containing 5% chromium,

$$\log (a_{\text{C}}) = \frac{10,830}{T} - 7.06 + \frac{1}{2} \log (5) + \frac{1}{4} \log (0.95), \quad (4-d)$$

$$\log (a_{\text{C}}) = \frac{10,830}{T} - 6.716.$$

At 1600°C  $\log (a_{\text{C}}) = -0.936$ ; at 1700°C  $\log (a_{\text{C}}) = -1.226$ . Neglecting solutes other than chromium, and neglecting the self-interaction of carbon, and assuming that the chromium-carbon interaction parameter is temperature independent,

$$\log (f_{\text{C}}) = (e_{\text{C}}^{\text{Cr}}) \% \text{Cr}. \quad (4-e)$$

From Table A-V,

$$\log f_{\text{C}} = -0.024(5) = -0.12. \quad (4-f)$$

Then at 1600°C

$$\log (\% \text{C}) = \log (a_{\text{C}}) - \log (f_{\text{C}}) = -0.816, \quad (\% \text{C})_{1600^\circ\text{C}} = 0.153.$$

However, at 1700°C,  $(\% \text{C})_{1600^\circ\text{C}} = 0.078$ .

At 1700°C, the limiting carbon content is one-half of that at 1600°C. Oxidation of the bath to achieve carbon levels below these values would only result in oxidation of the chromium into the slag.

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### Discussion Questions

1. Discuss the thermal balance involved in the copper reverberatory smelter-converter process. What variations in the material balance can be achieved and how will they influence total production rate?

2. Build-up of magnetite accretions on the floor of copper reverberatory smelting furnaces is a problem which limits productivity and can lead to excessive shut-down for furnace repairs. This magnetite formation is akin in many ways to magnetite formation in the copper converter which causes tuyere blockage. Can you suggest any means by which magnetite formation can be limited or magnetite which has formed can be removed and by a means which does not interfere with normal smelting operations?
3. Based on the following data, describe the smelting of tin.  
Ore—Cassiterite ( $\text{SnO}_2$  78.6% Sn)  
Metal—232°C melting point  
2687°C boiling point  
Carbon solubility in liquid metal is limited.
4. Discuss the gas-solid reactions in the iron blast furnace with respect to the specific effects of recently proposed methods for improving furnace operation and efficiency.
5. Briefly discuss the solution loss and carbon deposition reactions in the iron blast furnace with respect to:
  - (a) effect of pressure
  - (b) effect of temperature
  - (c) calcination of limestone
  - (d) reduction reactions
6. Briefly discuss the processing conditions which are desirable in order to obtain:
  - (a) a high degree of desulfurization in an open hearth bath,
  - (b) low phosphorus in iron blast furnace hot metal.
7. Basing the relationships on (1) production rate, (2) capital investment, (3) steel quality (S, P, N) and types, (4) charge materials:
  - (a) Compare the Top Blown (BOF), Rotor and Kaldo oxygen processes.
  - (b) Compare these oxygen processes as a group with the basic open hearth, electric, and basic Bessemer processes.
8.
  - (a) In the production of low-carbon steel in the open hearth, it is generally not feasible to tap at lower than 0.04% C. Explain.
  - (b) Ingot iron sheet averages below 0.02% C. Explain how this is accomplished.
  - (c) Explain why it is more difficult to make low-carbon stainless steel.
  - (d) Describe briefly a method for making 17% Cr steel containing 0.03% C max.
9. In the electric furnace practice, phosphorous is eliminated early in the oxidizing period before all of the carbon is eliminated. In the basic Bessemer, phosphorous is eliminated at the very end of the blow, after all of the carbon has been removed. Explain.
10. Compare air pollution control systems for fully integrated copper and steel producing plants.

## Problems

1. A copper converting operation is carried out in a Pierce-Smith converter at 1100°C. Matte of the composition given below is charged at an average rate of

20 tons/hr. If a constant air blast of 25,000 CFM (100°F and 30 inches Hg) is maintained, what is the efficiency of the oxidation reactions?

Matte Composition: 29% Cu  
38% Fe  
28% S  
5% impurities (gangue, inerts, etc.)

2. The separation of copper in the matte during the smelting of copper ores is highly efficient. Assuming that  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  behave ideally in the matte, and noting that the activity of iron oxide in a typical reverberatory slag is on the order of 0.5 (relative to liquid pure  $\text{FeO}$ ), justify this industrial experience on a thermodynamic basis.
3. Calculate the partial pressures of  $\text{S}_2(\text{g})$  and  $\text{O}_2(\text{g})$  under equilibrium conditions corresponding to converting of copper matte where two phases—matte and copper—coexist and are mutually saturated (assume  $a_{\text{Cu}} = a_{\text{Cu}_2\text{S}} = 0.8$ ). The pressure of  $\text{SO}_2$  is about 0.2 atm.
4. The activity of  $\text{SiO}_2$  in a slag is 0.0004 based on pure  $\text{SiO}_2$  as the standard state. What is the silicon content of carbon-saturated iron in contact with this slag at 1600°C at 1 atm total pressure ( $\text{CO} + \text{CO}_2$ )?
5. A roaster calcine charged to a reverberatory smelting furnace contains 27% iron pyrite ( $\text{FeS}$ ) and 32% chalcopyrite. The remainder is gangue. Assuming that  $\text{FeS}$  and  $\text{Cu}_2\text{S}$  form the matte and that the excess sulfur is removed with the flue gases, what grade of matte will be formed and in what quantity per ton of calcine?
6. Compare the relative quantities of air required for the two stages of the copper converting process for various matte grades (e.g. 20–70% Cu).
7. In preparing a thermochemical model for analysis and control of an iron blast furnace, the energy term “heat loss” is computed from carefully collected operating data. The “heat loss” term which is made up of the heat losses from the furnace and errors in the other terms of the heat balance is subject to variation caused by inaccuracies in the reference period data. Given the following:
 

2400 TPD (tons per day) furnace  
100,000 SCFM (60°F, 14.7 psia) blast rate  
1,700,000 BTU/NTHM (net ton hot metal) heat loss  
top gas composition: 2.4%  $\text{H}_2$   
0.6%  $\text{H}_2\text{O}$   
20%  $\text{CO}$   
18%  $\text{CO}_2$   
59%  $\text{N}_2$

estimate the variation in the “heat loss” term caused by:

  - (a) an error of 0.1 in top gas  $\text{CO}/\text{CO}_2$  ratio,
  - (b) a 20°F error in hot metal temperature.
8. A blast furnace is operated with blast enrichment using natural gas (primarily methane). The wind rate is decreased to keep the gas flow rate after combustion constant. Calculate the increase in tuyere zone temperature for each 1% of natural gas enrichment (present enrichment is based on orig-

inal blast flow rate). State all assumptions. *Hint*: See Appendix B, Example Problem 2.

9. (a) Estimate the activity of sulfur in hot metal containing 0.04% S, 4.0% C, 2% Si, and 1% Mn.  
(b) Calculate the solubility of MnS, as percent S:  
(1) at 1350°C in metal containing 4% C, 1% Si, 1% Mn,  
(2) at 1600°C in metal containing 0.5% C, 0.05% Si, 0.4% Mn.
10. At turndown of a basic oxygen steelmaking heat, the liquid steel contained 0.0005 wt% silicon and 0.06 wt% oxygen at 2920°F. Assuming equilibrium, calculate the activity of silica in the slag phase.
11. At the end of a basic oxygen heat, the FeO content of the slag is approximately 20% which corresponds to a mole fraction of 0.165. Assuming that the activity coefficient of FeO in the slag is unity and that the slag and finished steel are in equilibrium at 1600°C, estimate the carbon content of the metal bath.
12. Compute the required oxygen driving pressure for the following conditions: nozzle—Laval convergent-divergent, 1.825 inches throat diameter, blowing time = 18 min.

|                 | C    | Mn   | Si   | P     | Weight (lb) |
|-----------------|------|------|------|-------|-------------|
| Pig iron charge | 4.1  | 0.95 | 1.1  | 0.25  | 160,000     |
| Scrap charge    | 0.18 | 0.30 | 0.05 | 0.03  | 60,000      |
| Steel produced  | 0.08 | 0.25 | 0.05 | 0.015 | 200,000     |

Note: CO/CO<sub>2</sub> in effluent gas = 9.

13. Recognizing that oxygen cost increases markedly with increasing purity, specify the minimum oxygen purity for a basic oxygen process installation producing low nitrogen (0.004% N maximum) steels for deep drawing sheet.
14. The basic oxygen process is turned down at about 0.05 wt% carbon in the manufacture of low carbon steel. The carbon-oxygen product has been observed to be in equilibrium with 1.5 atm CO pressure. Assuming the slag to be saturated with lime (CaO) and calcium silicate (2CaO·SiO<sub>2</sub>), calculate the equilibrium silicon content of the steel bath.
15. In the basic oxygen process, the correct prediction of end-point temperature and composition is a primary goal for the control system. The end point composition in the production of low carbon steels is relatively easy for the operator to find by observing the "flame drop" which is indicative of a low carbon bath. The end-point temperature, however, depends upon a thermal balance between the enthalpy contents of the various phases, the heat generated by reactions, and heat losses. Computer control has been proposed for this purpose. A limitation placed on any computer "model" for the process is the accuracy of input data. Several variables appear to be of importance including the hot metal temperature and the scrap weight. Estimate the acceptable error in each of these variables which would *individually* cause the normally accepted

limit of error on the pouring temperature ( $\pm 20^\circ\text{F}$ ) to be exceeded, i.e., complete the table.

| Variable ( $\theta$ ) | Input value | Estimated error in $\theta$ | Change in tap temp. ( $^\circ\text{F}$ ) |
|-----------------------|-------------|-----------------------------|------------------------------------------|
| Hot metal temp        | 2500°F      | ?                           | 20                                       |
| Scrap weight          | 75,300 lb   | ?                           | 20                                       |

Base your calculations on the following heat:

|                  | Amount (lb) | Temperature ( $^\circ\text{F}$ ) |
|------------------|-------------|----------------------------------|
| Converter input  |             |                                  |
| Steel scrap      | 75,300      | 77                               |
| Pig iron         | 253,000     | 2500                             |
| Ore              | 2,870       | 77                               |
| Burnt lime       | 19,100      | 77                               |
| Oxygen gas       | 286,800 SCF | -60                              |
| Converter output |             |                                  |
| Steel            | 300,000     | 2900                             |
| Slag             | 42,000      | 3000                             |
| Flue gas         | —           | 3000                             |

16. Compute the tons of scrap which can be melted in a BOF under the following conditions:

- (a) Combustion gas is 100% CO at 3000°F.
- (b) Combustion gas is 90% CO<sub>2</sub> and 10% CO at 3500°F.

*Assumptions:* heat losses at  $2 \times 10^6$  Btu/hr,  
pig iron charged 80 tons,  
heat time 45 min,  
flue dust losses are 3% of hot metal charged.

Data:

|             | %Si                                            | %Mn  | %C   | %P   | Temperature ( $^\circ\text{F}$ ) |
|-------------|------------------------------------------------|------|------|------|----------------------------------|
| Hot metal   | 0.8                                            | 1.30 | 4.40 | 0.13 | 2500                             |
| Blown metal | 0.01                                           | 0.20 | 0.05 | 0.02 | 3000                             |
| Scrap       | 0.01                                           | 0.20 | 0.05 | 0.02 | 77                               |
| Oxygen      | 99.5% oxygen                                   |      |      |      | -60                              |
| Burnt lime  | Available CaO 92%                              |      |      |      | 77                               |
| Mill scale  | (0.15 lb/lb burnt lime) 50% FeO                |      |      |      | 77                               |
| Slag        | Basicity ratio (%CaO/%SiO <sub>2</sub> ) = 3.0 |      |      |      | 3000                             |

17. Preheating of scrap has been investigated in an attempt to develop a means for increasing the scrap melting capability of the basic oxygen converter. Develop a plot of scrap melting capability versus preheat temperature of the scrap for a given converter operation.
18. The recently developed spray steelmaking process can be used to produce steel or as a pretreating process to partially purify liquid pig iron (hot metal) prior to completion of refining by a conventional steelmaking process. Consider a pretreating process carried out with the following specifications:

Hot metal composition—4 wt% carbon; 1.4 wt% silicon.

Required final composition—carbon, 2 wt%; silicon, 0.8 wt%

$$D_{\text{C}} = 1.2 \times 10^{-4} \text{ cm}^2/\text{sec}, \quad D_{\text{Si}} = 6 \times 10^{-4} \text{ cm}^2/\text{sec}.$$

Estimate the minimum tower height required to accomplish this refining step, assuming that the metal droplets are 2 mm in diameter and spherical in shape, and that the only resistance to mass transfer is the diffusion of silicon and carbon to the surface of the droplet. The atmosphere can be assumed to be highly oxidizing. The diffusion out of a sphere may be described by

$$\left[ \frac{c - c_0}{c_s - c_0} \right] = 3.385 \frac{\sqrt{Dt}}{r}$$

where

$c$  = the mean concentration of the droplet at time,  $t$ ,

$c_0$  = the uniform initial concentration,

$c_s$  = a constant surface concentration,

$r$  = the radius of the sphere,

$D$  = the diffusion coefficient for the species under consideration.

## CHAPTER 5

### Pyrometallurgy IV: Refining Processes

This chapter considers the refining of liquid metals when the purification step involves the separation of a second phase. Initially, refining by separation of a liquid or solid phase from the liquid phase being treated will be presented. Later sections consider the purification of liquid metals based on vapor-liquid separation by distillation and by degassing techniques.

#### 5-1 Liquid Phase Refining

The use of a limited solubility of either a metallic phase, such as a precipitating solid solution or intermetallic compound, or by precipitation of a nonmetallic phase, such as an oxide, represents a purification or refining step that is used in nearly all of the metallurgical industries. These refining steps include the formation of an insoluble compound, such as in deoxidation or in reactions carried out between a slag and liquid metal phase; the precipitation of a metallic phase, as in liquation; and liquid-solid separations, as employed in purification by zone refining.

One of the principal methods of refining liquid metals is based on the relative insolubility of compounds in liquid metals. The addition of materials that result in the formation of an insoluble compound by reaction with an impurity element permits a refining separation to be carried out on liquid metals.

The calculation of addition requirements to effect a precipitation is based on the solubility product for the separating compound, or more precisely, in terms of the equilibrium constant for the reaction involving formation of the compound from solution by the dissolved reactants.

#### Deoxidation Equilibria

In view of the fact that oxygen plays a major role in many high-temperature metallurgical process operations, equilibria between dissolved oxygen and other elements in the base material being refined are of prime importance in describing liquid metal refining processes. It should be noted that the formation of insoluble oxides may serve as a refining step in removing either oxygen or the metallic component of the oxide. In addition, the formation of a nitride, sulfide, carbide, or other insoluble compound is also a refining operation that may be described in the same manner.

The reaction equilibrium between the dissolved element oxygen and the oxidation product (which is usually a nonmetallic "slag" or a gas, in the case of

carbon, hydrogen, or sulfur), may be expressed by the equation,



where  $\text{M}$  represents the element dissolved in the bulk metal;  $\text{O}$  is the dissolved oxygen, which may be present as oxygen atoms or in combination with bulk metallic atoms (e.g., oxygen dissolved in liquid iron may be considered to be present as dissolved  $\text{FeO}$ ); and  $\text{M}_x\text{O}_y$  is the oxide reaction product. The equilibrium constant for Eq. (5-1) is

$$K_1 = \frac{a_{\text{M}_x\text{O}_y}}{a_{\text{M}}^x \cdot a_{\text{O}}^y}. \quad (5-2)$$

Experimental determinations of deoxidation constants involve not only the thermodynamics of formation of the oxide product, but the formation of the solutions of oxygen and the reacting element in the bulk metal as well.

*Aluminum Deoxidation of Steel.* Consider the deoxidation of liquid steel by the addition of aluminum. The reaction is



with equilibrium being specified by the constant,

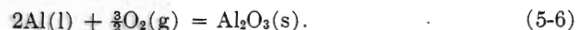
$$K_3 = \frac{a_{\text{Al}_2\text{O}_3}}{a_{\text{Al}}^2 \cdot a_{\text{O}}^3}. \quad (5-4)$$

Then since  $\Delta G^0 = -RT \ln K$

$$\log K = -\frac{\Delta H^0}{4.575 T} + \frac{\Delta S^0}{4.575}. \quad (5-5)$$

The aluminum deoxidation relationship given in Eq. (5-3) requires three thermodynamic relationships describing (1) the formation of alumina, (2) the solution of aluminum in iron, and (3) the solution of oxygen in iron. The development of Eq. (5-3) is presented from this standpoint in the following paragraphs.

I. Formation of  $\text{Al}_2\text{O}_3$  from pure elements.



At high temperatures, i.e., near 1900°K, Elliott and Gleiser<sup>1</sup> give

$$\begin{aligned} \Delta G^0 &= -255,200 \\ \Delta H^0 &= -401,400 \end{aligned}$$

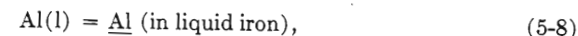
$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T = -77.0$$

Thus the free energy for Eq. (5-6) is given by

$$\Delta G_1^0 = -401,400 + 77.0 T \quad (5-7)$$

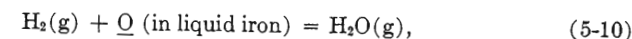
II. Solution of aluminum in iron. The activity of aluminum in liquid iron has

been determined by combining data on the activity of aluminum in liquid silver with the results of measurements of the distribution of aluminum between liquid layers of silver and iron. The distribution measurements were reported by Chipman and Floridis,<sup>2</sup> who computed a free energy of solution of aluminum in iron where the activity of aluminum is expressed in wt%. The chemical equation and the thermodynamic relationship is given as



$$\Delta G_{II}^0 = -12,900 - 7.70 T. \quad (5-9)$$

III. Solution of oxygen in liquid iron. The solution of oxygen in iron may be considered in terms of the equilibrium between  $\text{H}_2/\text{H}_2\text{O}$  gas mixtures and oxygen dissolved in liquid iron, which also has been measured by Floridis and Chipman.<sup>3</sup> That equilibrium may be expressed as



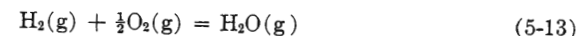
where

$$K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} \cdot a_{\text{O}}}. \quad (5-11)$$

It was found that

$$\Delta G^0 = -32,200 + 14.63 T. \quad (5-12)$$

However, the formation of water from the pure elements is given as



and

$$\Delta G^0 = -60,200 + 13.94 T \quad (5-14)$$

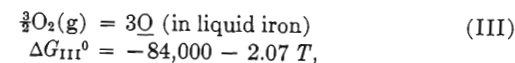
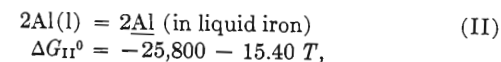
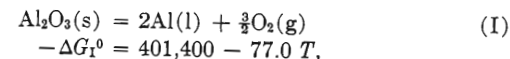
The difference between Eqs. (5-13) and (5-10) gives

$$\frac{1}{2}\text{O}_2(g) = \text{O} \quad (5-15)$$

with the free energy change,

$$\Delta G_{III}^0 = -28,000 - 0.69 T. \quad (5-16)$$

IV. Combination of I, II, and III. By combining

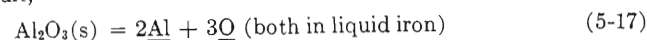


<sup>2</sup> John Chipman and T. P. Floridis, *Acta Metallurgica* 3, 456 (1955).

<sup>3</sup> T. P. Floridis and John Chipman, *Trans. Met. Soc. AIME*, 212, 549 (1958).

<sup>1</sup> J. F. Elliott and M. Gleiser, *Thermochemistry for Steelmaking*, Vol. 1, Addison Wesley, Inc., Reading, Mass., 1960.

one obtains the result,



$$\Delta G_{\text{IV}}^0 = 291,600 - 94.47 T, \quad (5-18)$$

which may be expressed in terms of the deoxidation constant

$$\log K_{\text{IV}} = \frac{-63,700}{T} + 20.65. \quad (5-19)$$

The deoxidation constant may then be calculated at any temperature in the steel-making range, e.g.,  $K_{\text{IV}}$  at  $1600^\circ\text{C} = 4.35 \times 10^{-14}$ .

**Summary of Deoxidation Data.** A summary presentation of the free energies of formation of oxide compounds is given in Table A-II. Also included are data for nitrides, sulfides, and carbides, compounds which also may be formed upon removal of an impurity.

In addition to the standard free energies of formation of the insoluble compounds, the standard free energies of formation of the solution containing the reactants also is required. Table A-IV presents the free energy relations for the formation of dilute solutions in liquid iron. The data for other solvent metals is less complete, with only a few values being scattered throughout the literature.

In many cases, an estimation of the deoxidizing power of an element can be made by assuming that an ideal solution is formed between the element and the solvent metal (i.e., the mole fraction of the dissolved element may be substituted for its activity). However, if the free energy of formation of the solution between oxygen and the solvent metal is unknown, the equilibrium oxygen activity may only be specified in terms of an equivalent oxygen partial pressure in the gas phase. This information may be useful to the process engineer if the oxygen potential of the system is determined by other conditions which are known or can be fixed.

The equilibria presented have been derived for the pure reactant phase, e.g., solid pure  $\text{Al}_2\text{O}_3$ . These same basic relationships apply, however, in all cases, and the deoxidizing power of an element may be computed under conditions of equilibrium with complex slag mixtures, including those cases wherein the activity of the oxide formed is reduced below unity resulting in an improvement in deoxidizing power of the dissolved element. The use of silicomanganese as a deoxidizer is an illustration of this case. In this instance, the deoxidation product is an iron-manganese silicate slag in which the activities of the reaction products would be much lower than they would be if either pure silicon or manganese were used. In this manner the deoxidation can be made more complete and thus less deoxidizing material is required for the same degree of deoxidation. Application of vacuum to systems where a gaseous reaction product is formed (e.g., CO) also permits the reaction to reach a greater degree of completion.

These principles apply as well to the formation of nitrides, sulfides, carbides, and other insoluble compounds.

#### Precipitation Stoichiometry

The total amount of reacting material that must be added to remove an impurity from solution can be divided into two parts. First, a portion of the material

added reacts with the impurity, forming an insoluble precipitate that separates from the liquid alloy. A second portion is represented by the added material which remains in solution in sufficient quantity to satisfy the solubility product relationship, e.g., equilibrium between a saturated solution and the precipitate.

**Example Problem 5-1.** A 100-ton ladle of steel at  $1600^\circ\text{C}$  contains 0.03 wt% oxygen. Compute the minimum amount of pure aluminum that must be added to reduce the oxygen content of the steel to 0.001 wt%. Assume Henry's law behavior for both aluminum and oxygen in solution, and that equilibrium conditions are reached.

**Solution.** The deoxidation constant for aluminum, assuming the conditions given above and that pure alumina is the reaction product, was determined for  $1600^\circ\text{C}$  using Eq. (5-19).

$$K = 4.35 \times 10^{-14} = (\% \text{Al})^2 (\% \text{O})^3. \quad (5-a)$$

The equilibrium aluminum content is then

$$(\% \text{Al}) = \sqrt{\frac{4.35 \times 10^{-14}}{(0.001)^3}} = 6.6 \times 10^{-3}. \quad (5-b)$$

The residual aluminum in solution in pounds is

$$\text{Al}_{\text{dissolved}} = (100) \times (2000) \times \frac{6.6 \times 10^{-3}}{100} = 13.2 \text{ lb.} \quad (5-c)$$

The aluminum that reacted is given by the pounds of oxygen removed times the weight ratio in the reaction product, or

$$\text{Al}_{\text{reacted}} = \frac{(0.03 - 0.001)}{100} \times (100) \times (2000) \times \frac{(54)}{(48)} = 65.2 \text{ lb.} \quad (5-d)$$

The total aluminum required is given by the sum of the two amounts, or 78.4 lb.

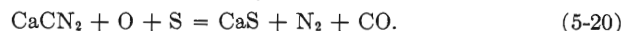
In steel plant practice the deoxidation requirements for a killed steel are often 5 or 6 times this calculated amount. The reasons for the additional aluminum include alloying inefficiency, i.e., all of the aluminum does not go into solution and some floats on the surface of the steel, and absorption from the air during the pouring operation of a considerable amount of oxygen which must be removed by deoxidation. It should be noted also that the deoxidation product is not always pure alumina but often may be an iron-aluminum-oxygen compound, such as hercynite.

#### Desulfurization of Molten Pig Iron

Liquid pig iron produced in the blast furnace (Pyrometallurgy III) often contains concentrations of sulfur that are too high for production of a low sulfur product in the steelmaking furnace to which the pig iron will be charged. External desulfurization, i.e., the intermediate treatment of molten pig iron with a desulfurizing agent, is sometimes employed to lower the sulfur content of the pig iron. Liquid basic slags and some alkalies, or a solid desulfurizing agent, can be used. The kinetics of the process are limited by the contact of the desulfurizing agent and the liquid

metal bath. Bubbling inert gases or shaking the ladle have been employed as mechanical means for increasing process rates.

Strong alkalis such as caustic soda (sodium hydroxide) or soda ash are sometimes used for external desulfurization. Preparation of a synthetic basic slag containing lime and fluxing agents also has been employed. Calcium cyanamide has been used to desulfurize molten pig iron according to the reaction,



Injection of the desulfurizing material, using an inert carrier gas such as argon, or nitrogen, has been used to promote contact between the molten bath and the desulfurizing agent. Calcium carbide acts as a desulfurizing agent according to the reaction,



Powdered lime injected into the bath in a gas stream is a very effective desulfurizing agent. The thermodynamics of this desulfurization technique is illustrated in the following example problem.<sup>4</sup>

**Example Problem 5-2.** Consider a pig iron containing no silicon and saturated with graphite at 1300°C. Estimate the equilibrium sulfur content when lime is injected in a nitrogen stream into the pig iron bath and desulfurization takes place according to the reaction



$$\Delta G_{1300^\circ\text{C}}^\circ = 27,050 - 27.55 T \text{ cal/g-atom}. \quad (5-b)$$

The sulfur activity is referred to the infinitely dilute solution and the activity coefficient of sulfur under these conditions is approximately 5.

*Solution.*

$$\log K_b = \log \frac{a_{\text{CaS}} P_{\text{CO}}}{a_{\text{CaO}} a_{\text{S}} a_{\text{C}}} = - \frac{27,050}{4.575(1573)} + \frac{27.55}{4.575} = +2.26 \quad (5-c)$$

The activity of the pure solids CaS and CaO can be taken as unity. The activity of carbon in graphite saturated iron is also one. The pressure of carbon monoxide can be assumed to be 1 atm, although the presence of nitrogen would markedly reduce this pressure. It should be noted that a lower effective carbon monoxide pressure would enhance desulfurization. Thus

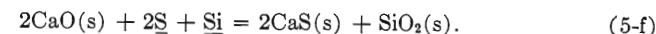
$$\frac{1}{a_{\text{S}}} = \frac{1}{(\%S)(f_{\text{S}})} = 182, \quad (5-d)$$

$$\%S = \left( \frac{1}{182} \right) \left( \frac{1}{5} \right) = 0.0011. \quad (5-e)$$

In actual practice, it is more likely that the pig iron would contain an appreciable amount of silicon such that desulfurization would occur according to the

<sup>4</sup> B. Trentini, L. Wahl, and M. Allard, *Trans. Met. Soc. AIME* 209, 1133 (1957).

reaction,



The equilibrium sulfur content would be lowered by about a factor of 50, because of formation of dicalcium silicate, and because of an increase in the activity coefficient of sulfur resulting from the presence of silicon.

### Parkes Process

In a manner very much parallel to deoxidation, the removal of an alloying element from a liquid metal can be effected by precipitation of an intermetallic compound. This is illustrated by the Parkes process for desilverization of liquid lead with zinc. Zinc readily combines with silver to form a zinc-silver intermetallic compound that is highly insoluble in liquid lead. This process is carried out by adding a sufficient amount of zinc (up to 2 wt%) to lead bullion at about 550°C. The liquid lead is agitated and permitted to cool slightly, and a crust that is rich in silver forms on the bath. The crust contains up to 70% lead along with the silver and zinc.

In operating practice, a two-stage desilverization often is carried out wherein the zinc is added in two batches. The first stage of the refining process produces a crust that is fairly rich in silver, whereas the second crust contains an excess of zinc and is used to remove as much silver from the lead as possible. The zinc-rich crust formed in the second phase of the process is used as a source of zinc for the first stage of the Parkes process on a fresh kettle of lead bullion.

Desilverization of lead bullion with zinc also can be carried out in a continuous manner, as in the Williams continuous process.<sup>5</sup>

Some lead bullions also contain gold. Gold is even stronger in its affinity for zinc than is silver. A two-step refining process can be carried out in which a small addition of zinc is made to the lead bullion to separate the gold, and then a second addition of zinc removes the silver.

To illustrate the thermodynamics involved in carrying out the Parkes process, the following example problem is posed. It should be noted that the compositional relationships may be made more complex in operating practice, in that the crust that forms at the process temperature may actually consist of a ternary alloy of lead, silver, and zinc, rather than the intermetallic silver-zinc compound plus entrained lead.

**Example Problem 5-3.** A liquid lead bullion initially free of zinc and containing 250 troy ounces of silver per ton is treated at 500°C with zinc to remove the silver. Assume that the reaction product is pure  $\text{Ag}_2\text{Zn}_3$ . Calculate the zinc addition in pounds per ton of lead bullion required to remove 98% of the silver.

|                                                                   |                |
|-------------------------------------------------------------------|----------------|
| $(\gamma_{\text{Zn}}^\circ)_{\text{Pb}} = 11$                     | Atomic Weights |
| $(\gamma_{\text{Ag}}^\circ)_{\text{Pb}} = 2.3$                    | Ag 107.9       |
| $2\text{Ag(l)} + 3\text{Zn(l)} = \text{Ag}_2\text{Zn}_3$          | Pb 207.2       |
| $\Delta G_{500^\circ\text{C}}^\circ = -30,500 \text{ cal/g-mole}$ | Zn 65.4        |

<sup>5</sup> G. K. Williams, *Trans. Met. Soc. AIME* 121, 226 (1936).

*Solution.* Converting troy ounces to pounds,

$$(250) \frac{(31.1035)}{(28.3495)(16)} = 17.125 \text{ lb Ag/ton bullion}, \quad (5-a)$$

$$\frac{(\text{troy oz/ton})(\text{gm/troy oz})}{(\text{gm/avoir oz})(\text{avoir oz/lb})}$$

Basis: 1 Ton Lead Bullion.

Initial Composition:

$$\frac{17.125}{107.9} = 0.159 \text{ lb moles Ag/ton bullion},$$

$$\frac{1982.875}{207.2} = 9.60 \text{ lb moles Pb/ton bullion}.$$

Equilibrium Constant at 500°C:

$$\log K = -\frac{\Delta G^0}{2.3RT} = \frac{30,500}{(4.575)(773)} = 8.62, \quad (5-b)$$

$$K = 4.17 \times 10^8 = \frac{a_{\text{Ag}_2\text{Zn}_3}}{a_{\text{Ag}}^2 a_{\text{Zn}}^3}. \quad (5-c)$$

Assuming that the reaction product is  $\text{Ag}_2\text{Zn}_3$  at unit activity,

$$a_{\text{Ag}}^2 a_{\text{Zn}}^3 = 2.4 \times 10^{-9}, \quad (5-d)$$

$$X_{\text{Ag}}^2 \gamma_{\text{Ag}}^0 X_{\text{Zn}}^3 \gamma_{\text{Zn}}^0 = 2.4 \times 10^{-9}. \quad (5-e)$$

The final silver content is

$$(1 - 0.98)(0.159) = 0.00318 \text{ lb moles Ag/ton bullion}. \quad (5-f)$$

The mole fraction of silver is

$$X_{\text{Ag}} = \left( \frac{0.00318}{9.60} \right) = 3.31 \times 10^{-4}. \quad (5-g)$$

The equilibrium mole fraction of zinc in the bullion in contact with pure  $\text{Ag}_2\text{Zn}_3$  from Eq. (5-e) is

$$(X_{\text{Zn}}) = \sqrt[3]{\frac{(2.4 \times 10^{-9})}{(3.31 \times 10^{-4})^2 (2.3)^2 (11)^3}}, \quad X_{\text{Zn}} = 0.0146 \quad (5-h)$$

The residual zinc content is given to a very good approximation (neglecting the residual silver and assuming that the zinc concentration is small) by the product,

$$(0.0146)(9.6)(65.4) = 9.15 \text{ lb Zn/ton refined bullion}. \quad (5-i)$$

The zinc reacting with silver is

$$\frac{(0.98)(17.125)(3)(65.4)}{(2)(107.9)} = 15.25 \text{ lb zinc}. \quad (5-j)$$

The zinc required to carry out the refining to 98% of completion is given by the sum of the zinc remaining in solution and the zinc reacting with silver  $(9.15 + 15.25) = 24.4 \text{ lb/ton bullion}$ . In practice, the actual zinc requirement is slightly greater than predicted by the foregoing analysis. Failure to achieve equilibrium and a reduction in the activity of the zinc-silver compound by the presence of lead in the crust could both contribute to the differences. The residual zinc content of the lead bullion is on the order of 0.6 wt% or about 12 lb/ton of bullion, and the total addition often approaches 40 lb/ton.

#### Kinetics of Nucleation of a Separating Phase

The principal barrier to reaching equilibrium often manifests itself in the rate of nucleation of the separating phase. This is particularly true for crystallization processes, where large degrees of supercooling often have been noted. The surface energy between the precipitate and the solution must be considered, particularly for solids, in addition to the difference in free energies of the bulk phases. For homogeneous nucleation of spherical particles, the total free energy change may be expressed as

$$\Delta G = \frac{4\pi r^3}{3} \Delta G_v + 4\pi r^2 \gamma, \quad (5-22)$$

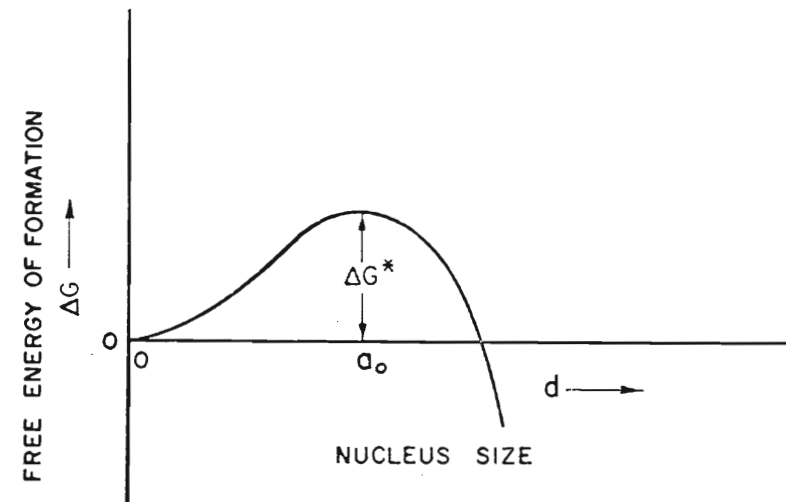


Fig. 5-1. Free Energy of Nucleus Formation as a Function of Nucleus Size

where

- $\Delta G_v$  = bulk free energy change,  
 $\gamma$  = surface energy of a unit area of interface between parent liquid and crystal nucleus,  
 $r$  = radius of a spherical particle.

It should be noted that these terms vary with the specific geometry of the nucleus. The geometrical factors introduce a size effect into the problem, and, since  $\Delta G_v$  is negative for a supercooled melt, these factors determine the critical size for a nucleus. When the nuclei are small, the positive term predominates, and the curve shown in Fig. 5-1 rises to a maximum as the size increases. A nucleus is stable if the size is greater than  $r^*$ , the critical nucleus size, since the free energy decreases if the nucleus grows. The free energy change for the formation of a nucleus of critical size is called the "work of nucleus formation." The nucleus of critical size,  $r^*$ , is in unstable equilibrium with the parent phase since any change in its size results in a decrease in free energy, and a tendency either to grow or disappear.

The work of formation is determined by  $r^*$ , which may be evaluated by maximizing  $\Delta G$ .

$$\frac{\partial(\Delta G)}{\partial r} = 4\pi r^2 \Delta G_v + 8\pi r \gamma = 0, \quad (5-23)$$

$$r^* = -\frac{2\gamma}{\Delta G_v}. \quad (5-24)$$

Substitution in Eq. (5-22) gives

$$\Delta G^* = \Delta G_{(a-a^*)} = \frac{4}{3}\pi \left(\frac{-2\gamma}{\Delta G_v}\right)^3 \Delta G_v + 4\pi \left(\frac{-2\gamma}{\Delta G_v}\right)^2 \gamma, \quad (5-25)$$

$$\Delta G^* = \frac{\beta \gamma^3}{(\Delta G_v)^2}, \quad (5-26)$$

where the coefficient  $\beta = \frac{16}{3}\pi$  for a sphere. If the nucleus were a cube,  $\beta$  would be equal to 32, where  $r$  is the cube edge.

The value of  $\Delta G^*$ , which corresponds to the critical size, represents an energy barrier that must be overcome by a nucleus before it is stable. The energy required can come only from momentary local fluctuations of both concentration and energy. The energy fluctuations are statistical in nature and are of the usual kinetic type that give rise to homogeneous reactions. The concentration fluctuation requires movement of the requisite number of molecules close enough to one another by molecular diffusion to form a nucleus large enough to equal or exceed the critical size. Becker<sup>6</sup> proposed the following equation for nucleation rate,

$$\frac{dN}{dt} = ce^{-Q/kT}e^{-A(T)/kT}, \quad (5-27)$$

<sup>6</sup> R. Becker, *Ann. Phys.* **27**, 128 (1938).

where

$$\frac{dN}{dt} = \text{nucleation rate, number/unit volume-unit time,}$$

- $Q$  = activation energy for diffusion,  
 $A(T)$  = work required to form a nucleus,  
 $T$  = absolute temperature,  
 $c$  = a constant,  
 $k$  = Boltzmann constant.

The work of nucleation,  $A(T)$ , increases markedly with decrease in supersaturation and is infinite at the saturation point. The term  $e^{-Q/kT}$  decreases with decreasing temperature. The plot of  $N$  versus  $T$  thus has a pronounced maximum that corresponds to a definite supersaturation. However, if enough time is allowed, homogeneous nucleation will, in theory, eventually occur at any supersaturation. The presence of foreign particles or of seed crystals can increase appreciably the nucleation rate by inoculation. The alteration of surface energies caused, e.g., by the presence of trace amounts of surface active elements also can drastically affect the rate of nucleation. These effects occur because of the change in the surface energy term of the nucleation rate equation.

It may be concluded from the foregoing discussion that heterogeneous nucleation caused by the presence of seed crystals or inoculating agents that promote nucleation will occur prior to homogeneous nucleation. This is desirable in phase separation processes since a rapid nucleation of the precipitating phase promotes the kinetics of phase separation, and prevents nucleation of the precipitate from becoming rate-limiting. In practice, it is often necessary to "seed" the melt with foreign particles to promote heterogeneous nucleation (see Bayer Process, nickel reduction from aqueous solution, Chapter 6, Hydrometallurgy). Agitation in the form of vigorous stirring or vibrating techniques also has been used to induce nucleation.

#### Growth and Flotation of a Separating Phase

The limitation on the effectiveness of a phase separation may reside in the rate of growth of the precipitate and its subsequent separation from the bulk liquid. The rate of growth of the inclusion will be limited by the process of diffusion of reactants from the bulk liquid to the surface of the nucleated precipitate. Simultaneous with the diffusion process established at the surface of the particle is the relative motion of the particle in the bulk liquid.

The precipitating phase usually will have a different density than the bulk liquid and consequently will tend to rise (or sink). If the particle size is fixed, the terminal velocity of the particle can be estimated from Stokes law concepts. However, because the particle can grow during its residence in the liquid metal, its velocity will continuously increase. Nevertheless, Stokes law is applicable because of the relatively low Reynolds numbers encountered in situations of this nature (see Degassing). The additional possibility of collision and coalescence of small particles also exists. For the specific situation of deoxidation of liquid steel, theo-

retical<sup>7</sup> and experimental<sup>8</sup> studies have been carried out on the rate of growth and separation of the deoxidation product.

### Liquid Phase Separation

Liquid phase separation in metallic systems often is described by the term "liquation." Liquation refers to the separation of a liquid phase both by liquid immiscibility and by melting point difference. The recovery from steel of lead, solders, or low melting alloys by liquation consists of heating a steel scrap charge to a temperature above the melting point of the low melting alloys, but below the melting point of steel, and permitting the low melting alloy to drain from the scrap. Liquation carried out by slowly cooling a liquid metal to permit a second phase, either liquid or solid, to separate is a common technique in the refining of nonferrous metals.

**Processing Operations—Lead-Silver System.** The recovery of silver from lead may be accomplished by cooling the silver-containing lead bullion (Pattinson Process). Consider a lead-silver alloy containing 0.9 wt% silver (260 troy ounces per ton). As shown in the phase diagram, Fig. 5-2, high purity lead will precipitate from lead-silver solutions at a temperature slightly above 320°C and will continue to do so until the eutectic point is reached at 304°C and a liquid phase composition of 2.5 wt% silver. At this point, the liquid which has been enriched in silver can be separated; hence, crystals of alpha phase (pure or nearly pure lead) separate, contaminated only by mechanical attachment or "wetting" by the high silver alloy, which is still liquid. This process is no longer used industrially but has been replaced by the Parkes Process in treating lead bullion for recovery of silver.

**Lead-Copper System.** A first step in the refining of lead is removal of copper by kettle drossing. The copper-lead phase diagram is shown in Fig. 5-3. This system exhibits a low melting point eutectic in which 99.8% lead as a liquid is in equilibrium with solid pure copper. Although lead bullion may contain less than 1% copper, most of this copper can be removed effectively by slowly cooling the lead from 450–350°C. A copper-rich dross appears on the surface of the molten lead. Commercial practice of the "drossing" of liquid lead is shown in Fig. 5-4.

**Zinc Recovery by Liquid Phase Separation.** An example of the commercial application of liquation in a continuous process involving separation of two liquid phases is the recovery of zinc from the Imperial Smelting Process, a combined zinc-lead blast furnace. A diagram of the process is shown in Fig. 5-5. The zinc recovery system and operating conditions are given in Fig. 5-6. Ores that are high in zinc are smelted in a lead blast furnace, producing a stack gas containing up to 6% zinc. The stack gases are passed through a splash-condenser containing lead, which absorbs the zinc from the vapor phase. Under typical conditions, the gas entering the condensers contains 5.9% zinc at a temperature of 1000°C, which represents over 90% of the zinc charged. The lead enters the condenser at 450°C and leaves at about 560°C. It is saturated with zinc on entering, 2.15 wt%. During

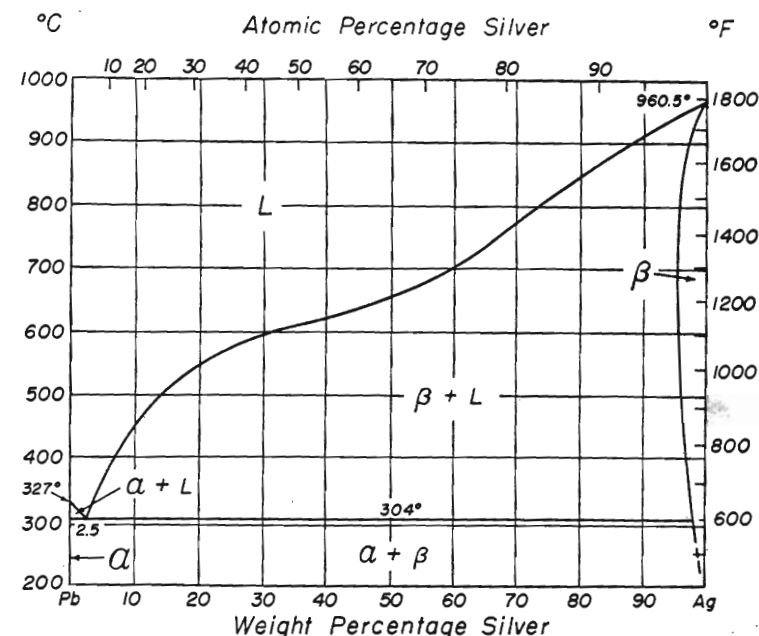


Fig. 5-2. Phase Diagram for the Lead-Silver System

Source: *Metals Handbook*, edited by Taylor Lyman, American Society for Metals, Metals Park, Ohio, 1948, p. 1153.

the condensation, the lead is heated and dissolves an additional 0.25% zinc. The lead is then circulated through a cooling launder. The concentration of zinc, 2.4%, is far below the saturation point on exiting from the condenser, i.e., 4.4% at 560°C. However, on cooling, at 470°C essentially pure liquid zinc begins to precipitate out from the lead, and the additional 0.25% absorbed in the condensers separates out. The upper liquid layer of zinc is then separated by means of a weir or baffle, and the underflow of lead-rich alloy is recirculated.

**Engineering Design.** The major considerations of a phase separation which concern the engineer are: (1) the yield of a given product, (2) the purity of the product, (3) the energy requirements, (4) the rate of production.

**Process Yield.** The yield of the product may be estimated by constructing a material balance for the system, assuming that equilibrium conditions prevail. This would represent the maximum yield, a quantity that is given in pounds by

$$Y = W_0 \frac{c_2^I - c_2^0}{c_2^I - c_2^{II}}, \quad (5-28)$$

<sup>7</sup> E. T. Turkdogan, *J.I.S.I.* 204, 914–919 (1966).

<sup>8</sup> G. C. Duderstadt and R. D. Weller, *J. Metals*, 18, No. 6, 714–718 (1966).

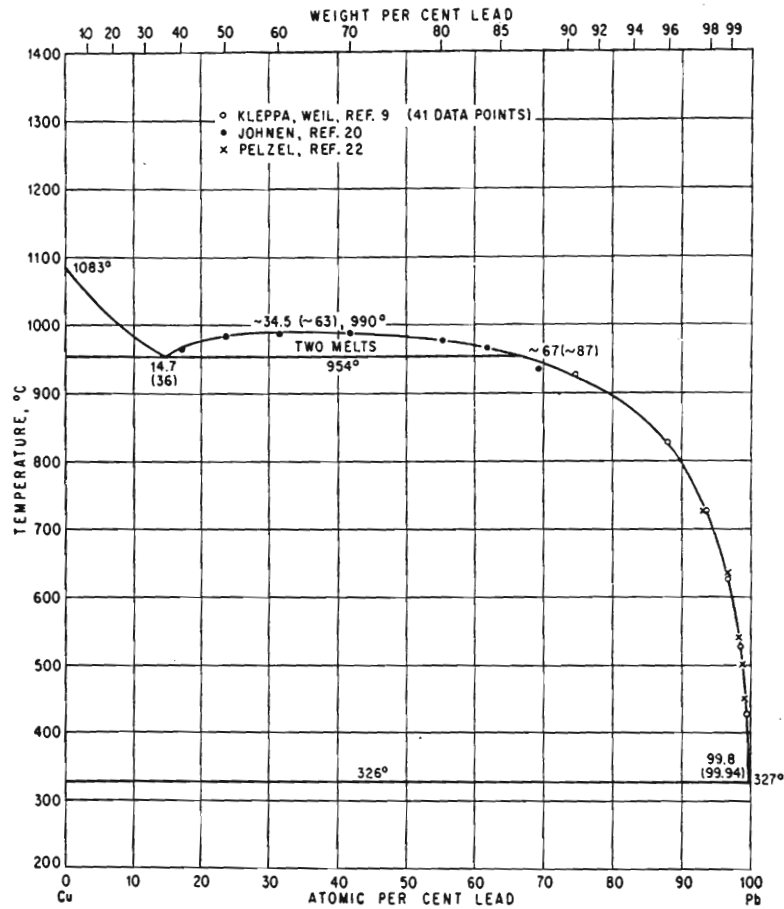


Fig. 5-3. Phase Diagram for the Copper-Lead System

Source: Hansen, *Constitution of Binary Alloys*, McGraw-Hill Book Company, New York, 1961, p. 610.

where

$W_0$  = initial weight of the charge, lb,

$c_2^I$  = equilibrium concentration, in wt% of component 2 in the parent phase at the lower temperature.

$c_2^0$  = concentration, in wt% of component 2 in the parent phase initially.

$c_2^{II}$  = equilibrium concentration, in wt% of component 2 in the precipitated phase at the lower temperature.

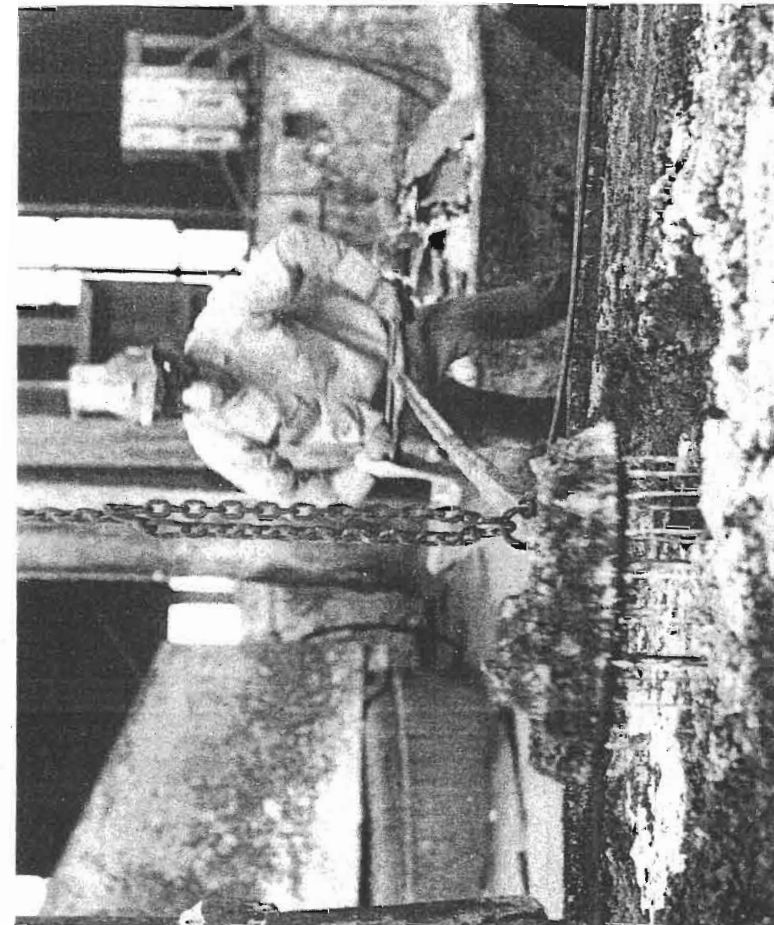


Fig. 5-4. Dross being removed from lead refining kettle. These drosses contain antimony, arsenic, copper, silver, tin and zinc, and are further processed to recover these elements. Courtesy of American Smelting and Refining Company.

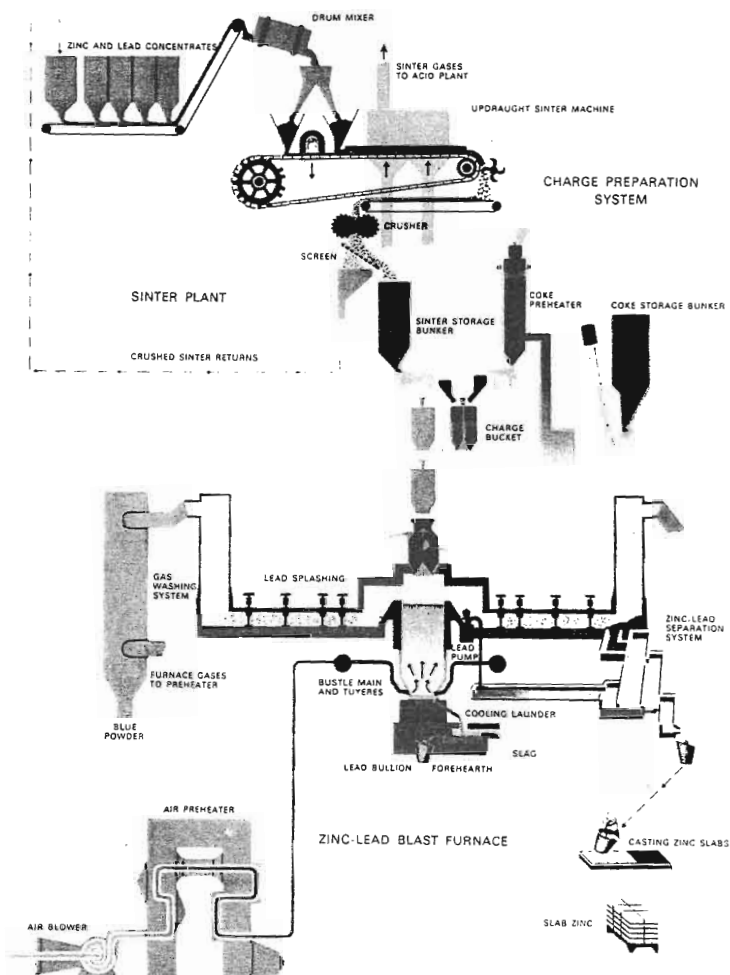


Fig. 5-5. Imperial Smelting Process

Courtesy of Imperial Smelting Processes Limited, Avonmouth, Bristol, England.

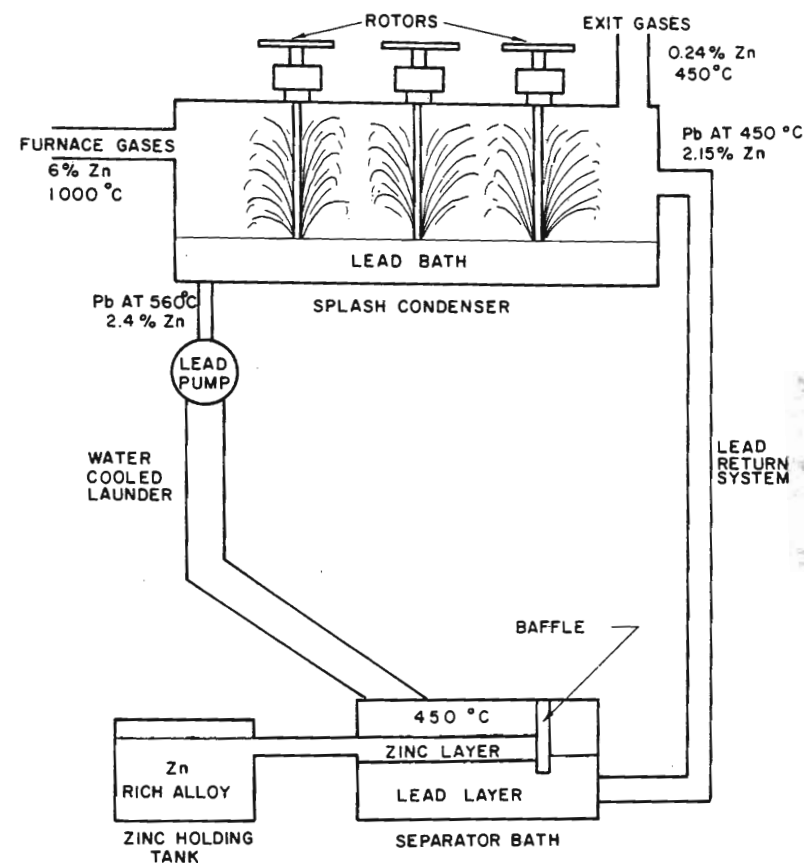


Fig. 5-6. Schematic Diagram of Zinc Recovery System for Zinc-Lead Blast Furnace

Equation (5-28) is an expression of the "lever-rule" as used in the study of binary phase equilibria. Mole fractions may be substituted for weight percentages and  $N_0$ , the total number of moles of initial solution, may be substituted for  $W_0$ . The yield then is expressed in moles, and the weight may be computed from the molecular weights of the solute and solvent and the concentrations in the product.

When the process involves a highly volatile solvent, or reactions occur between the lining of the process container and the material being processed, a correction for the losses must be made to the yield relation given above.

*Purity of Product.* For the equilibrium case, the purity of the product is given directly by the phase diagram. In practice, the adherence of the parent liquid to the precipitated crystals, or the entrainment of one phase within the other often

decreases the purity of the recovered material. The purity usually can be improved by repeating the separation on the product, at a correspondingly greater cost.

**Thermal Requirements.** The energy requirements for a phase separation can be calculated from a heat balance on the process. The cooling energy represents heat which must be removed from the system, and is given by the algebraic sum of the sensible heat change in the solution, plus the heat evolved during the separation of phases (a quantity which may be either negative or positive, and often is approximated by the heat of solution for dilute solutions whose composition does not vary greatly during the operation), minus the heat losses to the surroundings, and any other cooling effects, e.g., vaporization of the solvent.

**Process Kinetics.** The rate at which a phase separation can be carried out may be limited either by the kinetics of the process, by the capacities of the equipment, or both may play a role. The kinetics of nucleation, introduced in a previous section, may be applied to the case where the rate-limiting step is the nucleation of the second phase. The growth of the separating phase also may be rate-limiting.

The ability of the equipment to extract heat rapidly from the solution may be a primary factor in the rate of the process. The removal of the material from the equipment, or the charging methods, i.e., material handling, also may limit the operation. A consideration of these factors is of major importance in the engineering design of phase separation processes.

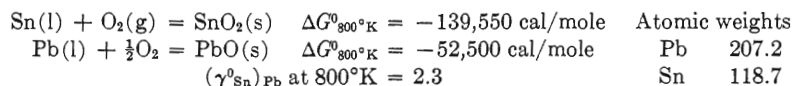
#### Refining by Oxidation

Application of slightly oxidizing (or sulfurizing) conditions to an impure metal can result in the removal of the impurity as an oxide (or sulfide). These operations are illustrated best by the practices of "softening" lead bullion. The removal of copper, antimony, arsenic, and tin result in softer or more ductile lead, hence use of the term "softening."

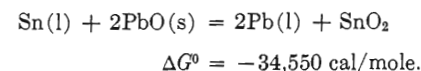
The initial removal of copper from lead bullion by drossing was described in a previous section. Complete removal of the copper is accomplished by the addition of sulfur. About 2 lb of sulfur per ton of lead is stirred into the bath and a second dross, made up primarily of cuprous sulfide, floats out of the bath and can be skimmed from the surface. This treatment can reduce the copper content of the bullion to less than 0.005 wt%. Some removal of arsenic, antimony, and iron also is accomplished in this process.

Antimony, arsenic, and tin oxidize more readily than lead. Oxidizing conditions, imposed by agitation of molten lead with compressed air in a small reverberatory furnace, produce a lead-bearing slag containing the oxides of these impurities.

**Example Problem 5-4—"Softening" of Lead-Removal of Tin.** Lead bullion containing tin is oxidized by bubbling compressed air through the liquid metal at 800°K. Assuming that the reaction products are pure PbO(s) and pure SnO<sub>2</sub>(s), what is the minimum tin composition that can be reached by this "softening" process?



**Solution.** For the combined reactions,



The equilibrium constant at 800°K is

$$\log K = \frac{34,550}{(4.575)(800)} = 9.44,$$

$$K = 2.76 \times 10^9 = \frac{a_{\text{SnO}_2} a_{\text{Pb}}^2}{a_{\text{Sn}} a_{\text{PbO}}^2}.$$

The bath is nearly pure lead, hence,  $a_{\text{Pb}} = 1$ . The respective oxides are assumed to be present as pure solids and at unit activity.

$$K = 2.76 \times 10^9 = \frac{1}{(X_{\text{Sn}}) \gamma_{\text{Sn}}^0},$$

$$X_{\text{Sn}} = \frac{1}{(2.76 \times 10^9)(2.3)} = 1.57 \times 10^{-10},$$

$$\% \text{Sn} = \frac{(100)(1.57 \times 10^{-10})(118.7)}{(207.2)} = 9 \times 10^{-9}.$$

The oxidation of tin from lead is a very effective refining process. In plant operations, tin is removed to the chemical "trace" level. The formation of compounds or solid solutions of the oxides would tend to lower the activity of the tin oxide and make the process even more effective. Agitation of the metal to promote reaction with the entire bath such that the tin is removed with a minimum lead loss is a primary objective in commercial practice.

Alternative oxidizing procedures for purifying lead can be carried out with a reduced loss of lead by using oxidizing agents such as sodium nitrate in fluxes of sodium hydroxide or sodium chloride to dissolve the alkaline stannates, antimonates, and arsenates.

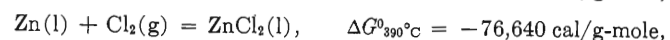
The fire refining of crude tin is carried out using liquation and drossing techniques to achieve high purity tin. Liquation can be used to remove iron, arsenic, and copper from tin, while oxidation with air or steam removes iron, aluminum, zinc, and nickel. The copper can be removed with sulfur additions, and formation of intermetallic compounds with aluminum additions removes antimony, arsenic, copper, and nickel. Further refining for the removal of lead and small remaining amounts of antimony and arsenic can be accomplished by electrolytic refining.

The use of chlorine gas to remove zinc from liquid lead as a chloride is the basis of the Betterton process. This means of zinc removal for purification of lead is illustrated in the following example problem.<sup>9,10</sup>

<sup>9</sup> H. H. Kellogg, *Trans. Met. Soc. AIME* 133, 862 (1950).

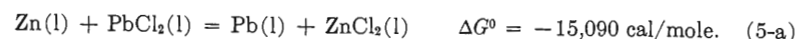
<sup>10</sup> R. D. Pehlke and K. Okajima, *Trans. Met. Soc. AIME* 239, 1351 (1967).

**Example Problem 5-5.** After the Parkes process in which an appreciable zinc concentration remains in the lead, chlorine gas is bubbled through lead bullion at 390°C. Calculate the limiting zinc concentration, assuming that the chlorides form an ideal solution, and that the mole fraction of zinc chloride in the salt formed is 0.983.



$$\log (\gamma^\circ_{\text{Zn}})_{\text{Pb}} = \frac{1215}{T^\circ\text{K}} - 0.418.$$

**Solution.** At 390°C,  $\log \gamma^\circ_{\text{Zn}} = 1.417$ ;  $\gamma^\circ_{\text{Zn}} = 26.1$



The equilibrium constant is given by

$$\log K_a = + \frac{15,090}{(4.575)(663)} = +4.97, \quad (5-b)$$

$$K_a = 93,500 = \frac{a_{\text{Pb}} a_{\text{ZnCl}_2}}{a_{\text{Zn}} a_{\text{PbCl}_2}}. \quad (5-c)$$

The activities of the chlorides are assumed to be given by the mole fractions

$$a_{\text{ZnCl}_2} = X_{\text{ZnCl}_2} = 0.983$$

and

$$a_{\text{PbCl}_2} = X_{\text{PbCl}_2} = 0.017.$$

The activity of the lead is unity, since the chloride is in contact with the purified bullion. The activity of zinc in equilibrium is given by

$$a_{\text{Zn}} = X_{\text{Zn}} \gamma^\circ_{\text{Zn}} = \frac{(1)(0.983)}{(0.017)(93,500)} = 6.18 \times 10^{-4}, \quad (5-d)$$

$$X_{\text{Zn}} = \frac{6.18 \times 10^{-4}}{26.1} = 2.37 \times 10^{-5}. \quad (5-e)$$

The theoretical wt% zinc remaining in the lead is then 0.00075. In actual practice, the residual zinc is usually below 0.005 wt% for these conditions. The kinetics of reaction of chlorine gas (or the salt phase) with the zinc remaining in very dilute solution in the lead limits the attainment of the calculated theoretical limit.

### Zone Refining

The advent of the semiconductor industry with its requirement for ultrahigh purity materials led to the development of zone refining. In zone refining, a small molten zone moves through a long charge of alloy or impure material. The differences in impurity concentration between liquid and crystallizing solid lead to segregation of impurities into the moving liquid zone and a corresponding purifica-

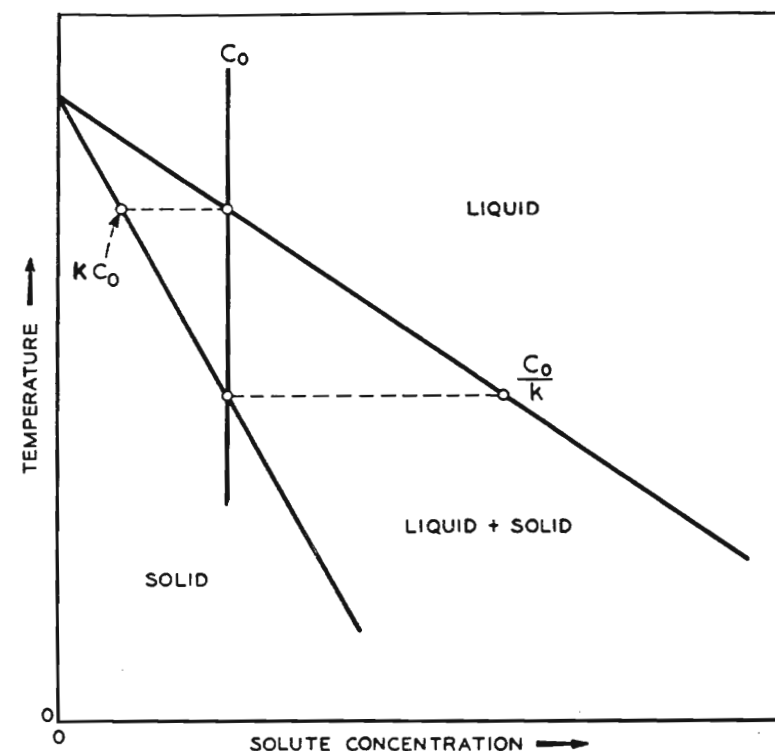


Fig. 5-7. Portion of Constitutional Diagram for a Solute Which Lowers the Freezing Point of the Solvent

Source: "Principles of Zone-Melting," W. G. Pfann, *Transactions AIME*, (Metals Branch), 1952, Vol. 194, p. 748.

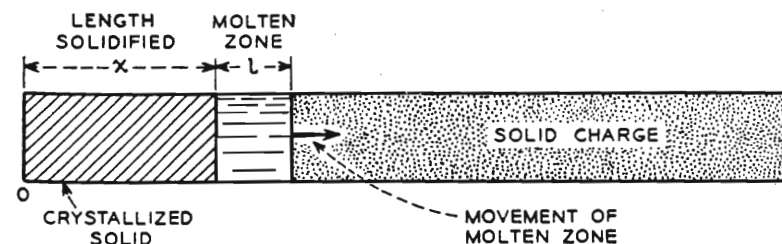


Fig. 5-8. Solidification by zone-melting

Source: "Principles of Zone-Melting," W. G. Pfann, *Transactions AIME*, (Metals Branch), 1952, Vol. 194, p. 748.

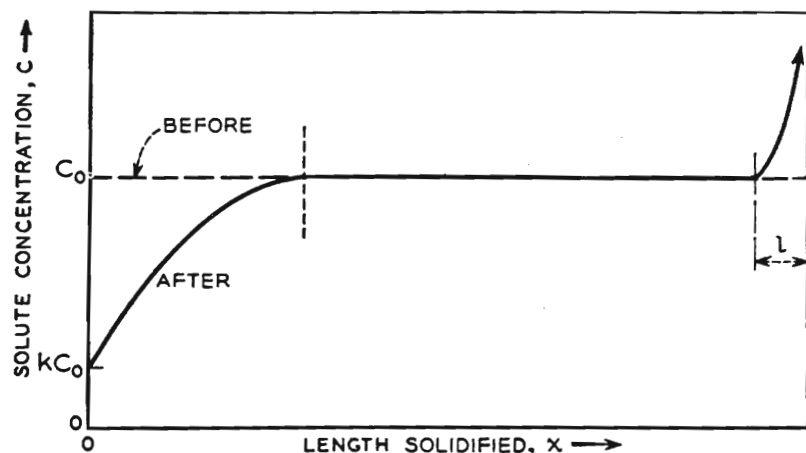


Fig. 5-9. Approximate Concentrations Before and After Single-Pass Zone-Melting

Source: "Principles of Zone-Melting," W. G. Pfann, *Transactions AIME*, (Metals Branch), 1952, Vol. 194, p. 748.

tion of the solidifying material.<sup>11,12</sup> Zone refining is used to purify not only metals but various inorganic and organic materials.

Refining by solidification is possible because impure metals solidify over a range of temperature with significant differences in the equilibrium composition of liquid and solid. This is illustrated in Fig. 5-7. For a liquid metal of initial composition  $C_0$ , the first solid to form would be of composition  $kC_0$ . The constant  $k$  of Fig. 5-7 is defined by the ratio of the equilibrium concentration of solute in the solid at the liquid-solid interface to the concentration of the liquid. In the case illustrated by Fig. 5-7, the distribution coefficient,  $k$ , is less than unity, and the liquid would be enriched in solute during solidification. In dilute solutions, the solidus and liquidus concentrations can be approximated closely by straight lines. Hence, the distribution coefficient remains constant over a range of compositions. The unequal distribution of solute between liquid and solid forms a basis for purification of metals, as well as being the cause of segregation in ingots and castings (see Chapter 8).

In a classic paper<sup>13</sup> W. G. Pfann first described zone melting and developed mathematical relationships for the redistribution of solute in a zone-melted material under various limiting conditions.

Zone refining by passing a single molten zone along a length of solid material is illustrated in Fig. 5-8. As the molten zone traverses the first zone length,  $l$ , a

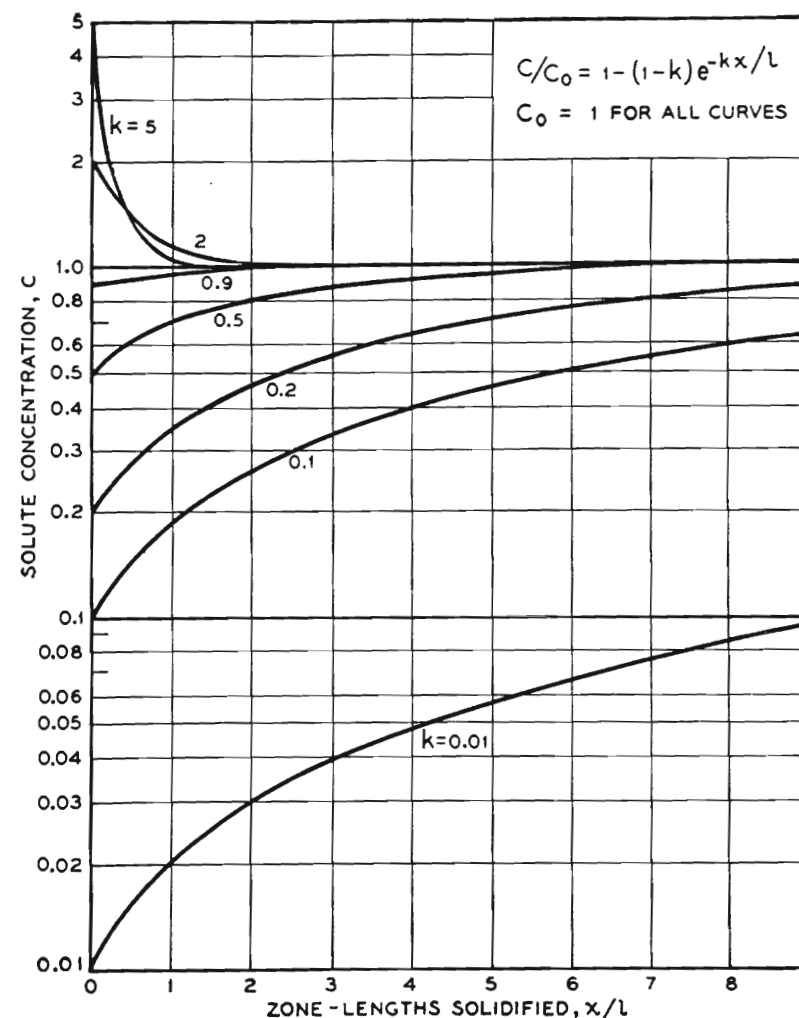


Fig. 5-10. Curves for Zone-Melting, Showing Solute Concentration in Solid as a Function of  $x/l$ , the Zone-Lengths Solidified, Calculated from Eq. 5-29, for Various  $k$ 's

Source: "Principles of Zone-Melting," W. G. Pfann, *Transactions AIME*, (Metals Branch), 1952, Vol. 194, p. 749.

<sup>11</sup> W. G. Pfann, *Zone Melting*, John Wiley, New York, 1958.

<sup>12</sup> H. Schildknecht, *Zone Melting*, Verlag Chemie, Academic Press, New York, 1966.

<sup>13</sup> W. G. Pfann, *Trans. Met. Soc. AIME* 194, 747 (1952).

solid with solute concentration  $kC_0$  freezes out as shown in Fig. 5-7. The molten zone is thus enriched in solute, and as the zone traverses along the ingot, it is continually enriched until its concentration reaches a value  $C_0/k$ . From this point on, the concentration of the zone remains unchanged since the concentration of unmelted solid entering the zone is the same as that freezing out. At the end of the pass, there is a build-up of solute. The concentration distribution after a single zone melting pass is shown in Fig. 5-9. The mathematical expression describing the concentration gradient of Fig. 5-9 is

$$\frac{C}{C_0} = 1 - (1 - k)e^{-kx/l}, \quad (5-29)$$

where

$C$  = solute concentration,  
 $C_0$  = initial solute concentration,  
 $k$  = distribution coefficient,  
 $x$  = total length solidified,  
 $l$  = length of molten zone.

The distribution coefficient,  $k$ , has a marked influence on the effectiveness of zone refining. As the distribution coefficient changes from unity, i.e., becomes either very large or very small, the purification, assuming equilibrium conditions between solid and liquid and complete mixing in the liquid, is more effective, as shown in Fig. 5-10.

Several passes, which can be carried out in a multiple zone-refining unit as shown in Fig. 5-11, or as a series of single passes, can be employed to reach high degrees of purification. Concentration curves after several passes for a system having a distribution coefficient of 0.1 are shown in Fig. 5-12.

Zone leveling is a zone melting procedure in which repeated passes are made through the rod in reverse directions or where repeated-pass zone melting is made on a circular charge. This results in a very uniform concentration in the material. Thus, zone leveling can be an important technique in homogenizing materials.

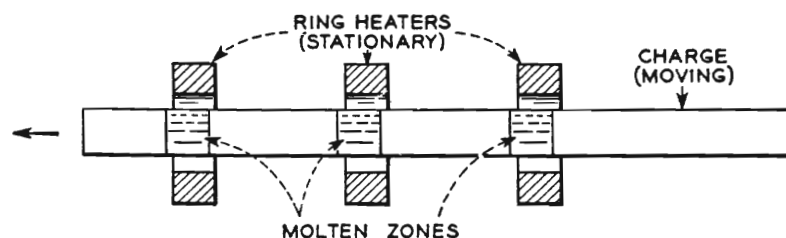


Fig. 5-11. Multiple-Zone-Refining, Using a Straight Charge

Source: "Principles of Zone-Melting," W. G. Pfann, *Transactions AIME*, (Metals Branch), 1952, Vol. 194, p. 750.

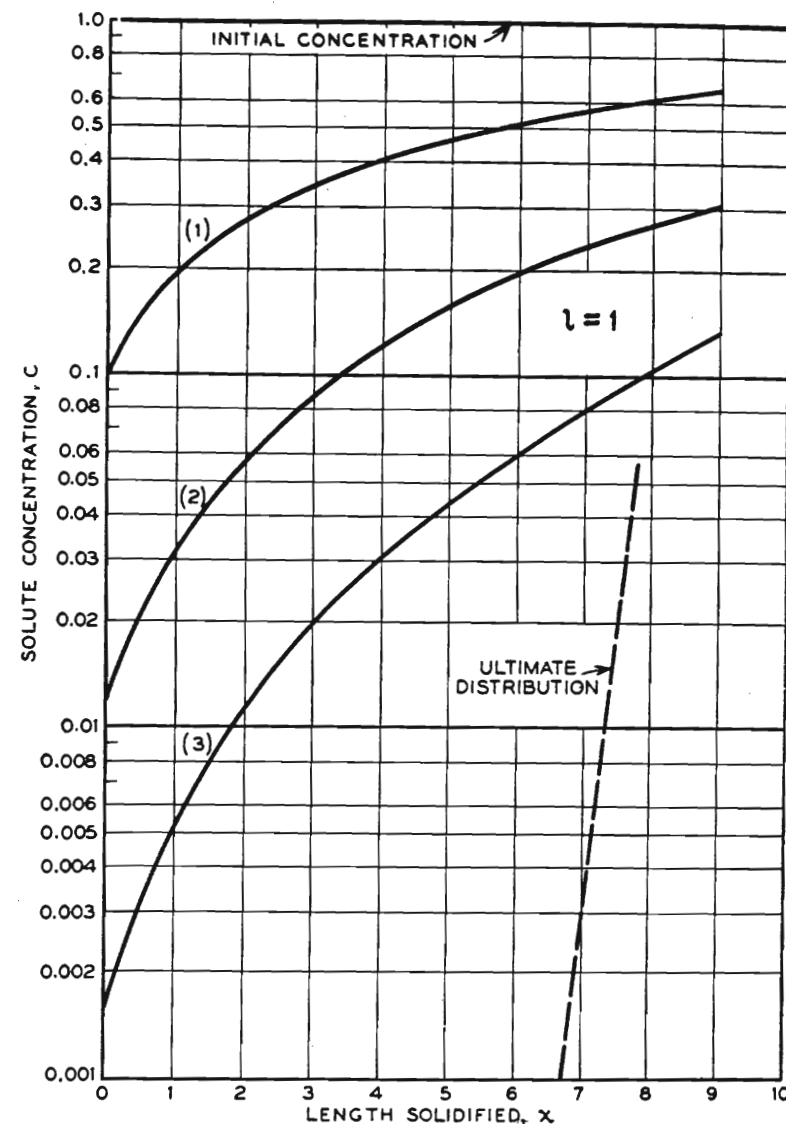


Fig. 5-12. Concentration Curves, Showing Concentration of Solute in Solid as a Function of  $x$ , the Length Solidified, After 1, 2, and 3 Successive Single-Zone Passes From Left to Right, Through an Initially Uniform Charge Ten Units in Length, for Unit Zone-Length.

Source: "Principles of Zone-Melting," W. G. Pfann, *Transaction AIME*, (Metals Branch), 1952, Vol. 194, p. 751.

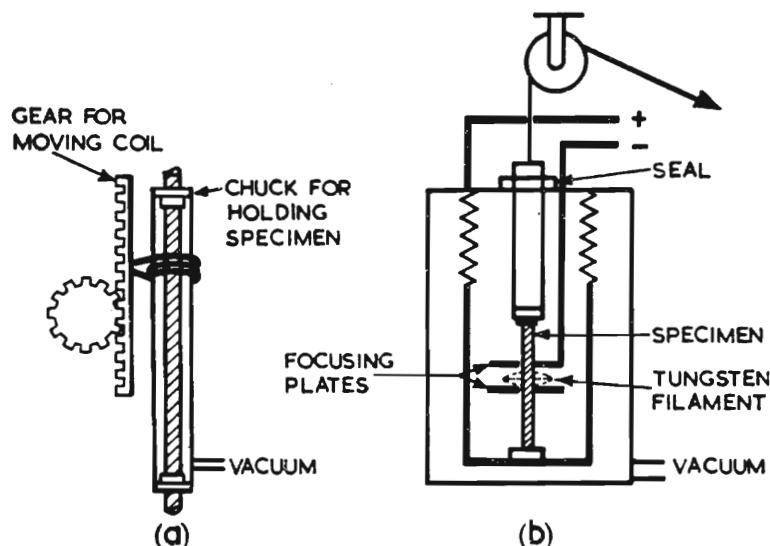


Fig. 5-13. Floating-zone Techniques

Source: W. H. Dennis, *Extractive Metallurgy*, Philosophical Library, New York, 1965, p. 321.

Zone refining is primarily employed in the semiconductor industry for refining of germanium and silicon. However, nearly all metals can be refined, including those which are highly reactive. To avoid reaction with refractory materials, the floating zone technique, Fig. 5-13, has been developed, in which surface tension of the metal is sufficient to contain the zone in a vertical rod, free from contact with any supporting material. Zone refining is usually employed in refining small batches of metals, but developments in this field point toward refining of larger masses of material and a more general use of this highly effective purification technique.

#### Secondary Metal Refining

A large segment of the metallurgical process industry is engaged in up-grading secondary and scrap materials to produce a prime metallurgical product. The recycle of scrap in the iron and steel industry as well as in most nonferrous industries is well known. Remelting and fire refining, using many of the techniques described in the previous paragraphs, are employed in up-grading secondary metallic material. Units for remelting copper, aluminum, and other nonferrous materials to make specific commercial alloys are an important part of the metallurgical industry.

### 5-2 Distillation Processes

Distillation is the separation of the constituents of a liquid mixture by partial vaporization, followed by separate recovery of vapor and residue. Distillation

processes are an important aspect of process metallurgical engineering. They play a principal role in the extractive metallurgy of zinc and mercury and have been used to remove volatile constituents from other metals, including metals with rather high melting points, such as iron. The impurity element arsenic is present in many iron ores, but no suitable method has been developed to lower its content in the liquid iron produced from these ores. Fractional distillation, however, has been shown to be a possible method for the removal of this element from liquid iron.<sup>14</sup>

The engineering design of a distillation process requires a knowledge of the partial pressures of the vapor constituents in equilibrium with the condensed phase. Relatively few directly measured data are available on the vapor pressures of elements in liquid metallic solutions. However, the vapor pressures of pure elements are known to a relatively high degree of accuracy. The equations giving the vapor pressures of several metals are presented in Appendix A as Table A-VII.

If the vapor pressure of the pure element is known, the partial pressure of that element in equilibrium with a metallic solution can be computed, provided the activity coefficient is known, using the relation,

$$P_a = P_a^0 \gamma_a x_a, \quad (5-30)$$

where

$P_a^0$  = vapor pressure of pure component  $a$  at the temperature under consideration,

$\gamma_a$  = activity coefficient of component  $a$  in solution,

$x_a$  = mole fraction,

For dilute solutions, the activity coefficient of the solvent may be taken as one; also, if the solution is known to have ideal behavior, the activity coefficient of the solute is one. Otherwise, specific experimental data are required to determine the activity coefficient of the solute. The vapor pressures of several alloying elements over dilute solutions in liquid iron at 1600°C are presented in Table 5-1.

#### Clausius-Clapeyron Equation

From a combined statement of the first and second laws of thermodynamics, one may derive for a vapor-liquid equilibrium the relationship,

$$(S_v - S_l) dT = (V_v - V_l) dP \quad (5-31)$$

or

$$\frac{dP}{dT} = \frac{\Delta S_v}{\Delta V_v} = \frac{\Delta H_v}{T \Delta V_v} \quad (5-32)$$

The relation is known as the Clausius-Clapeyron equation. Its integration requires an experimental knowledge of  $\Delta H_v$  and  $\Delta V_v$ . If the volume of the liquid is small in comparison to that of the vapor, then  $\Delta V_v \cong V_v$ , and if the vapor behaves ideally, then  $V_v = RT/P$ , assumptions that are reasonable for metals at elevated tem-

<sup>14</sup> M. Olette, "Vacuum Distillation of Minor Elements from Liquid Ferrous Alloys," *Proc. Physical Chemistry of Process Met. Conf., Pittsburgh, 1959*, Vol. 2. G. K. St. Pierre (ed.), pp. 1065-1087, Interscience, New York, 1961.

TABLE 5-1  
Thermodynamic Data for Some Metallic Elements

| Elements | Atomic wt.<br>$A_v$ | Vapor pressure for pure<br>elements at 1600°C <sup>a</sup><br>mm Hg, $P_0$ | Activity<br>coefficient<br>in dilute Fe<br>solutions, $\gamma^0$<br>at 1600°C | Source of data<br>for $\gamma^0$         | Vapor pressure over dilute<br>Fe solutions at 1600°C <sup>a</sup><br>mm Hg |               |         | Evaporation<br>coefficient $\alpha'$<br>$= \gamma^0(P_0/P_0^0) \sqrt{M_{Fe}} / \sqrt{M_v}$ |
|----------|---------------------|----------------------------------------------------------------------------|-------------------------------------------------------------------------------|------------------------------------------|----------------------------------------------------------------------------|---------------|---------|--------------------------------------------------------------------------------------------|
|          |                     |                                                                            |                                                                               |                                          | 0.050%                                                                     | 0.2%          | 1%      |                                                                                            |
| Pb       | 207.21              | 340                                                                        | 1                                                                             | Assuming ideality                        | 0.046                                                                      | (two liquids) | (3000)  |                                                                                            |
| Mn       | 54.94               | 42                                                                         | 1.3                                                                           | Sanbongi and Masa-<br>yasu               | 0.028                                                                      | 0.11          | 0.55    | 900                                                                                        |
| Al       | 26.98               | 1.9                                                                        | 0.031                                                                         | Chipman and Floridis                     | 0.00006                                                                    | 0.00024       | 0.0012  | 1.4                                                                                        |
| Cu       | 63.54               | 1.0                                                                        | 8.0                                                                           | Morris and Zellars,<br>Koros and Chipman | 0.0035                                                                     | 0.014         | 0.070   | 125                                                                                        |
| Sn       | 118.70              | 0.8                                                                        | 1                                                                             | Assuming ideality                        | 0.00019                                                                    | 0.00076       | 0.0038  | 9.1                                                                                        |
| Si       | 28.09               | 0.42                                                                       | 0.0072                                                                        | Chipman et al.                           | 0.000003                                                                   | 0.000012      | 0.00006 | 0.07                                                                                       |
| Cr       | 52.01               | 0.19                                                                       | 1                                                                             | Assuming ideality                        | 0.0010                                                                     | 0.004         | 0.020   | 3.3                                                                                        |
| Fe       | 55.85               | 0.060                                                                      | 1                                                                             |                                          |                                                                            | 0.060         | 1       | 1                                                                                          |
| Ni       | 58.71               | 0.043                                                                      | 1                                                                             | Assuming ideality                        | 0.00002                                                                    | 0.00008       | 0.00041 | 0.7                                                                                        |
| Co       | 58.94               | 0.031                                                                      | 1                                                                             | Assuming ideality                        | 0.000015                                                                   | 0.00006       | 0.0003  | 0.5                                                                                        |

<sup>a</sup> Approximate values.

Source: Michel Olette, Vacuum distillation of minor elements from liquid ferrous alloys, *Physical Chemistry of Process Metallurgy, Part 2*, Vol. 8, p. 1069, 1961, copyright AIME.

peratures. Substitution in Eq. (5-32) gives

$$\frac{dP}{P} = \frac{\Delta H_v}{R} \left[ \frac{dT}{T^2} \right] \quad (5-33)$$

By further assuming that  $\Delta H_v$  is independent of temperature and pressure, i.e.,  $\Delta H_v$ , the enthalpy change accompanying the transformation from the liquid to the vapor state at equilibrium is essentially equal to that accompanying the change from liquid to vapor at the boiling point,  $\Delta H_v^0$ , Eq. (5-33) can be integrated to the form,

$$\ln \frac{P_2}{P_1} = - \frac{\Delta H_v^0}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \quad (5-34)$$

This relationship may be used to extrapolate vapor pressure data to any desired temperature.

Eq. (5-33) may be integrated to a general form,

$$\log P = - \frac{A}{T} + B, \quad (5-35)$$

where  $A$  and  $B$  are constants whose values depend upon the units in which the vapor pressure,  $P$ , and the absolute temperature,  $T$ , are expressed. This relationship permits the vapor pressures of materials to be tabulated in the form of two constants. Since  $\Delta H_v^0$  is not entirely independent of temperature, an improved fit for the vapor pressure relationship can be made by adding additional terms, e.g.,  $C \log T$  as given in Table A-VII.

#### Relative Volatility

The term volatility is used to compare the vapor pressure of one pure substance with another. However, since the vapor pressure is a function of the presence of other components, the vapor pressure of a pure component does not in itself define the ease of component separation from solutions. The partial pressure ratio of two components over a solution is given by the relationship,

$$\text{Partial pressure ratio} = \frac{\gamma_a x_a P_a^0}{\gamma_b x_b P_b^0} \quad (5-36)$$

The criterion for successful distillation is that the molar (or mass) ratio of a component to be separated must be greater in the vapor phase than in the condensed phase. From Eq. (5-36), the coefficient of the molar ratio in solution may be termed  $\alpha$  where

$$\alpha = \frac{\gamma_a P_a^0}{\gamma_b P_b^0} \quad (5-37)$$

The relative volatility,  $\alpha$ , is thus a direct measure of the ease of component separation by a distillation process. If  $\alpha$  is unity, no separation is possible, since the concentration of the two components in the vapor will be the same as in the con-

densed phase. Substances that can be readily separated show either large or small values of  $\alpha$ .

The relative volatilities of certain elements in liquid iron solutions are included in Table 5-1. The computed values of  $\alpha$  indicate that lead, manganese, copper, tin, and chromium may be distilled from liquid iron but that it would be impossible to remove silicon, nickel, or cobalt from liquid iron; that is, the relative volatility of iron is greater than that of the alloying element in these solutions. The calculations also indicate that aluminum has a relative volatility of one and thus cannot be separated.

The relative volatility of two components changes with temperature. Viewed from the standpoint of ease of separation alone, the optimum temperature range in which to conduct the distillation is that in which the value of  $\alpha$  is maximum.

Equation (5-36) may be used to derive the following relationship between the

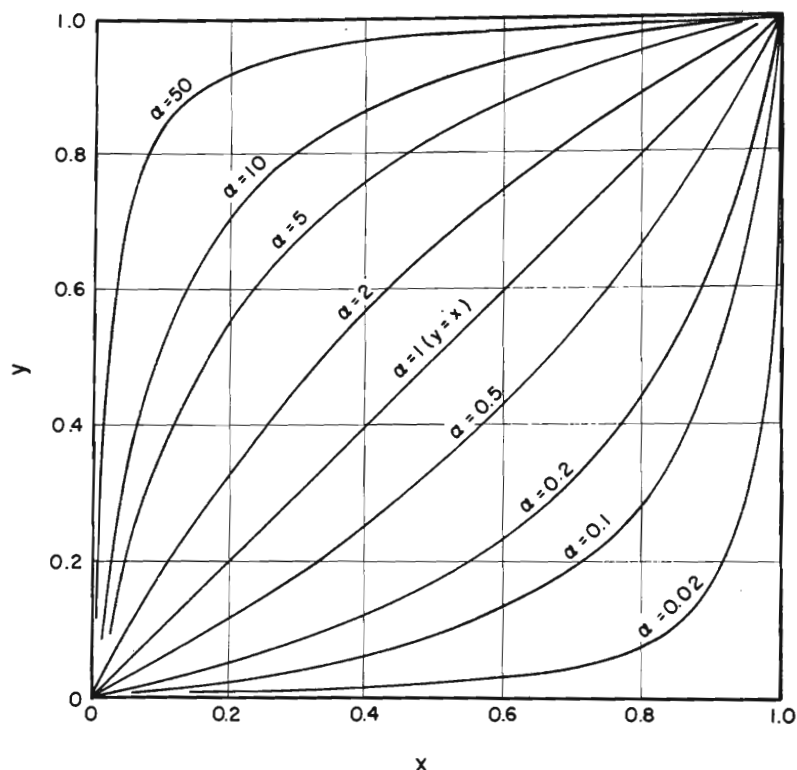


Fig. 5-14. Relationship Between  $X$  and  $Y$  for Various Values of  $\alpha$

concentration of the volatile component in the vapor phase,  $y_a$ , and in the liquid phase,  $x_a$ :

$$y_a = \frac{\alpha x_a}{1 + x_a(\alpha - 1)} \quad (5-38)$$

Figure 5-14 shows a plot of  $y$ , the vapor phase mole fraction, versus  $x$ , the liquid phase mole fraction for a given component at various constant values of  $\alpha$ .

**Example Problem 5-6.** Calculate the equilibrium partial pressures of the three components cadmium, bismuth, and lead over a ternary bismuth-rich solution containing 20 mol% lead and 20 mol% cadmium at 500°C. Compare the volatilities of lead and cadmium in this solution. The activity coefficients are:  $\gamma_{Bi} = 0.9$ ,  $\gamma_{Cd} = 1.2$ ,  $\gamma_{Pb} = 0.9$ .

**Solution.** From Table A-VII the vapor pressures of the three metals can be calculated. For pure cadmium,

$$\begin{aligned} \log P_{Cd}^0 (\text{mm Hg}) &= -\frac{5819}{773} + 12.287 - 1.257(\log 773) \quad (5-a) \\ &= -7.525 + 12.287 - (1.257)(2.888) \\ &= 1.127 \\ P_{Cd}^0 &= 13.4 \text{ mm Hg.} \end{aligned}$$

The partial pressure of cadmium over the alloy is given by the relationship,

$$P_{Cd} = X_{Cd} \gamma_{Cd} P_{Cd}^0 = (0.2)(1.2)(13.4) = 3.22 \text{ mm Hg} \quad (5-b)$$

Similarly for lead and bismuth

$$P_{Pb} = X_{Pb} \gamma_{Pb} P_{Pb}^0 = (0.2)(0.9)(1.64 \times 10^{-5}) = 2.95 \times 10^{-6} \text{ mm Hg,} \quad (5-c)$$

$$P_{Bi} = X_{Bi} \gamma_{Bi} P_{Bi}^0 = (0.6)(0.9)(1.82 \times 10^{-5}) = 9.83 \times 10^{-6} \text{ mm Hg.} \quad (5-d)$$

The relative volatility of cadmium and lead in this alloy is given by Eq. (5-37):

$$\alpha = \frac{(1.2)(13.4)}{(0.9)(1.64 \times 10^{-5})} = 1.09 \times 10^6. \quad (5-e)$$

A similar calculation for bismuth yields a correspondingly large ratio, thus indicating that cadmium can be separated from these elements by distillation. The extent of purification depends, of course, on the concentration levels as indicated by Eq. (5-36).

#### Equilibrium Distillation

Simple batch distillation is the principal method of distillation used in metallurgical processes. In this technique increments of vapor upon formation are removed from the remaining liquid solution. If the operation is not conducted under high vacuum conditions, and under the assumption that the vapor coming off the solution is in equilibrium with the bulk liquid, the following mathematical analysis may be applied, as first done by Rayleigh.<sup>15</sup>

<sup>15</sup> Rayleigh, *Philosophical Magazine* 4, 521 (1902).

The mass balance of such a process may be written in terms of a differential equation, the Rayleigh equation, derived as follows: assume a solution of two components, the total moles of which are  $L$ . Let the mole fraction of the more volatile component be  $x$  in the liquid and  $y$  in the vapor phase. Let  $dL$  moles be vaporized. The liquid will lose and the vapor will gain a differential quantity of the more volatile component. By a material balance,

$$(L - dL)(x - dx) + (y + dy) dL = Lx. \quad (5-39)$$

Neglecting differentials of second order and rearranging,

$$\frac{dL}{L} = \frac{dx}{y - x}. \quad (5-40)$$

Integrating Eq. (5-40) between limits

$$\ln \frac{L_1}{L_2} = \int_{x_2}^{x_1} \frac{dx}{y - x}, \quad (5-41)$$

where

$L_1$  = moles of original charge,

$L_2$  = moles of residual charge after  $L_1 - L_2$  have been distilled off,

$x_1$  = the mole fraction of more volatile component in the original charge  $L_1$ ,

$x_2$  = mole fraction of more volatile component in the residual charge  $L_2$ .

Consistent weight units may be substituted for the molar units in Eq. (5-41).

If experimental data for the relationship between  $y$  and  $x$  are available, the right side of Eq. (5-41) may be integrated graphically. If a mathematical relationship exists between  $y$  and  $x$ , the integration may be carried out analytically, as in the following cases. For example, during a simple batch distillation at constant pressure, the temperature may rise as the residual liquid becomes poorer in the more volatile component. If  $\alpha$  does not vary with temperature, Eq. (5-38) may be substituted in Eq. (5-41) with the integrated result

$$\ln \frac{L_1}{L_2} = \frac{1}{\alpha - 1} \left[ \ln \left[ \frac{x_1}{x_2} \right] + \alpha \ln \left[ \frac{1 - x_2}{1 - x_1} \right] \right]. \quad (5-42)$$

If Henry's law applies to the solute that is being removed from the solution by distillation, the relationship  $y = kx$  may be substituted with the result,

$$\ln \frac{L_1}{L_2} = \frac{1}{k - 1} \ln \left[ \frac{x_1}{x_2} \right]. \quad (5-43)$$

It is important to note that Henry's law is an isothermal relationship, and in order to assure valid use of Eqs. (5-42) and (5-43), one should be aware of any temperature influences on the relationships involved.

The application also may be made to multicomponent mixtures. In the event that only one of the components of the complex solution is highly volatile, the solution may be treated as a pseudo binary. However, if two or more components

have a volatility of the same order, one may compute the concentrations. The mathematics are more involved, but the principles remain the same.

### Molecular Distillation

In most metallurgical distillation operations, particularly those carried out under high vacuum conditions, the rate of distillation is controlled by the rate of evaporation of atoms from the surface of the melt, and therefore it is not valid to assume that equilibrium is maintained between the concentrations in the vapor and in the liquid. The process conducted under these conditions is termed molecular distillation, and under conditions of complete nonreturn condensation, the quantitative rate of distillation is given by the Langmuir equation.

In 1913 Langmuir<sup>16</sup> using the kinetic theory of gases derived a relationship for the rate of evaporation of single component systems in terms of the vapor pressure. Under isothermal conditions there is a maximum rate at which a volatile substance will evaporate from an exposed surface. From the kinetic theory of gases, the rate of collision of vapor molecules with the surface can be calculated from the pressure of the vapor. Assuming that the vapor molecules obeyed a Maxwell-Boltzmann velocity distribution, and by making use of the ideal gas law, Langmuir showed that the mass of vapor molecules, striking a unit area of surface per unit time is given by the relation,

$$\mu = P \sqrt{\frac{M}{2\pi RT}} \quad (5-44)$$

where

$P$  = pressure of vapor,

$R$  = gas constant,

$M$  = molecular or atomic weight of the vapor species.

The number of molecules returning to the surface can be assumed to be the same as the number striking it, i.e., all of the molecules striking the surface are held there. Under equilibrium conditions between vapor and liquid, this rate will be the same as the maximum rate of evaporation. Therefore,

$$w_0 = P_0 \sqrt{\frac{M}{2\pi RT}}, \quad (5-45)$$

where

$w_0$  = rate of evaporation, g/cm<sup>2</sup> per second,

$P_0$  = saturation pressure, mm Hg at solution temperature,

$T$  = absolute temperature, °K,

$M$  = molecular or atomic weight.

Evaporation can occur at a rate of  $w_0$  only in a perfect vacuum and then only when the rate of evaporation is so small that the mean-free-path of the vapor

<sup>16</sup> I. Langmuir, *Phys. Rev.* 2, 329 (1913).

molecules exceeds the distance between the evaporating and condensing surfaces. At appreciable rates of evaporation, the vapor molecules will collide with each other. Some will rebound to the surface, so the actual rate of evaporation will be the difference between  $w_0$  and the rate of return to the surface  $w_1$ . The net rate of evaporation will then be

$$w = w_0 - w_1. \quad (5-46)$$

The two rates  $w_0$  and  $w_1$  are related to the pressures  $P_0$  and  $P_1$ . Therefore, the net rate of evaporation is given by

$$w = (P_0 - P_1) \sqrt{\frac{M}{2\pi RT}}, \quad (5-47)$$

where  $P_1$  is the partial pressure of the vapor at the evaporating surface.

The ratio between  $P_1$  and  $P_0$  is termed  $\phi$ , the degree of saturation of the vapor; it varies from 0 to 1 as the evaporating conditions vary from molecular to equilibrium vaporization. The degree of saturation is related in the following way to the relation between  $w$ , the observed rate, and  $w_0$ , the maximum rate of evaporation.

$$\phi = \frac{P_1}{P_0} = 1 - \frac{w}{w_0}. \quad (5-48)$$

For the case of multicomponent systems, the relation given in Eq. (5-47) is modified and is referred to as the Langmuir-Knudsen equation:

$$W_A = (P_A^0 - P_A') \gamma_A X_A \sqrt{\frac{M_A}{2\pi RT}}. \quad (5-49)$$

where

- $W_A$  = rate of evaporation of component  $A$  from a multicomponent solution,
- $P_A^0$  = equilibrium partial pressure of pure component  $A$ ,
- $P_A'$  = effective partial pressure of component  $A$  in the vapor phase,
- $\gamma_A$  = activity coefficient of component  $A$  in the liquid phase,
- $X_A$  = mole fraction of component  $A$  in the liquid phase,
- $M_A$  = atomic or molecular weight of component  $A$ .

**Example Problem 5-7.** Using the Langmuir-Knudsen equation, estimate the concentration of manganese in a 1% Mn steel after holding in a high vacuum at 1600°C for 10 min. Assume the maximum rate of molecular distillation. The melt is inductively stirred, is 70 mm deep, and is contained in a 40-mm ID crucible.

**Solution.** From Table 5-1

$$P_{Mn}^0 = 42 \text{ mm Hg}, \quad \gamma_{Mn}^0 = 1.3, \quad M_{Mn} = 54.94.$$

Neglecting iron evaporation, the maximum evaporation rate for manganese is

$$W = 0.0583 P_{Mn}^0 \gamma_{Mn} X_{Mn} \sqrt{\frac{M}{T}}. \quad (5-a)$$

Since the atomic weights of manganese and iron are nearly the same, the mole fraction can be converted directly to wt%.

$$\frac{d(\%Mn)}{dt} = \frac{(0.0583)S}{V\rho} P_{Mn}^0 \gamma_{Mn} \sqrt{\frac{M}{T}} (\%Mn). \quad (5-b)$$

Rearranging and integrating,

$$\log_{10} \left[ \frac{(\%Mn)_{t=0}}{(\%Mn)_t} \right] = \frac{0.0583 S}{2.3 V\rho} P_{Mn}^0 \gamma_{Mn} \sqrt{\frac{M}{T}} t, \quad (5-c)$$

where

$S$  = surface area of the melt,  $\text{cm}^2$

$V$  = volume of the melt,  $\text{cm}^3$

$\rho$  = density of the melt,  $7.1 \text{ gm/cm}^3$

$t$  = time, sec.

$$\log \left[ \frac{1}{(\%Mn)_t} \right] = \frac{(0.0583)}{(2.3)(7.1)(7)} (42)(1.3) \sqrt{\frac{54.94}{1873}} (600) = 2.87,$$

$$(\%Mn)_{t=600 \text{ sec}} = 0.00135\%.$$

The Langmuir-Knudsen equation describes distillation phenomena with good accuracy under conditions where the vapor pressure of the component is reflected by the bulk concentration, i.e., the rate of mass transport is controlled by vaporization at the surface. In commercial operations, attempts to achieve high distillation rates often create situations that place the Langmuir-Knudsen equation in error. One cause of the discrepancy between the Langmuir-Knudsen theory and observed distillation rates has been ascribed to depletion of the surface which occurs if liquid diffusion is the rate-limiting step which controls mass transfer to the surface. Furthermore, the surface may be covered with oxides that restrict mass transfer to the vapor, or the distillation rate may be limited by the rate of heat transfer to the surface which provides the necessary heat of evaporation.

In commercial operations the rate of distillation also may be controlled by the rate of transfer of vapor away from the surface. This rate of transfer is not as easy to calculate as the rate of evaporation. Factors which must be considered are (1) pressure gradient of vapor, (2) effective pressure of permanent gas in the system, and (3) dimensions of still and condensing system.

Finally, it should be noted that the vapor pressure is difficult to treat analytically in a gas stream whose molecules are moving predominately in one direction. In general, thermodynamic quantities are defined for systems at equilibrium and cannot be used rigorously under other conditions. Despite these limitations and the fact that conditions which lead to deviations from the Langmuir-Knudsen theory are difficult to describe analytically, these factors may become important in commercial operations, and must be considered in analyzing or modeling a distillation process.

## Vacuum Dezincing of Desilverized Lead Bullion

The first commercial vacuum dezincing process for the purification of lead was developed by the St. Joseph Lead Company.<sup>17</sup> This process is used to remove zinc remaining in the lead after the Parkes desilverizing process.

The lead bullion is refined in batches at a temperature of 450–500°C. The surface exposed to vacuum is free of dross, and, since distillation is more rapid than diffusion of zinc through the molten lead, vigorous agitation must be employed to prevent surface depletion of zinc and also to prevent a temperature drop at the surface caused by radiation and energy consumed as latent heat of vaporization of zinc. In the St. Joseph batch operation, agitation is produced by a mechanical stirrer. In the continuous process used by the Broken Hill Associated Smelters, in Australia, agitation is produced by circulating a thin stream of lead in turbulent flow. The zinc is condensed as a solid from these operations.

The amount of lead distilling over with the zinc increases with temperature because the relative difference in vapor pressures becomes less at higher temperatures. Consequently, the best separation of zinc from lead is obtained at the lowest temperatures. However, the zinc recovered from the lead bullion is recycled for desilverizing, so that contamination of lead in this instance is of little practical consequence. Operating practice shows that the lead in the condensate is less than 10%, which represents less than 0.05% of the lead treated. This is not a great circulating load for the process. It is also important that oxygen be avoided. A vacuum of 200  $\mu$  or less is adequate to provide a distillate that is shiny in appearance. The rate of distillation in these processes has been quantitatively treated and compared with the Langmuir equation.<sup>18</sup> The actual operating times are on the order of 5 hr, or approximately 10 times the theoretical treatment time based on the Langmuir equation. This discrepancy may result from surface depletion of zinc or from inefficient condensation, which permits the zinc vapor to condense and fall back into the lead bath. In the continuous process used in Australia, a horizontal flow of vapor from the liquid lead surface to the condenser prevents precondensed zinc droplets from falling back into the bath, with the result that the distillation rates more closely approach the theoretical limit.

## Observations on Liquid Iron Alloys

Under conditions of molecular distillation, the influence of the molecular weights of the components on the rate of evaporation must be considered. Thus, for distillations from iron baths the relative volatility coefficient,  $\alpha$ , as defined in Eq. (5-37), may be modified to the form,

$$\alpha' = \frac{\gamma_A}{\gamma_{Fe}} \left[ \frac{P_A^0}{P_{Fe}^0} \right] \sqrt{\frac{M_{Fe}}{M_A}}, \quad (5-50)$$

<sup>17</sup> W. T. Isbell, *Trans. Met. Soc. AIME* **182**, 186 (1949).

<sup>18</sup> T. R. A. Davey, *J. Metals* **5**, 991 (1953).

where

$M_{Fe}$  = atomic weight of iron,

$M_A$  = atomic weight of solute.

In a dilute solution, iron (the solvent) obeys Raoult's law and hence,  $\gamma_{Fe}$  is unity. Also, the solute  $A$  at low concentrations obeys Henry's law, and  $\gamma_A$  is nearly constant and equal to  $\gamma_A^0$ . (It would be equal to one if the solution were ideal). Under such conditions,  $\alpha'$  becomes

$$\alpha' = \gamma_A^0 \left[ \frac{P_A^0}{P_{Fe}^0} \right] \sqrt{\frac{55.85}{M_A}}. \quad (5-51)$$

A comparison is made in Table 5-1 between the computed values of  $\alpha'$  and those measured experimentally on liquid iron solutions. Although there is some discrepancy, it should be noted that the comparative evaporation coefficients remain in the same order. The unusual results for silicon (and also for aluminum, where it was noted that in some cases aluminum was highly volatile and in other cases did not distill at all) are explained in terms of the formation of a highly volatile suboxide.<sup>19</sup> This effect also has been noted by Floridis,<sup>20</sup> who showed that the vacuum distillation of sulfur from liquid iron was greatly enhanced by the presence of silicon, presumably because of the formation of a volatile silicon sulfide, which assists in removing both elements from solution.

## 5-3 Degassing Operations

An important problem in producing a suitable metal product is that of gas control. Hydrogen is a particularly troublesome gas—causing bleeding ingots, embrittlement, low ductility, and the presence of blow holes. Nitrogen also may have a desirable or undesirable effect on the properties of a metal, particularly steel, depending upon the metal's composition, subsequent treatment, and intended use. Oxygen, as a principal refining agent, plays a role in determining the final composition and properties of metals. In addition to these simple gases, the metallurgist must also cope with complex gases, those which contain more than one type of atom in the molecule, principally CO, CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>O. In the design of processes to control these gases in metals, data are required on the solubility, rates of solution, and chemical reactions involved in formation or decomposition in the metal, particularly in the liquid state. Much of this information is presently available, and an attempt will be made in this section to apply that data to the design of degassing operations as refining processes.

## Fundamentals of Gas-Metal Reactions

**Diatomic Gases.** The solubility of a gas in a metal is a function of the pressure of that gas in equilibrium with the liquid metal. The solubility of a diatomic gas,

<sup>19</sup> M. Olette, Vacuum Distillation of Minor Elements from Liquid Ferrous Alloys, *Proc. Physical Chemistry of Process Met. Conf., Pittsburgh*, 1959, Vol. 2. G. K. St. Pierre (ed.), pp. 1065–1087, Interscience, New York, 1961.

<sup>20</sup> T. P. Floridis, *Trans. Met. Soc. AIME* **215**, 870 (1959).

e.g., nitrogen, is proportional to the square root of the pressure of nitrogen, which is in equilibrium with the melt. This relationship has come to be known as Sieverts' law,<sup>21</sup> and follows directly from consideration of the equilibrium of the reaction,



where the equilibrium constant may be expressed as

$$K_{s2} = \frac{a_N}{\sqrt{P_{N_2}}} = \frac{f_N(\%N)}{\sqrt{P_{N_2}}}. \quad (5-53)$$

Since the solubility of nitrogen is directly proportional to the square root of the nitrogen pressure as shown in Fig. 5-15 for nitrogen dissolving in liquid iron, the activity coefficient of nitrogen in the liquid pure metal is unity and independent of concentration, i.e., nitrogen pressure, up to several atmospheres pressure. From this behavior, it follows that a diatomic gas, such as nitrogen, dissolves monatomically in a liquid metal at high temperatures. Eq. (5-53) can be rewritten in Sieverts' law form as

$$\%N = K_{s2}\sqrt{P_{N_2}}. \quad (5-54)$$

Similar relationships can be rewritten for hydrogen and other diatomic gases.

The solubility of a gas in an alloy is also a function of the concentrations of solutes in the alloy. As an example, the influence of alloying elements on the solubility of nitrogen in liquid iron is shown in Fig. 5-16. Since the equilibrium constant,  $K_{s2}$  of Eq. (5-53), remains fixed, a change in solubility of nitrogen occasioned by the presence of an alloying element may be represented by a corresponding change in the activity coefficient,  $f_N$ . Customarily the infinitely dilute solution of nitrogen is taken as the reference state,

$$\lim \left[ \frac{a_N}{\%N} \right]_{\%N \rightarrow 0} = f_N = 1. \quad (5-55)$$

Since nitrogen solution follows Sieverts' law in Fe-N solutions,  $f_N$  remains unity and the self-interaction parameter for nitrogen,  $e_N^N$ , is zero. As a result of the reference state taken, the activity coefficient of nitrogen in an Fe-j alloy is obtained by the following equation:

$$f_N = \left[ \frac{\%N(\text{pure Fe})}{\%N(\text{alloy})} \right]_{P_{N_2}, T}. \quad (5-56)$$

A plot of the logarithm of the activity coefficient of nitrogen in liquid iron as a function of added third elements is shown in Fig. 5-17. The slope of a curve of Fig. 5-17, taken as the alloying element approaches zero concentration, represents the interaction parameter  $e_N^j$ .

A summary of the standard free energy changes for the solution of various gases in liquid metal solvents is presented in Table 5-2. Additional interaction data for solutes in liquid iron is presented in Table A-V of Appendix A.

<sup>21</sup> A. Sieverts, *Z. Phys. Chem.* **60**, 129 (1907).

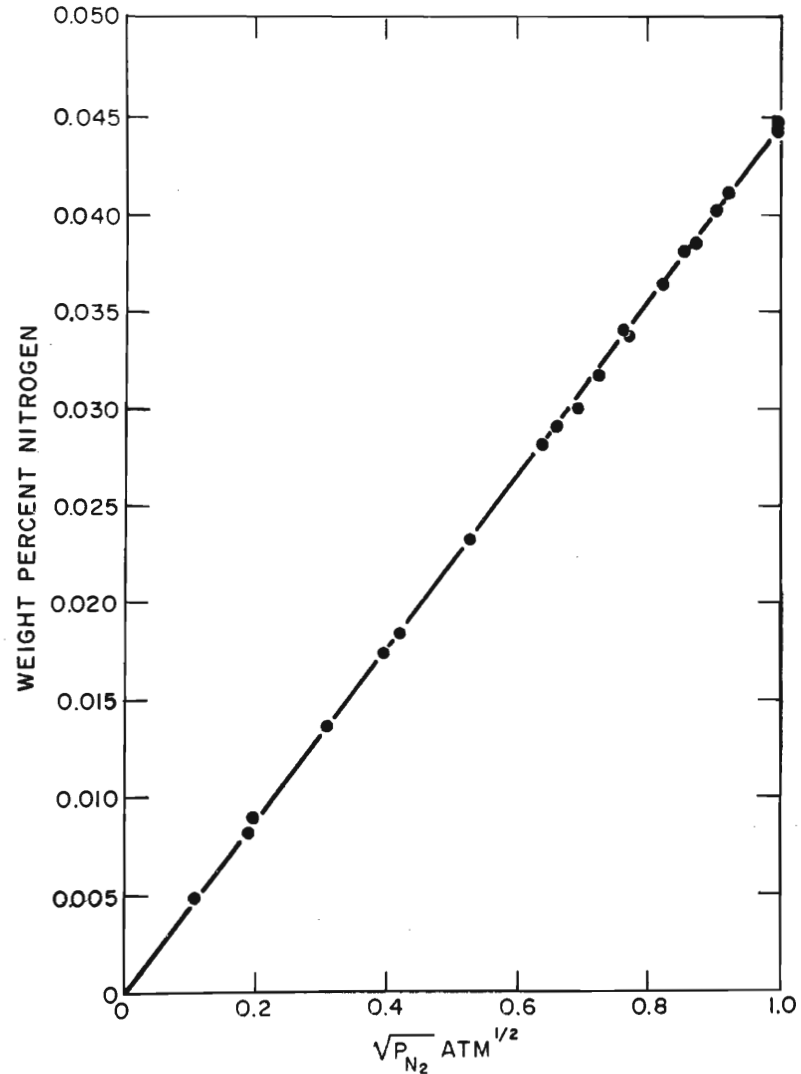


Fig. 5-15. Adherence to Sieverts' Law,  $\%N \propto \sqrt{P_{N_2}}$ , Nitrogen Dissolved in Pure Iron at 1606°C

Source: "Solubility of Nitrogen in Liquid Iron Alloys," R. D. Pehlke and J. F. Elliott, *Trans. Met. Soc. AIME*, 1960, Vol. 218, p. 1091.

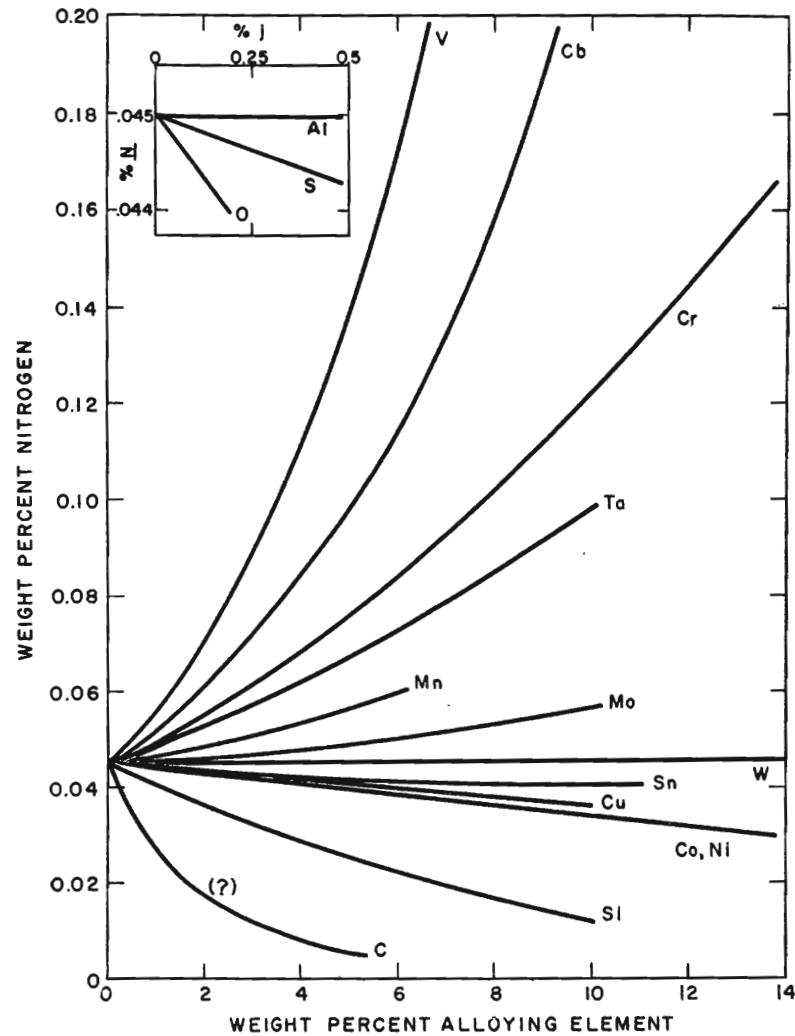


Fig. 5-16. Summary of the Solubility of Nitrogen in Liquid Binary Fe-j Alloys at 1600°C and 1-atm N<sub>2</sub> Pressure

Source: "Solubility of Nitrogen in Liquid Iron Alloys," R. D. Pehlke and J. F. Elliott, *Trans. Met. Soc. AIME*, 1960, Vol. 218, p. 1099.

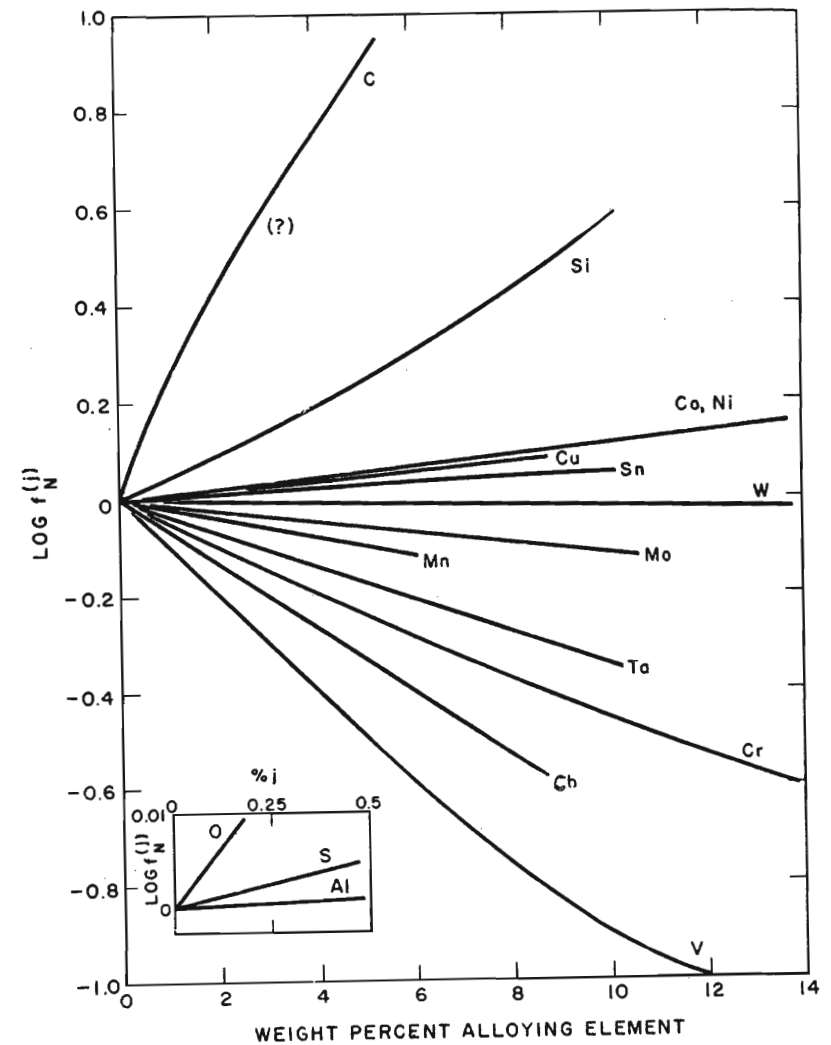


Fig. 5-17. Effect of Alloying Elements on the Activity Coefficient of Nitrogen in Binary Fe-j Alloys at 1600°C

Source: "Solubility of Nitrogen in Liquid Iron Alloys," R. D. Pehlke and J. F. Elliott, *Trans. Met. Soc. AIME*, 1960, Vol. 218, p. 1100.

TABLE 5-2

Standard Free Energy of Solution of Gas Forming Solutes in Various Liquid Metal Solvents

(Standard state in solvent is hypothetical 1 wt% solution)

| Solvent  | Element                                      | $\Delta G^\circ$ cal/g-atom | Reference      |
|----------|----------------------------------------------|-----------------------------|----------------|
| Aluminum | Hydrogen $\frac{1}{2} \text{H}_2 = \text{H}$ | $11,650 + 6.55 T$           | 1              |
| Cobalt   | Hydrogen $\frac{1}{2} \text{H}_2 = \text{H}$ | $9,800 + 7.03 T$            | 2              |
|          | Nitrogen $\frac{1}{2} \text{N}_2 = \text{N}$ | $10,000 + 5.24 T$           | 3              |
|          | Oxygen $\frac{1}{2} \text{O}_2 = \text{O}$   | $-14,700 - 4.91 T$          | 4              |
| Copper   | Hydrogen $\frac{1}{2} \text{H}_2 = \text{H}$ | $10,400 - 10.8 T$           | 5              |
|          | Oxygen $\frac{1}{2} \text{O}_2 = \text{O}$   | $-18,150$                   | 6              |
| Iron     | Carbon C(g) = $\text{C}$                     | $5100 - 10.0 T$             | See Table A-VI |
|          | Hydrogen $\frac{1}{2} \text{H}_2 = \text{H}$ | $8715 + 7.28 T$             | 7              |
|          | Nitrogen $\frac{1}{2} \text{N}_2 = \text{N}$ | $860 + 5.71 T$              | See Table A-VI |
|          | Oxygen $\frac{1}{2} \text{O}_2 = \text{O}$   | $-28,000 - 0.69 T$          | See Table A-VI |
|          | Sulfur $\frac{1}{2} \text{S}_2 = \text{S}$   | $-31,520 + 5.27 T$          | See Table A-VI |
| Nickel   | Hydrogen $\frac{1}{2} \text{H}_2 = \text{H}$ | $4800 - 9.9 T$              | 5              |
|          | Oxygen $\frac{1}{2} \text{O}_2 = \text{O}$   | $-11,920 - 2.28 T$          | 4              |

1. W. R. Opie and N. J. Grant, *Trans. AIME* **188**, 1237-1241 (1950).
2. F. E. Woolley and R. D. Pehlke, *Trans. AIME* **233**, 1454-1461 (1965).
3. R. G. Blossey and R. D. Pehlke, *Trans. AIME* **236**, 28-31 (1966).
4. E. S. Tankins, N. A. Gokcen, and G. R. Belton, *Trans. AIME* **230**, 820-826 (1964).
5. M. Weinstein and J. F. Elliott, *Trans. AIME* **227**, 285-286 (1963).
6. G. R. Belton and E. S. Tankins, *Trans. AIME* **233**, 1892-1898 (1965).
7. M. Weinstein and J. F. Elliott, *Trans. AIME* **227**, 382-393 (1963).

**Compound Gases.** Equilibrium constants may be written for the reactions between gases dissolved in metals and other constituents in solution. For example, the equilibrium partial pressure of CO over liquid steel is a function of the carbon and oxygen activities in the liquid metal. This may be seen from the expression,



where the equilibrium constant is written as

$$K_{57} = \frac{P_{\text{CO}}}{a_{\text{C}} \cdot a_{\text{O}}}. \quad (5-58)$$

This expression may be rewritten in the form,

$$P_{\text{CO}} = K_{57} \cdot a_{\text{C}} \cdot a_{\text{O}}, \quad (5-59)$$

which indicates that the partial pressure of CO in equilibrium with the steel is determined by the equilibrium constant and the product of the activities of carbon and oxygen in solution.

Equation (5-59) implies a hyperbolic relationship between the concentrations of carbon and oxygen in liquid iron at a given pressure of CO. In Fig. 5-18 this form of relationship is shown for equilibrium at 1 atm carbon monoxide pressure. Figure

5-18 also shows average values from electric and open hearth furnaces where the steel bath compositions are slightly above equilibrium with 1 atm pressure of carbon monoxide. (See Appendix B, Example Problem 9.) Since the activity coefficients for oxygen or carbon can be influenced by the concentrations of the other element, the relationship is not perfectly hyperbolic. The presence of other solutes will also slightly influence the shape of the equilibrium curve while the location of the equilibrium curve of Fig. 5-18 is determined by the CO pressure.

As another case, consider the dissolution of a compound which contains an atomic species of a gaseous component. For example, the solubility product of aluminum nitride is given by the reaction



where the activity of the nitride is taken as unity and the equilibrium constant is expressed as

$$K_{60} = \frac{a_{\text{Al}} \cdot a_{\text{N}}}{a_{\text{AlN}}} = a_{\text{Al}} \cdot a_{\text{N}}. \quad (5-61)$$

Combining this expression with Eq. (5-53), one can compute the partial pressure

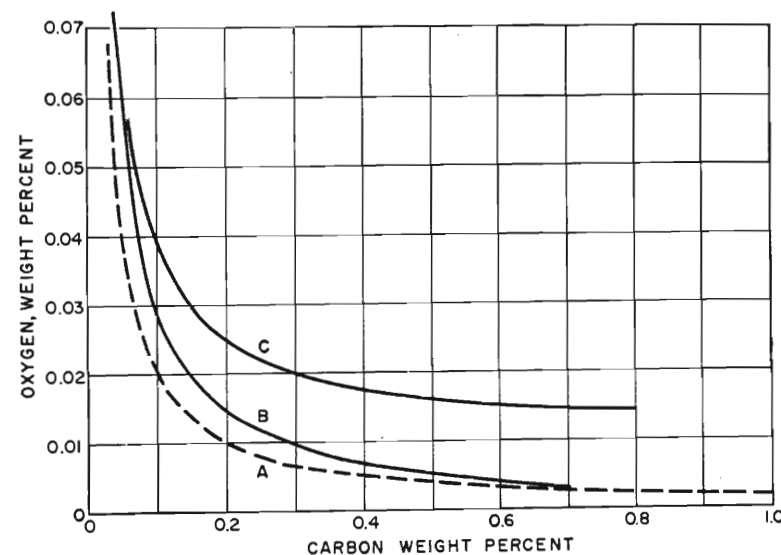


Fig. 5-18. Carbon-Oxygen Equilibrium in Steel Furnaces

- Source: *Electric Furnace Steelmaking, Vol. II: Theory and Fundamentals*, edited by Clarence E. Sims, Interscience Publishers, New York 1963, p. 126, copyright AIME
- A. Equilibrium at 1600°C and 1 atmosphere CO pressure
  - B. Electric Furnaces, Marsh J., *Electric Furnace Proc. AIME*, 1944, Vol. 16, p. 135.
  - C. Open Hearth, Fetter K., and J. Chipman, *Trans. AIME*, 1940, vol. 140, p. 170.

of nitrogen in equilibrium with a melt containing a given wt% aluminum, and in contact with aluminum nitride, provided the activity coefficients for the solution are known. The reaction would be expressed as

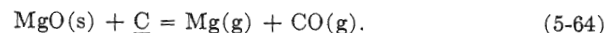


where the equilibrium relationship is given by

$$K_{62} = \frac{K_{60}}{K_{52}} = \sqrt{(P_{\text{N}_2})f_{\text{Al}}}(\% \text{Al}). \quad (5-63)$$

The activity coefficient of aluminum,  $f_{\text{Al}}$ , is a function of the composition of the melt and is determined by the concentrations of dissolved nitrogen and aluminum and any other alloying elements that may be present. This activity coefficient can be estimated using interaction parameters.

During degassing of steel melts, dissolved carbon can react with the refractories. An example of this is given by the following reaction:



Experimental support for this phenomenon has been developed by Bennett et al.,<sup>22</sup> who showed that carbon was lost by reaction with a magnesia refractory under vacuum. Similar reactions can take place with silica and alumina. The refractories used for degassing should be as resistant as possible to this type of attack. The greater thermodynamic stability of alumina under vacuum degassing conditions (note that aluminum reaction product would not vaporize as magnesium does) supports the practical experience that high alumina refractories are preferable for this application.

#### Inert Flush Degassing

Inert flush degassing is a process for removing a dissolved gas from a liquid metal by bubbling an inert or insoluble gas through the liquid metal. The solubility of the dissolved gas is a function of the partial pressure of that component in the gas phase with which the metal is in contact. Exposure of a melt to an atmosphere which is very dilute in the dissolved gas will provide a driving force for elimination of the dissolved gas. The mechanism for elimination of a dissolved gas from the liquid metal involves diffusion to the surface of the melt, reaction at the surface, and subsequent removal from the melt. Consequently, any process which provides a dilute atmosphere and which also shortens the diffusion path, or provides a greater surface area, should provide a more rapid means for removing the dissolved gas. The blowing of an inert flush gas through a liquid metal as a fine dispersion of bubbles is such a process. A schematic diagram of an argon degassing operation is shown in Fig. 5-19.

*An Equilibrium Process.* The process engineer is interested in the rate at which inert flush degassing will remove a dissolved gas. If it is assumed that the flush gas is in equilibrium with the melt when it leaves the melt surface, i.e., that the partial

<sup>22</sup> G. H. J. Bennett et al., *J.I.S.I.* 195, 174-180 (1960).

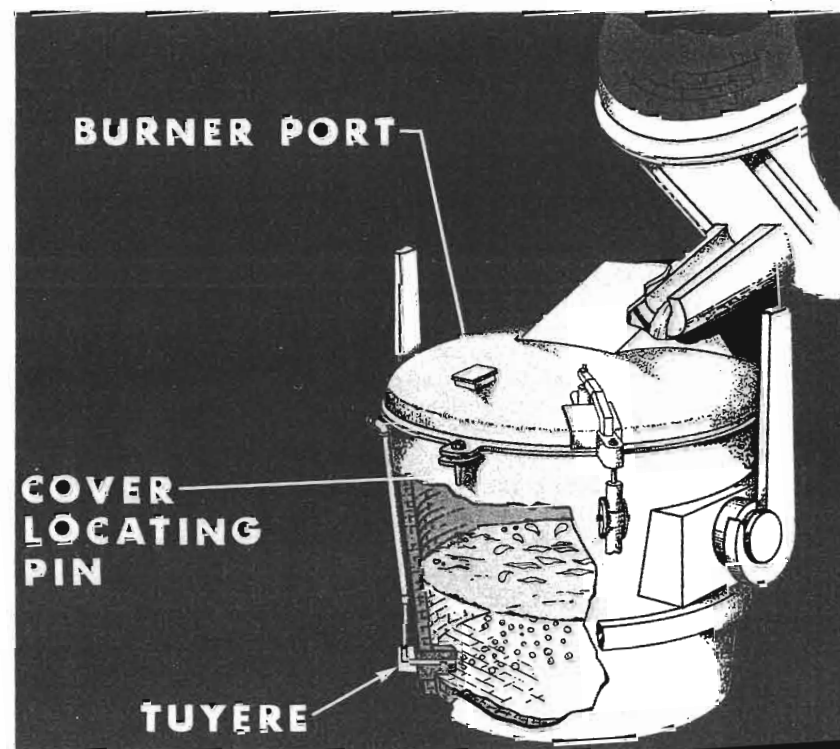


Fig. 5-19. Argon Degassing Vessel

Source: "Argon Degassing Practice and Results," R. J. Choulet, R. L. W. Holmes, and L. R. Chrzan, *J. of Metals*, 1966, 18, p. 73.

pressure of dissolved gas in the bubble leaving the melt is equal to the equilibrium partial pressure for the instantaneous concentration of dissolved gas in the melt, the following differential relationship applies

$$-dN_G = (dN_F + dN_G) \left[ \frac{P_G}{(P_G + P_F)} \right], \quad (5-65)$$

where

$N_G$  = cubic feet of dissolved gas,

$N_F$  = cubic feet of flushing gas,

$P_G$  and  $P_F$  = respective partial pressures in the existing gas bubble.

If the total pressure on the system is 1 atm, then  $(P_G + P_F)$  is equal to 1, and Eq. (5-65) may be rewritten as

$$dN_F = -dN_G \left[ \frac{1 + P_G}{P_G} \right]. \quad (5-66)$$

Converting from standard cubic feet of dissolved gas to wt%

$$dN_F = - \left[ \frac{(379)(2000)(W)}{(100)(M)} \right] \left[ \frac{1 + P_G}{P_G} \right] dC_G, \quad (5-67)$$

where

$W$  = tons of metal,  
 $C_G$  = concentration of dissolved gas,  
 $M$  = molecular weight of the dissolved gas.

For the case where the dissolved gas is diatomic, the equilibrium pressure of dissolved gas,  $P_G$ , is related to the concentration of dissolved gas by Sieverts' law,

$$C_G = K_G(P_G)^{1/2}, \quad (5-68)$$

where the concentration is expressed in wt% and the pressure in atmospheres. [The Sieverts' law constant is given in the units  $\% / (\text{atm})^{1/2}$ .] The partial pressure of dissolved gas is then

$$P_G = \left[ \frac{C_G}{K_G} \right]^2. \quad (5-69)$$

Equation (5-67) may be integrated in the form,

$$\int_0^{V_F} dN_F = - \left[ \frac{7580 W}{M} \right] \int_{C_0}^C \left( dC_G + K_G^2 \frac{dC_G}{C_G^2} \right). \quad (5-70)$$

The volume of flush gas in standard cubic feet,  $V_F$ , required to reduce the dissolved gas content in wt% from  $C_0$  to  $C$  is

$$V_F = \left[ \frac{7580 W}{M} \right] \left[ \frac{(C_0 - C)(K_G^2 + C C_0)}{C C_0} \right]. \quad (5-71)$$

In most cases of inert flush degassing, the concentration of dissolved gas in the bubble leaving the melt is very much less than that of the purge gas. Hence, Eq. (5-65) can be rewritten in the form,

$$-dN_G = dN_F \left[ \frac{P_G}{P_F} \right] \quad (5-72)$$

and when  $P_F = 1$  atm, then

$$dN_F = - \left[ \frac{7580 W}{M} \right] \left[ \frac{dC_G}{P_G} \right], \quad (5-73)$$

which integrates in a simpler form,

$$\int_0^{V_F} dN_F = \left[ \frac{7580 W}{M} \right] K_G^2 \int_{C_0}^C - \left[ \frac{dC_G}{C_G^2} \right], \quad (5-74)$$

$$V_F = \left[ \frac{7580 W}{M} \right] K_G^2 \left[ \frac{1}{C} - \frac{1}{C_0} \right]. \quad (5-75)$$

Equations of slightly different form result when other types of gases are considered. Deoxidation of liquid iron can be carried out by inert flush degassing to purge the melt of carbon monoxide. If the exiting gas is assumed to leave at 1 atm with a very small CO content and the carbon content is low, but large relative to the oxygen content, such that it remains nearly constant; and the process is assumed to be carried out at equilibrium, then

$$dN_F = - \left[ \frac{7580 W}{M} \right] \left[ \frac{1}{K_{57} \% C} \right] \left[ \frac{dC_O}{\% O} \right], \quad (5-76)$$

$$V_F = \left[ \frac{7580 W}{M} \right] \left[ \frac{1}{(K_{57})(\% C)} \right] \ln \left[ \frac{(\% O)_{\text{initial}}}{(\% O)_{\text{final}}} \right]. \quad (5-77)$$

In cases where the carbon content is of the same order as the oxygen content, the concentrations of both components will decrease during degassing and hence the carbon content cannot be assumed to remain constant. The equilibrium degassing relationships become more complex under these circumstances.

The foregoing equations, describing an equilibrium process, define the minimum volume of flushing gas required for a given degree of degassing. In actual practice, the exiting bubble does not reach equilibrium with the melt, and a larger volume of flushing gas is required than predicted by equilibrium calculations. Geller,<sup>23</sup> in his original work on this subject, corrected the equilibrium calculations with an empirical efficiency factor. An alternative approach is to consider the mechanism by which dissolved gas is transferred to the rising gas bubbles.

**Boundary Layer Model.** The transfer of dissolved gas from the liquid melt to the inert flush bubble is controlled by diffusion of the dissolved species through a boundary layer surrounding the bubble. Since the diffusion coefficient is finite and the residence times for bubbles are relatively small, it is quite conceivable that the exiting bubble would not have sufficient time to reach equilibrium. If it is assumed that the melt remains homogeneous throughout the flush process, and that the concentration of dissolved gas in the flush bubble leaving the melt is quite small, i.e., that the concentration gradient through the boundary layer film surrounding the bubble is essentially given by the concentration of the bulk metal divided by the boundary layer thickness, a mass transfer model may be derived. It should be noted that this selection of the concentration gradient through the boundary layer film assumes that the concentration in the boundary layer at the bubble surface is zero. Under these conditions, a linear concentration gradient, approximated as

<sup>23</sup> W. Geller, *Z. Metallkunde* **35**, 213 (1943).

$\Delta C/\Delta x$ , is equal to  $(C - O)/\delta$ . The kinetics of inert flush degassing are described by the relation,

$$-\frac{dC}{dt} = \left[ \frac{DA_B}{\delta V_M} \right] F t_R C, \quad (5-78)$$

where

- $D$  = diffusion coefficient of atomic species of the gas in the metal,
- $A_B$  = average surface area of a gas bubble,
- $\delta$  = boundary layer thickness,
- $V_M$  = volume of liquid metal phase,
- $F$  = flow rate of flush gas,
- $t_R$  = residence time of average gas bubble,
- $C$  = instantaneous concentration of dissolved gas in metal.

The expression integrates to the form,

$$\log \left[ \frac{C_0}{C} \right] = k't, \quad (5-79)$$

where  $k'$  is a constant which may be evaluated from the factors given on the right side of Eq. (5-78). In general, one can estimate a diffusion coefficient and a boundary layer thickness and determine the remaining quantities from the geometry of the degassing equipment. It should be noted that  $t_R$ , the residence time, is a constant which represents the time required for a gas bubble to leave the source which is injecting the flush gas and rise to the surface of the melt.

The boundary layer model, which expresses the concentration of dissolved gas in the melt in the general form of Eq. (5-79), is in excellent agreement with experimental results as shown in Fig. 5-20.

**Calculation of Residence Time.** The residence time may be computed by assuming that the bubble is a sphere and then writing a force balance about the bubble. The forces on the bubble are the buoyant force, its weight, and the friction force caused by viscous drag. Thus,

$$F = ma = wg - mg - F_d, \quad (5-80)$$

where

- $g$  = acceleration due to gravity,
- $w$  = mass of fluid displaced by the bubble, i.e., having the same volume,
- $m$  = mass of the bubble.

Hence,

- $wg$  = buoyant force on the bubble,
- $mg$  = gravitational force,
- $F_d$  = resisting force caused by friction effects in the viscous fluid.

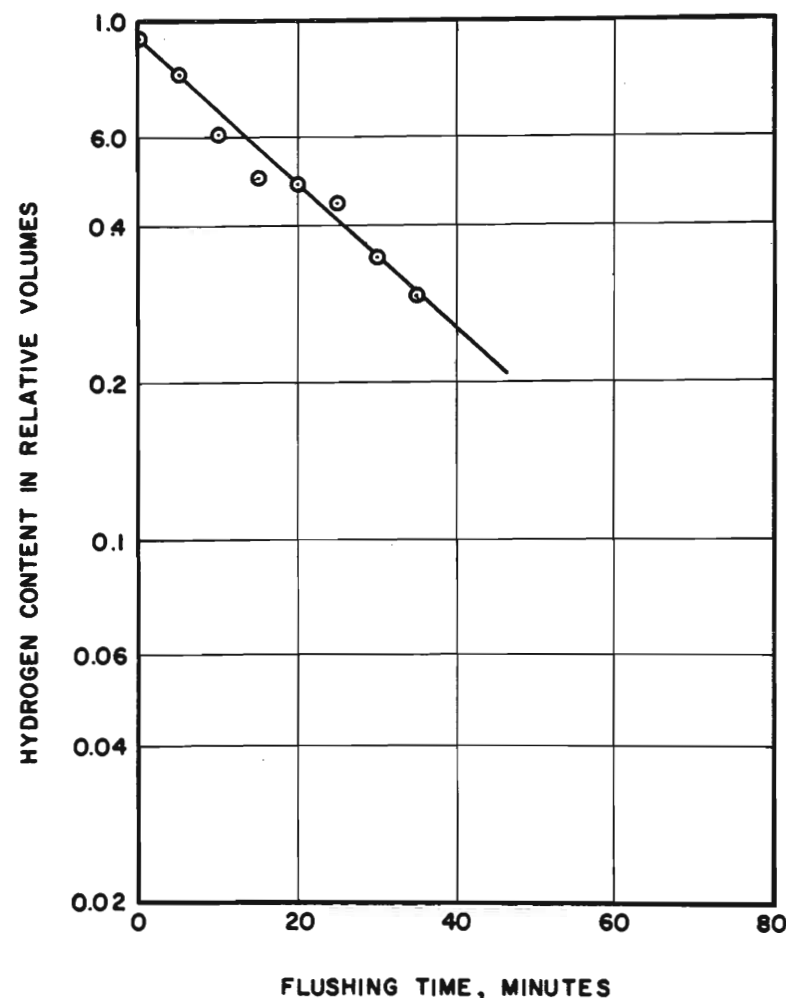


Fig. 5-20. Hydrogen Content Versus Flushing Time with Argon

Based on *Electric Furnace Steel Proceedings*, C. E. Sims, "Flushing Molten Steel With Neutral Gases," 1949, Vol 7, p. 311.

Combining the first two terms of Eq. (5-80),

$$\frac{dv}{dt} = \left[ \frac{\rho_L - \rho_B}{\rho_B} \right] g - \left[ \frac{3f_D \rho_L v^2}{4d\rho_B} \right], \quad (5-81)$$

where

$d$  = diameter of bubble,  
 $\rho_B$  = density of bubble,  
 $v$  = velocity of bubble in vertical direction,  
 $\rho_L$  = density of liquid metal,  
 $f_D$  = drag coefficient, which is given as a function of Reynolds number in Table 5-3.

If a bubble is assumed to reach its terminal velocity instantaneously and to rise with no rapid changes in acceleration, the velocity at any point is given as

$$v = -\frac{dh}{dt} = \frac{4(\rho_L - \rho_B)gd}{3\rho_L f_D}, \quad (5-82)$$

where  $h$  is instantaneous depth in the melt. Rearranging Eq. (5-82), the residence time,  $t_R$ , is given by the integral,

$$t_R = \int_H^0 \frac{-dh}{4(\rho_L - \rho_B)gd/3\rho_L f_d}, \quad (5-83)$$

where  $H$  is the depth at which the flush gas is discharged.

Equation (5-83) may be evaluated in either of two ways. First, an average value can be taken for the density of the gas in the bubbles as they are released,

TABLE 5-3

Drag Coefficient as a Function of Reynolds Number for Air Bubbles  
Rising at Their Terminal Velocity (Average of Various Liquids)

| $f_d$  | $R_e$                 |
|--------|-----------------------|
| $10^7$ | $2 \times 10^{-6}$    |
| $10^6$ | $2 \times 10^{-5}$    |
| $10^5$ | $1.8 \times 10^{-4}$  |
| $10^4$ | $1.75 \times 10^{-3}$ |
| $10^3$ | $2 \times 10^{-2}$    |
| $10^2$ | $1.8 \times 10^{-1}$  |
| 10     | 2.0                   |
| 1      | 35                    |
| 0.2    | 200                   |
| 0.18   | 300                   |
| 0.2    | 350                   |
| 0.3    | 400                   |
| 0.9    | 900                   |
| 2.5    | 2000                  |
| 2.5    | 10,000                |

Source: W. L. Haberman and R. K. Morton, *An Experimental Investigation of the Drag and Shape of Air Bubbles Rising in Various Liquids*, Report No. 802, Naval Ship Research and Development Center, September 1953, p. 25.

and an average value estimated for the bubble diameter based on the size of the discharge orifices and the flow rate. Then the average velocity of the bubbles upward through the melt can be computed using a trial and error solution involving the drag coefficient and the Reynolds number. Alternatively, a more rigorous approach may be taken. The density of the gas can be expressed as a function of atmospheric pressure and depth in the melt, and perhaps temperature as well, since the bubble is heated during its passage through the liquid metal. The diameter of the bubble can be expressed in terms of the density and mass of gaseous material in the bubble. These expressions may be substituted in the integral of Eq. (5-83), which then can be evaluated graphically. Instead, using the expressions for bubble diameter and density, the velocity may be determined at several depths in the melt using Eq. (5-82). The average of these velocities would give a reasonable value for the velocity up through the melt, at least a more reliable value than one calculated using the first procedure outlined. In the event that the velocity remains essentially constant, the assumption of negligible acceleration is valid, and the residence time is given by the expression

$$t_R = \frac{H}{v}. \quad (5-84)$$

In analyzing the removal of a dissolved gas by inert flushing on a small scale, e.g., the degassing of aluminum in small ladles prior to casting, one must also consider losses of hydrogen from the surface. Two paths exist for removal of hydrogen: (1) the diffusion through the surface to the atmosphere above, and (2) the diffusion into the inert flush bubbles. This problem has been considered in detail and an analysis has been presented in the literature for this particular case.<sup>24</sup>

#### Vacuum Degassing

An operation that is capable of producing liquid metals containing extremely low concentrations of dissolved gases is that of vacuum degassing. In this process, the liquid metal is held in a closed container under extremely low pressures. The mechanism by which the dissolved gases are removed is essentially the same as that previously described, namely, diffusion through a boundary layer at the surface and evaporation from that surface into the vapor space above. Since the partial pressure of dissolved gases above the surface of the melt is extremely low in the vacuum and remains so throughout the operation, the process is a very effective way of removing dissolved gases.

Assuming the rate-controlling step to be diffusion of atomic species of the gaseous component through a boundary layer in the metal, the kinetics of vacuum degassing processes may be described by the equation,

$$\frac{dC}{dt} = -\frac{DA}{\delta V} C, \quad (5-85)$$

<sup>24</sup> R. D. Pehlke and A. L. Bement, Jr., *Trans. AIME* 214, 1237-1242 (1962).

where

$A$  = area of the gas-metal interface (generally taken as the cross-sectional area of the container)

$V$  = volume of melt

$C$  = concentration of dissolved gas.

Since the concentration at the gas-metal interface is assumed to be in equilibrium with the gas phase, in this case a vacuum, the concentration gradient is given by the ratio  $C/\delta$ . If the process is carried out at reduced pressures rather than under vacuum, the gradient is given by  $(C - C_e)/\delta$ , where  $C_e$  is the concentration of dissolved gas in equilibrium with its reduced partial pressure in the process atmosphere (Fig. 5-21).

Eq. (5-85) can be integrated to

$$\log \left( \frac{C_0}{C} \right) = \frac{DA}{2.3 \delta V} t. \quad (5-86)$$

It should be noted that according to this model, as long as the reaction taking place at the surface of the melt is much more rapid than the rate of diffusion through the liquid boundary layer, the degassing rate is independent of the molecular form of the gas species formed in the vapor space above the melt.

Figure 5-22 shows the concentration of hydrogen in a melt of steel as a function of time under vacuum.<sup>25</sup> The slope of the curve,  $k'$ , i.e., the reaction rate constant for degassing, is given by the coefficient of Eq. (5-86).

$$k' = \frac{DA}{2.3 \delta V}. \quad (5-87)$$

Assuming that  $D$  equals  $6 \times 10^{-3} \text{ cm}^2/\text{min}$ ,  $\delta$  equals 0.003 cm, and noting that  $V/A$  was approximately 50 cm, the predicted rate constant is

$$k' = \frac{6 \times 10^{-3}}{(2.3)(0.003)(50)} = 0.017 \text{ min}^{-1}, \quad (5-88)$$

which is in approximate agreement with the average slope of the curve in Fig. 5-22, about 0.02  $\text{min}^{-1}$ .

The desulfurization of a liquid 80% Ni-20% Co alloy under a vacuum of  $10^{-5}$  atm is shown as a function of time in Fig. 5-23. The mechanism of desulfurization in this case was shown to be by evolution of  $\text{SO}_2$  gas. However, the rate limiting step in the presence of dissolved oxygen was shown to be diffusion of sulfur. In the case under consideration, the melt was 10 cm deep, and if a diffusion coefficient for sulfur of  $3 \times 10^{-5} \text{ cm}^2/\text{sec}$  and a boundary layer thickness of 0.003 cm are selected, the estimated rate constant is

$$k' = \frac{3 \times 10^{-5}}{(2.3)(0.003)(10)} = 4.3 \times 10^{-4} \text{ sec}^{-1}. \quad (5-89)$$

<sup>25</sup> A. M. Aksoy, *Thermodynamics and kinetics in vacuum induction melting*, Vacuum Metallurgy (R. S. Bunshah, Ed.), Reinhold Publishing Corp., New York, 1958.

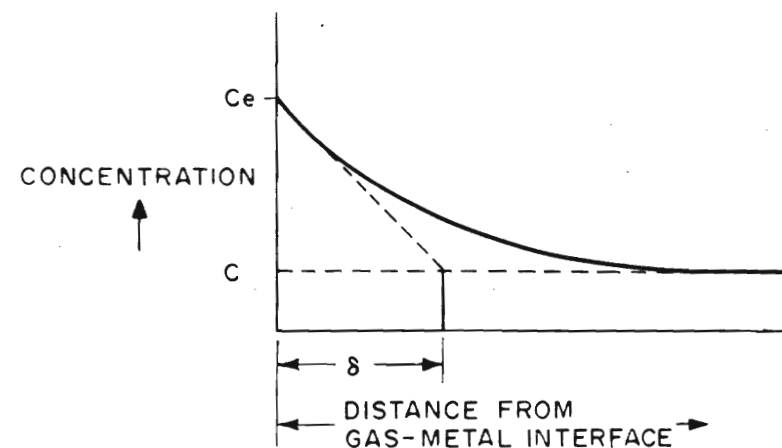


Fig. 5-21. Diagrammatic Representation of Static Boundary Layer Model

An average observed value of  $2.1 \times 10^{-4} \text{ sec}^{-1}$  is in reasonable agreement with the predicted result.

These examples serve to illustrate the general validity of the assumption that diffusion is the rate controlling step in the kinetics of vacuum degassing processes at high temperatures. However, under some circumstances, the rate limiting step may be the reaction at the metal surface, and other kinetic models must be used.

An alternative model can be developed for the case of the surface degassing of a liquid metal where diffusion is rate controlling and the presence of a boundary layer is unlikely because of the marked difference in viscosity of the two fluids, gas, and metal. Here the surface degassing can be described in terms of semiinfinite diffusion into a continuously renewed surface layer.<sup>26,27</sup> The melt is assumed to be made up of rigid quanta of fluid that appear on the surface, absorb or desorb gas, and then are stirred into the melt. This concept is particularly applicable where induction stirring is present, but also can be applied to cases where the rate of surface renewal can be specified.

The rate of degassing of a melt under these conditions can be described using relationships which assume that the liquid metal is moving without shear gradients, i.e., as a "rigid body" at the gas-metal interface. The rigid body motion, referred to as streamline flow, is assumed to be maintained until the melt adjacent to the gas-metal surface is no longer in contact with the gas phase. The streamline flow layer is assumed to be free of convective currents and to be of sufficient thickness such that the mathematical assumption of diffusion into a semiinfinite medium is valid for the absorption of atoms into the streamline flow layer. Under these condi-

<sup>26</sup> P. V. Danckwerts, *Ind. Eng. Chem.* **43**, 1460 (1951).

<sup>27</sup> E. S. Machlin, *Trans. AIME* **218**, 314 (1960).

tions, transport into the metal is normal to the direction of flow as illustrated in Fig. 5-24. After the surface element has been in contact with the atmosphere, as shown in Fig. 5-24 for position *A*, the surface concentration is  $C_s$ , the concentration in equilibrium with the gas phase, and a sharp concentration gradient exists to  $C$ , the concentration of the bulk phase. This gradient extends down into the streamline flow layer but does not extend below this volume, which is treated as a rigid body. At a later time, the volume element has reached position *B*, shown in Fig. 5-24. The concentration gradient is less steep and goes further into the element, but still extends from  $C_s$  at the surface down to  $C$ , the bulk concentration of the

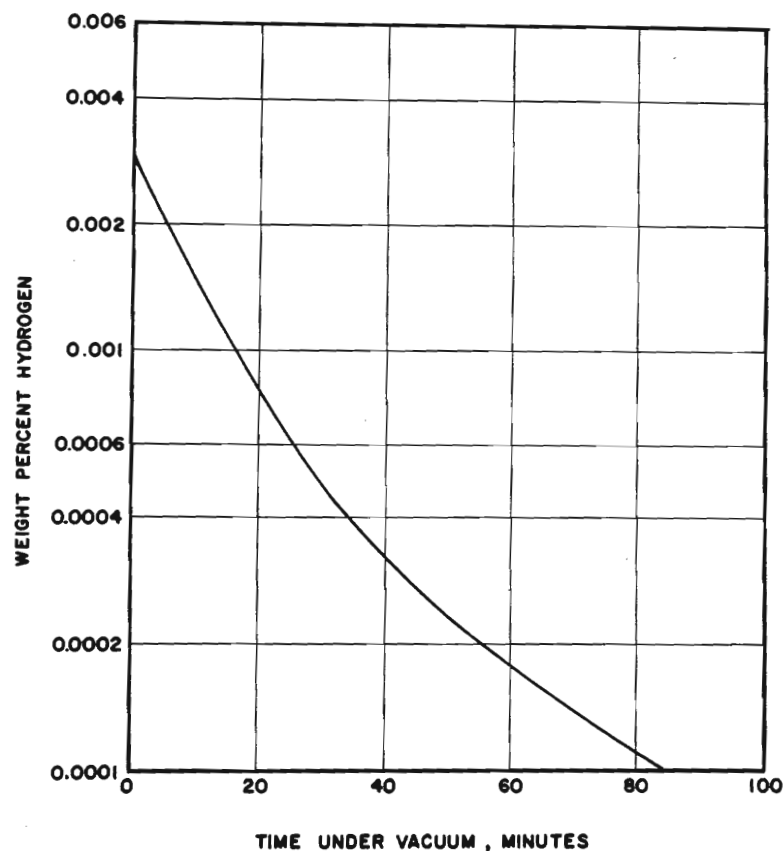


Fig. 5-22. Vacuum Degassing of Liquid Iron in Magnesia Crucible

Based on R. F. Bunshah, *Vacuum Metallurgy*, Reinhold Book Corporation, a subsidiary of Chapman-Reinhold, Inc., New York, 1958, p. 68.

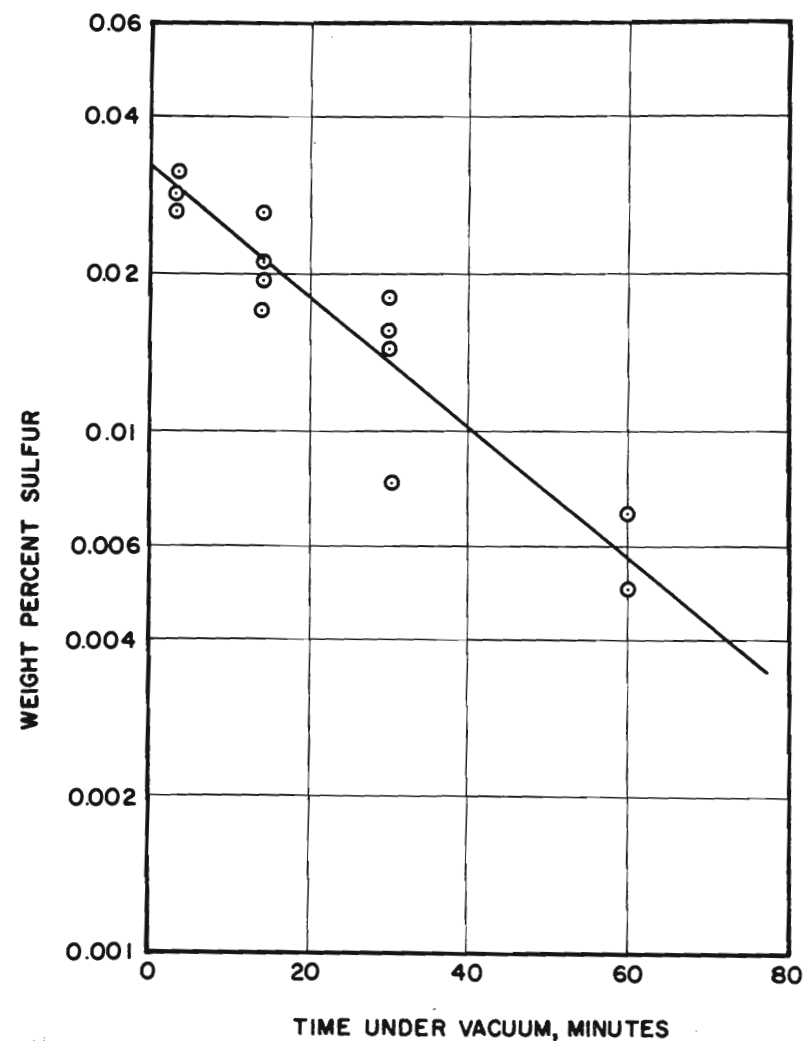


Fig. 5-23. Desulfurization of an 80% Ni-20% Co Alloy at 1520°C by Vacuum Treatment

Based on "Kinetics of Vacuum Induction Refining-Theory," E. S. Machlin, *Trans. Met. Soc. AIME*, 1960, Vol. 218, p. 315.

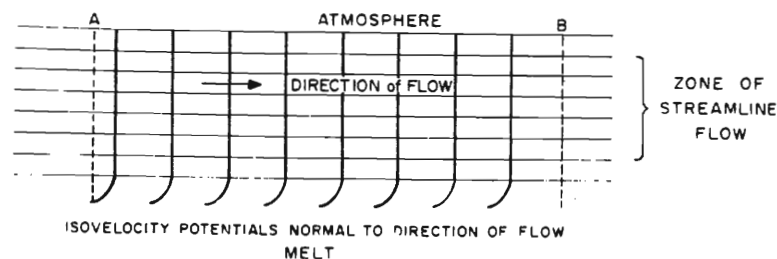


Fig. 5-24. Diagrammatic Representation of Streamline Flow Model

Based on "Kinetics of Vacuum Induction Refining-Theory," E. S. Machlin, *Trans. Met. Soc. AIME*, 1960, Vol. 218, p. 315.

melt at the time the surface element was created. Under these boundary conditions, the equation for diffusion into a semiinfinite medium, as derived by Darken,<sup>28</sup> may be applied:

$$\frac{dM}{dA} = 1.1284 (C_e - C) (Dt')^{1/2}, \quad (5-90)$$

where

$\frac{dM}{dA}$  = change in solute per unit area of gas-metal surface,

$C_e$  = concentration of solute in the metal in equilibrium with the gas phase (expressed in consistent units, e.g., cubic centimeters at STP per cubic centimeter of liquid metal),

$C$  = concentration of solute in the bulk phase of metal at any time,  $t$ , in the same units as  $C_e$ .

<sup>28</sup> L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, p. 445, McGraw-Hill, New York, 1952.

$D$  = diffusion coefficient of solute in the liquid metal,

$t'$  = time interval during which the solute is transferred from the surface element.

Converting variables

$$\frac{dc}{dt} = \frac{dM}{dA} \times \frac{dA}{dt} \times \frac{1}{V}, \quad (5-91)$$

where

$\frac{dc}{dt}$  = rate of change of solute concentration in liquid metal,

$\frac{dA}{dt}$  = rate of creation of gas-metal interface,

$V$  = volume of melt.

Considering the case where inductive stirring exists and the flow of metal is upward at the center and out toward the walls, the life of the element,  $t'$ , may be expressed as  $x/v$ , the ratio of the distance traveled (approximately one-half the crucible radius) to the flow velocity. For cylindrical geometry, the volume of the melt is equal to  $\pi r^2 h$ , where  $r$  is the radius of the melt and  $h$  is the depth. The rate of creation of surface  $dA/dt$  is also the rate of disappearance of melt surface, which may be expressed by the relation,

$$\frac{dA}{dt} = 2\pi r v \quad (5-92)$$

If Eqs. (5-90), (5-91), and (5-92) are combined

$$\frac{dC}{dt} = \left[ \frac{2.56 D v}{r h^2} \right]^{1/2} (C_e - C), \quad (5-93)$$

which integrates to

$$\log \left[ \frac{C_e - C_0}{C_e - C} \right] = \frac{1}{2.3} \left[ \frac{2.56 D v}{r h^2} \right]^{1/2} (t - t_0). \quad (5-94)$$

Equation (5-94) thus takes a form similar to that derived for the boundary layer diffusion model, excepting that the adjusting parameter,  $\delta$ , is absent. However, there is an uncertainty as to the true velocity of streamline flow. If the surface elements are to move as rigid bodies, the velocity of streamline flow must be smaller at the periphery of the melt than near the center, where the surface is being generated. Furthermore, the distance the element travels has been approximated by one-half the radius, which must be considered only as a reasonable guess. Thus the adjustable parameter of the boundary layer model has been replaced with other parameters which are not well defined. It should be noted, however, that the streamline flow model more closely describes the physical system which exists in the process of degassing an inductively stirred melt.

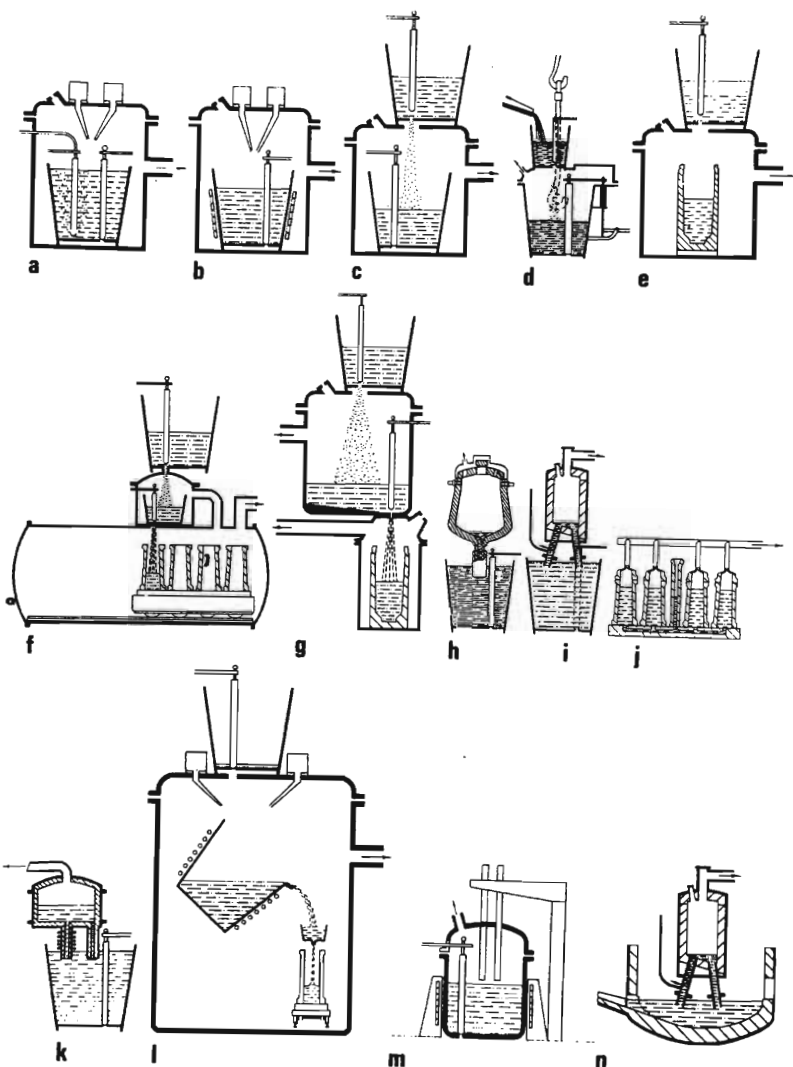


Fig. 5-25. Methods of Degassing—*a* purging gas; *b* induction stirring; *c* ladle to ladle; *d* tap degassing; *e* ladle to mold; *f* ladle to multiple mold; *g* two-stage treatment; *h* vacuum lift; *i* circulation by gas lift; *j* ingot degassing; *k* circulation by induction; *l* combination process; *m* arc heating; *n* treatment in the furnace.

Source: "Vacuum Degassing 1955-1965 . . .", J. H. Flux, *J. Iron and Steel Inst.*, 1965, Vol. 203, p. 1196.

Application of Eq. (5-94) to one of the preceding examples, the desulfurization of a nickel-cobalt alloy, is appropriate since the stirring conditions and melt geometry were reasonably well defined.<sup>29</sup> In that experiment, the desulfurization was carried out in a 6.4 cm dia crucible with a melt height of 10 cm, and under inductive stirring conditions where the velocity on the surface was between 1 and 10 cm/sec. A range for the rate coefficient may be defined using Eq. (5-94).

Since

$$k' = \frac{1}{2.3} \left[ \frac{2.56 Dv}{rh^2} \right]^{1/2}$$

then it follows that

$$\frac{1}{2.3} \left[ \frac{(2.56)(3 \times 10^{-5})(1)}{(3.2)(10)^2} \right]^{1/2} < k' < \frac{1}{2.3} \left[ \frac{(2.56)(3 \times 10^{-5})(10)}{(3.2)(10)^2} \right]^{1/2}$$

$$2.1 \times 10^{-4} < k' < 6.7 \times 10^{-4} \text{ sec}^{-1}. \quad (5-95)$$

This result compares favorably with the observed value of  $2.4 \times 10^{-4} \text{ sec}^{-1}$  (Fig. 5-24).

#### Other Degassing Processes

Several other degassing processes have been proposed which utilize vacuum, or a combination of vacuum and inert flushing to produce a larger gas-metal surface area and, consequently, an increased rate of degassing. Several of these processes are shown in Fig. 5-25. An increased degassing rate is particularly important in the treating of liquid metals, since the metal temperature decreases during the operation thus limiting the time available for processing.

The Dortmund-Hörder degassing process<sup>30,31</sup> is used to remove dissolved gases and control the extent of the carbon-oxygen reaction in liquid steel. The process utilizes a vacuum chamber into which low carbon steel is drawn up by vacuum from a ladle and then released to flow by gravity back to the ladle. Only a small fraction of the liquid metal in the ladle can be drawn up into the vacuum chamber, and to obtain extensive degassing, several cycles of the process are required. A schematic description of the process is shown in Fig. 5-26 and also in Fig. 5-25-h.

The question facing the process designer who is considering use of the Dortmund-Hörder process is, "How many cycles of the degassing operation may be required to lower the gas content of the metal in the ladle to a desired level?" In the face of deficient thermodynamic and kinetic data, the assumption that a given reaction goes to completion within the allotted process time often is used as a basis for design purposes. This approach to the Dortmund-Hörder process results in the assumption that the metal drawn up into the vacuum chamber is completely degassed, and, upon being returned to the ladle, is completely mixed with the ladle material. For this case, the material balance for the degassing operation is given

<sup>29</sup> E. S. Machlin, *Trans. AIME* **218**, 314 (1960).

<sup>30</sup> F. Harders, H. Knuppel, and K. Brotzmann, *J. Metals* **12**, 398 (1960).

<sup>31</sup> P. J. Wooding and W. Sieckman, *Metal Progress* **77**, 1-116 (1960).

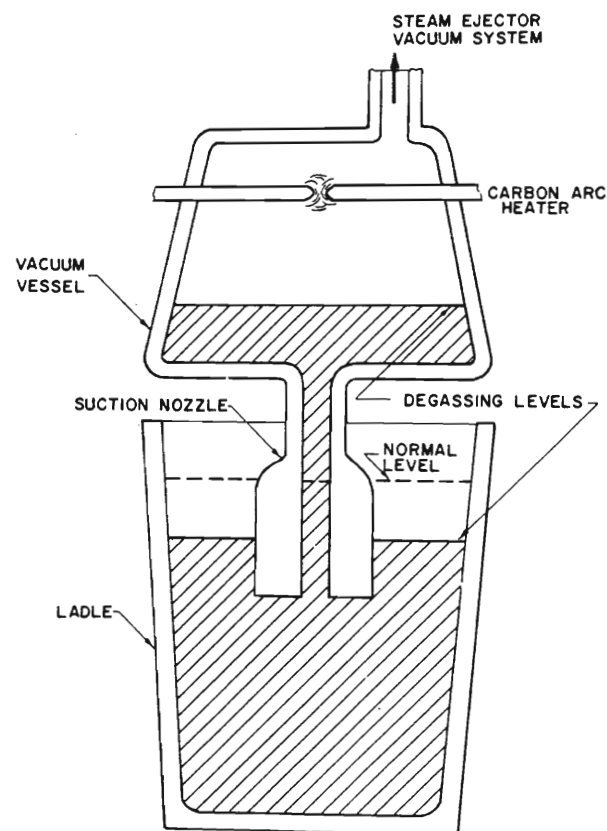


Fig. 5-26. Schematic View of Dortmund-Hörder Hüttenunion Vacuum Treating Process

by the relation,

$$C = C_0(1 - X)^n, \quad (5-96)$$

where

- $n$  = number of cycles,
- $C$  = concentration of gas in the metal in the ladle after the  $n$ th cycle,
- $C_0$  = initial gas concentration in the metal,
- $X$  = fraction of ladle material which is drawn into the vacuum chamber during each cycle.

The results of actual data taken from the operation of the process are compared with Eq. (5-96) in Fig. 5-27. The agreement between the two curves shows the assumption to be quite reasonable.

A process has been developed in Germany called the Ruhrstahl-Heraeus Continuous Vacuum Process. This process, shown in Fig. 5-25-i, is used in ladle degassing. The ladle of molten steel is placed in a pit, and the vacuum apparatus positioned above it by an overhead crane. Tubes are lowered into the melt while the vacuum chamber is being pumped out by a multiple stage pumping system. Argon is introduced into one of the tubes, and causes the liquid steel to move up in this tube. The metal then splashes into the vacuum chamber where it is degassed. The time required to degas 100 tons of liquid steel is 15–20 min, and the temperature drop during this period is only about 30°C. If necessary, it is possible to heat the liquid steel by auxiliary equipment during the vacuum treatment.<sup>32,33</sup>

Several other vacuum degassing techniques include vacuum degassing in the

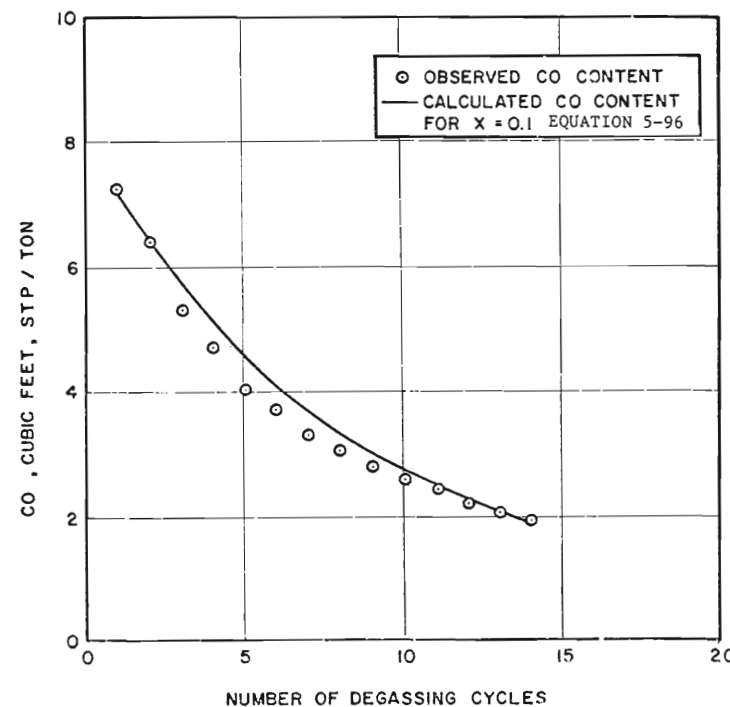


Fig. 5-27. Removal of CO from Liquid Steel by DHHU Vacuum Treating Process

Based on P. J. Wooding and W. Sieckman, *Metal Progress*, 77, (1960), p. 121.

<sup>32</sup> H. W. Balster, *Elect. Furnace Steel Proc. AIME* 16, 192 (1958).

<sup>33</sup> F. W. Starratt, *J. Metals* 10, 465 (1958).

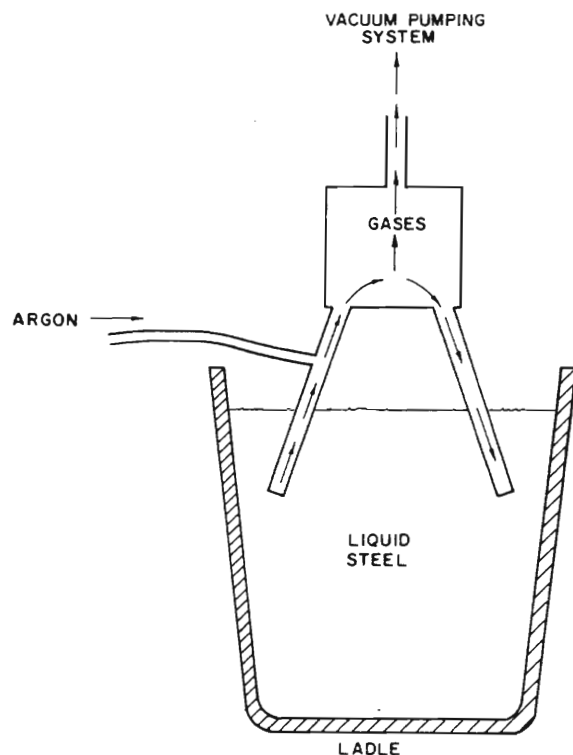


Fig. 5-28. Schematic Diagram of Vacuum-Flow Steel Degassing Process

ladle, a process devised by A. Finkl and Sons Co., Chicago.<sup>34</sup> This vacuum degassing technique is shown in Fig. 5-28. Vacuum stream degassing is another method of bringing more of the surface of the melt in contact with the vacuum. In this process a bottom-pouring ladle of steel is placed over a vacuum chamber and the liquid metal is permitted to flow into the vacuum chamber. The reduced pressure causes the gases to diffuse from the metal, which is received in another ladle below, from which in turn it can be poured into an ingot mold. The thin stream of molten metal flowing into the evacuated chamber allows an excellent chance for the vacuum to degas the melt quickly and efficiently. Results by this method have been as low as two parts per million residual hydrogen.<sup>35</sup>

Another effective method of controlling dissolved gases (particularly for oxygen

<sup>34</sup> C. W. Finkl, *Metal Progress* 76, 111 (1959).

<sup>35</sup> A. Tix, *Elect. Furnace Steel Proc. AIME* 13, p. 70 (1955).

and nitrogen) is that of adding a scavenging element, such as titanium or zirconium. These elements form stable nitrides or oxides which are insoluble in liquid metals. The principles involved here are the same as those outlined in previous sections of this chapter. Inert flush degassing may also be accomplished by placing a volatile solid in the liquid melt, which then forms purging gases that are evolved in the bulk of the metal.

The effectiveness of the methods outlined here and continued development effort in perfecting degassing techniques will result in a rapid increase in the use of degassing processes as a refining operation in the metallurgical industries.

#### Temperature Drop of the Melt During Degassing

The temperature drop of a melt during degassing may be estimated from a consideration of the radiative and convective heat losses from the metal surface during the degassing operation. Absorption of heat into the refractory lining of the ladle or other degassing equipment also can represent a significant heat loss, although preheating of the refractories can diminish this latter source. The heat effect caused by the removal of the dissolved gas from solution (and in the case of inert flush degassing, the sensible heat lost to the flush gases) is negligible compared with the principal source of heat loss, direct radiation from exposed metal surfaces. This is true especially for steels. The loss of heat by direct radiation is enhanced further by the agitation and stirring occasioned by gas evolution. Indeed, the bubbling of argon through liquid steel in the ladle often is used to cool heats prior to tapping. The agitation and breaking of the insulating slag cover results in direct radiation from the metal surface, which can reduce the temperature by 10–15°F within 1 min or less. A balance between the various sources of heat loss and any energy input such as by induction or arc heating (see Fig. 5-25-b, -h, -m) permits an evaluation to be made of the time available for degassing, or the required superheat of the metal.

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### Discussion Questions

1. Silico-manganese, an alloy containing silicon and manganese, is made in several grades including a 3% carbon, 15% silicon, 65% manganese, balance iron grade. What are the advantages and disadvantages of using this material versus either aluminum or silicon as a deoxidizer?
2. Briefly describe economically and technically feasible liquid phase techniques for:
  - (a) removing cadmium from lead at cadmium concentrations below 1 wt%,
  - (b) removing bismuth from lead,
  - (c) removing oxygen from steel,
  - (d) removing hydrogen from aluminum.
3. A secondary metals company has purchased large quantities of scrap bearings at a very low cost. The bearings consist of cylinders of an alloy (80% Cu, 10% Pb, 10% Zn) mounted in steel sleeves. Outline an integrated process for recovering the various metals.
4. Discuss the potential success and feasibility of processes for external desulfurization of iron blast furnace hot metal using magnesium, calcium carbide, or lime.
5. The impurities in gold bullion are sometimes removed by bubbling chlorine gas through the impure liquid gold. What information is required to thermodynamically describe this process?
6. Although thermodynamics shows distillation processes to be very favorable for refining in many metallurgical systems, they are not often used. Why?
7. Present a more general statement of Sieverts' Law which is modified to include the solution behavior of compound gases such as  $\text{CO}_2$  or  $\text{SO}_2$ .

### Problems

1. Compute the minimum theoretical weight of ferro-silicon (75% Si) required to deoxidize 150 tons of basic oxygen blown steel with a turndown carbon content of 0.05 and temperature of 2900°F to an oxygen content of 0.01 wt%. Make the same calculation for pure vanadium and chromium.
2. In a recent experiment, liquid pure iron was held in a silica crucible at 1600°C under an argon atmosphere. After several hours, the melt was quenched in an argon blast. Chemical analysis revealed that the metal was of the following composition:

|         |            |
|---------|------------|
| Silicon | 0.0120 wt% |
| Oxygen  | 0.0550 wt% |
| Iron    | Remainder  |

- (a) Is this experimental result in agreement with tabulated data?
  - (b) Is silicon a suitable deoxidizer for steels and how does it compare with aluminum?
3. Calculate the equilibrium activity of nickel oxide in a slag in contact with a liquid iron alloy containing 4 wt% nickel and 0.05 wt% oxygen at 1600°C. Specify the reference state for nickel oxide.

4. Can a low carbon steel be desulfurized to concentrations of 0.01% S or below by treatment with magnesium at 1600°C?
5. Chemical analyses for silicon in low carbon steels (below 0.10% C) produced in the BOF are usually reported as "nil." Explain.
6. The following quotation appears in *Trudy Leningradskogo Politekhn. Instituta*, Im. M. I. Kalinina No. 125, 1963, pp. 143-148:

"It has often been established that when pig iron is transferred in ladles from the blast furnace to the mixer or casting ladle, the sulfur content is reduced, the more so when the initial sulfur and manganese contents of the pig iron are high and when it is frequently shaken up during transit by rail, at switches and rail joints. This is explained by the associated acceleration of the coalescence of the manganous sulfide particles. Moreover, a reduction in the sulfur content leads to a displacement of the state of equilibrium of the reaction in favor of the formation of manganous sulfide as the pig iron cools upon removal from the furnace and during its stay in the ladles. The high melting point of manganous sulfide (1620°C-2950°F) and its low solubility in pig iron result in its separation in the form of solid particles. There is no direct experimental confirmation of such mechanism."

The article further reports that a pig iron of the composition 0.6% Si, 0.2% Mn, 4.0% C and 0.143% S showed a final composition of 0.03% S and 0.06% S after adding sufficient manganese to raise the Mn content to 2% and cooling over a period of 17 min to temperatures of 1200 and 1350°C, respectively.

Evaluate the thermodynamic feasibility of precipitation of manganese sulfide from liquid pig under these two circumstances.

7. Desulfurization of an alloy was accomplished by contacting the metal in the liquid state with a sulfur-free basic slag. The metal bath was 7.5 cm deep and the slag-metal interfacial area was 20 cm<sup>2</sup>. The sulfur concentration of the metal was observed to be:

| Time (min) | % S    |
|------------|--------|
| 0          | 0.03   |
| 10         | 0.02   |
| 20         | 0.013  |
| 30         | 0.0086 |
| 40         | 0.006  |
| 50         | 0.005  |
| 60         | 0.0045 |

- (a) Explain the concentration-time behavior.
  - (b) Assuming sulfur diffusion in the metal is rate limiting, estimate the diffusion coefficient of sulfur in the liquid alloy.
8. A steel containing 0.40 wt% carbon (AISI 1040) is held in an alumina crucible under an atmosphere of CO at a pressure of 760 mm Hg. Estimate the equilibrium aluminum content of the metal. Neglect interaction between solutes.
  9. A steel company proposes to deoxidize low carbon heats with vanadium. If the grade specification calls for oxygen below 0.01 and vanadium below 2 wt%, is this a feasible process?

10. Phosphorous often is used to deoxidize liquid copper. The solubility product for this reaction at 1200°C is

$$\log [(\%P)(\%O)^{2.5}] = -11.07.$$

What concentration of phosphorous will limit the oxygen concentration to 0.0005% at 1200°C? What will be the volume percent of phosphorus rich phase in the solidified copper (if any)?

11. Starting with a value of 62,360 mm Hg-cm<sup>3</sup>/°K g-mole for  $R$ , the gas constant, make a conversion of units to develop the value of  $R$  used in Eq. 5-44.
12. What fraction of a 3 wt% Mn steel would have to be evaporated at 1600°C under equilibrium conditions to reduce the manganese concentration to 0.5 wt%.
13. In the vacuum dezincing of lead bullion at 600°C, estimate the maximum evaporation rates for bullion containing 0.5 and 0.05% zinc.
14. Estimate the lead contamination of the zinc condensate for a lead bullion being vacuum treated at zinc concentrations of 0.5 and 0.05 wt%.
15. Calculate the thermal requirement (exclusive of heat losses) to remove 0.5 wt% zinc from lead bullion by distillation. The lead bath is at 600°C and the zinc is condensed to a solid at 200°C.
16. Calculate the relative volatility at 700°C for a lead alloy dilute in cadmium.
17. The solubility of N<sub>2</sub> in liquid Fe has been reported as 0.0447 wt% at 1535°C and 1 atm pressure of nitrogen, and 0.0368 wt% at 1760°C and 0.639 atm of nitrogen pressure. Express this information as a  $\Delta G^0$  equation.
18. The solubility of nitrogen at 1 atm pressure in liquid pure iron at 1600°C is 36 CC (STP)/100 g Fe. The total dissolved gas (H<sub>2</sub> + N<sub>2</sub>) under a 20% H<sub>2</sub>-80% N<sub>2</sub> mixture at 1 atm total pressure in 100 g of pure liquid iron at 1600°C is 45 CC (STP). Compute the total amount of dissolved gas CC(STP) in 100 g of the following alloy at 1600°C under a gas mixture of 5% H<sub>2</sub>-1% N<sub>2</sub>-94% Ar at 1 atm total pressure.

| Element | Wt%     |
|---------|---------|
| Cb      | 2       |
| Co      | 3       |
| Ni      | 4       |
| Si      | 2       |
| Fe      | Balance |

19. Steel, tapped from a steelmaking furnace at 2920°F, contains 0.003% nitrogen. Will the steel tend to pick up or lose nitrogen from the atmosphere?
20. The solubility product (%C × %O) is approximately 0.0022 at 2850°F for medium and low carbon steels. Calculate the equilibrium oxygen content in a steel at 2850°F having the following carbon content:
- (a) 0.60% C
- (b) 0.40% C

- (c) 0.10% C
- (d) 0.06% C
- (e) 0.02% C

In actual steelmaking practices, a heat entering the ladle often may have either more or less oxygen than the solubility product would indicate. List a number of conditions which can lead to this.

21. Calculate the partial pressure of SO<sub>2</sub> over a bath of low carbon steel containing 0.05% S and 0.10% O at 1600°C. Comment on the feasibility of removing S by vacuum treatment.
22. What is the total volume of dissolved gas in 100 lb of liquid iron containing 4% silicon in equilibrium with a gas at 1 atm pressure consisting of 50% H<sub>2</sub> and 50% N<sub>2</sub>?
23. Calculate the interaction parameter,  $e_H^{Si}$ , based on the measurement: 20.4 cc H<sub>2</sub> (STP)/100 gm in a 3% Si-Co alloy at 1600°C and 1 atm H<sub>2</sub> pressure.
24. Calculate the degassing time required to remove 95% of the dissolved hydrogen from liquid copper held in a zirconia crucible at 1420°C. The pressure of the system is maintained at 1 mm Hg. The Sieverts Law constant for hydrogen in copper at 1420°C is 1.097 cc/100 g-(atm)<sup>1/2</sup>.

Operating Conditions:

weight of copper = 50 lb

$D_H$  in liquid copper at 1420°C =  $10^{-3}$  cm<sup>2</sup>/sec

$\delta$  = 0.003 cm

crucible diameter = 6 in.

$\rho$ , density of liquid copper = 7.68 gm/cc

initial hydrogen content = 0.8 cc/100 gm

25. An induction melting unit is stationed in a vacuum chamber. Five hundred pounds of cobalt alloy is melted and held under vacuum at 1600°C. The chamber then is pressurized to 800 mm Hg with hydrogen gas. The melt is maintained at 1600°C under the hydrogen atmosphere for 5 min. Then the chamber is pumped out and maintained at 5 mm Hg for 3 min. The alloy is immediately cast into a water-cooled copper mold. Estimate the final hydrogen content of the alloy given:

alloy = 10% Mo, 10% Ta, balance Co

$\rho_{\text{alloy}}$  at 1600°C = 10 gm/cm<sup>3</sup>

I.D. of crucible = 30 cm

$D_H$  in liquid cobalt =  $2 \times 10^{-3}$  cm<sup>2</sup>/sec

$\delta$  = 0.003 cm

26. A dilute liquid iron alloy is melted in a vacuum induction furnace. The alloy contains 5 ppm (by weight) of hydrogen. Estimate the degassing time required to reach 0.5 ppm of hydrogen given:

$D_H$  =  $2.5 \times 10^{-4}$  cm<sup>2</sup>/sec

$\delta$  =  $10^{-3}$  cm

weight of melt = 12 kg

$\rho_{\text{melt}}$  = 7.16 gm/cc

area of bath surface = 75 cm<sup>2</sup>

pressure in vacuum chamber = 48.5  $\mu$

27. Special heats of OFHC copper are prepared by treating liquid copper with hydrogen at 1 atm in an inductively heated crucible under a reducing slag. This treatment removes dissolved oxygen. The copper is then held under a vacuum to remove the dissolved hydrogen. Estimate the time required to decrease the dissolved hydrogen content to 0.5 cc  $H_2$ /100 gm (STP).

Data:

$$D_H = 5 \times 10^{-4} \text{ cm}^2/\text{sec}$$

$$\rho_{Cu} = 7.76 \text{ gm/cc}$$

melt—10 in. diameter  $\times$  15 in. deep

metal temperature—1300°C

vacuum system—1.0 mm Hg

Assume well stirred melt with rate limiting transport being diffusion across a boundary layer 0.01 cm thick in the metal phase.

28. Evaluate the thermodynamic feasibility of the following refining processes.
- Desulfurization of steel with manganese.  
Process conditions: maximum residual sulfur—0.03 wt%  
maximum residual manganese—0.5 wt%  
temperature—1600°C
  - Distillation of aluminum from silver.  
Process conditions: temperature—1000°C where  $\gamma_{Al}^0 = 0.11$   
maximum residual aluminum—1 mol%
  - Phase separation of zinc from lead.  
Process conditions: minimum temperature—350°C  
maximum residual zinc—1 wt%
  - Vacuum degassing of copper.  
Process conditions: minimum chamber pressure—0.1 mm Hg  
maximum residual hydrogen—0.1 cc(STP)/100 g  
temperature—1400°C
29. Estimate the volume of hydrogen which would have to be blown through a low-carbon steel at 1600°C to reduce the sulfur content from 0.04 to 0.02 wt%.
- $$H_2(g) + S = H_2S(g) \quad K_{1600^\circ C} = 5 \times 10^{-3},$$
- where  $K$  can be expressed as  $(\%)^{-1}$ .
30. A 100-ton ladle of liquid steel at 1600°C contains 0.04% C and 0.05% O. Argon is bubbled through the bath at a low rate in finely dispersed bubbles such that the gas mixture leaving the melt at 1 atm pressure is in equilibrium with the bath at all times.
- How much argon (ft<sup>3</sup> STP) must be blown into the bath to reduce the carbon content to 0.01%?
  - What will the oxygen content be when the carbon content just reaches 0.01%?
31. A 100-ton heat of copper is fire-refined in a fuel-fired reverberatory furnace; the furnace atmosphere contains 20% (by volume) water vapor. At tap, the oxygen content of the copper is 0.03% and the temperature is 1227°C. The heat is tapped into a holding ladle, during which operation the temperature

falls to 1177°C and thereafter may be assumed constant. Nitrogen is bubbled through the copper to lower the hydrogen content before casting. What is the hydrogen content after 200 ft<sup>3</sup> STP of  $N_2$  have been used?

$$H_2O(g) = 2H + O \quad \log K = \frac{-10640}{T} - 3.09.$$

Activities of H and O are in weight percent based on the infinitely dilute solution. The gas mixture leaving the copper may be assumed to have reached equilibrium with respect to its dissolved constituents. Any assumptions which are made to facilitate solutions should be stated.

32. An inert flush degassing operation supplies 100 ft<sup>3</sup> (STP)/min of argon at 100°F to a 100-ton ladle of steel at 3000°F to reduce the hydrogen content from 7.5 to 4 ppm in 30 min. Estimate in °F the difference in temperature decrease of the melt caused by inert flushing as compared to vacuum degassing for the same period and hydrogen removal.

$$C_p (\text{Fe liquid}) = 10.00 \text{ Btu/\# mole-}^\circ\text{F}$$

$$C_p (A) = 4.97 \text{ Btu/\# mole-}^\circ\text{F}$$

## CHAPTER 6

### Hydrometallurgy

Hydrometallurgy is that phase of metallurgy which involves the extraction and recovery of metals using aqueous or organic solutions. The unit processes of hydrometallurgy include the leaching of ores (particularly low-grade ores) for recovery of metals, the separation of the leaching solution from the spent ore, and also the recovery of the dissolved metal from the solution. A typical example is the recovery of copper from a sulfide ore (usually a low-grade ore containing less than 1.5 wt% copper that has been partially oxidized to copper sulfate) by extraction with a solvent such as water, subsequent washing of the ore with fresh water to recover all of the copper solution, and precipitation of copper from the dilute copper sulfate solution by "cementation," i.e., displacement of the copper ions in solution by iron on the surface of iron scrap.

Hydrometallurgical extraction always involves three steps:

1. The solvent or reacting solution must come in contact with the solid to be treated in order to transfer the soluble constituent to the solvent.
2. The solution is separated from the residual solid and the solid is washed. Liquid always adheres to the solids, which must be washed to prevent either the loss of solution or contamination of the solids, depending upon which is the desired material.
3. The desired solute is recovered from the solution, or in the case where the residual solid is the desired material, a process also must be provided for recovery of the solvent. The techniques employed to treat the enriched solution include evaporation, distillation, electrolysis, ion exchange, solvent extraction using an insoluble liquid, or precipitation, the latter being one of the most common in the metallurgical industries.

Further examples of hydrometallurgical operations include the extraction of gold and silver by cyanidation and precipitation of these elements from the cyanide solution with zinc. Leaching with acid is employed to dissolve zinc oxide and copper oxide as sulfates although copper oxide also can be dissolved in alkaline solutions of ammonia. Caustic soda is used to dissolve alumina, and uranium oxide can be dissolved with acid or carbonate. The recovery of these solutes can be accomplished by several methods. Copper is recovered from acid solutions by cementation with iron or by electrolysis. Uranium and vanadium are recovered from acid or carbonate solutions by solvent extraction or ion exchange, and metallic ions can be precipitated from aqueous solutions as insoluble sulfides.

In recent years interest in hydrometallurgical operations has been intensified, largely a result of the necessity for turning to lower grade raw materials that must

be concentrated for processing. Many of the new developments involve leaching and precipitation at elevated temperatures and pressures. The advantages in operating under these conditions are greatly increased rates of reaction, favorable displacement of thermodynamic equilibria, and the possibility of using certain gaseous or highly volatile reagents such as oxygen, hydrogen, or ammonia. Among the new processes which have resulted from the application of high-temperature and high-pressure techniques are direct leaching of nickel, copper, and cobalt sulfides with ammonia; carbonate leaching of uranium ores; leaching of certain sulfide ores with water; precipitation of metallic nickel, cobalt and copper from aqueous solutions of their salts by hydrogen reduction; and precipitation of uranium and vanadium oxides from aqueous carbonate solution by hydrogen reduction. Although there is a demand for advances relating to the chemistry of some of the older hydrometallurgical processes, undoubtedly the employment of higher temperatures and pressures in conjunction with new extraction techniques will bring the greatest advances to the field.

## 6-1 Hydrometallurgical Processes

### Leaching

In preparation for leaching, the ore is usually reduced to a small size by crushing and grinding; in some cases, chemical treatment may be necessary to render the ore to its optimum state for recovery. Thus, zinc sulfide and cobalt sulfide, e.g., are insoluble in most solvents, but with an oxidizing roast they can be converted to water soluble sulfates, and roasting the ore with salt can convert the metallic material to a water-soluble chloride. The material selected for a leaching process is usually a low-grade ore, but in some instances may be concentrates, calcines (sulfide materials converted to oxides by roasting), sulfides, alloys, etc.

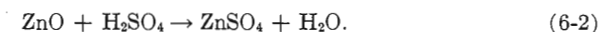
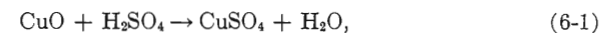
The leaching of low-grade ore is a large scale operation and requires large volumes of solvent and great quantities of ore. The solvent must be inexpensive and capable of being cheaply regenerated. If the ore is concentrated, the solvent or reactant costs are not too significant because of the high metallic yield of the ore, and more expensive reactants (such as concentrated acids) often are used. Furthermore, concentrated acid leaching of concentrates results in rapid solution rates and requires a smaller installation.

Ores are prepared to two general conditions, sands or slimes. Sands refer to ores that are coarse enough to permit circulation of the solvent through the void spaces between the ore particles. Metallics in ores of this type are recovered by percolating the leaching solution through the ore. Very fine ore products which are not suitable for a "percolating" leach are called slimes; leaching of slimes is carried out by agitating the slime and solvent together in a tank.

As mentioned earlier, sulfide ores must be roasted by heating in contact with an oxidizing gas to convert the sulfide to an oxide or a sulfate, thus transforming the metal into a soluble form. The process volatilizes certain soluble impurities and also renders the ore porous enough so the metallic compounds are readily attacked by the solvent. Roasting is a pyrometallurgical operation (see Pyrometallurgy I) and

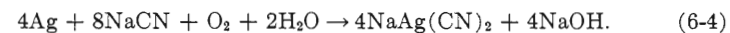
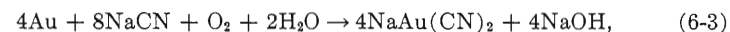
is relatively expensive; hence, roasting is limited in its application to high-grade, concentrated ore. Low-grade sulfide ores can be oxidized to oxide by natural weathering—the slow oxidation of sulfides by the action of the atmosphere, accomplished by outdoor exposure of crushed ore. This process is slow and inefficient, and because it requires the storage of a large amount of metallic material for a long time, the technique is expensive. Of course, the advantages in weathering are that as a process, it is inexpensive, and the technique has been used to advantage with certain copper ores that are thus converted into water soluble sulfates.

Solvents are liquids which from an engineering point of view should be inexpensive, capable of regeneration, and able to dissolve rapidly the desired minerals, thus separating them from the gangue material. Several solvents are used in leaching operations. The most important solvent for sulfate minerals is water; for example, rain water or natural mine waters have been used to recover copper sulfate from ore. Another solvent is dilute sulfuric acid, used to dissolve copper and zinc oxides according to the reactions,



Hydrochloric and nitric acids also have been utilized as solvents.

Alkaline solutions such as ammonium hydroxide with oxygen or ammonium carbonate plus ammonium hydroxide are used to leach native copper ores and metallic carbonates. The advantage of using an alkaline leaching solution with a carbonate gangue is that the alkaline solution does not attack the carbonate, whereas the use of an acid leach would consume a considerable quantity of acid by extraneous reaction with the carbonate. When copper is leached with an alkaline solution containing ammonia, the copper can be precipitated as CuO by heating, which also drives the ammonia and carbon dioxide out of solution and allows recovery of these gases. Sodium hydroxide is used in the Bayer process for the purification of bauxite. Cyanide solutions, such as NaCN, are used to dissolve gold and silver according to the reactions,



Sulfite and chloride solutions are used for recovery of metallic chlorides.

### Leaching Techniques

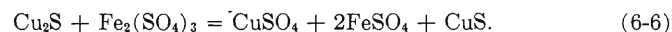
Copper ores often are leached *in situ* by circulating water through underground copper deposits. Exposure of the ore body to water and oxygen oxidizes the sulfide to a sulfate, which dissolves in the water percolating through the ore. The water is collected then and the dissolved copper recovered, usually by precipitation (cementation) on iron scrap. The "cemented" copper is loosely adherent to the scrap and can be flushed off the scrap into a collecting tank.

Heap leaching also depends upon oxidation of sulfide minerals by exposure to

water and air. Ore is placed above ground in large heaps which are exposed to the atmosphere and water, either natural rain water or water sprays. The solution percolates through the ore, which usually contains iron, and by one postulated mechanism, the pyrite is oxidized according to the reaction,



The ferric sulfate then reacts with the copper converting it to a soluble sulfate as



An extraction carried out in this manner may require several years and the loss of metal in solution which seeps into the ground represents an inherent inefficiency.

Leaching is more commonly carried out in a tank, either by *percolation* through a sand or by *agitation*, either mechanically or with compressed air, with a slime.

A continuous method of leaching and separation of the enriched solution from the gangue is *counter-current decantation* (C.C.D.). This process was used originally in the cyanide extraction of silver and gold but now is used in several other hydrometallurgical applications. The technique employs a series of thickening tanks arranged to permit counter-current flow of solids and liquid solution as illustrated in Fig. 6-1. The underflow or sludge is pumped to each succeeding tank at a higher elevation, while the overflow solution is permitted to move in the opposite direction. The pulp or gangue material is stripped of the desired metal as it moves toward the discharge, while the liquid solution moving counter-current is enriched.

Pressure leaching is carried out in a autoclave at high pressures and at higher temperatures than are feasible in open tanks. The advantages of this technique are that gaseous reagents, such as oxygen, can be used and the high pressure enhances the solubility of the gas in the leaching solution. Oxygen is necessary for the solution of gold by a cyanide solution (Eq. 6-3) and the rate of reaction between the cyanide solution and the gold is increased by increased oxygen pressure. Sulfides can be directly dissolved in acid or alkaline solutions at higher temperatures and higher

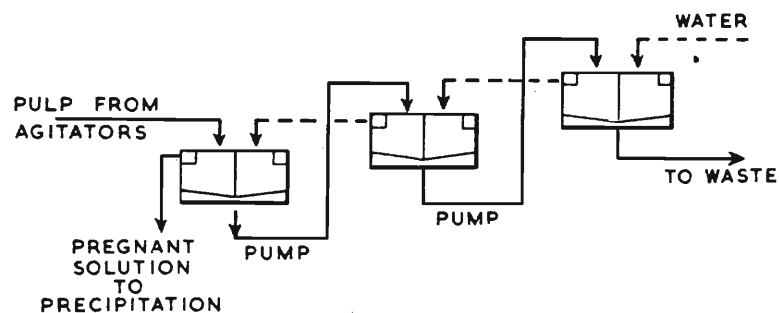


Fig. 6-1. Counter-Current Decantation

Source: W. H. Dennis, *Extractive Metallurgy*, Philosophical Library, Inc., New York, 1965, p. 245.

oxygen pressures. Cobalt and cobalt-nickel sulfides, as well as certain uranium ores, are treated by pressure leaching.

The chemistry of high pressure leaching of sulfides is very complex. Nickel and cobalt sulfides are leached in sulfuric acid and air under high pressure (100 psig) and high temperature (250°F) conditions. The sulfides are oxidized to sulfates which may be described by the simplified overall reactions:

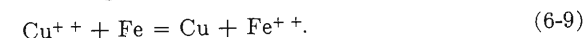


Liquid-solid separation techniques are required to remove the leaching solution from the residual gangue. Several methods are employed including decanting, thickening, and filtering.

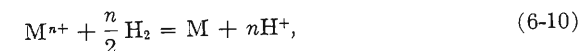
#### Recovery of Metal from Solution

Several techniques are available for recovering metals from leaching solutions. The most important industrial process is electrolytic deposition (see Electro-metallurgy), but other methods include gaseous reduction, precipitation, solvent extraction, and ion exchange. The development of commercial processes for gaseous reduction of metallic ions from aqueous solutions has been a major metallurgical advance in recent years. This technique, although known for many decades, only recently has achieved a significant industrial status. The thermodynamic aspects of the process are reasonably well understood, and are developed in some detail in the following paragraphs.

*Thermodynamics of Reduction of Metals from Aqueous Solution.* The use of chemical displacement reactions to precipitate metals from ionic solutions is a time-worn practice in the metallurgical art. The classical example of such a reduction is the "cementation" process in which copper is displaced from aqueous solution by reaction with metallic iron according to the ionic reaction,



Recently developed hydrometallurgical processes employing reducing gases at high pressure to precipitate metals from aqueous solutions are based on the same concepts. These gaseous reduction processes are carried out at elevated temperatures (over 100°C) and at pressures ranging up to several hundred psi. Although the principal reducing agent in these processes is gaseous hydrogen, other reducing gases, such as carbon monoxide or hydrogen sulfide, can be used; the technique has been applied primarily in the production of cobalt and nickel, but with these other gases, however, the formation of undesirable by-products and high cost are disadvantages. Many other metals can be recovered by this process. A generalized representation of the reaction for hydrogen reduction of a metallic ion in aqueous solution is



where M is the metallic element and  $n$  is the valence of the metallic ion in aqueous solution.

The feasibility of these reduction processes can be tested on the basis of metal-metal ion potentials in aqueous solutions.

**Electrode Potentials.** The equilibrium relation for a displacement reaction in aqueous solution can be developed from standard free energies of reaction, but it is more convenient to use electrode potentials as a measure of the free energy change, since the tabulated data appear in this form, and in fact, for the most part are based on electrode potential measurements.

Standard electrode potentials have been determined for aqueous electrolytes at ambient temperature. The standard potential for several metal-metal ion electrodes and their corresponding reactions can be defined from experimental measurements of the potential of such electrodes relative to a *standard* cell whose potential is defined by the hydrogen electrode (zero potential at 1 atm hydrogen gas and 25°C). A summary of the standard electrode potentials for several half-cell reactions is presented in Table A-VIII of Appendix A.

Cell potentials depend not only upon the temperature, the materials making up the electrodes, and the overall cell reaction, but also upon the activities of the participating ions in solution. Utilizing the definition of net electrical work, which is equivalent to free energy,

$$\Delta G = -nF\epsilon, \quad (6-11)$$

where

$$\begin{aligned} n &= \text{number of equivalents transferred,} \\ F &= \text{Faraday's constant, 23066 cal/V-g equiv,} \\ \epsilon &= \text{emf of cell.} \end{aligned}$$

And considering the reaction isotherm for a reaction

$$aA + bB + \dots = cC + dD + \dots, \quad (6-12)$$

where

$$\Delta G = \Delta G^0 + RT \ln \left[ \frac{a_C^c a_D^d \dots}{a_A^a a_B^b \dots} \right]. \quad (6-13)$$

Then

$$-nF\epsilon = -nF\epsilon^0 + RT \ln \left[ \frac{a_C^c a_D^d \dots}{a_A^a a_B^b \dots} \right] \quad (6-14)$$

and

$$\epsilon = \epsilon^0 - \frac{RT}{nF} \ln \left[ \frac{a_C^c a_D^d \dots}{a_A^a a_B^b \dots} \right]. \quad (6-15)$$

**The Hydrogen Electrode.** The hydrogen electrode is defined by the half-cell reaction,



The potential of the hydrogen electrode is defined by the concentration of hydrogen ions in solution and the hydrogen pressure. The potential of a hydrogen electrode,

according to Eq. (6-15), is given by the expression,

$$\epsilon_{\text{H}_2} = \epsilon_{\text{H}_2}^0 - \frac{RT}{2F} \ln (a_{\text{H}^+})^2 + \frac{RT}{2F} \ln (P_{\text{H}_2}). \quad (6-17)$$

[The pressure of hydrogen in atmospheres is commonly substituted for fugacity. At 100 atm hydrogen pressure, the fugacity is 106.1 atm, which changes the last term of Eq. (6-17) by only 1%.] The activity of the hydrogen ions in solution is defined in terms of the pH scale by the relationship,

$$\text{pH} = -\log_{10} (a_{\text{H}^+}) = -\frac{\ln (a_{\text{H}^+})}{2.303}. \quad (6-18)$$

Since the standard potential for the hydrogen electrode,  $\epsilon_{\text{H}_2}^0$ , is zero by definition, Eq. (6-17) at 25°C reduces to

$$\epsilon_{\text{H}_2} = 0.0592 \text{ pH} + 0.0296 \log_{10} (P_{\text{H}_2}). \quad (6-19)$$

**Metal-Metal Ion Electrode Potentials.** The electrode potential for a metallic ion in aqueous solution is determined by the standard electrode potential for the metal-metal ion half-cell and the activity of the ion in solution. The cell potential for a half-cell reaction,



is given by the relationship,

$$\epsilon_{\text{M}} = \epsilon_{\text{M}}^0 - \frac{RT}{nF} \ln (a_{\text{M}^{n+}}). \quad (6-21)$$

The activity of the metal ion in solution is related to the concentration according to the relationship,

$$a_{\text{M}^{n+}} = f_{\text{M}^{n+}} (\text{M}^{n+}). \quad (6-22)$$

The standard state is chosen so that the activity coefficient,  $f_{\text{M}^{n+}}$ , approaches unity at infinite dilution. Thus, by definition

$$f_{\text{M}^{n+}} = \left[ \frac{a_{\text{M}^{n+}}}{(\text{M}^{n+})} \right]_{(\text{M}^{n+}) \rightarrow 0} \rightarrow 1. \quad (6-23)$$

The concentration in Eq. (6-22) is expressed in terms of molality (moles per 1000 g of solvent). A one molal solution which is common in hydrometallurgical processes, may *not* result in a cell potential,  $\epsilon_{\text{M}}$ , which is equal to the standard cell potential,  $\epsilon_{\text{M}}^0$ , since the activity coefficient *could* be much less than unity. Although the concentration would be unity, the activity would not be, and the last term in Eq. (6-21) would alter the cell potential. The activity coefficients for aqueous sulfates and chlorides, common metallurgical processing solutions, are usually less than one, even in relatively dilute solutions, as illustrated in Table 6-1.

**Example Problem 6-1.** Compute the half-cell potential at 25°C for the reaction,



in a 0.1 molal solution of nickel sulfate.

TABLE 6-1  
Activity Coefficients in Some Metal Salt Solutions

| Salt              | Activity Coefficients in solutions of molality |       |       |      |      |      |      |      |       |       |
|-------------------|------------------------------------------------|-------|-------|------|------|------|------|------|-------|-------|
|                   | 0.001                                          | 0.002 | 0.005 | 0.01 | 0.02 | 0.05 | 0.1  | 0.2  | 0.5   | 1.0   |
| MgSO <sub>4</sub> | —                                              | —     | —     | 0.40 | 0.32 | 0.22 | 0.18 | 0.13 | 0.088 | 0.064 |
| NiSO <sub>4</sub> | —                                              | —     | —     | —    | —    | —    | 0.18 | 0.13 | 0.075 | 0.051 |
| CuSO <sub>4</sub> | 0.74                                           | —     | 0.53  | 0.41 | 0.31 | 0.21 | 0.16 | 0.11 | 0.068 | 0.047 |
| ZnSO <sub>4</sub> | 0.70                                           | 0.61  | 0.48  | 0.39 | —    | —    | 0.15 | 0.11 | 0.065 | 0.045 |
| MgCl <sub>2</sub> | —                                              | —     | —     | —    | —    | —    | 0.56 | 0.53 | 0.52  | 0.62  |
| FeCl <sub>2</sub> | 0.89                                           | 0.86  | 0.80  | 0.75 | 0.70 | 0.62 | 0.58 | 0.55 | 0.59  | 0.67  |
| CuCl <sub>2</sub> | 0.89                                           | 0.85  | 0.78  | 0.72 | 0.66 | 0.58 | 0.52 | 0.47 | 0.42  | 0.43  |
| ZnCl <sub>2</sub> | 0.88                                           | 0.84  | 0.77  | 0.71 | 0.64 | 0.56 | 0.50 | 0.45 | 0.38  | 0.33  |

Source: B. Meddings and V. N. Mackiw, Gaseous reduction of metals from aqueous solutions, *Applications of Fundamental Thermodynamics to Metallurgical Processes*, p. 110, Gordon and Breach Science Publishers Inc., New York, 1967.

*Solution.* Using Eq. (6-21) and the cell potential from Table A-VIII

$$\epsilon_{Ni} = 0.236 - \frac{0.0592}{2} \log_{10} (a_{Ni^{++}}). \quad (6-b)$$

From Table 6-1,  $f_{Ni^{++}} = 0.18$ , and Eq. (6-b) yields

$$\begin{aligned} \epsilon_{Ni} &= 0.236 - 0.0296 \log_{10} [(0.18)(0.1)] \\ \epsilon_{Ni} &= 0.236 + 0.052 = 0.288 \text{ V} \end{aligned} \quad (6-c)$$

*Hydrogen Reduction of Metal Ions.* The generalized hydrogen reduction reaction, Eq. (6-10), may be considered to be made up of two half-cell reactions, as given by Eqs. (6-16) and (6-20). The corresponding cell potentials are given by Eqs. (6-17) and (6-21). If the cell potential for the oxidation of metal, Eq. (6-20), is greater than for the oxidation of hydrogen, Eq. (6-16), then the metal will oxidize and go into solution and hydrogen gas will be liberated. If, however, the cell potential for the reaction of Eq. (6-16) is the larger, the metal will precipitate from solution and hydrogen will be oxidized.

It is especially important to note that the cell potentials are independent of the number of electrons taking part in the oxidation or reduction reaction. This is evident from rewriting Eq. (6-11) in the form,

$$\epsilon = - \frac{\Delta G}{nF}. \quad (6-24)$$

The total free energy change is dependent upon the number of gram atoms, moles, or equivalents taking place in a reaction but the corresponding emf is independent of the form in which the equation is written. Thus, Eqs. (6-10) and (6-20) can be

combined to yield



As stated above, at constant temperature the potential of the hydrogen electrode is dependent only on the pH and the hydrogen pressure. Thus, for a given condition, the cell potential for Eq. (6-16) and for Eq. (6-25) are the same, regardless of the value assigned to  $n$  in Eq. (6-25). This is evident from Eq. (6-17).

The thermodynamic feasibility of a reduction by hydrogen can be determined by comparing cell potentials. The cell potential for reduction of a pure metal is dependent upon the concentration of the metallic ion in solution, and the cell potential for the hydrogen reaction is dependent upon pH and hydrogen pressure. Figure 6-2 presents a comparison of the hydrogen potentials at 25°C for 1 and 100 atm on a pH scale with the potentials for reduction of various metallic ions at two levels of concentration. Activities rather than concentrations have been used for calculation of the metal-metal ion potentials, yielding smaller slopes. Since the values of pH, hydrogen pressure, and metal ion concentration cover the range normally encountered in industrial operations, copper can always be reduced by hydrogen whereas zinc cannot. Reduction of zinc, iron, and cadmium are considered in the following example problem.

*Example Problem 6-2.* Compare the hydrogen pressures required to precipitate  $\text{Zn}^{++}$ ,  $\text{Fe}^{++}$ , and  $\text{Cd}^{++}$  at 25°C in solutions of pH 6 and 10. The potentials for precipitation can be taken as 0.83, 0.50, and 0.47 V for  $\text{Zn}^{++}$ ,  $\text{Fe}^{++}$ , and  $\text{Cd}^{++}$ , respectively.

*Solution.* At pH 6, 25°C, and 1 atm hydrogen pressure, the hydrogen potential, from Eq. (6-19) is

$$\epsilon_{\text{H}_2} = \epsilon^{\circ}_{\text{H}_2} + 0.0592(\text{pH}) + 0.0296 \log_{10} (P_{\text{H}_2}), \quad (6-a)$$

$$\epsilon_{\text{H}_2} = +0.0592(6) = 0.36 \text{ V}. \quad (6-b)$$

The potentials for reduction of  $\text{Zn}^{++}$ ,  $\text{Fe}^{++}$ , and  $\text{Cd}^{++}$  are thus 0.47, 0.14, and 0.11 V above the hydrogen potentials, respectively. The emf of the hydrogen half-cell can be increased by increasing the hydrogen pressure by an amount calculable from the last term of Eq. (6-19)

$$\Delta \epsilon = 0.0296 \log_{10} (P_{\text{H}_2}). \quad (6-c)$$

The corresponding pressures at pH 6 ( $\epsilon^{\circ}_{\text{H}_2} = 0.36$ ) and at pH 10 ( $\epsilon^{\circ}_{\text{H}_2} = 0.592 \text{ V}$ ) are

|                  | Equilibrium Hydrogen Pressure in Atmospheres |                   |
|------------------|----------------------------------------------|-------------------|
|                  | pH = 6                                       | pH = 10           |
| $\text{Zn}^{++}$ | $8 \times 10^{15}$                           | $1.1 \times 10^8$ |
| $\text{Fe}^{++}$ | $5.4 \times 10^4$                            | $1^a$             |
| $\text{Cd}^{++}$ | $5.2 \times 10^4$                            | 1                 |

<sup>a</sup> Above a pH of 8.5, ferrous ions are unstable with respect to hydrolysis. The equilibrium solubility product for ferrous hydroxide is on the order of  $10^{-14}$  and hence the ferrous ion concentration would be about  $10^{-10}$  mole/liter and the hydrogen pressure would have to be increased to about  $10^6$  atm to precipitate metallic iron under these circumstances.

At pH 10,  $\epsilon_{Zn^{++}}$  is still much greater than  $\epsilon_{H_2}$ , and it is unlikely that zinc will ever be recovered by hydrogen reduction. However, cadmium could be precipitated at less than 1 atm hydrogen pressure.

It should be noted that as the reduction reaction is carried out, there is a limiting concentration of metallic ion at which the cell potential for the reduction of the metal ion and the oxidation of hydrogen become equal. For 1 atm hydrogen pressure and 25°C this potential is

$$\epsilon_{H_2} = 0.0592 \text{ pH} = \epsilon_M^0 - \frac{0.0592}{n} \log_{10} (a_{M^{n+}}). \quad (6-26)$$

At low ion concentrations, the activity of the metal ion can be replaced by concentration. Eq. (6-26) then becomes

$$-\log_{10} (C_{M^{n+}}) = (n) (\text{pH}) - \frac{(n) (\epsilon_M^0)}{0.0592}. \quad (6-27)$$

For a concentration of  $10^{-2}$  mole/liter of metallic ion and at 1 atm hydrogen pressure and 25°C, the equilibrium pH values calculated by Eq. (6-27) are tabulated in Table 6-2. As reduction of the metal ion continues, hydrogen ions are released in the solution and the pH decreases. It is evident from Table 6-2 that precautions must be taken to assure that the pH is maintained above the desired level. This is particularly true for metals with positive  $\epsilon^0$  values.

It is apparent from Fig. 6-2 that reduction by hydrogen is favored at higher pH values. However, in alkaline solutions, the solubility of many metal cations is limited particularly for the transition metals. In commercial practice the metal ions are "complexed" by adding ammonia, which raises the pH and forms a soluble amine. The addition of ammonia to solutions containing cobalt ions, e.g., would cause formation of a series of amines with increasing cobalt-to-ammonia ratios. The formation of the first amine is given by the equation,

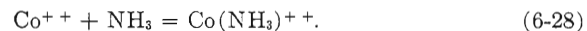


TABLE 6-2

Equilibrium pH Values at  $C_{M^{n+}} = 10^{-2}$  Molar

| Ion              | $E^0$  | pH    |
|------------------|--------|-------|
| Zn <sup>++</sup> | 0.762  | 13.9  |
| Fe <sup>++</sup> | 0.440  | 8.5   |
| Cd <sup>++</sup> | 0.403  | 7.8   |
| Co <sup>++</sup> | 0.267  | 5.5   |
| Ni <sup>++</sup> | 0.241  | 5.1   |
| Cu <sup>++</sup> | -0.337 | -4.7  |
| Ag <sup>+</sup>  | -0.799 | -11.5 |

Source: B. Meddings and V. N. Mackiw, Gaseous reduction of metals from aqueous solutions, *Applications of Fundamental Thermodynamics to Metallurgical Processes*, p. 114, Gordon and Breach Science Publishers Inc., New York, 1967.

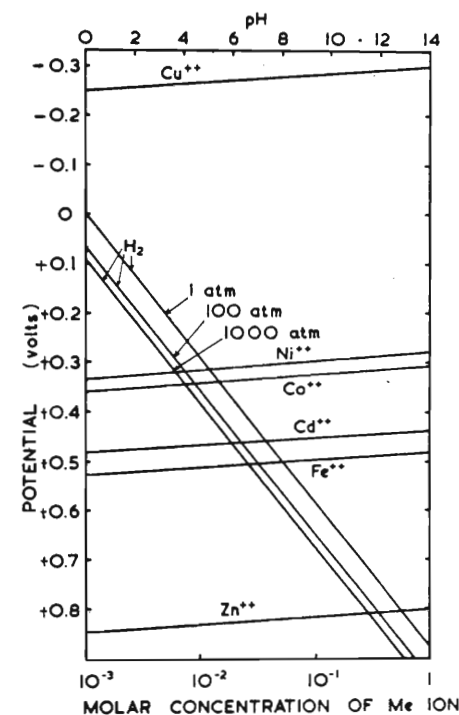


Fig. 6-2. Variation of Hydrogen and Metal Electrode Potentials with Ion Concentration in Sulfate Solutions (corrected for solute activity interactions)

Source: D. J. I. Evans, "Advances in Extractive Metallurgy", Symposium Volume, p. 881, American-Elsevier, England, 1968.

The distribution of types of amines in the solution determines the reduction potential for the cobalt ion. The greatest driving force occurs near the ratio  $\text{NH}_3/\text{Co}^{++} = 2$ , and it is this concentration which is usually employed in industrial processing of both cobalt and nickel.<sup>1</sup> The addition of ammonia and formation of an alkaline solution for the high pressure reduction of metals from aqueous solutions has a further practical advantage in that the extremely corrosive conditions existing in acid solutions under hydrogen pressure are avoided.

*Kinetics of Gaseous Reduction in Aqueous Solutions.* The rate of reduction of a metallic ion from aqueous solution can be limited by a number of factors; nucleation of solid particles; area of the nucleation surface; the thermodynamic factors of hydrogen pressure, pH, or metal ion concentration; etc. The rate limiting step in

<sup>1</sup> T. M. Kaneko and M. E. Wadsworth, *J. Phys. Chem.* **60**, 457 (1956).

the conversion varies with the system and the stage of the recovery process. The significant kinetic factors for a few industrial hydrometallurgical processes are outlined in the following paragraphs.

Nucleation of a precipitate is often a rate limiting step in the reduction process. The reduction of nickel is a heterogeneous process and requires the presence of nuclei. Nickel powder usually is suspended in the solution and vigorously agitated. Ferrous sulfate also can be used. The rate of reduction of cobalt also is nucleation dependent.<sup>2</sup> The reduction rate of nickel has been shown to be proportional to the surface area of the nickel "seed" particles.<sup>3</sup>

The pressure of hydrogen is also important in determining the rate of reaction. The thermodynamic equilibrium depends upon the hydrogen pressure; for example, the rate of reduction of nickel from an ammoniacal solution varies with the first power of the hydrogen pressure,<sup>4</sup> such that

$$-\frac{d(\text{Ni}^{++})}{dt} = kA(P_{\text{H}_2}), \quad (6-29)$$

where

$k$  = temperature dependent rate constant,

$A$  = area of nucleating surface,

$P_{\text{H}_2}$  = pressure of hydrogen in atm.

In a closed reduction vessel, the pressure decreases with time in direct proportion to the nickel reduced, so that

$$-\frac{dP_{\text{H}_2}}{dt} = k'A(P_{\text{H}_2}), \quad (6-30)$$

where  $k'$  is a constant combining the rate constant  $k$  and the volume of the system, volume of solution, etc. Eq. (6-30) can be integrated to

$$\log_{10} \left[ \frac{(P_{\text{H}_2})_{t=0}}{(P_{\text{H}_2})_t} \right] = \frac{k'At}{2.303}. \quad (6-31)$$

Catalysts, such as anthraquinone in the case of nickel reduction, have been used to increase the rate of reaction.

The rate of reduction is *temperature dependent* and Arrhenius plots have been used to determine activation energies. In the case of nickel reduction the activation energy was 10,200 cal/mole.<sup>5</sup>

To achieve success in industrial practice, the hydrogen pressure, pH, and metallic ion concentration are well above those predicted by equilibrium calculations. The actual equilibria are complicated by complexing reactions in ammoniacal solutions. Agitation and the presence of nuclei, particularly in the cases

<sup>2</sup> J. Halpern and A. G. Webster, *J. Phys. Chem.* 61, 1245 (1957).

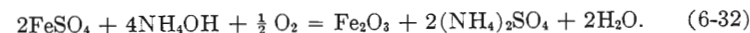
<sup>3</sup> V. N. Mackiw, W.C. Lin, and W. Kunda, *Trans. AIME* 209, 786 (1957).

<sup>4</sup> Ibid.

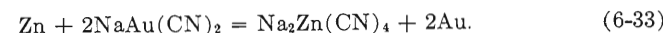
<sup>5</sup> Ibid.

of nickel and cobalt reduction, are especially important in assuring a reasonably rapid reaction and the precipitation of the desired sand-like deposit.

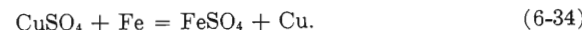
**Other Recovery Methods.** The precipitation of a metal ion from a solution by formation of an insoluble compound is a well-known technique in chemical analysis. It can be applied to the recovery of metals from leaching solutions or for the separation of elements if the leaching solution contains more than one element, as in the sulfuric acid-oxygen leaching of nickel-cobalt-iron sulfides. By using ammonia to raise the pH to approximately 5 and oxidizing the solution with air at atmospheric pressure, the ferrous ions are oxidized to ferric ions and precipitated as hydrated ferric oxide. This separation process is described by the reaction,



Another example of this technique is in the precipitation of gold or silver from cyanide solutions by using zinc dust. The cyanide solution is agitated with zinc dust under conditions which are relatively oxygen-free. The zinc precipitates the gold (or silver) according to the reaction,



The long-standing technique for recovery of copper from dilute solutions has been by cementation. These dilute solutions of copper usually contain large quantities of impurities that would make electrolytic refining difficult. Precipitation of the copper is accomplished by bringing the solution in contact with low-cost scrap iron. The copper precipitates as a finely divided, loosely adherent sponge according to the reaction,



Any adherent copper is easily removed from the iron by blasting with high pressure water. The cemented copper is not very pure (50-75% copper). In theory, it requires less than 1 lb of iron to precipitate a pound of copper, but because of reaction with the acid solution and reduction of ferric ions, the consumption of iron ranges from 1.5-2 lb per pound of copper precipitated.

The efficiency of copper recovery by cementation depends upon the surface area of iron exposed to the solution, extent of agitation of the solution, and length of contact. A standard gravity launder provides 90% recovery of copper, but a recently designed cone precipitator (see Fig. 6-3) improved cementation efficiencies such that over 93% of the copper is recovered. The use of shredded scrap iron in the cone precipitator with its turbulent action zone where kinetic factors are favorable results in the improvement. The automatic recovery of the cemented copper is also a marked advantage in this process.

**Example Problem 6-3.** In the cementation of copper, the copper concentration in the leaching solution can be reduced to very low levels. Assume a dilute sulfuric acid solution in which the activity coefficient of the ferrous ion is 0.2. The solution leaves the cementation launder at 25°C and contains 0.6 g/liter of iron. Estimate the residual equilibrium copper content of the exit stream.

**Solution.** The displacement reaction is given by Eq. (6-9).



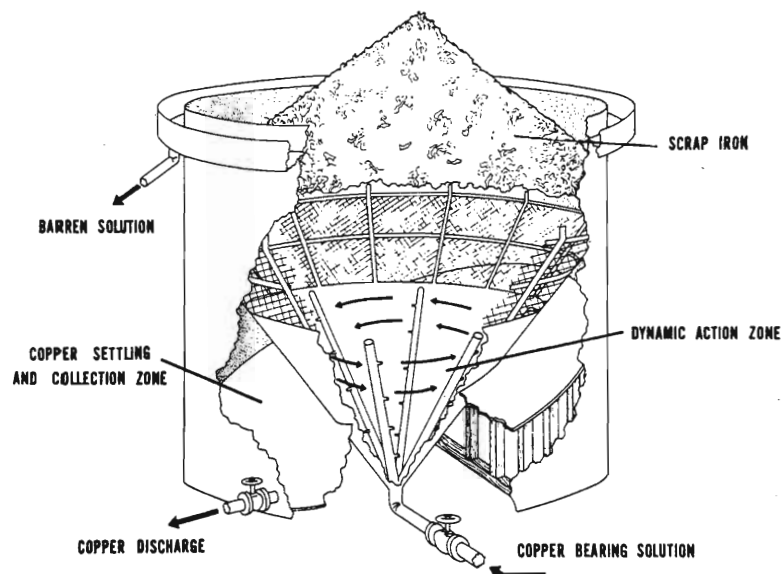


Fig. 6-3. Sketch of Cone Precipitator Showing Solution Inflow and Copper Precipitate Discharge  
Source: "Cone-Type Precipitators for Improved Copper Recovery," H. R. Spedden, E. E. Malouf, and J. D. Prater, *J. of Metals*, 1966, Vol. 18, p. 1139.

The half-cell potential for iron is

$$\epsilon = \epsilon^0 - \frac{4.575 T}{(2)(23066)} \log_{10} (a_{Fe^{++}}). \quad (6-b)$$

From Table A-VIII,  $\epsilon^0_{Fe} = 0.441$ , and

$$\epsilon = 0.441 - 0.0296 \log_{10} (0.2) \frac{0.6}{55.85}, \quad (6-c)$$

$$\epsilon = 0.441 + 0.0795 = 0.521 \text{ V.} \quad (6-d)$$

At equilibrium, the copper half-cell must have the same potential, and

$$\epsilon = \epsilon^0_{Cu} - 0.0296 \log_{10} (a_{Cu^{++}}). \quad (6-e)$$

From Table A-VIII,  $\epsilon^0_{Cu} = -0.3441$ . Assuming that the activity coefficient of copper is unity in the dilute solution and substituting concentration for activity,

$$\log_{10} (C_{Cu^{++}}) = - \frac{(0.521 + 0.3441)}{0.0296} = -29.2. \quad (6-f)$$

The molality is  $6.3 \times 10^{-30}$  which corresponds to  $4 \times 10^{-28}$  g/liter.

The cementation process is highly favored thermodynamically, and in practice is a very efficient way to recover copper from dilute aqueous solutions. The extent of recovery in practice is limited by the effectiveness of contact between the copper solution and the scrap iron, and the spent solution usually contains more than 0.06 g of Cu/liter.

Solvent extraction has been used for many years in the chemical and oil industries, and has become increasingly important in the metals field, particularly with the advent of uranium ore processing. This method also is referred to as liquid-liquid extraction. The solvents used with aqueous solutions are usually organics, since it is necessary that the extracting solution be relatively insoluble in the leaching solution and also be capable of a clean separation, that is, it is important

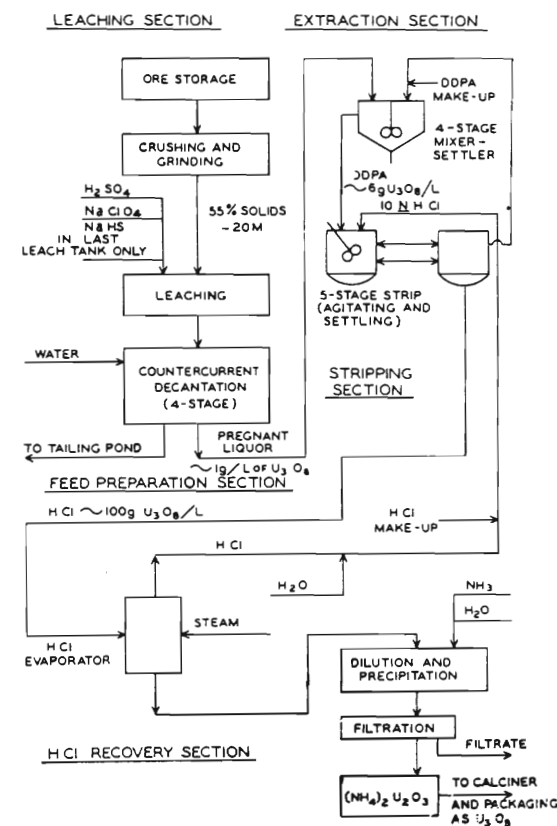


Fig. 6-4. Scheme for DDPA Extraction and Recovery of Uranium

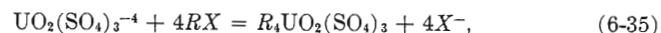
Source: W. D. Wilkinson, *Uranium Metallurgy*, Vol. 1, "Uranium Process Metallurgy", Interscience Publishers; John Wiley and Sons, Inc., New York, 1962, p. 141.

that the extracting solution does not form an emulsion. The extractant must be highly selective in its ability to react with or absorb the desired material.

In a system for processing uranium ores, di(2-ethylhexyl) phosphoric acid (EHPA) is dissolved in kerosene and contacted with the leaching solution containing uranium. The phosphoric acid forms an extractable complex with uranium, and the extraction is carried out with various types of mixing units, such as stirred tanks, columns, etc. A typical acid-leach system employing a similar phosphoric acid compound as an extractant for uranium is diagrammed in Fig. 6-4.

Ion exchange is another technique for recovering metals from leaching solutions, and this method also has received considerable impetus from the processing of uranium ores. The same technique is used in water softeners, in which a zeolite (a sodium aluminate-silicate) removes calcium or magnesium ions by exchanging them with sodium ions. Ion exchangers used in most hydrometallurgical operations are synthetic resins made up from organic polymers.

In the processing of uranium ores, an anionic exchanger is used because the uranium is present in the solution as a complex anion. An ion exchange process for recovery of uranium from sulfate solutions is shown schematically in Fig. 6-5. This permits an effective separation of the uranium since the other metals in solution, aluminum, cobalt, nickel, etc., are present as cations. The active group on the surface of the resin exchanges with the complex ion according to the reaction,



where  $R$  indicates the resin and  $\text{X}^-$  is a negative ion. Adsorption takes place rapidly until the surface of the resin is fully reacted and the leaching solution passing through the resin begins to show traces of dissolved uranium. When the resin has fully reacted, it is brought into contact with a strong solution of chloride or nitrate ions ( $\text{X}^-$  ions), which puts the uranyl ions back into solution and recharges the

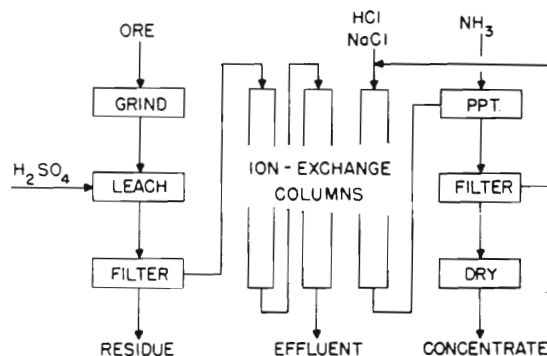


Fig. 6-5. Uranium Ore Processing—Ion-Exchange for Sulfate Solutions

Source: W. D. Wilkinson, *Uranium Metallurgy*, Vol. I: *Uranium Process Metallurgy*, Interscience Publishers; John Wiley and Sons, Inc., New York, 1962, p. 111.

surface of the resin. This solution (eluate) is treated subsequently for recovery of the uranium.

Ion exchange is a process requiring several steps: absorbing metal ions from solution; removal of the retained ions by replacement reactions using a solution containing the proper ion (anion in the case of uranium processing), and, finally, recovering the metal from the eluate. Ion exchange is relatively expensive and has been restricted to separation processes like uranium extraction and the processing of rare-earth metals.

## 6-2 Industrial Hydrometallurgical Operations

In the following paragraphs, a brief description is given of some of the more important hydrometallurgical processes used in the metallurgical industries. The examples cited include the recovery of copper, gold and silver, uranium, zinc, nickel, cobalt, and the purification of alumina for production of metallic aluminum.

### Hydrometallurgy of Copper

As mentioned previously, the leaching of copper as a recovery process is usually practiced on low-grade ores. Dilute sulfuric acid is used to leach ores containing copper oxide, whereas water will leach copper sulfate from partially roasted, or weathered ores.

The presence of iron in sulfide minerals as ferric salts enhances the solution of copper. Copper is usually recovered by cementation or electrolysis.

### Gold and Silver Hydrometallurgy

The recovery of gold is classically described by stories of the old prospector and his panning operations. The placer deposits of gold where the waste material has been washed away leaving the gold behind permit recovery of the gold by panning. Large operations in Alaska use hydraulic mining, in which water is used to wash the gold bearing dirt into sluiceways where gravity separation is carried out.

Gold also is recovered by amalgamation. The solubility of gold in mercury is quite high, over 15 wt% at 100°C, and finely divided gold readily dissolves when brought into contact with a fresh mercury surface. By washing the gold-bearing material in a finely divided state over a copper surface coated with mercury, the gold is alloyed readily with the mercury for later recovery by distillation. Various types of milling operations are carried out in the presence of mercury to recover gold by amalgamation.

The chemical recovery of gold in a hydrometallurgical manner was formerly accomplished primarily by chlorination. However, in 1888, the McArthur-Forrest process for cyanidation was introduced, and since then this method has been a primary process for production of gold and other precious metals. Dissolution of gold in dilute cyanide solution according to Eq. (6-3) shows that oxygen is an important factor, and gold will not dissolve in cyanide solutions *unless* oxygen is present, i.e., as dissolved oxygen gas or possibly as an oxidizing agent. Sodium cyanide is used because it is less expensive than potassium cyanide, the original reagent material.

The solutions used contain approximately 0.1% sodium cyanide. One difficulty arising in cyanidation is the presence of cyanicides, a term given to materials (other than the precious metals) that react with and consume the cyanide solution. Acids or salts which react with strong bases often are present and react with cyanide. Also, most copper minerals react with sodium cyanide to form complex compounds. Zinc carbonate and iron also consume the cyanide. Cyanicides must be removed from the solution and this often can be accomplished after acid leaching by addition

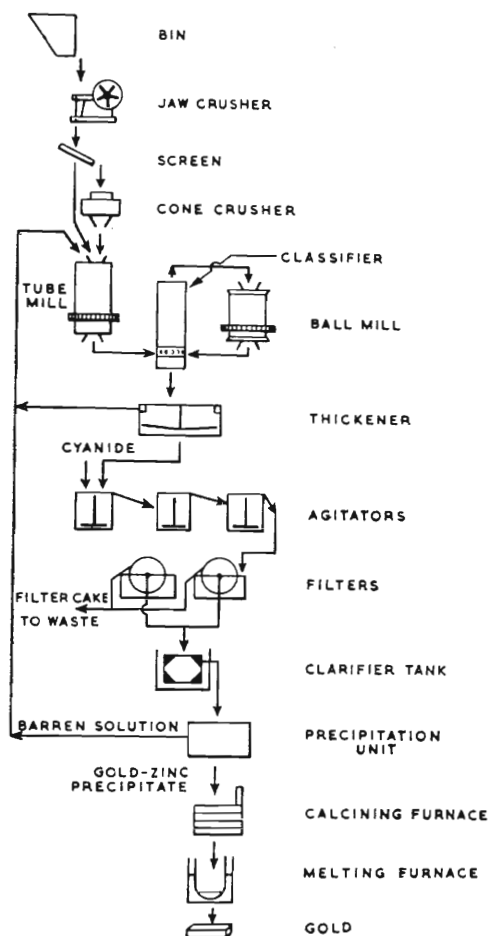
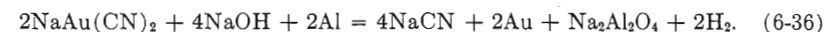


Fig. 6-6. Schematic Diagram Outline the All-sliming Gold-recovery Process

Source: W. H. Dennis, *Extractive Metallurgy*, Philosophical Library, Inc., New York, 1965, p. 251.

of lime, which neutralizes the free acid and precipitates some of the interfering metallic ions such as iron. A schematic diagram outlining a gold recovery process in which an ore slime is treated is shown in Fig. 6-6.

Gold is recovered from the leaching solution by precipitation with zinc [Eq. (6-33)]. Several metals could be used to displace the gold in an ionic reaction, and, in fact, sodium and potassium would be most desirable because they would regenerate the solution. Aluminum sometimes is used to produce sodium cyanide and a gold precipitate, but wide adoption of this method has not taken place because of the interference of calcium oxide, often used to supply alkalinity to the solution, which precipitates along with the gold. The reaction with aluminum is

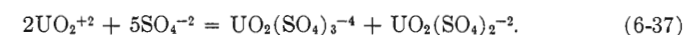


Charcoal also could be used. Nevertheless, in industrial practice because of its low cost and suitability, zinc is used most widely for this purpose.

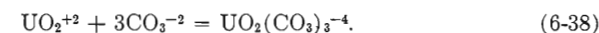
The gold precipitate is treated with sulfuric acid to dissolve the zinc, and the residual material then is fused with borax, sand, and soda to produce metallic gold in a pyrometallurgical operation. The gold thus produced is about 90% pure and usually contains silver. Further refining is carried out by electrolysis.

#### Uranium Hydrometallurgy

Uranium minerals usually are extracted by alkaline or acid leaching. In the acid process sulfuric acid is used, whereas in alkali leaching sodium carbonate and bicarbonate solutions are used. In acid leaching the uranium is dissolved according to the ionic equation,



In alkaline leaching the corresponding reaction would be



Alkali leaching is much slower but the kinetics can be enhanced by treating a finer material and using heated leaching solutions.

Acid leaching usually is employed and is carried out in the presence of an oxidizing agent to convert the uranium to  $\text{U}_3\text{O}_8$ . The concentration of uranium in the leaching solutions is relatively low, corresponding to about 1 g of uranium oxide/liter. The dissolved uranium is present in complex anions that can be advantageously treated with ion exchange or solvent extraction processes. Direct precipitation of the uranium is possible but is not desirable because of the diluteness of the solution and the fact that the resulting precipitate would be contaminated by the metallic impurities present. Anionic removal of the uranium using ion exchange, although expensive, is very effective in purifying the uranium oxide.

Uranium as a molten metal is extremely reactive but can be produced by electrolysis of fused salts, the uranium being present as  $\text{KUF}_5$ . Calcium hydride also has been used to decompose uranium oxide, producing calcium oxide, hydrogen, and uranium powder upon reaction at about  $1000^\circ\text{C}$  in a vacuum or inert atmosphere.

### Zinc Hydrometallurgy

Zinc usually is found as a sulfide and such ores are roasted to convert the sulfide to an oxide which in turn is leached with sulfuric acid according to Eq. (6-2). The solution usually contains other impurities, such as copper, cadmium, etc. These metals are precipitated by displacement reactions upon agitating the solution with zinc dust. The zinc sulfate solution then is electrolyzed to produce metallic zinc. In

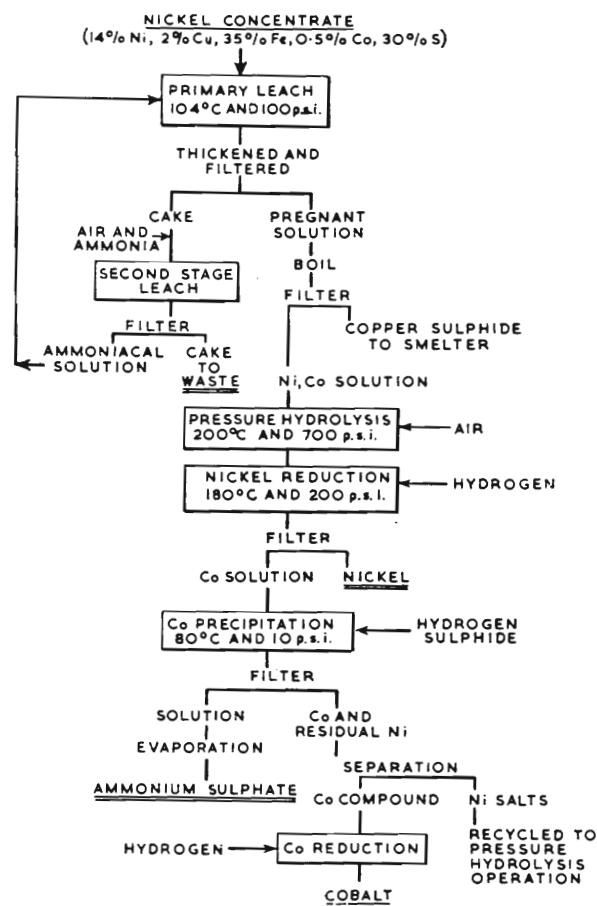


Fig. 6-7. Pressure Leach Separation of Copper, Nickel and Cobalt

Source: W. H. Dennis, *Extractive Metallurgy*, Philosophical Library, Inc., New York, 1965, p. 270.

### Hydrometallurgy

the electrolytic process, the sulfuric acid is regenerated and returned to the leaching operation.

### Hydrometallurgy of Nickel and Cobalt

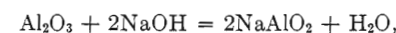
Sulfide minerals including nickel-cobalt-copper ores are dissolved readily in ammonia or sodium hydroxide solutions, or in sulfuric acid, under oxygen pressure at slightly elevated temperatures. This process for the recovery of nickel, cobalt, and copper has been practiced in Canada since the early 1950s. A flow sheet for the process is given in Fig. 6-7.

The finely ground concentrate is given a preliminary leach in an ammoniacal solution in an autoclave at about 100°C and 100 psi. Most of the copper and nickel are dissolved in this leach. After thickening and filtering, the pulp from the first leach is given a second leach under similar conditions. The iron is removed from solution as ferric hydroxide, which is filtered off with the residual ore. The "pregnant liquor" from the primary leach contains nickel, copper, and cobalt as amines and various ammonium salts. On heating this solution, ammonia is driven off and the copper is precipitated as a sulfide and filtered off. The solution which contains nickel and a small amount of cobalt is treated in an autoclave at 200°C under a high oxidizing pressure to decompose the complex ions containing sulfur. The solution then is treated in a two-step process at temperatures up to 200°C at high hydrogen pressures. Nickel is first precipitated. Precipitation is enhanced by addition of metallic nickel powder or by introduction of a suitable catalyst such as ferrous sulfate. The resulting solution contains cobalt and traces of nickel. By suitable adjustment of the temperature and pressure conditions, selective precipitation can be carried out in two stages on this solution. Overall recoveries are very high, ranging up to 90% or higher for nickel, about 90% for copper, and as high as 75% for the cobalt. This direct production of the metals eliminates electrolysis and the expensive pyrometallurgical processes that would have to be carried out to accomplish the same purification.

### Hydrometallurgy of Aluminum—Bayer Process

The commercial production of high purity aluminum (99+% or pure) by electrolysis in the Hall cell is made possible through the use of high purity alumina. The alumina for use in the Hall process is produced from bauxite ores using the Bayer process, a chemical process producing sodium aluminate that is soluble in alkali solutions. The aluminate is decomposed to produce aluminum hydroxide, which then is calcined to alumina. A schematic flow chart for the Bayer process is shown in Fig. 6-8. The steps in this process can be outlined as follows:

1. The bauxite is dried, calcined, and ground.
2. The bauxite powder is digested in a concentrated sodium hydroxide solution. To facilitate this digestion the reaction,



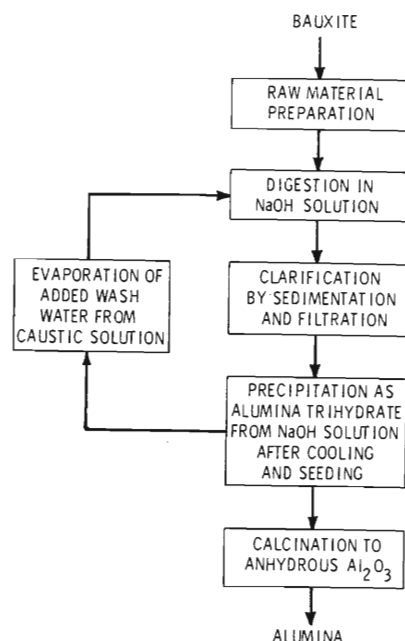


Fig. 6-8. Bayer Process Flow Sheet

is carried out in autoclaves at 50 to 70 lb psi pressure and a temperature of 160–170°C.

3. The solution and any residue is transferred to settling tanks where undissolved ferric oxide, silica, and sodium–aluminum silicates settle out.
4. The sodium aluminate solution is cooled to 25–35°C, precipitating the Al(OH)<sub>3</sub> and regenerating NaOH. Freshly precipitated aluminum hydroxide sometimes is stirred into the solution to “seed” the reaction. The sodium hydroxide is recirculated, concentrated by evaporation and new sodium hydroxide is added to compensate for losses.
5. The aluminum hydroxide is calcined at about 1100°C to produce alumina.

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## Discussion Questions

1. Uranium ore is leached with acid under an oxygen pressure of 10–15 psi according to the reaction,
 
$$\text{U}_3\text{O}_8 + \frac{1}{2} \text{O}_2 + 3\text{H}_2\text{SO}_4 = 3\text{UO}_2\text{SO}_4 + 3\text{H}_2\text{O}.$$
 What influence do the following variables have on the rate of pressure leaching?
  - (a) mesh size of ore
  - (b) temperature
  - (c) oxygen pressure
2. Describe briefly the influences of temperature, bath agitation, solute concentrations, and particle geometry on the kinetics of leaching.
3. Bacterial oxidation offers considerable potential as a mechanism which can enhance leaching of various ores. Discuss the mechanism and outline possible application of leaching reactions involving microorganisms.
4. Hydrometallurgical processes involving the gaseous reduction of metals from solution have been successfully operated on a commercial scale since 1955. However, production in the first decade or more has been limited to nickel, cobalt and copper. Discuss the reasons for this and project the potential for application of this processing operation to other metals.
5. The extension of hydrogen reduction of metals from aqueous solution to production of coated metallic powders and intimate mixtures of finely subdivided materials has been proposed. Discuss the technology and possible market for these processes.
6. Discuss Fig. 6-2 in terms of separating copper, nickel and cobalt. What is the possibility of developing a process for hydrogen reduction of zinc from aqueous solution?
7. Nearly all of the alumina used for metal production is prepared by the Bayer process. A recent investigation of the rate of solution of Gibbsite, the most important aluminum mineral in natural bauxites, in sodium hydroxide has shown that the reaction is reaction rate limited. In deriving a kinetic model, what variables should be included?
8. Discuss the economic and technological advantages and disadvantages of regeneration, neutralization, and disposal as alternative treatments for acid leaching solutions.

Problems

1. The rate of leaching of a copper ore with sulfuric acid has been measured under the following conditions:

| Rate (Mg Cu <sup>++</sup> /cm <sup>2</sup> -min) | Temperature (°C) | Acid concentration (Molarity) |
|--------------------------------------------------|------------------|-------------------------------|
| 1.09                                             | 40               | 0.685                         |
| 1.86                                             | 49.5             | 0.685                         |
| 0.554                                            | 40.9             | 0.103                         |
| 1.37                                             | 50.1             | 0.353                         |
| 1.83                                             | 41               | 1.377                         |

- Derive an equation or equations describing the rate of leaching as a function of temperature and acid concentration.
2. Copper, cadmium, and silver are recovered from a leaching solution by precipitation with excess zinc dust. Assuming that the zinc ion concentration is 114 g/liter and that its activity coefficient at this concentration level is close to unity, estimate the residual ionic concentrations of the recovered metals.
  3. Under certain circumstances, cementation of copper on nickel powder can be carried out economically, e.g., the cementation of copper with nickel from a nickel-rich electrolyte and recovery of nickel by conventional means. If during precipitation of copper with nickel powder in a sulfate solution the nickel ion concentration is 15 g/liter, estimate the residual copper ion concentration.
  4. A copper ore containing 0.63% CuO and 0.39% Cu<sub>2</sub>S is leached with a sulfuric acid-ferric sulfate solution. Upward percolation is carried out in a 9000 T (ore) vat. The system is on an 8-day leach—1-day wash cycle with the overflow composition averaging 23.4 g Cu/liter, 12.5 g H<sub>2</sub>SO<sub>4</sub>/liter and 2.2 g of Fe<sup>+++</sup> ion/liter. Calculate the composition of the original leaching solution if 90% of the oxide and 45% of the sulfide is recovered.
  5. The rate of cementation of copper with iron follows first-order kinetics with no appreciable back reaction. Derive a relation describing this behavior. What additional variables are likely to influence the cementation rate and how could they be measured?
  6. (a) What is the ionic activity of nickel under equilibrium conditions following precipitation of metallic nickel from a solution of pH = 5.5 in contact with 1 atm of hydrogen gas at 25°C?  
(b) Is this activity increased or decreased with  
(1) a decrease in pH of the solution.  
(2) an increase in hydrogen pressure.  
(c) In part (a), what would be the corresponding activity of ferrous ion?
  7. Separation of nickel and cobalt in acid solution depends on the pH and hydrogen pressure. At low concentrations, calculate the equilibrium ratio of nickel to cobalt in solution. What can be done to decrease the ratio?

8. What is the limiting equilibrium residual cobalt ion activity for precipitation from aqueous solution (pH = 6.6) with hydrogen at 50 atm?
9. What is the electrode potential for nickel-nickel ion (0.005 molal) in a sulfate solution at 25°C? At what pH would hydrogen at 10 atm be in equilibrium with the solution and pure nickel?

## CHAPTER 7

### Electrometallurgy

#### 7-1 Principles of Electrolysis

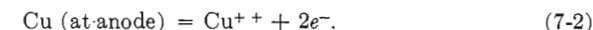
The use of electrical energy to win metals from ores, to recover metals from leaching solutions, and to refine metals establishes electrochemistry as an extremely important part of extractive metallurgy. Electrochemical engineering is employed in the separation of materials in electrolyzing solutions (as in the copper and zinc industries), in electro-refining of metals (as in the production of electrolytic copper, nickel, lead, etc.), and in the electrolysis of fused salt electrolytes (for the production of aluminum, magnesium, and alkali metals). Additional extensions of this science are found in electric furnace operations and in the conversion of chemical to electrical energy.

##### Half-Cell Reactions

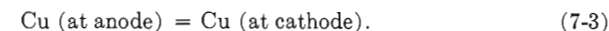
The relation between the chemical and electrical nature of the reactions taking place during electrolysis may be represented by electrochemical equations. Consider, for example, two strips of pure copper immersed in a copper sulfate solution. If an external circuit is set up so electrons flow between the two copper pieces, one will be the cathode in an electrolytic cell and the other will be the anode. Under the influence of the electrical potential between the two electrodes, copper ions in solution will migrate to the more negatively charged electrode, the cathode in this instance. At the cathode,<sup>1</sup> electrons are released which combine with the positively charged copper ions in the electrolyte to form atoms of copper deposited on the cathode. This half-cell reaction is represented by the relationship,



At the anode, to which the negatively charged sulfate ions are migrating, the reverse reaction occurs:



The copper ions combine with the sulfate ions in solution to form copper sulfate which in turn dissolves in the electrolyte and ionizes. Combining reactions (7-1) and (7-2), one obtains the overall cell reaction,



<sup>1</sup> As a general principle of electrochemistry, the cathode is the electrode where electrons enter the cell, and the anode is the electrode where electrons leave the cell.

This cell reaction represents the process occurring in electrolytic refining of copper. The theoretical voltage required to activate this cell reaction is infinitesimal, but in actual practice a finite voltage must be applied to the cell to force the reaction, as well as to overcome cell inefficiencies and losses that are described later.

### Faraday's Laws

The research of Michael Faraday (1791-1867) led to quantitative relationships describing the amount of electricity passing between electrodes in an electrolyte and the amount of material separated from or deposited on the electrodes. These relationships are defined by two laws which state that

1. The quantity of material released at an electrode is directly proportional to the quantity of electricity passed through the cell.
2. The same quantity of electricity will release the same number of equivalents of a substance.

The electrochemical equivalent of a substance is the number of grams of that substance released by 1 C (A-sec) of electricity. Thus, Faraday's second law says that chemical equivalents (atomic weight/valence) are proportional to electrochemical equivalents. The proportionality factor is Faraday's constant, given by the ratio of the gram equivalent weight to the electrochemical equivalent. This ratio, as determined for silver, is

$$\frac{107.88 \text{ g/g equiv}}{0.0011180 \text{ g/C}} = 96,496 \text{ C/g-equiv.}$$

TABLE 7-1  
Electrochemical Equivalent of Metals

| Metal    | Atomic weight | Valency | Chemical equivalent (atomic wt/valency) | Amount deposited (g/Ah) | Electrochemical equivalent (mg/C) |
|----------|---------------|---------|-----------------------------------------|-------------------------|-----------------------------------|
| Aluminum | 26.98         | 3       | 8.99                                    | 0.3358                  | 0.0930                            |
| Antimony | 121.76        | 3       | 40.58                                   | 1.4949                  | 0.2523                            |
| Cobalt   | 58.94         | 2       | 29.47                                   | 1.1000                  | 0.3054                            |
| Copper   | 63.54         | 2       | 32.77                                   | 1.1858                  | 0.3290                            |
| Gold     | 197.00        | 3       | 65.67                                   | 2.4524                  | 2.041                             |
| Hydrogen | 1.008         | 1       | 1.008                                   | 0.0376                  | 0.0104                            |
| Iron     | 55.85         | 3       | 18.62                                   | 0.6946                  | 0.2394                            |
| Lead     | 207.21        | 2       | 103.6                                   | 3.8654                  | 0.5368                            |
| Nickel   | 58.71         | 2       | 29.35                                   | 1.0946                  | 0.0340                            |
| Silver   | 107.88        | 1       | 107.88                                  | 4.0258                  | 1.1180                            |
| Tin      | 118.70        | 2       | 59.35                                   | 2.2144                  | 0.6150                            |
| Zinc     | 65.38         | 2       | 32.69                                   | 1.2192                  | 0.3385                            |

Source: Dennis, W. H., *Extractive Metallurgy*, p. 275, Philosophical Library, New York, 1965.

The quantity of electricity required to release 1 g equivalent weight of any substance is 1 F or 96,496 C (23066 cal/V-g equiv). Table 7-1 summarizes these electrochemical quantities for several common metals.

Faraday's second law may be expressed in differential form,

$$W = \frac{M i t}{nF}; \quad \frac{dW}{M} = dm = \frac{i}{nF} dt, \quad (7-4)$$

where

- $dW$  = weight of metal deposited, grams in time interval  $dt$ ,
- $M$  = atomic weight of metal deposited,
- $dm$  = number of gram moles of metal deposited in time interval  $dt$ ,
- $n$  = valence of metallic ion in electrolyte,
- $i$  = current, amp,
- $t$  = time, sec,
- $F$  = Faraday's constant, 96,496 abs C/equiv.

Thus the rate of deposition or flux of material proportional to the electrical current is

$$\frac{dm}{dt} = \frac{i}{nF}. \quad (7-5)$$

Integration of Eq. (7-4) yields an expression for the maximum theoretical quantity of material that can be liberated by a given amount of current, i.e., at 100% current efficiency.

### Reversible Cell Potential

Cell potentials depend not only upon the materials making up the electrodes and the overall cell reaction, but also upon the activities of the participating ions in solution and the temperature. Utilizing the definition of net electrical work which is equivalent to free energy,

$$\Delta G = -nF\epsilon, \quad (7-6)$$

where

- $n$  = number of equiv transferred/g-atom,
- $F$  = Faraday's constant,
- $\epsilon$  = cell emf;

and considering the reaction isotherm for a reaction,

$$aA + bB + \dots = cC + dD + \dots, \quad (7-7)$$

where

$$\Delta G = \Delta G^0 + RT \ln \left[ \frac{a_C^c a_D^d \dots}{a_A^a a_B^b \dots} \right], \quad (7-8)$$

then

$$-nF\epsilon = -nF\epsilon^0 + RT \ln \left[ \frac{a_C^c a_D^d \dots}{a_A^a a_B^b \dots} \right] \quad (7-9)$$

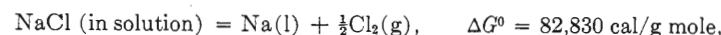
which yields the Nernst equation,

$$\epsilon = \epsilon^0 - \frac{RT}{nF} \ln \left[ \frac{a_C^c a_D^d \dots}{a_A^a a_B^b \dots} \right] \quad (7-10)$$

The standard free energy change is constant at constant temperature, and hence  $\epsilon^0$  is constant at constant temperature.

**Example Problem 7-1.** Calculate the reversible cell potential for the electrolysis of sodium and chlorine (1 atm pressure) from a molten mixture of sodium and calcium chlorides at 600°C. The sodium chloride is present in the salt solution at an activity of 0.4. The standard free energy of formation of liquid pure NaCl at 600°C is -82,830 cal/mole. The liquid pure chloride freezes at 800°C, but the data on "supercooled" liquid can be used to represent the thermodynamics of NaCl in the liquid electrolyte.

**Solution.** This situation is representative of conditions in the Downs cell during production of sodium and chlorine. Using Eq. (7-10) applied to the cell reaction,



$$\epsilon = \epsilon^0 - \frac{RT}{nF} \ln \left[ \frac{a_{\text{NaCl}_2^{1/2}}}{a_{\text{NaCl}}} \right].$$

The sodium and chlorine are released at unit activity, hence

$$\begin{aligned} \epsilon &= -\frac{\Delta G^0}{nF} + \frac{RT}{nF} \ln (a_{\text{NaCl}}) \\ &= -\frac{(82,830)}{(1)(23066)} + \frac{(4.575)(873)}{(1)(23066)} \log_{10} (0.4) \\ &= -3.59 - 0.069 = -3.66 \text{ V.} \end{aligned}$$

The reversible cell potential would be -3.59 V if the NaCl were at unit activity. Since the activity of the NaCl is reduced in the salt solution, the reversible cell potential is more negative by 69 mV. However, the actual cell voltage is approximately 6 V.

Standard electrode potentials have been determined for aqueous electrolytes at ambient temperature. By experimentally measuring the potential of metal-metal ion electrodes relative to a standard cell whose potential is defined by the hydrogen electrode (zero potential at 1 atm hydrogen gas and 25°C, the standard potential for several metal-metal ion electrodes and for other cell reactions can be defined. A summary of the standard electrode potentials for several half-cell reactions is presented in Appendix A, Table A-VIII.

#### Cell Voltages

Cell voltages are comprised of several components: (1) the  $IR$  drop to overcome the resistance of the electrolyte, bus bars, connections, etc., (2) the reversible

cell potential, (3) polarization, and (4) over-voltage. The total cell voltage is the sum of these four potentials.

**Ohmic Resistance.** From Ohm's law,  $E = IR$ , the contribution of ohmic resistance of the solution to the cell voltage may be computed.  $R$ , the resistance of the electrolyte in question, may be calculated from the equation,

$$R = \rho \frac{L}{A}, \quad (7-11)$$

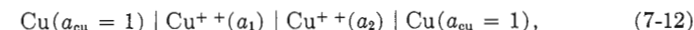
where

$L$  = average length of flow path,  
 $A$  = cross-sectional area,  
 $\rho$  = resistivity of electrolyte.

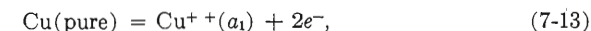
**Reversible Cell Potential.** The reversible cell potential can be calculated from Eq. (7-10).

**Polarization.** A polarization potential arises from a concentration difference between ions in the neighborhood of the electrode and those in the bulk of the electrolyte solution. The concentration of ions in the bulk phase can be measured directly, while the concentration at an electrode surface often can be estimated, thus permitting a calculation of the concentration polarization potential. The basis for the relationships by which the polarization potential may be computed are shown in the following manner.

Consider, e.g., a cell of the type,



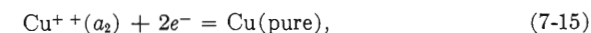
consisting of two pure copper electrodes immersed in solutions of copper-containing electrolyte in which the activities of the copper ions are equal to  $a_1$  and  $a_2$ , respectively. The electrode reaction on the left side is



with  $\epsilon$  given by

$$\epsilon_{13} = \epsilon^0_{\text{Cu}} - \frac{RT}{2F} \ln (a_1). \quad (7-14)$$

Again, for the reduction on the right side



$$\epsilon_{15} = -\epsilon^0_{\text{Cu}} - \frac{RT}{2F} \ln \left( \frac{1}{a_2} \right). \quad (7-16)$$

The overall cell reaction may be represented as



and the cell emf is

$$\epsilon_{17} = (\epsilon_{13} + \epsilon_{15}) = -\frac{RT}{2F} \ln \left( \frac{a_1}{a_2} \right). \quad (7-18)$$

Since  $a_1$  (concentration near the anode) is greater than  $a_2$  (concentration near the cathode), the sign of  $\epsilon_1$  will be negative. This decrease in cell potential indicates that any applied potential would have to increase, i.e. the polarization potential opposes the applied potential. The decrease in cell emf reflects the fact that at the anode the copper ions are being dissolved in a solution whose concentration is greater than the bulk electrolyte liquid and at the cathode copper ions are being removed from solution at a concentration level which is below that of the bulk electrolyte liquid.

A practical example of such a concentration cell may exist in an electrolytic processing operation if the solution near the anode builds up in metallic ion concentration or if there is a depletion of ions in the solution at the cathode. The case of a build-up of ionic concentration at the anode and a simultaneous depletion at the cathode is illustrated in Fig. 7-1. The concentration difference between the solution near the electrodes creates a potential difference that must be overcome and acts to increase the total cell voltage.

From Eq. (7-18), it is evident that the emf of this concentration cell arises from a transfer of copper ions from the solution where the ionic activity is  $a_1$  to the solution where the ionic activity is  $a_2$ . Furthermore, emf depends only on the ratio of the activities of copper ion at the electrode surfaces and not on the absolute value of the ionic activity. In the final cell emf, Eq. (7-18),  $\epsilon^0$  does not appear. This is true of all concentration cells. It may be concluded therefore, that for concentration cells,  $\epsilon^0$  is 0, and the emf equation takes on the simplified form,

$$\epsilon = - \frac{RT}{nF} \ln \left( \frac{a_1}{a_2} \right). \tag{7-19}$$

Since in cells of the type under discussion,  $a_2$  and  $a_1$  refer to the activities of the

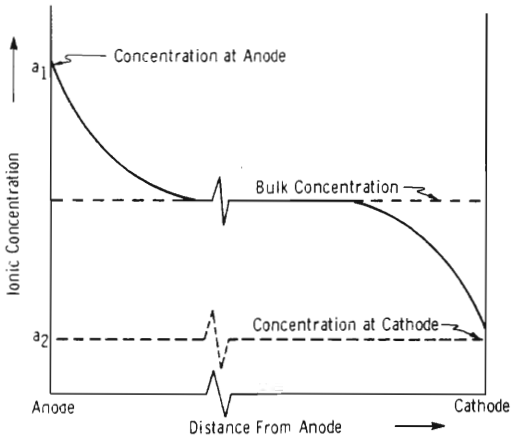


Fig. 7-1. Concentration Polarization in Electrolytic Cell.

metallic ion in solution, we may assume that for dilute solutions, these are essentially equal to or are proportional in the same manner to the concentrations,  $c_1$  and  $c_2$ . Thus, Eq. (7-19) may be written approximately as

$$\epsilon \simeq - \frac{RT}{nF} \ln \left( \frac{c_1}{c_2} \right). \tag{7-20}$$

The equation in this form may be used to calculate the concentration polarization potential of a cell where  $c_1$  refers to the surface concentration of the metallic ion in solution at the anode and  $c_2$  refers to the surface concentration at the cathode. Since we are interested in the ratio of the two concentrations, any consistent units may be used to express them.

**Over-Voltage.** In general, it is not possible to compute accurately the cell voltage contribution arising from gas over-voltage. The over-voltage is related to the potential required for evolution of gas on an electrode. The over-voltage has been found to increase with increasing current density and to decrease with increasing temperature.

The over-voltage is also a function of the nature of the electrode. The hydrogen over-voltage in ambient temperature, aqueous electrolyte cells for refining lead, mercury, zinc, and tin is high. These metals are poor catalysts for the reaction,



This over-voltage, however, is quite low for platinum, iron, and silver—metals which are good catalysts for the above reaction.

Other factors influencing the over-voltage are roughness of surface and electrode impurities. A rough surface has a low over-voltage, presumably because of the ability of the surface to act as a nucleating agent for the formation and evolution of the gas. And the hydrogen over-voltage tends toward the over-voltage of those impurities which are present in the electrodes. The source of impurities may lie not only in the electrodes themselves, but in traces of metal ions in the electrolyte which may plate out at the cathode.

### 7-2 Electrolysis of Fused Salts

An important process for the production of reactive metals is the electrolysis of fused salts. Such processes are carried out at relatively high temperatures, and consequently, differ in some aspects from electrolytic processes carried out in aqueous solutions, even though the principles involved are essentially the same for both. The engineering approach to processes used for electrolytic purification, or for the recovery of metals from leaching solutions are parallel to those for fused salt electrolysis and are described in the following sections.

Since highly electropositive metals tend to react at high temperatures with most materials, common pyrometallurgical processes cannot be used for smelting them. A straightforward method for producing these metals is first to purify a salt of a reactive metal and then electrolyze the salt for recovery of the metallic element. This technique is used for the production of aluminum, magnesium, beryllium,

cerium, lithium, sodium, potassium, and calcium. It also could be used to produce less reactive materials, although usually without economic advantage.

The electrolysis of a fused salt bath requires a container for the bath equipped with a device for collecting the metal produced, and a cathode and an anode to deliver the electric power for decomposition. A direct current is passed through the molten bath. The bath may be the pure salt of the metal or the salt of a more reactive metal into which a compound containing the desired metallic element is dissolved. Examples of these two cases would be the production of sodium from pure liquid sodium chloride, and the production of aluminum from a fused cryolite bath ( $\text{AlF}_3\text{-3NaF}$ ) in which a small amount of alumina is dissolved, respectively.

The salt or oxide of the element to be produced must be pure. If less electrochemically active impurities were present in the electrolyte, they would be reduced and migrate to the cathode, thus contaminating the element being produced. Furthermore, displacement reactions could occur at the cathode, causing transfer of impurities from the electrolyte into the reduced metal. Consequently, one of the critical steps in fused salt electrolysis is purification of the electrolyte. For example, the Bayer process for producing pure alumina from bauxite ores has permitted the electrolytic production of high purity aluminum on a commercial basis.

Some of the engineering aspects and operating characteristics of fused salt electrolytic cells are presented in the following examples. Descriptions of commercial production cells are given for aluminum, magnesium, and sodium.

### Aluminum

Aluminum is produced by electrolysis of alumina from a bath of fused cryolite. This process was developed independently in 1886 by Hall in the United States and Heroult in France. Cryolite melts just below  $1000^\circ\text{C}$ , and because of a depressed freezing point in the dilute solution region, is able to dissolve from 4–20 wt% alumina while remaining liquid at temperatures above  $980^\circ\text{C}$ . Beyond a concentration of 20 wt% alumina, the melting point rises rapidly. Aluminum production cells use commercial cryolite, which consists of aluminum fluoride and sodium fluoride in a 1–3 molar ratio. Potassium or calcium fluorides also can be substituted for the sodium fluoride. Since these fluoride solutions are highly corrosive, successful development of the electrolysis technique depended upon coping with this material's corrosive nature. The problem was solved by using an iron vessel lined with carbon as a cathode and a carbon electrode as an anode, a design still in use today.

The commercial production of high purity aluminum (99+ % or pure) requires high purity alumina. The alumina for use in the Hall process is produced from bauxite ores using the Bayer process (see Hydrometallurgy).

**Hall (Heroult) Process.** A cross-sectional view of an aluminum reduction cell is shown in Fig. 7-2. This cell consists of a steel shell with a thin lining of insulating brick. Inside the refractory lining is a carbon lining several inches thick which serves as the cathode. The anodes are carbon and project through a crust of electrolyte frozen at the surface. Modern cells use the continuous Soderberg electrode, a single anode in which a mixture of carbon and pitch is continuously fed from above through a rectangular metal box. The heat of the cell bakes the mixture and forms a continuous graphite anode.

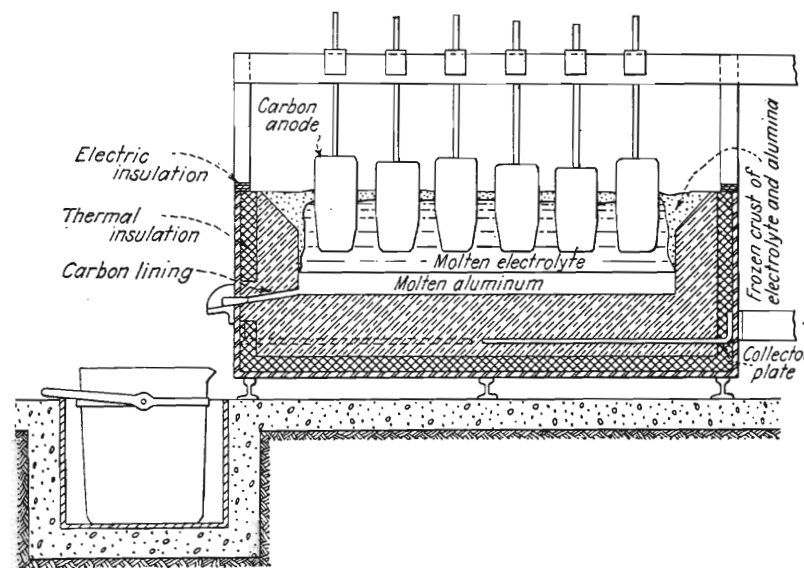
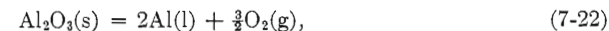


Fig. 7-2. Early Aluminum Cell

Source: Electrochemical Engineering, C. L. Mantell, McGraw-Hill Book Company, Inc., New York, 1960, p. 379.

The alumina concentration in the electrolyte ranges from  $2\frac{1}{2}$ –20 wt%. The cell temperature is in the vicinity of  $900$ – $1000^\circ\text{C}$ . The cell operating voltage is  $6$ – $7\frac{1}{2}$  V, and the current density ranges up to  $1000$  A/ft<sup>2</sup> of cathode. At 100% current efficiency this current density would produce  $\frac{3}{4}$  lb metal/hr-ft<sup>2</sup> of cathode; the actual current efficiency in the Hall cell is 80–90%. Anode consumption ranges 0.6–0.8 lb of carbon/lb of alumina, and the alumina requirements are approximately 2 lb of alumina per pound of aluminum. The total amperage for an aluminum cell varies with the size and cell design but may range up to 50,000 A or higher. An operating aluminum cell is shown in Fig. 7-3.

**Cell Potential.** The reversible cell potential can be calculated using the principles outlined in the previous chapter. At the cathode, pure aluminum (99+ %) is deposited as a liquid. At the anode, pure oxygen gas is liberated, which immediately reacts with the carbon anode material giving off carbon monoxide and some carbon dioxide gas. These reactions may be summarized as



$$\Delta G^\circ = +401,400 - 77.0 T \text{ cal/mole}; \quad (7-23)$$



$$\Delta G^\circ = -28,200 - 20.16 T \text{ cal/mole}. \quad (7-25)$$

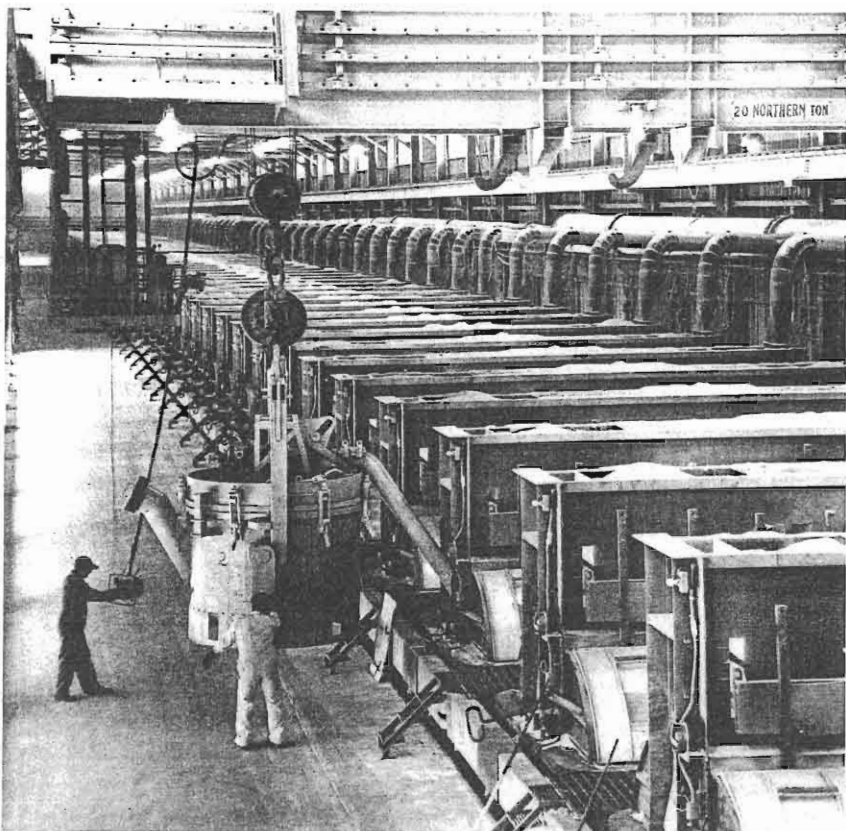


Fig. 7-3. Electrolytic Cells for Aluminum Production at Badin Smelting Works  
Courtesy of Aluminum Company of America

A crane-man at Alcoa's Badin (N.C.) Smelting Works is manipulating a large crucible into position to tap one of the electrolytic cells containing molten aluminum. Assisting him is a pot serviceman. One spout of the crucible is lowered into the pot, then, through vacuum, molten metal is drawn into the crucible from the pot bottom.

At cell operating temperatures the  $\text{CO}/\text{CO}_2$  mixture in equilibrium with graphite is nearly pure  $\text{CO}$  (actual  $\text{CO}/\text{CO}_2$  ratios are on the order of 0.5-1). In calculating the theoretical minimum voltage at which aluminum will be deposited at the cathode in the Hall process, it may be assumed that the anode gas is essentially pure carbon monoxide and that the salt bath is saturated with alumina. Calculating the free energy of the sum of the reactions given in Eqs. (7-22) and (7-24),



$$\Delta G^\circ = 316,800 - 137.48 T \text{ cal/mole.} \quad (7-27)$$

The decomposition potential,  $\epsilon$ , (in this case,  $\epsilon^\circ$ , since reactants and products are in their standard states) is related to the free energy of reaction by the relation,

$$\Delta G^\circ = -nF\epsilon^\circ. \quad (7-28)$$

For the above case, at  $900^\circ\text{C}$ , the result is

$$\epsilon^\circ = -1.13 \text{ V.} \quad (7-29)$$

There is still considerable speculation about how much effect the oxidation of the carbon anode has on the reaction voltage of the aluminum cell. The point in question is the influence of the energy of formation of the carbon monoxide and carbon dioxide formed at the anode.

The reversible cell potential at  $900^\circ\text{C}$ , (assuming that the carbon-oxygen reaction at the anode does *not* influence the cell potential) is  $-2.24 \text{ V}$  for the decomposition of alumina into liquid aluminum and gaseous oxygen. However a typical operating cell potential is  $6 \text{ V}$  or more. This additional voltage is due to over-voltage at the anode and ohmic drop through the bus bars, cathode lining, electrolyte, and anode. The over-voltage at the anode is a function of current density, while the resistance of the electrolyte varies with alumina concentration. In addition the decomposition voltage will increase as the alumina activity decreases, i.e., as the concentration of alumina decreases from the saturation value. Optimum operation of the reduction cell requires that changes be made in operating conditions as the alumina concentration changes.

Another interesting aspect of Hall cell operation is the "anode effect," a sharp increase in voltage across the cell which raises the cell potential from about  $6 \text{ V}$  to something over  $30 \text{ V}$ . The "anode effect" occurs when the electrolyte does not wet the anode, creating a gas-filled gap between the anode and the electrolyte. The voltage increase is localized in this region and the cell requires stirring or the addition of alumina to correct the condition.

### Magnesium

Approximately 85% of the world's magnesium is produced electrolytically and the remaining 15% is produced by thermal reduction processes. Early production of magnesium by electrolysis was carried out from a fused salt bath in a manner similar to the Hall process for producing aluminum. This process is not used at the present time, and magnesium is produced electrolytically from anhydrous  $\text{MgCl}_2$  or from  $\text{MgCl}_2$  containing about 25% water.

The Dow Chemical Company, primary producer of magnesium in the United States, developed its first magnesium processing plant at Midland, Michigan, using brine from wells. Electrolysis of the solution of mixed salts magnesium chloride, sodium chloride, and calcium chloride yields magnesium metal and chlorine gas. A typical electrolyte composition is 25%  $\text{MgCl}_2$ , 15%  $\text{CaCl}_2$ , and 60%  $\text{NaCl}$ . A schematic diagram of the Dow Magnesium Cell is shown in Fig. 7-4. The temperature in the cell is maintained between  $700$  and  $750^\circ\text{C}$  by controlled firing of natural gas. The graphite anodes are inserted from the top. The cathodes in the Dow Cell are coiled iron liners spaced very closely and symmetrically around each

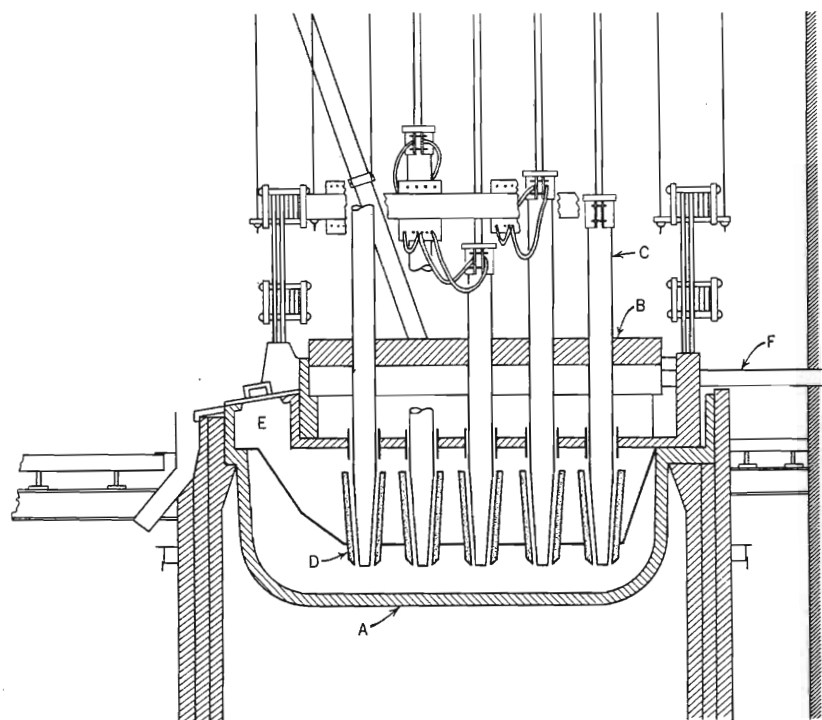


Fig. 7-4. Diagram of Dow Magnesium Cell—The steel container (A) is equipped with ceramic cover (B) through which pass graphite anodes (C). The magnesium is deposited on the cathodes (D) and is diverted as it rises into collection sump (E). The chlorine is withdrawn through vent (F).

Courtesy of Dow Chemical Company

graphite anode. The cell voltage ranges from 5–8 V, and typical Dow Cell currents may range up to 100,000 A. The power requirement is approximately 10 kWhr/lb of magnesium produced.

The magnesium is lighter than the salt electrolyte and after being released on the cathode shell, it floats to the surface where it is trapped in inverted troughs. Magnesium is recovered as a liquid and in subsequent handling it is protected from atmospheric oxidation with a chloride flux or by molten sulfur. Chlorine gas is evolved at the anodes and is collected for use in other chemical operations, principally in the production of hydrochloric acid.

The present primary source of magnesium is from seawater. At Freeport, Texas, the Dow Chemical Company, using calcined oyster shells as a source of calcium hydroxide, precipitates magnesium from seawater as magnesium hydroxide. The magnesium hydroxide is treated with HCl and the  $MgCl_2$  slurry is dried to

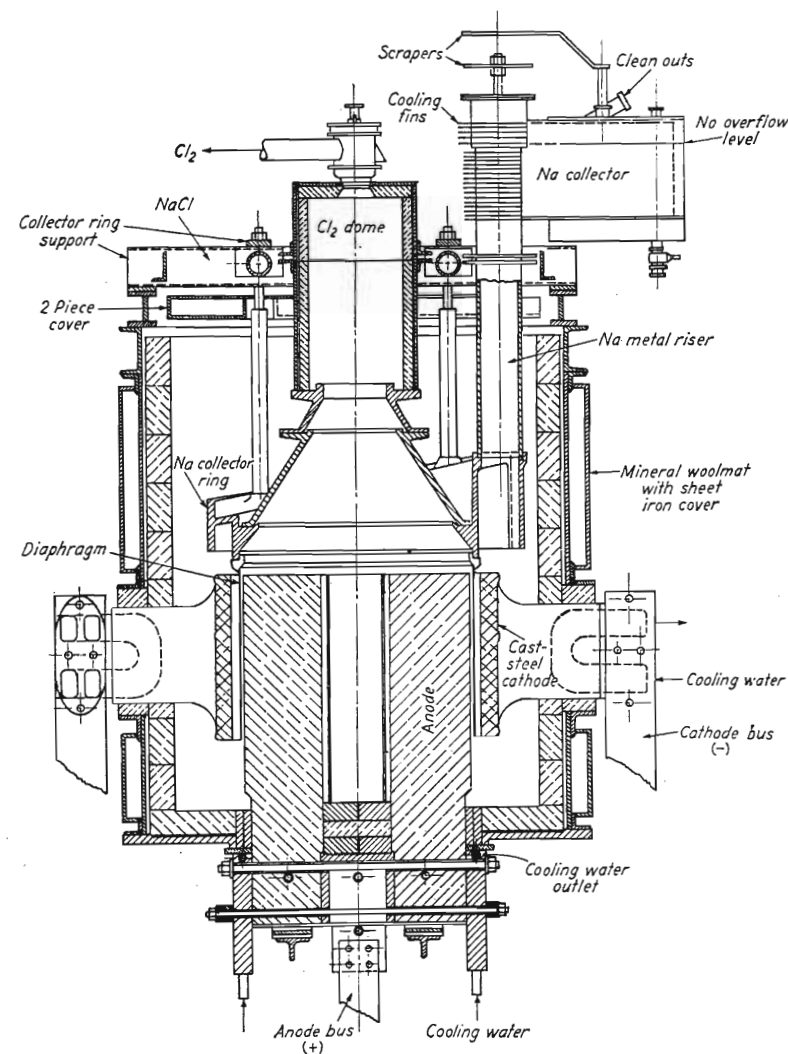
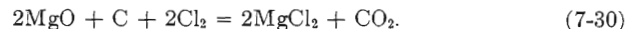


Fig. 7-5. Knapsack Sodium Cell

Source: *Electrochemical Engineering*, C. L. Mantell, McGraw-Hill Book Company, Inc., New York, 1960, p. 413.

$\text{MgCl}_2 \cdot 1.5 \text{H}_2\text{O}$ . It is not necessary to dry the  $\text{MgCl}_2 \cdot 1.5 \text{H}_2\text{O}$  further, and this material is added directly to the chloride electrolyte of the magnesium cell. Chlorine gas,  $\text{HCl}$ , and water vapor are liberated at the anodes. The water vapor driven out of the electrolyte attacks the graphite electrodes, whereas in an anhydrous magnesium chloride cell operation, the carbon anodes are permanent since they are not attacked by the liberated chlorine gas.

The magnesium industry in Norway employs a chlorination process to produce  $\text{MgCl}_2$  using magnesium oxide [ $\text{Mg}(\text{OH})_2$  is precipitated from sea water and dried to  $\text{MgO}$ ] and carbon, which are heated in an atmosphere of chlorine gas according to the reaction,



The magnesium chloride is treated in a cell similar in principle to that shown in Fig. 7-4, except that the cell is of refractory construction and utilizes anode and cathode compartments to keep the liquid magnesium and chlorine gas separated.

### Sodium

Metallic sodium is produced in a Castner cell by electrolysis of sodium hydroxide or in a Downs cell by electrolysis of sodium chloride dissolved in calcium chloride. The design of the two cells is fairly similar. A Downs cell is shown in Fig. 7-5.

The Downs cell operates at temperatures near  $600^\circ\text{C}$ . The cell current furnishes sufficient thermal energy for the cell to maintain an electrolyte of approximately 60% calcium chloride and 40% sodium chloride in the liquid state. Sodium is collected at wire gauze diaphragms and the chlorine is collected in a dome at the top of the cell. Current efficiencies are in the area of 75–80%, and cell amperages may range as high as 50,000 A. The advantages of sodium chloride electrolysis over sodium hydroxide electrolysis lie primarily in use of a cheaper raw material and production of chlorine gas as a by-product. Approximately 5 kWhr of electricity are expended per pound of sodium recovered.

## 7-3 Electrolytic Refining

The electrolysis of solutions containing metallic ions often is employed to refine metals or to recover them from the products of leaching operations. Solutions containing metallic ions are electrolyzed to deposit the element in metallic form. By taking advantage of the difference in electrode potentials between various metals, it is often possible to separate several metallic elements from the same solution by electrolytic means.

Electrolytic refining usually is carried out by passing a current through an ionic solution between an anode partially refined by some other process and a cathode. The anode is electrochemically dissolved in the electrolyte to form ions of the desired element, which are transported through the electrolyte to the cathode where they are deposited as atoms, thus effecting the refining of the anode material. A design engineer dealing with electrolytic processes is interested in the power and voltage requirements, plating rates, effects of impurities, size of the operation

(i.e., the number of tanks, the volume of solution, number of cathodes and anodes), and other factors that influence the economics of the operation.

Electrolytic refining is used throughout the metallurgical industry, but it is the principal refining method used for copper, nickel, and much of the lead produced. This type of refining also permits recovery of precious metals and other impurities as by-products. Electrolytic refining is practiced to some extent for purification of other metals such as iron, cobalt, tin, silver, and gold.

### Copper Refining

Electrolytic refining yields the very pure copper used by the electrical industry. In addition, gold, silver, and the platinum metals are recovered from the crude copper supplied to the electrolytic cell. The primary source of selenium is from the anode slimes of copper refining cells, while nickel, arsenic, antimony, tellurium and other metals also are recovered as impurities. Based on average analyses, 1 million lb of crude copper may contain on the order of 400 oz of gold, and 25,000 oz of silver, as well as a few ounces of palladium and platinum. Concentrations are quite low, but because of the large volume of copper handled, this source of precious metals is extremely significant. About 75% of the total world production of silver comes as a by-product of copper and lead refining. A flow sheet for a copper refinery is presented in Fig. 7-6.

**Anode Preparation.** Blister copper, the product of a converter or a blast furnace, is usually porous and brittle if directly cast into anodes. If further refining to improve physical properties is necessary, the blister copper is remelted in large reverberatory furnaces and subjected to oxidizing conditions to remove various impurities, particularly the residual iron and sulfur. The oxygen often is supplied from air blown through steel pipes into the furnace below the surface of the copper. The oxygen oxidizes some of the copper and also reacts with iron and sulfur, with the iron and copper oxides combining with silica present to form a slag. The charge then is subjected to a reducing stage in which the oxygen dissolved in the copper is removed by reaction with a reducing agent, carbon or a hydrocarbon gas. At this point the copper is cast into an anode weighing 500–700 lb and measuring about 3 ft square; the anodes contain less than 1% total impurities. Figure 7-7 is a picture of copper anodes, while a Walker casting machine for continuous production of anodes is shown in Fig. 7-8.

**Refining Systems.** Several basic electrical hook-ups, each with its own advantages, are possible in electrolytic process equipment. The two principal systems, parallel (multiple) and series, are shown in Fig. 7-9. A parallel system is one in which the electrode plates within each tank are connected in parallel so that the voltage drop across the entire tank is the same as that between any pair of plates in the tank. The advantage of this system is that there is a smaller voltage drop than in the series connections and, therefore, fewer losses due to short circuiting.

A series connection is one in which the electrodes within the tanks are connected in series. Consequently, the total voltage drop across the cell is the sum of the voltage drops between each electrode. In the series system, each plate acts as an anode on one side and a cathode on the other, whereas in the parallel system, each

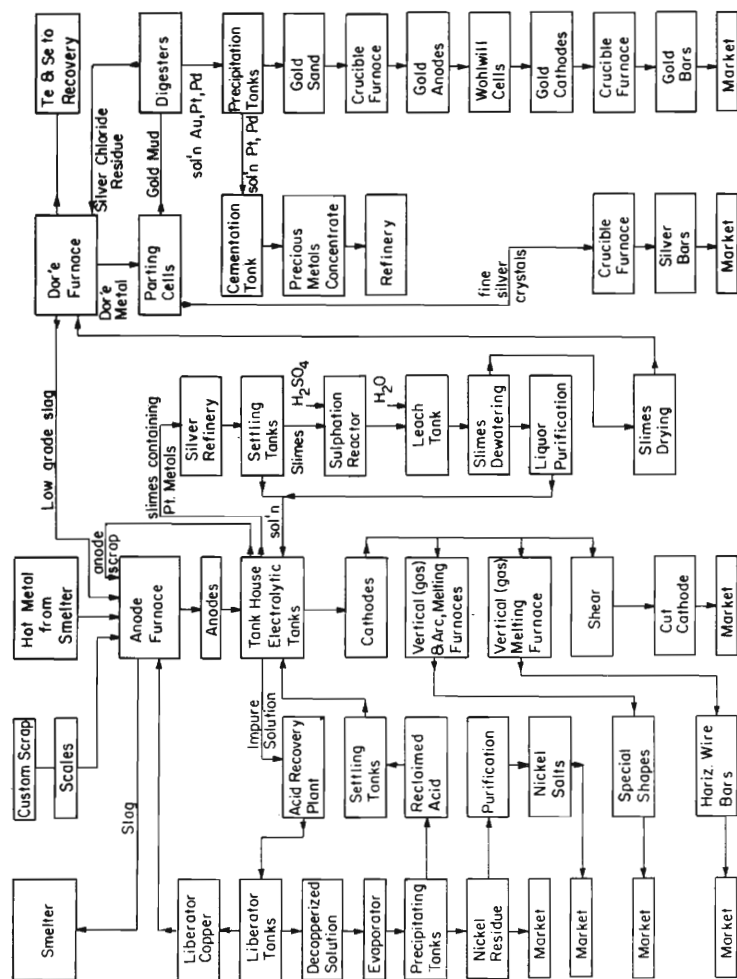


Fig. 7-6. Flowsheet of Copper Refinery  
Courtesy of International Nickel Company of Canada

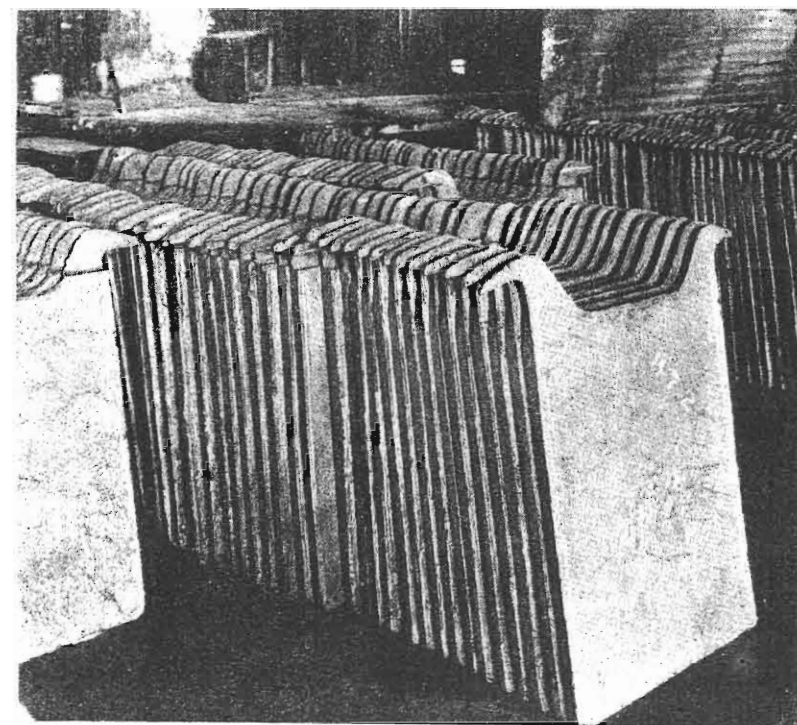


Fig. 7-7. A Stack of Copper Anodes at Anconda

Source: C. Hayward, *Outline of Metallurgical Practice*, D. Van Nostrand Company, Inc., New York, 1952, p. 95.

electrode behaves wholly as either a cathode or an anode, the reaction taking place on both surfaces. Thus, less space is required for the series arrangement, and there is no necessity for preparing special starting sheets. Furthermore, the tanks themselves are usually connected in series with the total number in the circuit being determined by the supply voltage and power of the generator.

Although the pure series system is used in a few large refineries, the system that is most commonly employed in metallurgical plants is the multiple system. In this system, the plates within each tank are connected in parallel, but the tanks themselves are connected in series. In the multiple system, cathode starting sheets are required. These sheets are approximately  $\frac{1}{8}$  in thick and the same shape as the anodes. The cathode starting sheets are prepared in special stripper cells where a copper deposit is built up on oiled copper blanks and subsequently stripped off for starting the cathode in a refining cell. Hard-rolled copper blanks often are used as cathode starting sheets.

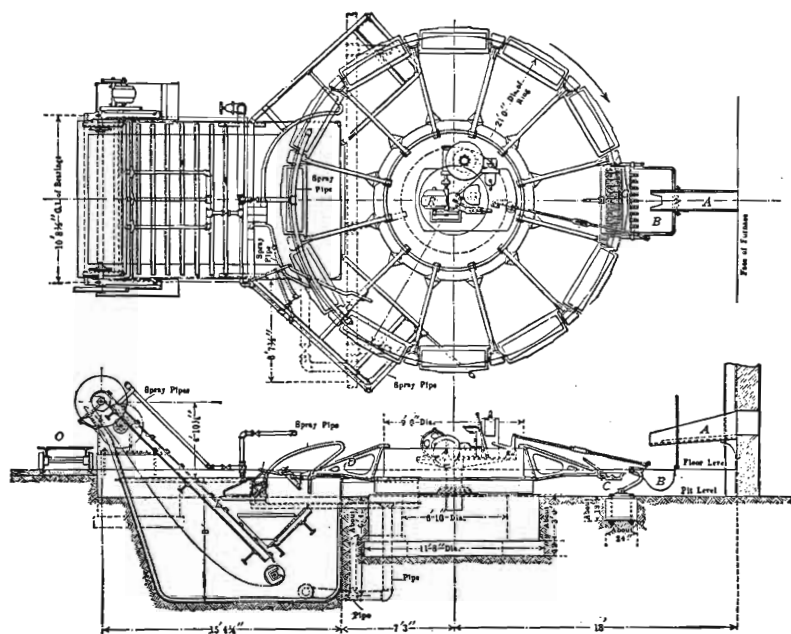


Fig. 7-8. Walker Casting Machine for Copper—Note the furnace spout *A* delivering metal to tipping ladle *B* which fills the molds *C*. The wheel is rotated in a clockwise direction by a motor controlled by an operator. When solid the copper passes under a water spray. The molds are automatically dumped at the left and the copper falls into a water bosh, from which it is withdrawn by endless metallic belt *L* and discharged to car *O*. The inverted empty mold is sprayed with clay, bone ash or special wash, righted and again passes under the ladle. Various details are shown in the figure.

Source: C. Hayward, *Outline of Metallurgical Practice*, D. Van Nostrand Company, Inc., New York, 1952, p. 93.

**Tank House Practice.** A typical tank house is shown in Fig. 7-10. The tanks are usually constructed of concrete and are lined with antimonial lead (3–6% antimony), but considerable research is being carried out on plastic and fiberglass linings for tanks.

The tanks contain from 20–40 cathodes and anodes in most instances. The electrolyte is a copper sulfate solution (40–50 g/liter) containing 100–200 g/liter of sulfuric acid. The electrolyte is circulated to permit temperature control and purification and also to minimize concentration polarization at the surfaces of the electrodes. Purification of the electrolyte is required since soluble impurities such as iron, zinc, nickel, and arsenic tend to accumulate in the solution, and there may be some build-up of copper concentration. Electrolysis often is used in a separate system to purify the electrolyte.

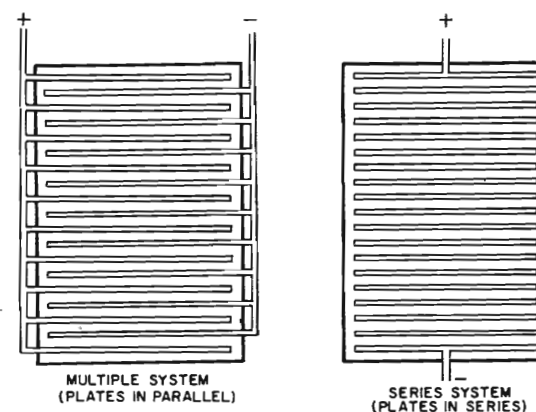


Fig. 7-9. Electrical Connections for Electrolytic Refining Cells

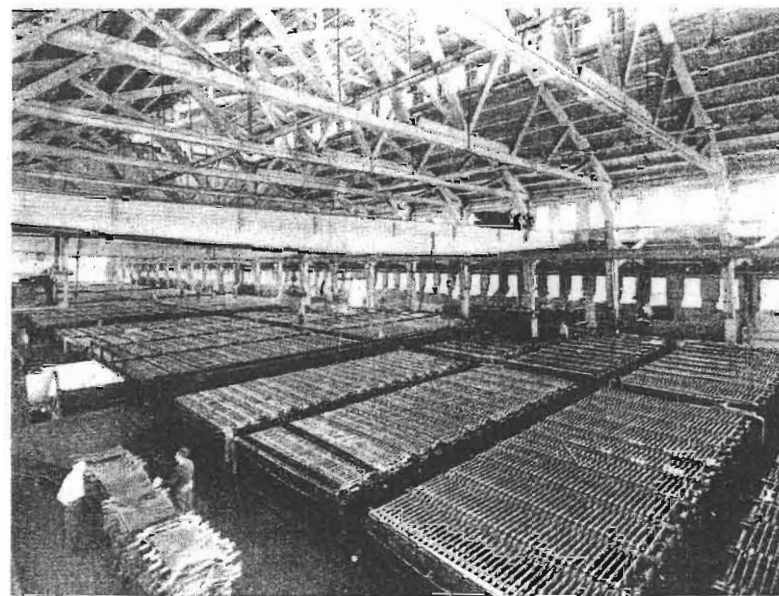


Fig. 7-10. Tank Room in an Electrolytic Copper Refinery

Source: J. Newton, *Extractive Metallurgy*, John Wiley and Sons, Inc., 1959, New York, p. 459.

In a typical large refinery operation, the electrolyte is circulated at a rate of approximately 4–5 gal/min. The tanks are 10–12 ft long, 3–4 ft wide, and about 4 ft deep. The electrolyte is maintained at a temperature of 45–60°C, since the resistance of the solution to passage of current accounts for over one-half of the total cell resistance, and this resistance decreases with increasing temperature. Glue and other additives are added to the electrolyte to improve the physical characteristics of the cathode deposit. Other chemical additives may be put into the electrolyte to depress the deposition of impurity ions.

The current density on the cathode usually ranges between 20 and 30 A/ft<sup>2</sup>. Low current densities offer the advantages of a better grade of cathode copper, more efficient recovery of precious metals, and a lower power cost of electrolysis. On the other hand, a larger plant then is required for a given copper production; however, an economic optimum exists for all these cost factors.

The voltage per tank varies with the current density and the resistivity of the solution. The theoretical cell voltage is zero, but the usual plant voltage is on the order of 0.2–0.4 V per tank. The cathodes are changed every 10–15 days, and the anode life is approximately twice that of the cathode. The anodes are removed from the tank when approximately 10–15% of the original weight remains; this material is returned to the anode furnace for remelting. The tanks are periodically drained and the slimes washed out, filtered, and processed for the recovery of selenium, tellurium, and precious metals.

**Example Problem 7-2.** How much copper is plated out in a copper refining tank operating at 20 A/ft<sup>2</sup> (current density at cathode). The cell is arranged in a parallel circuit and contains 38 anodes and 39 cathodes. The cathodes are 36 in. square and current efficiency for the tank is 90%.

**Solution.** On a per day basis for 1 ft<sup>2</sup> of operating surface

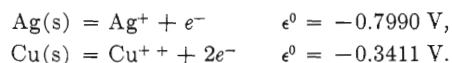
$$\begin{aligned}\text{Copper Deposited} &= (0.90)(20)(24 \times 3600) \frac{(63.6/2)}{(96500)} \\ &= (\text{current efficiency}) \left( \frac{\text{A}}{\text{ft}^2} \right) (\text{time, sec}) \left( \frac{\text{g/equiv wt}}{\text{A sec/equiv wt}} \right) \\ &= 512 \text{ g Cu/ft}^2 \text{ day}\end{aligned}$$

With this cell arrangement the area is

$$\begin{aligned}(38)(2)(3 \times 3) &= 684 \text{ ft}^2 \\ \frac{(512)(684)}{453.6} &= 770 \text{ lb Cu/day.}\end{aligned}$$

**Example Problem 7-3.** Copper is electrolytically refined at 60°C using an electrolyte containing 42 g/liter of copper. The voltage drop from anode to cathode is 0.03 V. At what silver ion concentration in the electrolyte could silver be plated out at the cathode?

**Solution.** Considering the half-cell reactions, from Table A-VIII,



The half-cell potential for the oxidation of copper is

$$\epsilon = \epsilon^0 - \frac{RT}{nF} \ln \left[ \frac{a_{\text{Cu}^{++}}}{a_{\text{Cu}}} \right].$$

The concentration of copper ion is (42/63.6) = 0.66 g-atom/liter. Substituting concentrations for activities and noting that the metals are at unit activity,

$$\begin{aligned}\epsilon_{\text{half-cell}} &= -0.3441 - \frac{(1.987)(333)(2.303)}{(2)(23066)} \log_{10}(0.66) \\ &= -0.3441 + 0.0060 \\ &= -0.3381.\end{aligned}$$

The half-cell potential for the reduction of silver is

$$\epsilon = - \left( \epsilon^0 - RT \ln \left[ \frac{a_{\text{Ag}^+}}{a_{\text{Ag}}} \right] \right).$$

The overall cell potential is

$$\begin{aligned}\epsilon_{\text{cell}} &= \epsilon_{\text{anode}} + \epsilon_{\text{cathode}}, \\ -0.03 &= -0.3381 + 0.7990 + \frac{RT}{nF} \ln(a_{\text{Ag}^+}).\end{aligned}$$

Substituting concentration for activity,

$$\begin{aligned}-0.4909 &= \frac{(1.987)(333)(2.303)}{(1)(23066)} \log(C_{\text{Ag}^+}), \\ \log(C_{\text{Ag}^+}) &= - \frac{(0.4909)(23066)}{(1.987)(333)(2.303)} = -7.43, \\ C_{\text{Ag}^+} &= 3.7 \times 10^{-8} \text{ g-atom/liter.}\end{aligned}$$

This low concentration of silver is not reached because of the presence of a small amount of chloride ion in the electrolyte that precipitates any electrolyzed silver as AgCl. The silver also is found in the anode mud as Ag<sub>2</sub>Se.

**Treatment of Insolubles.** The “anode mud” or slime accumulating in a copper refining cell may contain slightly less than 1% gold, from 5–25% silver, and from 15–40% copper. The remainder consists of selenium (often 5–20%) and small concentrations of tellurium, arsenic, antimony, lead, and traces of nickel and other metallics. A typical slime analysis is given in Table 7-2.

Special treatment of the “anode mud” is carried out, particularly for the recovery of silver, gold, platinum, palladium, selenium, and tellurium. The raw slime is washed, filtered, and roasted in an oxidizing atmosphere at 700°F. This converts the copper to copper oxide which is leached out with sulfuric acid. The slime then is filtered, and melted and refined in a small “Dore” reverberatory furnace. During refining in the Dore furnace, the lead is oxidized to a slag, and antimony and some

TABLE 7-2  
Analysis of Blister Copper, Anodes, and Cathodes

| Analysis  | Blister      | Anode        | Cathode     |
|-----------|--------------|--------------|-------------|
| Copper    | 99.0140%     | 99.4220%     | 99.9800%    |
| Oxygen    | 0.6910%      | 0.1540%      |             |
| Sulfur    | 0.0185%      | 0.0026%      |             |
| Arsenic   | 0.0464%      | 0.0435%      | 0.0010%     |
| Antimony  | 0.0350%      | 0.0317%      | 0.0010%     |
| Lead      | 0.0039%      | 0.0042%      | Nil         |
| Selenium  | 0.0184%      | 0.0176%      | 0.0003%     |
| Tellurium | 0.0122%      | 0.0122%      | 0.0002%     |
| Nickel    | 0.0140%      | 0.0146%      | 0.0010%     |
| Silver    | 63.31 oz/ton | 62.44 oz/ton | 0.30 oz/ton |
| Gold      | 0.265 oz/ton | 0.265 oz/ton |             |

Log of Tank House (One Tank)

|                             |           |
|-----------------------------|-----------|
| Total weight of anodes      | 14,065 lb |
| Weight of anode scrap       | 1,678 lb  |
| Weight corroded from anodes | 12,387 lb |

|                                            |           |
|--------------------------------------------|-----------|
| Total electrolysis, 31 days, 17 hr, 55 min |           |
| Weight of deposited copper                 | 11,837 lb |
| Average amp during run                     | 6,700     |
| Current efficiency, %                      | 91.3      |

|                                           |             |
|-------------------------------------------|-------------|
| Slime                                     | 51 lb 13 oz |
| Pounds of slime per ton of copper refined | 8.37        |

|                |         |                  |
|----------------|---------|------------------|
| Slime analysis |         |                  |
| Copper         | 18.80%  |                  |
| Silver         | 51.008% | 14,877.73 oz/ton |
| Gold           | 0.2171% | 63.32 oz/ton     |
| Arsenic        | 3.90%   |                  |
| Antimony       | 8.04%   |                  |
| Lead           | 1.06%   |                  |
| Selenium       | 4.37%   |                  |
| Tellurium      | 2.99%   |                  |
| Nickel         | 0.05%   |                  |

Source: C. L. Mantell, *Electrochemical Engineering*, p. 165, McGraw-Hill, New York, 1960.

selenium and tellurium are volatilized and recovered as flue dust. Selenium and tellurium are removed primarily by alkaline fluxes. The product, Dore metal, often contains over 98% silver, approximately 1% gold (sometimes as high as 10%) and a small amount of other metallic impurities. The crude silver is cast into anodes and electrolyzed to remove silver in Thum or Moebius electrolytic cells. The electrolyte in these cells is a solution of silver nitrate. These two refining systems, shown in Fig. 7-11, employ canvas diaphragms to retain the gold slime and prevent

mixing with the cathode deposit. The silver deposit is very pure, often 99.99% silver. The Wohlwill process employs a hot acidic gold chloride solution for electrolyzing gold anodes which are prepared from the slime of the Thum or Moebius cells. Since platinum and palladium are soluble in the Wohlwill process electrolyte, they are permitted to accumulate and then are precipitated with ammonium chloride.

*Refining of Copper Cathodes.* The cathodes produced in the electrolytic refining of copper are of extremely high purity but contain some sulfur. This impurity is removed by remelting the copper, usually in an electric furnace.

Oxygen content also is important since it controls the "set" (shape of cast surface) of the copper. The oxygen concentration in the cathodes is very low, of the order of 10 ppm or less. Usually no care is taken to keep the oxygen concentration low, and often it is necessary to leave 0.03–0.05 wt% oxygen in the finished copper to produce a casting with a level surface, especially if bars for wire drawing are cast from the remelted cathodes. Alternatively, very low oxygen contents are often desired.

Copper, free from oxygen, is used in electrical products. The very low concen-

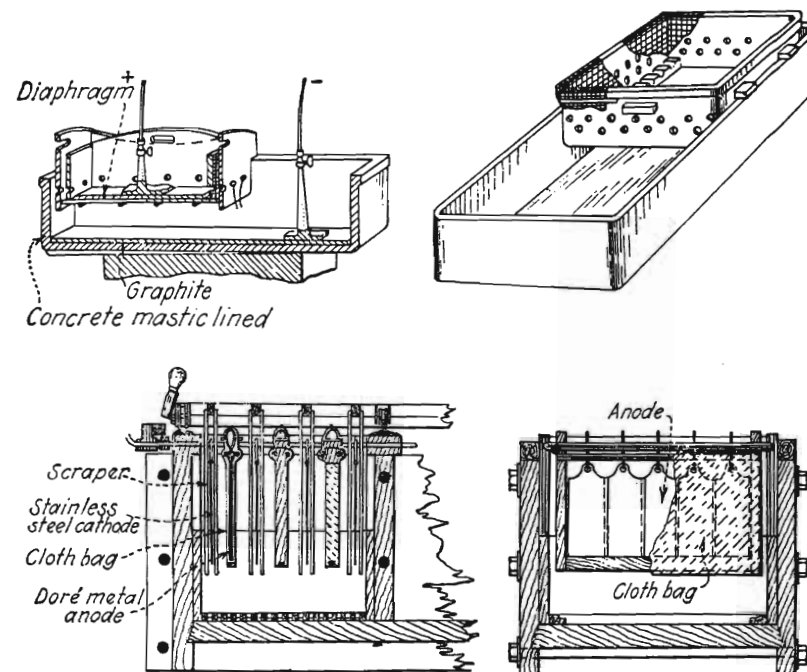


Fig. 7-11. Thum and Moebius Cells for Separating Silver from Other Noble Metals

Source: *Electrochemical Engineering*, C. L. Mantell, McGraw-Hill Book Company, Inc., New York, 1960, pp. 163–9.

trations of oxygen can be reached by removing oxygen from the molten copper in several ways: (1) by using carbon and casting under reducing conditions, (2) by using a deoxidizing agent other than carbon, usually phosphorus, or (3) by extruding directly an electrolytically deposited brittle cathode. The removal of oxygen with carbon or reducing gases, and casting under reducing conditions produces oxygen-free, high-conductivity copper.

#### Nickel and Lead Refining

Nickel is electrolytically refined in a nickel sulfate solution containing about 50 g/liter nickel, 20 g/liter boric acid and 50 g/liter sodium chloride. The anodes are approximately 95% nickel and contain 2–2½ wt% copper together with small amounts of iron and sulfur. The current density ranges from 12–15 A/ft². Precautions are taken to avoid contamination of the cathode with the principal impurities of the nickel anode, copper, and iron. As with silver recovery, each cathode is enclosed in a canvas diaphragm, and the electrolyte is circulated to minimize iron and copper contamination of the cathode. Then the copper and iron are removed from the electrolyte, the copper by "cementing out" on an iron surface, and the iron by oxidation with air precipitating it as a hydrate.

The electrolytic refining of lead is carried out by the Betts process, in which cast lead anodes are electrolyzed in a solution containing lead fluosilicate ( $\text{PbSiF}_6$ ) and free hydrofluosilicic acid ( $\text{H}_2\text{SiF}_6$ ). The process produces a very pure lead, and practically all the impurities accumulate as anode mud. This method is particularly significant in that it permits removal of bismuth from the lead.

#### Electro-Winning Metals from Leaching Solutions

Many low-grade ores are treated for recovery of metallics by leaching the mineral with an acidic solution which then is electrolyzed. The metal is recovered by electrolytic precipitation and the electrolyte is regenerated as fresh leaching solution. Two distinctly different reactions are involved at the electrodes. At the cathode, the metallic ion is reduced to the metal. At an inert anode, acid is formed by hydrolysis of an anion in the electrolyte. Hence, the overall cell voltage is usually much larger than the cell potentials of a few tenths of a volt encountered in electrolytic refining. In electro-winning of copper, the cell voltage is approximately 2 V, whereas it is 3–3.7 V for zinc, 2.5–3 V for antimony, and about 5 V for manganese.

There are many copper ores found in the world that are very low in metallic value, containing less than 0.5% copper. Sulfuric acid is used to leach copper from the ore. Prior to electrolysis the leaching liquors are dechloridized. Agitation with "cement" copper often is employed to remove the chlorine by formation of insoluble  $\text{CuCl}$ . This treatment also reduces the ferric ions to ferrous ions. Electro-winning cells employ inert anodes, which may be either copper or lead alloys for electrolysis in sulfate solutions.

The control of electrolyte composition in electro-winning is particularly important. This may be emphasized by considering the deposition of zinc from sulfate solutions. The feed to the electrolytic cells may contain about 100 g of

recoverable zinc/liter, and the cell would correspondingly discharge over 100 g of sulfuric acid/liter of electrolyte. The presence of antimony in the electrolyte is particularly troublesome, since a concentration of as low as 1 mg/liter will result in a poor cathode deposit. Arsenic and cobalt cause similar problems. Other electrolyte reactions, such as oxidation of ferrous or reduction of ferric ions, often cause fluctuations of current efficiency and may cause redissolution of the deposit. The presence of iron in zinc ores requires a high acid concentration in the leaching solution to dissolve the zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ). The use of concentrated acid results in the solution of more iron, which precipitates arsenic and antimony. Copper, cadmium, and cobalt often are removed from zinc leaching solutions by agitating the electrolyte with zinc dust at a temperature of about 80°C. These metals are precipitated by the zinc, so that the purified solution is relatively free of these elements. The starting cathodes for zinc recovery are made of aluminum sheet with an aluminum conductor bar welded to them, and the cathodes are stripped approximately once a day. Current densities range from 50–100 A/ft².

High purity (99.98%) manganese is produced by electro-deposition. The potential of manganese in the electromotive force series makes it difficult to deposit electrolytically, and requires considerable care in controlling electrolyte composition and temperature. Preliminary concentration of manganese ores usually is made by gravity methods. The ores are leached with sulfuric acid, and the leaching solution is purified by depositing copper on iron. Iron and arsenic are removed by oxidizing with air and adding  $\text{MnO}_2$ . Copper and nickel are removed by addition of potassium or sodium ethyl xanthate. Electrolysis is carried out with lead anodes and stainless steel cathodes separated by canvas diaphragms. Current density is on the order of 20 A/ft². Current efficiency is only 50–60% and the electrical energy required ranges from 3.5–5.5 kWhr/lb manganese. This is 2–3 times the requirement for electro-deposition of copper.

Electro-winning is a very effective and efficient means for recovering metals from low-grade ores. The electrolytic refining of copper, lead, and nickel is carried out primarily for recovery of precious metals. In the case of copper, electrolytic refining is the only practical method for removing gold and silver. However, in the case of lead, the Parkes process represents an alternative approach.

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## Discussion Questions

- What are the reasons for electrorefining nickel? What is the theoretical voltage per cell? Account for the differences between the theoretical voltage and the practical operating voltage. If a nickel ion of the type  $(\text{Ni complex})^+$  could be electrodeposited, would there be any advantage?
- Discuss the electrowinning of metals from aqueous chloride solution as contrasted with electrolysis of sulfate solution.
- Discuss possible improvement of the Hall cell by development of inert anodes. What are the material requirements? What materials might be used? How would cell operation be affected?
- Describe a process which would permit continuous metal reduction from a fused salt bath.
- Consider the electrolysis of magnesium chloride.
  - Why is magnesium never electrolyzed from pure  $\text{MgCl}_2$ ?
  - Why are high concentrations of  $\text{KCl}$  to be avoided in the salt bath?
  - What happens to impurities such as  $\text{Al}$ ,  $\text{Cu}$ ,  $\text{Ni}$ , and  $\text{Zn}$  in the bath?
- The feed analysis to a magnesium reduction cell based on a feed of 5200 lb and the production of 1000 lb of magnesium is:

| Salt            | Feed Analysis | Impurities<br>lb Added | Sludge<br>lb Removed |
|-----------------|---------------|------------------------|----------------------|
| $\text{NaCl}$   | 1.0%          | 52                     | 152                  |
| $\text{CaCl}_2$ | 0.75%         | 39                     | 38                   |
| $\text{MgCl}_2$ | 75.0%         |                        | 63                   |
| $\text{MgO}$    | 3.0%          | 156                    | 65                   |

What is happening in the cell in addition to reduction of magnesium? What measures should be taken to provide for continuous production?

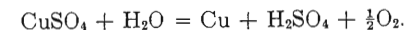
- What pollution control techniques are available for disposal of aqueous electrolyte solutions?

## Problems

- Determine the potential for a cell composed of a hydrogen electrode and a copper-aqueous copper chloride electrode.
- Nickel is electrolytically refined at  $40^\circ\text{C}$  using an electrolyte containing 50 g/liter of nickel ion. The impure anodes contain  $2-2\frac{1}{2}\%$  wt% copper which can plate out at the cathode. At what level of copper ion must the electrolyte be

maintained to avoid copper contamination of the cathode?

- Quantitatively define a procedure for electrolytically separating copper, nickel, and iron from an anode which is essentially an impure copper containing about 1% iron and 5% nickel.
- Starting sheets are used in a lead electrolytic refining process with a submerged cross section of  $32 \times 27$  in. The potential drop between anodes and cathodes is maintained at 0.4 V. The average current density is  $18.5 \text{ A/ft}^2$ .
  - At a current efficiency of 85%, calculate the time required to deposit 420 lb of lead per starting sheet?
  - Compute the energy required per pound of refined lead.
- A copper refining cell is operating with an electrolyte which contains 0.05 mole/liter of stannous ion. At what concentration of cupric ion will the tin start to precipitate in preference to copper?
- The overall reaction describing electrowinning of copper from a sulfate solution is:



The anode reaction has a standard electrode potential of +1.23 V. Calculate the reversible cell potential if the pH is 0.4 and the concentration of copper ion is 40 g/liter. In a commercial operation of this type, the cell voltage is on the order of 2 V. Explain the difference, if any, between the theoretical and the operating voltages.

- Compute the minimum theoretical voltage for electrolytically reducing magnesium in the cell described below.

|              |                                                                                                                  |
|--------------|------------------------------------------------------------------------------------------------------------------|
| Cell:        | Steel shell construction<br>Natural gas fired at $700^\circ\text{C}$<br>Cathode—steel shell<br>Anode—carbon rods |
| Electrolyte: | 25% $\text{MgCl}_2$<br>60% $\text{NaCl}$<br>15% $\text{CaCl}_2$                                                  |
| Product:     | Liquid magnesium floating on bath<br>Gaseous chlorine evolved at anode                                           |

Assume the electrolyte behaves ideally.

- Compute the reversible cell potential required to reduce cadmium from a liquid chloride melt containing  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{CdCl}_2$  at  $500^\circ\text{C}$  if the cadmium chloride activity is 0.25.
- An aluminum reduction cell may be regarded as operating so that the gas evolved at the carbon anodes is in equilibrium with graphite at the operating temperature.
  - Calculate anode carbon consumption per pound of aluminum produced when the operating temperature is  $800^\circ\text{C}$ .
  - At an operating temperature of  $1000^\circ\text{C}$ , the anode gas is essentially pure  $\text{CO}$ . The cell bath is saturated with  $\text{Al}_2\text{O}_3$ . What is the theoretical minimum voltage at which aluminum will be deposited at the cathode?

## CHAPTER 8

### Melting, Pouring, and Solidification

#### 8-1 Melting Practice

The advantages of a molten phase make it desirable to produce and refine metals in the liquid state. Subsequent to this, the metal is poured into a mold of desired shape and permitted to solidify in either a casting or an ingot form.

##### Thermal Requirements for Melting

The minimum power required to raise a metal from room temperature to some temperature above its melting point is equivalent to the enthalpy increase that the metal experiences in changing from the lower to the higher temperature. However, the actual power requirements are much greater than this, and may be determined from an overall heat balance for the melting process. In writing such a heat balance, several factors must be considered: (1) the energy input, (2) the sensible heat of the metal before and after the operation, (3) the sensible heat increase of the melting unit itself, and (4) the heat losses, which include not only radiation and convection from the exposed surfaces of the melting unit, but also any heat removed by the cooling water that often is used to protect critical areas of the melting unit. The heat balance is written most conveniently for a given period of time. The calculation of the required power input then depends upon the type of unit used.

##### Melting Units

Two types of electrical melting units are schematically represented in Fig. 8-1. The induction melting unit, Fig. 8-1A, is quite efficient since the thermal energy is generated directly in the metal. The charge is placed in a crucible surrounded by a coil which is supplied with a rapidly alternating current. The rise and fall of alternating current flowing through the coil causes a varying magnetic inductive force; this force produces electrical eddy currents in the metal which are dissipated in the form of heat. The power taken up from the coil by the metal is thus dependent upon the induction coil, its size and number of turns, crucible geometry and frequency of the electrical input, and also upon the electrical properties of the metal being melted.

Metals such as copper, brass, or aluminum, which are not melted easily by induction because of their relatively low resistivity, may be placed in a container made of a material such as carbon, which can be heated by the induction coil. Or, if a reaction would take place between the metal and the carbon crucible, it is possible to surround a refractory oxide crucible with an inductively heated cylinder. The cylinder, usually a high melting point metal, is called a susceptor. A material



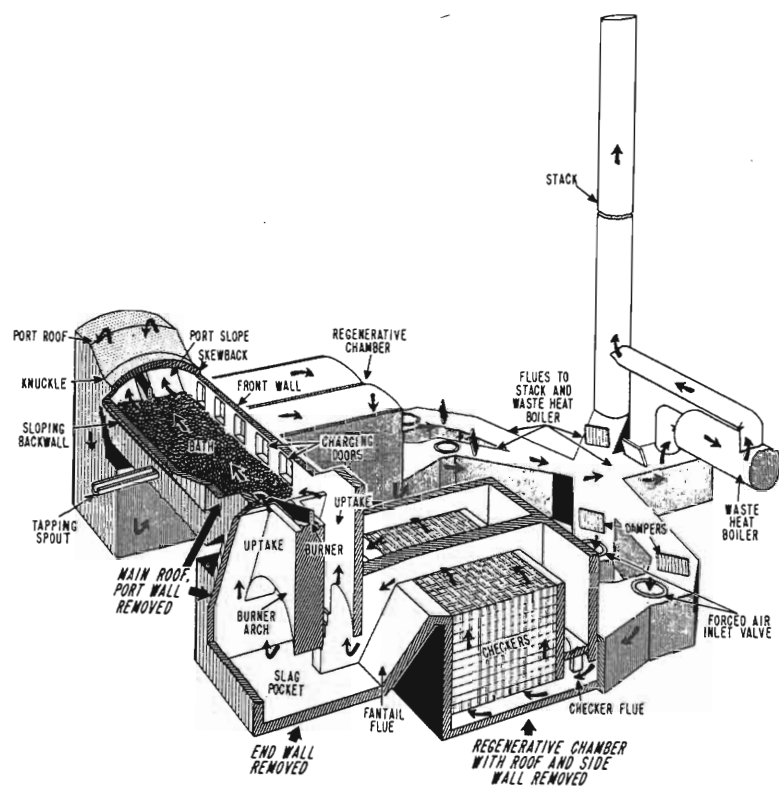


Fig. 8-3. Open Hearth Furnace

Source: *The Making, Shaping and Treating of Steel*, edited by Harold E. McGannon, Pittsburgh, United States Steel Corporation, 9th edition, 1971, p. 508.

A third type of electrical melting unit, one utilizing resistance heating elements, is sometimes used to melt metals, but usually is restricted to low-melting metals or small laboratory melts. Several different types of resistance melting units are in use, but the energy generally is supplied by radiation from a heating element. For operation at relatively low temperature, oxidation-resistant alloys (usually nickel-chromium base) often are used as heating elements; for slightly higher temperatures, nonmetallic elements, such as silicon carbide may be employed; and for operation at very high temperatures (approaching 4000°F) carbon resistors may be used, provided they are protected by an inert atmosphere.

In contrast to the use of electric power, heat may be supplied to a melting furnace by burning a low-cost fuel such as natural gas, fuel oil, or coke. Such a furnace may be of the shaft, retort, or reverberatory type. However, the apparent

economic advantage of using these types of fuels often is offset by the deleterious effects of melt contamination by sulfur in the fuel, e.g., as in the case of steel or by the costs of gas cleaning equipment to prevent air pollution.

Nevertheless, a large portion of the steelmaking in the United States still is carried out in open-hearth furnaces, a gas or oil fired reverberatory type furnace shown in Fig. 8-3 (see also Fig. 4-1 for reverberatory type furnace). Heat transfer in the open hearth furnace includes all of the common heat flow mechanisms—conduction, convective heat transfer in liquids and gases, and radiation from the gas flame and the hot interior refractories. In an effort to obtain a high flame temperature, the open hearth employs a regenerative heat transfer system, as seen in Fig. 8-4. By periodically reversing the direction of firing in the furnace, the hot combustion gases are passed out of the furnace through a set of brick checkers that recover heat from the expended combustion gases. The incoming air is passed through the previously heated checker work at the opposite end of the furnace before being fed to the burner. This technique for preheating the combustion air in the regenerative type of furnace provides fuel economy.

The cupola melting unit, a coke-fueled shaft furnace, is shown in Fig. 8-5. This furnace is used primarily in foundries for the melting of cast iron, although it is sometimes used to prepare a modified pig iron for use in steelmaking operations. Modern furnaces often employ a water-cooled shell and an air blast that is preheated before being blown into the furnace to react with the coke. The reaction chemistry of the melting zone of the cupola is shown in Fig. 8-6.

The choice of a melting unit depends upon economics and the required metallurgical and temperature control. The replacement of Bessemer steelmaking facilities by open hearths at the turn of the century, and the present replacement of open hearths by basic oxygen steelmaking furnaces are examples of improved melting techniques which provide economy of operation and improved product quality. In the iron foundry industry, at the present time the electric furnace is replacing in part or supplementing the melting capacity normally carried by the cupola furnace.

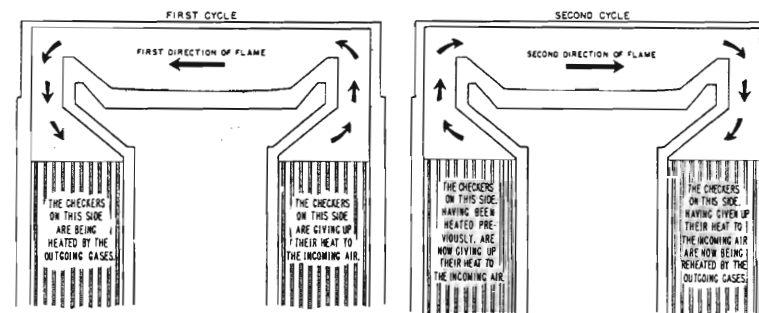


Fig. 8-4. Preheating Combustion Gases in Regenerative Furnaces

Source: *The Making, Shaping and Treating of Steel*, edited by Harold E. McGannon, Pittsburgh, United States Steel Corporation, 9th edition, 1971, p. 505.

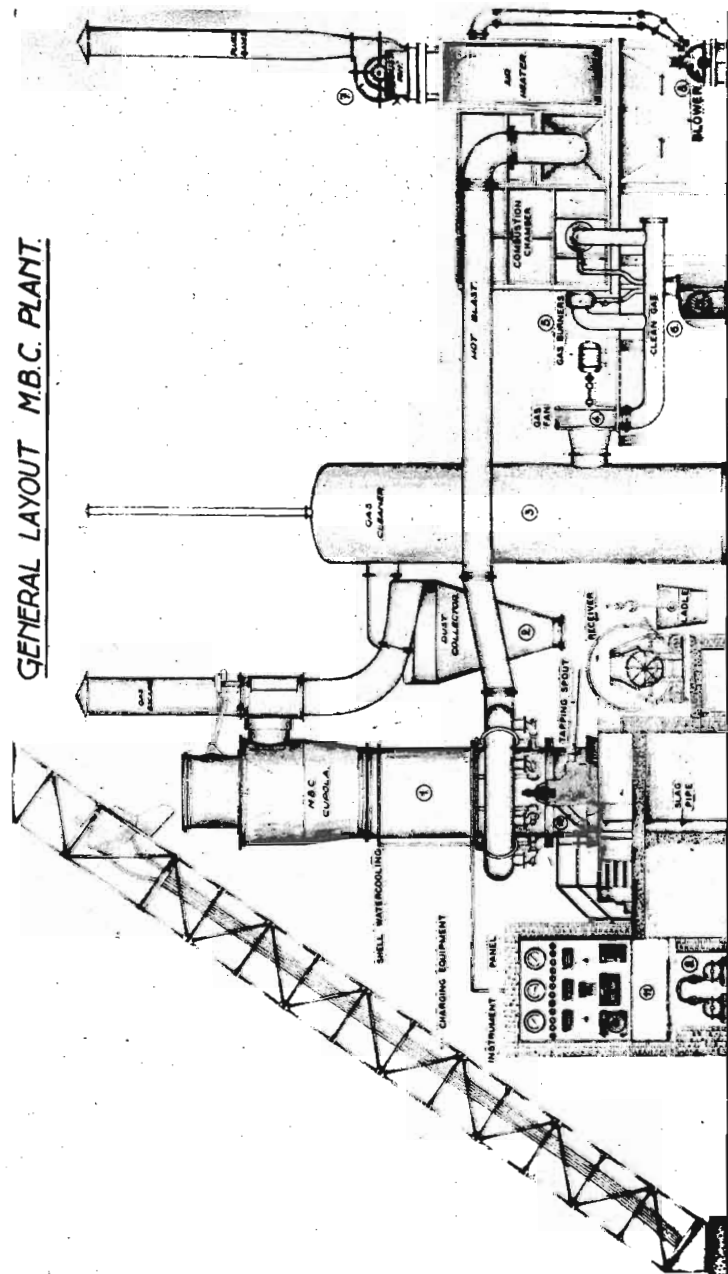


Fig. 8-5. General Layout and Charging System for Metallurgical Blast Cupola Plant

Source: *The Cupola and Its Operation*, 3rd edition, The American Foundrymen's Society, 1965, p. 30.

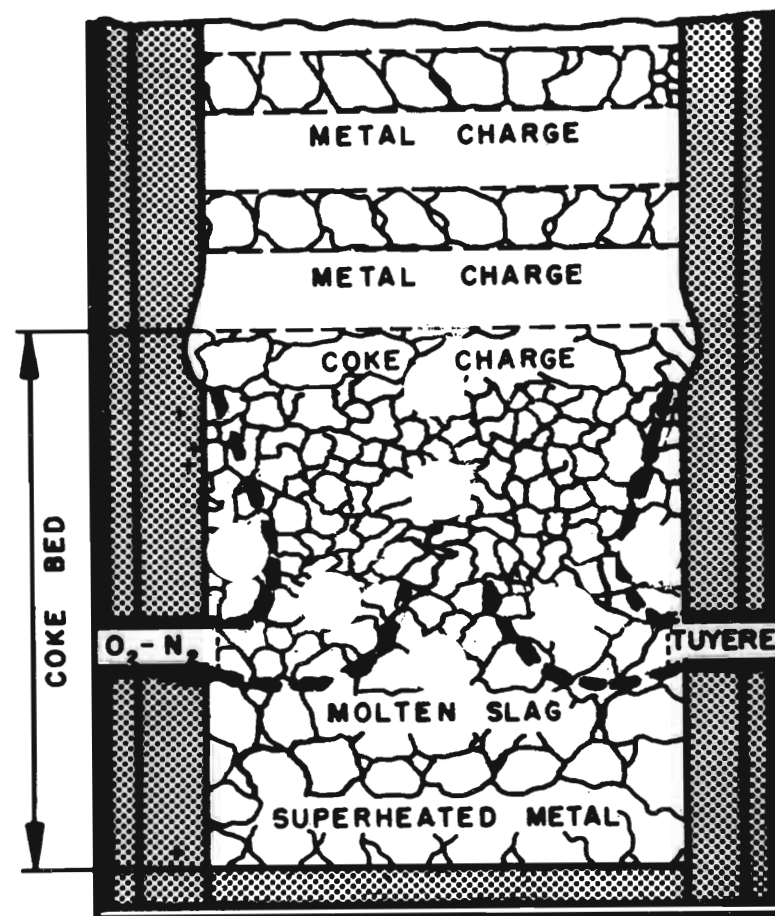


Fig. 8-6. Cross-section of Cupola Showing Reaction Areas

Source: *The Cupola and Its Operation*, 3rd edition, The American Foundrymen's Society, 1965, p. 26.

The greater metallurgical control, as well as greater production flexibility for the electric arc furnace, has increased industry interest in the electric furnace as a prime melting unit. The cost of electrical power, and the melting capacity which influences capital costs, are important factors in optimizing the economics of a melting facility.

#### Sensible Heat of the Metal

The sensible heat of the metallic charge may be calculated from a knowledge of the input and output temperatures of the charge and its specific heat. A more convenient method for handling such data is to tabulate the enthalpy increments for a given amount of metal, e.g., 1 lb mole. Table A-IX, Appendix A, gives the enthalpy increments for several metallic elements.

To compute the rate of heating, one must know the total heat transferred from the hot internal surfaces of the melting unit to the metal, or the heat transferred from the burning fuel or direct arc to the metal. One of the most important modes of heat transfer is radiation.

#### Sensible Heat of the Melting Unit

The temperature increase of various portions of the melting unit also must be included in the heat balance. If the operation is carried out on a continuous or semi-continuous basis, the temperature distribution in the melting unit can be assumed constant. In this case, sensible heat changes in the equipment itself are negligible. However, the change in enthalpy of the melting unit can be considered in evaluating the heat balance. To do this, it is necessary to know the temperature distribution and also the enthalpy increments as a function of temperature for the materials making up the furnace. Another approach that often is satisfactory, but less accurate, is to assign a factor to this quantity such that the sensible heat increase of the melting unit is represented by a fraction of the heat energy taken up by the metal. One may then multiply the sensible heat of the metallic charge by a factor ranging from 1.1–1.5, for most cases.

#### Heat Losses

The principal heat losses in melting operations are the radiation and convection losses from the exposed surfaces of the furnace. These losses may be computed by balancing the heat loss through the walls of the furnace with that lost by radiation and convection from the surface. This may be represented by the conservation relation,

$$q_{\text{cond}} = q_{\text{conv}} + q_r \quad (8-1)$$

A trial-and-error approach to this problem is necessary where one solves the following equation for the interface temperature  $T_0$ :

$$q = \frac{kAm}{\Delta x} (T_i - T_0) = h_c A_0 (T_0 - T_s) + \sigma e_0 A_0 (T_0^4 - T_s^4), \quad (8-2)$$

where

- $T_i$  = temperature of internal surface of furnace,
- $T_0$  = interface temperature between outer surface of the melting unit and surroundings,
- $T_s$  = temperature of surroundings,
- $k$  = thermal conductivity of furnace lining,
- $Am$  = mean area of lining,
- $\Delta x$  = thickness of lining,
- $\sigma$  = Stefan-Boltzmann constant,  $.173 \times 10^{-8}$  Btu/ft<sup>2</sup>·hr·°R<sup>4</sup>,
- $e_0$  = emissivity of the outer surface and surroundings, assumed equal,
- $A_0$  = outer area of melting unit,
- $h_c$  = convective coefficient from surface of unit (which may be taken on the average as being  $0.3 [T_i - T_s]^{0.25}$  for plane surfaces).

An example problem utilizing computer techniques for solution is presented in Appendix B (Problem 6).

In addition to heat losses from the exterior surfaces of a melting unit, heat may be lost to cooling water that is used to maintain low temperatures in certain critical areas of the furnace. In the case where the metal surface is exposed directly to the surroundings, one may compute the heat losses on the basis of radiation from that surface.

#### Mass and Energy Balance on Melting Unit

A material and energy balance on the cupola melting furnace is presented below to illustrate the engineering approach and point out the factors which must be considered in preparing a mass and heat balance on a melting unit.

The mass balance is the first step in providing a quantitative description of the melting operation. The streams entering the cupola are the blast, metallic charge, coke, and flux. The streams leaving the process are the stack gas, liquid metal, and slag. In order to reduce the material balance to its simplest form, and for ease in treating the energy balance, the materials are broken down into element or compound form for each stream. Material flow in the cupola furnace is illustrated schematically in Fig. 8-7. A material balance for a small cupola (approximately one order of magnitude smaller than the modern hot-blast, water-cooled cupola used in large foundry operations) is presented in Table 8-1.

The energy balance for the system can be calculated using thermochemical data for the compounds entering and leaving the process. The total enthalpy balance may be written as

$$H_{\text{blast}} + H_{\text{charge}} + H_{\text{flux}} + H_{\text{coke}} = H_{\text{top gas}} + H_{\text{metal}} + H_{\text{slag}} + H_{\text{losses}} \quad (8-3)$$

Each of the enthalpy terms in the foregoing equation can be calculated from a reference temperature, and are based on two terms—the energy of reaction to form the compounds in the stream, and the sensible heat in the stream relative to the selected base temperature.

TABLE 8-1  
Reference Period Data<sup>a</sup> on Cupola Furnace

| Material       | Molten metal<br>(wt. lb/net ton) | Chemical analyses, (Wt %) |                                |        |      |       |       |         |       |       |                  |
|----------------|----------------------------------|---------------------------|--------------------------------|--------|------|-------|-------|---------|-------|-------|------------------|
|                |                                  | Si                        | S                              | Mn     | P    | C     | Fe    |         |       |       |                  |
| Charge         |                                  |                           |                                |        |      |       |       |         |       |       |                  |
| Hematite pig   | 596.85                           | 2.940                     | 0.00                           | 0.940  | 0.09 | 4.00  | 92.03 |         |       |       |                  |
| Low P pig      | 198.95                           | 2.610                     | 0.00                           | 0.800  | 0.24 | 3.17  | 93.18 |         |       |       |                  |
| Return scrap   | 795.80                           | 2.000                     | 0.00                           | 0.730  | 0.14 | 3.30  | 93.83 |         |       |       |                  |
| Steel scrap    | 397.90                           | 0.040                     | 0.00                           | 0.600  | 0.05 | 0.10  | 99.21 |         |       |       |                  |
| Ferromanganese | 7.16                             | 0.000                     | 0.00                           | 50.000 | 0.00 | 0.00  | 50.00 |         |       |       |                  |
|                |                                  | SiO <sub>2</sub>          | Al <sub>2</sub> O <sub>3</sub> | CaO    | MgO  | P     | Fe    | Fixed C | S     | Vols  | Ash              |
|                |                                  |                           |                                |        |      |       |       |         |       |       | H <sub>2</sub> O |
| Coke           | 265                              | 4.51                      | 2.09                           | 0.15   | 0.06 | 0.016 | 0.98  | 91.25   | 1.18  | 0.95  | 7.80             |
|                |                                  |                           |                                |        |      |       |       |         |       |       | 3.00             |
|                |                                  | SiO <sub>2</sub>          | Al <sub>2</sub> O <sub>3</sub> | CaO    | MgO  | P     | Fe    |         |       |       |                  |
| Flux           |                                  |                           |                                |        |      |       |       |         |       |       |                  |
| Limestone      | 87                               | 1.81                      | 0.12                           | 51.80  | 1.86 | 0.000 | 0.000 | 0.000   | 0.000 | 0.000 | 0.000            |
| Lining loss    | 55                               | 84.10                     | 15.40                          | 0.05   | 0.15 | 0.000 | 0.000 | 0.000   | 0.000 | 0.000 | 0.000            |

|         |     | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO              | MgO   | S               | Mn             | C        | Fe               | CaF <sub>2</sub> | Temp, °F |
|---------|-----|------------------|--------------------------------|------------------|-------|-----------------|----------------|----------|------------------|------------------|----------|
|         |     | 48.30            | 10.96                          | 33.90            | 0.80  | 0.000           | 2.47           | 0.00     | 2.22             | 0.00             | 2642     |
| Slag    | 136 |                  |                                |                  |       |                 |                |          |                  |                  |          |
|         |     | Si               | S                              | Mn               | P     | C               | Fe             | Temp, °F |                  |                  |          |
|         |     |                  |                                |                  |       |                 |                |          |                  |                  |          |
| Metal   | —   | 1.79             | 0.000                          | 0.79             | 0.130 | 3.33            | 93.96          | 2642     |                  |                  |          |
|         |     | O <sub>2</sub>   | N <sub>2</sub>                 | H <sub>2</sub> O | CO    | CO <sub>2</sub> | H <sub>2</sub> | Temp, °F | Blast Rate, scfm |                  |          |
|         |     |                  |                                |                  |       |                 |                |          |                  |                  |          |
| Blast   | —   | 20.658           | 77.714                         | 1.627            | —     | —               | —              | 77       | 3293             |                  |          |
| Top gas | —   | —                | 70.62                          | 0.30             | 15.04 | 12.86           | 1.18           | 442      | —                |                  |          |

<sup>a</sup> Based on mass balance presented in Report of Sub-committee TS 52, Developments in the melting of metals for foundries, *Institute of British Foundrymen* 54, 103 (1961).

Source: R. D. Pehlke, Thermochemical Model for Computer Prediction of Cupola Performance, *Modern Castings* 44, 583 (1963).

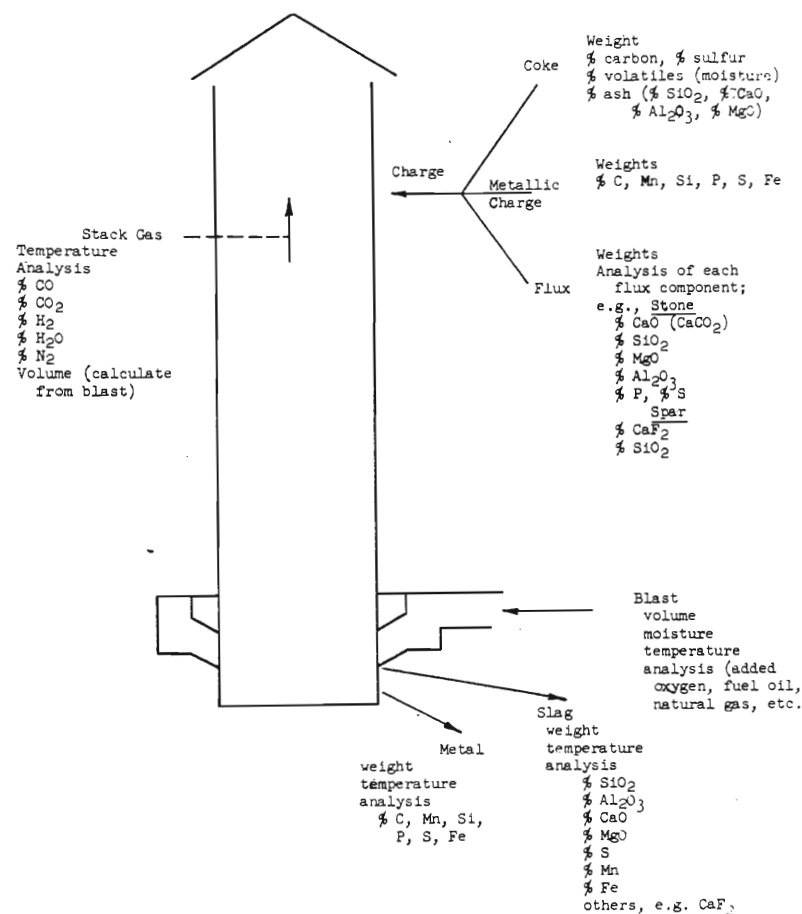


Fig. 8-7. Material Flow in the Cupola Melting Furnace

Source: Thermochemical Model for Computer Prediction of Cupola Performance," R. D. Pehlke, *Modern Castings*, 1963, Vol. 44, p. 582.

A summary of the enthalpies of the streams presented in the material balance of Table 8-1 are shown in Table 8-2. The weights of materials are given on a pound basis and the enthalpy terms are expressed in BTU/lb of product. The energy balance is used to calculate the heat loss per net ton of metal produced by the furnace.

TABLE 8-2  
Energy Balance for Reference Period of Operation<sup>a</sup>

|                                                            | lb Prod-<br>uct/Ton<br>Metal | H, Btu/<br>lb Product<br>Metal | H, Btu/<br>lb Product<br>Metal | lb Prod-<br>uct/Ton<br>Metal | H, Btu/<br>lb Product<br>Metal                        |
|------------------------------------------------------------|------------------------------|--------------------------------|--------------------------------|------------------------------|-------------------------------------------------------|
| Blast (77 F)                                               |                              |                                |                                |                              |                                                       |
| H <sub>2</sub> + ½ O <sub>2</sub> → H <sub>2</sub> O       | 18.67                        | -109,630                       |                                | 295                          | -473,475                                              |
|                                                            |                              |                                |                                | 397                          | -1,493,910                                            |
|                                                            |                              |                                |                                | 1.68                         | +2,135                                                |
|                                                            |                              |                                |                                | 3.63                         | -20,360                                               |
|                                                            |                              |                                |                                | 1385                         | +126,035                                              |
|                                                            |                              |                                |                                |                              | H-Stack gas = -1,859,575                              |
| Flux (77 F)                                                |                              |                                |                                |                              |                                                       |
| CaO + C + O <sub>2</sub> → CaCO <sub>3</sub>               | 80.18                        | -197,800                       |                                | 136                          | +111,790                                              |
| MgO + C + O <sub>2</sub> → MgCO <sub>3</sub>               | 3.55                         | -9,250                         |                                | 82.8                         | -27,320                                               |
|                                                            |                              |                                |                                | 3.22                         | -624                                                  |
|                                                            |                              |                                |                                | 6.81                         | +6,230                                                |
|                                                            |                              |                                |                                |                              | H-Slag = +90,076                                      |
| Charge (77 F)                                              |                              |                                |                                |                              |                                                       |
| loss by oxidation                                          |                              |                                |                                |                              |                                                       |
| Si(77 F) + O <sub>2</sub> (77 F) → SiO <sub>2</sub> (77 F) | -61.56                       | +39,700                        |                                | 1879                         | +1,031,571                                            |
| Mn(77 F) + ½ O <sub>2</sub> (77 F) → MnO(77 F)             | -2335                        | +6,300                         |                                | 35.7                         | -20,956                                               |
| Fe(77 F) + ½ O <sub>2</sub> (77 F) → FeO(77 F)             | -1598                        | +5,260                         |                                | 2.6                          | -6,776                                                |
| C(77 F) → C(77 F)                                          | +1750                        | +99,450                        |                                | 15.8                         | +9,116                                                |
|                                                            |                              |                                |                                | 66.5                         | +132,135                                              |
|                                                            |                              |                                |                                |                              | H-Metal = +1,145,090                                  |
|                                                            |                              |                                |                                |                              | Heat Loss (by difference) = 458,439 Btu/Net Ton Metal |

<sup>a</sup> Based on Table 8-1 with a reference temperature of 77°F.

Source: R. D. Pehlke, Thermochemical model for computer prediction of cupola performance, *Modern Castings*, 44, 583 (1963).

## 8-2 Pouring Operations

Liquid metals are transported in metallurgical plants by ladles, cylindrically shaped vessels consisting of a steel shell lined with refractories. The type of refractory in most common use is fire clay for pig or cast iron, and magnesia for steel. Ladles vary in capacity from 10 lb to 300 ton. Smaller ladles usually are lip-poured, but in the case of large heats of steel, the metal usually is bottom-poured to allow non-metallic inclusions to float out of the metal. (See Fig. B-8, of Example Problem 7, Appendix B.) With this method of pouring, a stopper assembly acts as a valve to control the flow of metal through a nozzle at the bottom of the ladle.

One of the most important factors affecting the surface of metal cast into an ingot mold, and the subsequent product made from that ingot, is the rate of rise of metal in the mold, which depends on the rate of flow of the pouring stream and the size of the mold. The pouring rate is determined by nozzle size, the height of metal in the ladle, and the erosion of the stopper and nozzle. For example, in the case of steel, the optimum pouring rate is determined by the type of product, but is also dependent upon mold design and temperature of pour. In general, a slow pour minimizes ingot cracking but increases the tendency toward rippled ingot surfaces. The rapid rise of molten steel in the mold prevents a rippled ingot surface. However, a rapidly poured ingot will result in a thin shell of steel frozen at the mold surface that shrinks away from the mold wall, thus losing its support against the pressure caused by the liquid iron contained in it. Since the shell is thin and hot and consequently very weak, it cannot stand the pressure of the liquid metal; as a result it ruptures, permitting fresh liquid to break through to the mold surface. This produces a fold in the ingot surface that may open on cooling or subsequent forming operations.

An intermediate pouring vessel is often used in lieu of casting the metal directly from the ladle to the mold. Such vessels are called pouring baskets, pouring boxes, or tundishes. This method usually involves pouring from the teeming (pouring) ladle into a vessel that has a nozzle leading into the ingot mold. Tundish or basket pouring is more expensive than conventional top pouring, but has the advantages of a greater opportunity for separation of nonmetallic inclusions from the metal and less splashing in the mold.

Some of the disadvantages of top-pouring mentioned above may be eliminated through the use of a bottom-pour mold assembly. The metal is cast into a runner system and finally emerges at the bottom of the mold through a special outlet. In bottom pouring, the metal rises steadily in the mold with very little agitation. Bottom pouring is much more expensive than top pouring, but is occasionally used to ensure optimum surface quality.

### Rate of Pouring

Since the rate of pouring greatly influences the quality of a cast ingot, much attention is given to the control of this factor. By considering the flow of metal through the nozzle of a bottom pour ladle in terms of the generalized flow equation, the rate at which metal is entering the mold at any time during the pouring opera-

tion can be estimated.<sup>1,2</sup> Since the nozzle is eroded by the liquid stream, it is necessary to have some relationship which indicates the size of the nozzle as a function of the amount of metal which has passed through it. Such correlations often may be obtained from plant data. If estimates for the entrance orifice coefficient and the friction factor also are available, the rate of pouring may be computed.

The gradual enlargement of the nozzle due to erosion has an effect that is desirable, i.e., the rate of pouring does not decline as rapidly with the ferrostatic head in the ladle as it would if the nozzle opening remained constant. While the head of metal has been decreasing, the diameter of the orifice has been increasing, and the rate of pouring can remain nearly constant or even increase slightly. Since the rate of pouring has a significant influence on the structure of the ingot, this is an important aspect in the design of the pouring operation. Knowing the behavior of several materials that are available for nozzles, the process engineer can select the material that provides a relatively constant pouring rate throughout the casting operation. Application of the generalized flow equation to the estimation of teeming rates from a bottom pour ladle is illustrated by Example Problem 7, Appendix B.

### Temperature Drop

Metal temperature during the pouring of steel into ingot molds is an important process variable. The furnace tapping temperature is controlled to establish the desired teeming temperature, but is not sufficient of itself to define the temperature during pouring into ingot molds. Several factors control the temperature drop that occurs between tapping and teeming. The principal factors are:

1. Radiation and convection losses from the steel surface, or slag surface, during the time the metal is in the ladle.
2. Heat losses from the tapping stream.
3. Heat losses into the brick lining of the ladle. These heat losses may be estimated in several ways. One assumption that can be made is that the brick lining acts as a semi-infinite heat sink and that heat continually diffuses into the refractory lining of the ladle. During both tapping of the furnace and teeming into ingot molds, the steel is in contact with the refractory near the bottom of the ladle for a longer period than it is in contact with the upper surfaces of the ladle. One way of treating the heat absorption process is to divide the lining into zones, the more zones the more precise the calculation, and to assign different times for contact with these zones during the filling and emptying of the vessel.
4. Thermal effects of deoxidation, including the energy required to heat the deoxidizing material up to temperature, and the heat of reaction.

Samways and Dancy<sup>3</sup> have reported on the temperature drop of liquid steel

<sup>1</sup> J. G. Henzel, Jr., and J. Keverian, *Modern Castings* 50, 69 (1966).

<sup>2</sup> R. D. Pehlke, Digital computer simulation of a bottom pouring ladle, *Computers in the Mineral Industries*, pp. 227-236 Stanford University School of Earth Sciences, Palo Alto, Calif., 1964.

<sup>3</sup> N. L. Samways and T. E. Dancy, *J. Metals* 12, 331 (1960).

between tapping and teeming and have compared statistically derived relationships describing plant practice with theoretically derived values.

### 8-3 Casting and Solidification

After pouring into molds, the liquid metal is permitted to solidify; the solidified castings are called ingots. The eventual use of the ingots may be in any of several mechanical forming operations, or may even include remelting and recasting to a desired shape. The mechanical forming operations used in the metallurgical industries are extensive subjects in themselves; discussion in this section consequently will be limited to the casting of ingot shapes for use in further forming operations and will be concerned chiefly with rates of solidification, ingot structure, and some consideration of special casting processes.

#### Rate of Solidification

There are two fundamental approaches to the mathematical treatment of solidification rates. One method involves development of rigorous equations describing the solidification process and the solution of these equations by analytical techniques. The equations, however, are usually complex and their solution is difficult and sometimes impossible to obtain for even the simplest of cases. Alternatively, approximate relationships can be developed that are representative of a given practical situation. With the assistance of high-speed computers, such approximations can be made to approach very closely actual conditions. Numerical approximations are much more versatile and do not require the limiting assumptions often necessary to develop a soluble analytical expression. As an example, the use of finite difference approximations to simulate heat flow in a slab is presented in Appendix B, Example Problem 8.

In order to indicate the nature of the analytical method, the following semi-quantitative approach to solidification is developed. The unidirectional unsteady state heat flow in a homogeneous solid is given by the relationship,

$$\frac{\partial T}{\partial t} = \left[ \frac{k}{C_p \rho} \right] \frac{\partial^2 T}{\partial x^2}, \quad (8-4)$$

where

- $T$  = temperature in the heat-conducting medium,
- $t$  = time,
- $k$  = thermal conductivity,
- $C_p$  = specific heat,
- $\rho$  = density,
- $x$  = distance.

The quantity  $k/C_p \rho$  is termed the thermal diffusivity and usually is represented by the symbol  $\alpha$ .

The solution for Eq. (8-4) depends upon the boundary conditions chosen. Where the heat-conducting medium is taken as semi-infinite, at an initial uniform tempera-

ture  $T_0$ , and at time  $t = 0$ , has its boundary temperature instantaneously raised to and maintained at  $T_i$ , the ensuing temperature distribution through the medium is given by the expression,

$$T_x = T_0 + (T_i - T_0) \operatorname{erfc} \left[ \frac{x}{2\sqrt{\alpha t}} \right], \quad (8-5)$$

where

- $T_x$  = temperature at a distance  $x$  in heat-conducting medium,
- $\alpha$  = thermal diffusivity as defined above,

$$\operatorname{erfc} \left[ \frac{x}{2\sqrt{\alpha t}} \right] = \left[ 1 - \text{error function of } \frac{x}{2\sqrt{\alpha t}} \right] \text{ as defined in Table A-X,}$$

Appendix A.

Ruddle,<sup>4,5</sup> and Feild<sup>6</sup> have developed a parabolic rate equation for solidification of an ingot using Eq. (8-5) in the following manner. Assuming that the mold into which liquid metal is cast meets the boundary conditions for Eq. (8-5), the temperature distribution in the mold is given by Eq. (8-5) where  $T_x$  is the temperature in the mold material at any distance,  $x$ , from the mold-metal interface. The rate of heat transfer across the mold-metal interface is given by the relationship,

$$\frac{q}{A} = -k \left[ \frac{\partial T}{\partial x} \right]_{x=0}, \quad (8-6)$$

where

$$\frac{q}{A} = \text{heat transfer rate per unit area,}$$

$k$  = thermal conductivity of mold material,

$$\left[ \frac{\partial T}{\partial x} \right]_{x=0} = \text{thermal gradient in mold material at mold-metal interface.}$$

Differentiating Eq. (8-5) with respect to  $x$  and evaluating the differential at  $x = 0$  yields

$$\left[ \frac{\partial T_x}{\partial x} \right]_{x=0} = \frac{T_i - T_0}{\sqrt{\pi \alpha t}}. \quad (8-7)$$

Then

$$\frac{q}{A} = \frac{1}{A} \left[ \frac{\partial Q}{\partial t} \right] = - \frac{k(T_i - T_0)}{\sqrt{\pi \alpha t}}, \quad (8-8)$$

<sup>4</sup> R. W. Ruddle, *The Solidification of Castings*, Institute of Metals Monograph and Report Series, 7, Institute of Metals, London, 1957.

<sup>5</sup> R. W. Ruddle, *J. Inst. Metals* 77, 1 (1950).

<sup>6</sup> A. L. Feild, *Amer. Soc. Steel Treating Trans.* 11, p 264 (1927).

where  $Q$  = total quantity of heat transferred; thus  $q = \frac{\partial Q}{\partial t}$ . Integrating Eq. (8-8)

$$\frac{Q}{A} = \frac{2k(T_i - T_0)}{\sqrt{\pi\alpha}} \sqrt{t}. \quad (8-9)$$

Under these conditions, the heat removed is proportional to the square root of time. Assuming that the freezing thickness depends upon removing a given quantity of heat per unit area

$$d = \beta' \sqrt{t}, \quad (8-10)$$

where

$d$  = thickness of frozen metal,  
 $\beta'$  = solidification constant,  
 $t$  = freezing time.

For an infinite plate, the total freezing distance is one-half the plate thickness, which is also the volume to surface area ratio. Hence the total freezing time is

$$t_f = \gamma' \left[ \frac{V}{A} \right]^2 \quad (8-11)$$

where

$t_f$  = total freezing time,  
 $\gamma'$  = empirical constant,  
 $\frac{V}{A}$  = volume to surface area ratio.

Equations (8-10) and (8-11) can be applied to the solidification behavior of the simple shapes encountered in ingot casting, although they are not strictly rigorous since the boundary conditions assumed in deriving these relationships are not fully valid. Nevertheless, over a wide range of industrial conditions, the solidification thickness is observed to be linear with the square root of time, particularly during the early stages of solidification. Thus, if the empirical constants are evaluated from previous operating data, Eqs. (8-10) and (8-11) are useful for interpolating solidification thicknesses and freezing times under similar conditions.

#### 4 Ingot Structure

Important factors that affect ingot structure are metal composition and gas evolution. In addition, pouring conditions, such as temperature of the liquid metal, the nature, temperature and geometry of the mold, and the rate of pouring, influence the rate of heat removal and, hence, the ingot structure.

**Effect of Rate of Heat Removal on Ingot Structure.** A cast ingot will generally freeze in three zones. Near the surface of the ingot the structure consists of very fine, randomly oriented grains. This region is called the chill zone and its structure is the result of rapid solidification with high nucleation rates during the early stages

of freezing. Underneath this region is a second zone where the crystals are thin and elongated, being oriented perpendicular to the mold wall. This zone is called the columnar zone and is the result of relatively rapid heat removal, giving rise to directional solidification and grain growth. Underneath the columnar zone, the ingot has a structure consisting of randomly oriented crystals that are much coarser than in the chill zone. The increase in grain size occurs because of a lower rate of heat removal in the final stage of solidification. All ingots that do not evolve gas during solidification will show these three structures, with the extent and nature of the zones being a function of pouring conditions, composition, and average rate of solidification. The rate of solidification varies widely, being nearly infinite at the mold surface and decreasing to a very small value near the center of the ingot. It is the combination of the variation in cooling rate during ingot solidification, together with metal composition and gas evolution, which markedly influences ingot structure.

**Influence of Metal Composition.** Since most liquid metals involved in metallurgical operations are not pure, solidification occurs over a temperature range, so that the first liquid to solidify has a different composition than that which is last to solidify. The distribution of solutes between liquid and solid is described by a distribution coefficient,  $k$  (see Zone Refining, Chap. 5). The separation of solute between liquid and solid is the cause of segregation.

Most alloying elements lower the melting point of a liquid pure metal, and consequently upon freezing the first crystals of solid more closely approach the pure major component than the composition of the bulk liquid. However, as the first crystals of solid form, the adjacent liquid is left slightly less pure than the bulk liquid. The solidification of a metal containing a solute then can be visualized as a stepwise crystallization process in which the material separating out is more pure in the major component, and, because of the rejection of solute on solidification, is separated from the bulk liquid by a film of liquid metal that is less pure than the bulk liquid.

In the columnar zone of solidification, less pure liquid is trapped between the long columnar crystals. Since this liquid is enriched in solute, it freezes in the interstices between the columnar grains at a lower temperature than the crystallized solid, resulting in the phenomenon described as micro-segregation. Contrasted with microsegregation is macrosegregation, a term used to describe relatively large-scale segregation that may be visible on a polished section to the naked eye and is exemplified by differences in concentration existing in different areas of an ingot or casting.

As the solidification front in a metallic solution advances, solute is rejected to the liquid phase, e.g., where  $k$  is less than one. In order for solidification to take place, a temperature gradient must exist across the liquid-solid interface such that the interface is at a temperature below that where solid and liquid are in equilibrium. In addition, there is a temperature gradient in the liquid phase. Depending upon the temperature gradient and the liquidus temperature for the solute-enriched liquid existing ahead of the freezing interface, the temperature in the liquid phase ahead of the solidification front may drop below the liquidus temperature. This condition is referred to as constitutional supercooling<sup>7</sup> and can lead to the formation

<sup>7</sup> B. Chalmers, *Trans. Met. Soc. AIME* 200, p 519 (1954).

of solid crystals in the bulk liquid ahead of the normal solidification front. The formation of crystals in the supercooled liquid depends upon nucleation conditions, and it has been shown that in order for homogeneous nucleation to occur, extensive supercooling is required.<sup>8</sup> In actual operating practice, only a few degrees of undercooling are required to initiate solidification. This is ascribed to the presence of small nucleating particles, e.g., the products of deoxidation, etc. Hence, inclusions enhance the nucleation of solidification.

In the case of a liquid metal containing some solute, freezing may proceed in any of three ways: (1) At high rates of solidification, the liquid solidifies quite rapidly, so that the solidification process is not distinguishable from that of a liquid pure metal and no segregation occurs; (2) At lower rates of solidification, the boundary layer of pure liquid that builds up in front of the solidification front may delay solidification slightly; or (3) At low rates of solidification, the bulk liquid beyond the impure film may reach its liquidus temperature before the impure liquid which exists at the solidification front. In this latter circumstance, free crystals will form in the liquid and settle out to the bottom of the ingot. As the solidification rate changes during the freezing of an ingot, all three types of freezing can take place in sequential steps. In the absence of gas evolution, the segregation characteristics of an ingot are determined by its composition, its rate of cooling and the tendency of any alloying elements to segregate between liquid and solid.

These segregation characteristics are illustrated by the freezing of a killed steel ingot. Figure 8-8 illustrates the mechanism of solidification of a killed steel ingot. Figure 8-8A shows the initial solidified chill zone made up of small, randomly oriented crystallites. Certain crystals will have an orientation such that the preferred-direction of more rapid growth extends out into the liquid. These crystals (Marked "a" in Fig. 8-8A) become elongated and produce the columnar zone, and in trapping less pure liquid between the columnar crystals, as shown in Fig. 8-8B, create microsegregation in this area. As the freezing rate decreases and the temperature gradient becomes less steep through the liquid and solid, the temperature beyond the less pure liquid film at the solidification front drops below the liquidus temperature of the unaltered liquid metal near the center of the ingot. Free crystals then form in this supercooled region and drop to the bottom of the ingot. These falling crystals and the corresponding rise in liquid level along the solidification front lead to macrosegregation, as shown in Fig. 8-9. The conical zone of negative segregation in the lower portion of the ingot is caused by the settling of free crystals that are purer and more dense than the bulk liquid. As the free crystals settle, they cause an upward movement of less pure liquid along the side of the ingot near the solidification front, thus leading to positive segregation in this region. Similarly, the V-shaped zones of positive segregation in the upper central portion of the ingot are caused by the movement of less pure liquid down into the ingot cavity by shrinkage during the final stages of solidification.<sup>9,10</sup>

<sup>8</sup> J. H. Holomon and D. Turnbull, *Progress in Metal Physics*, Vol. 4, p 333, Pergamon Press, London, 1953.

<sup>9</sup> G. Derge, Ed., *Basic Open Hearth Steelmaking*, Chap. 10 and 11, AIME, New York, 1964.

<sup>10</sup> J. K. McCauley, and F. C. Langenberg, *J. Metals*, 17, 318 (1965).

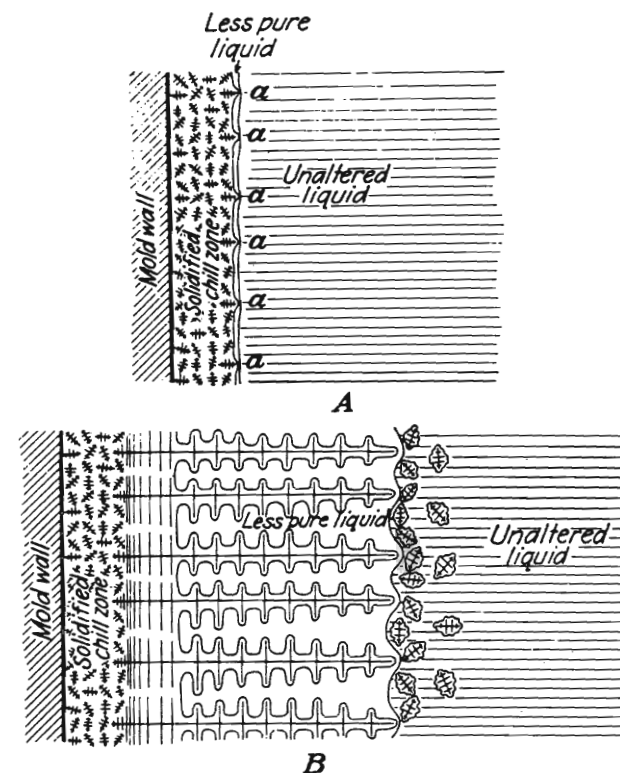


Fig. 8-8. Schematic Drawing Illustrating the Mechanism of Solidification in a Killed Ingot

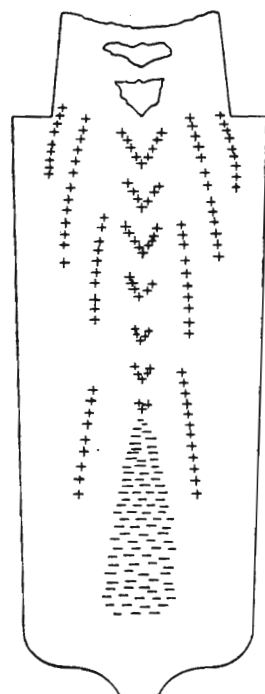
Source: *Basic Open Hearth Steelmaking*, edited by G. Derge, 1964, AIME, New York, Chapter 11, p. 440.

**Influence of Shrinkage.** The overall structure of cast ingots also is influenced by the change in specific volume of the metal with temperature. The change in volume of an ingot on casting occurs because of liquid shrinkage as the metal cools; shrinkage upon solidification, either at the melting point or over a small temperature range in the case of an alloy; and the thermal contraction of the solid material as it cools to room temperature. The volume contraction accompanying the transition from liquid to solid at the melting point depends upon the specific metal, but may range from 3-7%. The shrinkage in the liquid state depends upon the superheat and can be as high as 2%, whereas the solid state shrinkage for most metals averages about 3%.

These volume changes, particularly the shrinkage occurring during freezing, can lead to the formation of a large depression in the top of the ingot commonly

referred to as *pipe*. The exposed surface of a pipe will oxidize and will not weld during subsequent forming operations, necessitating that the upper portion of the ingot be cut off or *cropped*, leading to a decrease in ingot yield. One means for allowing for shrinkage on solidification is to provide an auxiliary liquid reservoir or *hot top* such that the top of the ingot remains liquid while solidification is promoted from the bottom of the mold. Other means for avoiding shrinkage pipe include controlled evolution of gases by control of the oxygen content in copper ingots to provide the proper set or by control of the carbon and oxygen contents in steel (such as in production of semikilled or rimming ingots), to counteract the contraction in volume by a controlled formation of gas within the ingot.

**Effect of Dissolved Gases.** The solubility of gases in both liquid and solid metals usually increases with temperature. However, at the melting point where liquid and solid exist in equilibrium, the solubility in the liquid is usually several times that of the solubility in the solid. If the concentration of the dissolved gas in the liquid metal exceeds the solid solubility, the metal thus will have a tendency to evolve gas upon solidification. This marked change in solubility at the melting point is illustrated in Fig. 8-10, where the solubilities of hydrogen and nitrogen at 1 atm pressure in iron are shown as functions of temperature. At the melting point, an approxi-



+ zones of positive segregation,  
- zones of negative segregation

Fig. 8-9. Segregation Pattern in Hot-topped Killed Steel Ingot

Source: *Basic Open Hearth Steelmaking*, edited by G. Derge, 1964, AIME, New York, Chapter 11, p. 441.

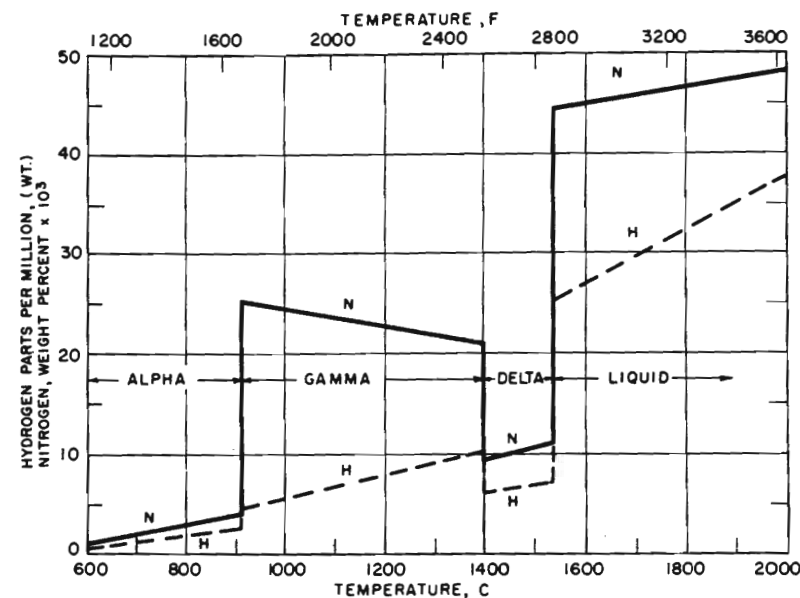


Fig. 8-10. Effect of Temperature on the Solubility of Hydrogen and Nitrogen at 1 atm Pressure in Iron

Source: *Basic Open Hearth Steelmaking*, edited by G. Derge, 1964, AIME, New York, Chapter 16, p. 646.

mately fourfold increase in the solubility of these gases exists in the liquid as compared with the solid.

The evolution of gas from an ingot during solidification may change not only its physical nature through formation of blowholes, but also may affect the segregation tendencies since the presence of a less dense gas phase results in fluid flow in the ingot during solidification. However, the presence of gas in an ingot is often an advantage since, as pointed out earlier, gas evolution can be used to compensate for shrinkage and to reduce or eliminate the ingot pipe, thus giving a higher yield.

In the casting of steel, the carbon-oxygen equilibrium and the influence of temperature on it are of primary importance in the control of ingot structure by gas evolution. Carbon and oxygen react to form carbon monoxide whenever the

activity product exceeds the equilibrium constant for the solution of the gas in liquid iron. The reaction may be written



where

$$K = \frac{P_{\text{CO}}}{(a_{\text{C}})(a_{\text{O}})} \quad (8-13)$$

The equilibrium constant is thus proportional to the pressure of CO, which in turn is a linear function of depth in the ingot mold. At atmospheric pressure near the top of the ingot, the equilibrium product of the carbon and oxygen activities would be one-half the value at a depth of 5 ft where the pressure is twice as great.

In practice, deoxidation in the ladle is used to control the oxygen content of liquid steel. As freezing of the ingot proceeds, carbon and oxygen become concentrated in the liquid, eventually resulting in gas evolution when the product of the oxygen and carbon activities exceeds the equilibrium value.

In a semikilled ingot, the concentration of oxygen is adjusted with deoxidizers in the ladle and also during the pouring operation in the mold, such that gas evolution compensates for shrinkage. After the top of the ingot freezes over, gas formation in the interior of the ingot is controlled by the pressure. As the steel shrinks during solidification, the pressure is relieved and additional gas is evolved.

Rimmed steels are characterized by rapid gas evolution that begins during the solidification of the chill zone at the mold wall. With the first solidification, marked gas evolution begins at the liquid-solid interface and the rising bubbles cause the liquid metal to move upward along the sides of the ingot and downward in the center. The motion of the liquid tends to limit columnar grain growth and keeps the interior liquid at a nearly uniform temperature. Just inside the rim zone of a rimmed ingot, a series of primary blowholes is found. The mechanism of formation of these blowholes has been described by Hultgren and Phragmen.<sup>11</sup> Gas is evolved from the solute-enriched liquid at the liquid-solid interface. As the rate of solidification decreases, the gas bubbles are not swept away but attach themselves to the solid and grow with the solidifying metal, resulting in a primary blowhole. After the top of the ingot freezes over, enough impure liquid accumulates at the solid-liquid interface to start gas formation in much the same manner as it occurs in semikilled ingots. This results in an interior series of spherical gas pockets called secondary blowholes.

The upward motion of the liquid along the solidifying wall sweeps away impure liquid and mixes it with the unsolidified body of the ingot. The eventual result is a large positive segregation in the upper central portion of the ingot, the last part to solidify.

The presence of other gases (especially hydrogen) may cause blowholes. In the case of copper, the evolution of hydrogen and water vapor or SO<sub>2</sub> may also influence ingot structure, as can hydrogen in aluminum and many other alloys. The control of gases in liquid metals is discussed in Chapter 5.

<sup>11</sup> A. Hultgren and G. Phragmen, *Met. Soc. Trans. AIME* 135, 133 (1939).

**Example Problem 8-1.** If a 3000 lb deoxidized copper cake solidifies slowly from a liquid containing 4 ppm (by weight) of dissolved hydrogen, how much hydrogen could be evolved?

**Solution.** At the freezing point the solubility of hydrogen in copper at 1 atm hydrogen pressure is about 1.3 ppm in the solid and 5 ppm in the liquid phase. The hydrogen evolved, neglecting any transfer between metal and the surrounding atmosphere and assuming that the freezing solid is saturated at 1 atm pressure, is  $4 - 1.3 = 2.7$  ppm. Converting to cubic feet at the freezing point,

$$\text{Volume of cake} = \frac{(3000) \text{ lb}}{(680) \text{ lb/ft}^3} = 4.42 \text{ ft}^3,$$

$$\text{Volume of H}_2 = \frac{(2.7 \times 10^{-6})(3000)(359)(1356)}{(2)(273)}$$

$$\frac{(\text{ppm})(\text{lb})(\text{ft}^3/\text{lb mole})(^{\circ}\text{K}_{\text{actual}})}{(\text{lb}/\text{lb mole})(^{\circ}\text{K}_{\text{reference}})} = \text{ft}^3$$

$$= 7.20 \text{ ft}^3,$$

$$\text{Relative volume} = \frac{7.2}{4.42} = 1.63.$$

In view of the limited solid solubilities of gases in metals, it is not surprising that the production of a gas-free casting is difficult.

In the case of rimming steel ingots, the relative volume of gas evolved at casting temperatures may be 30 or higher.<sup>12</sup> This large volume of evolved gas is utilized to promote better surface quality and higher yield.

**Defects in Ingots.** In addition to cavities caused by shrinkage or gas evolution, several other ingot defects have important influences on subsequent product quality.

Nonmetallic inclusions, depending upon their size, quantity, and distribution, can be detrimental to the properties of a metal in its service application. Nonmetallic inclusions originate from two primary sources and are designated accordingly as either indigenous or exogenous. Indigenous inclusions are the result of precipitation reactions within the metal itself, e.g., in the processing of steel, the entrapment of oxides formed during deoxidation or the precipitation of sulfides such as manganese sulfide during solidification. Exogenous inclusions are foreign particles trapped in the metal, such as particles of refractory eroded from linings, etc.

Another common defect in ingots is the formation of a plane of weakness along the diagonal of the cross section of the ingot. Since columnar grains form at right angles to the walls of the mold, their line of intersection represents a plane of weakness that can fail during mechanical working of the ingotism. This defect can be minimized by using rounded ingot mold corners and by promoting higher initial rates of solidification.

<sup>12</sup> A. Hayes and J. Chipman, *Met. Soc. Trans. AIME*, 135, 85 (1939).

## 8-4 Continuous Casting

Continuous casting processes have received a great deal of attention in recent years and have come into wide use in the casting of light alloy slabs and ingots; application is now being made in the processing of copper and steel. The purpose of continuous casting is to bypass conventional ingot casting and cast to a form that is directly rollable on finishing mills. Furthermore, there is good indication that use of this process should result in improvement in yield, in surface condition, and in internal quality of product.

Continuous casting involves the following sequence of operations:

1. Delivery of liquid metal to the casting strand.
2. Flow of metal through a distributor into the casting mold.
3. Formation of the cast section in a water-cooled mold.
4. Withdrawal of the casting from the mold.
5. Further heat removal from the casting, e.g., water spray beneath the mold.
6. Cutting and removal of the cast bars.

Several arrangements are now in commercial use to accomplish these objectives. The principal types of continuous casting machines are vertical, vertical with bending, and curved mold, as shown in Fig. 8-11A, -B, and -C. A curved mold continuous casting machine is shown in greater detail in Fig. 8-12.

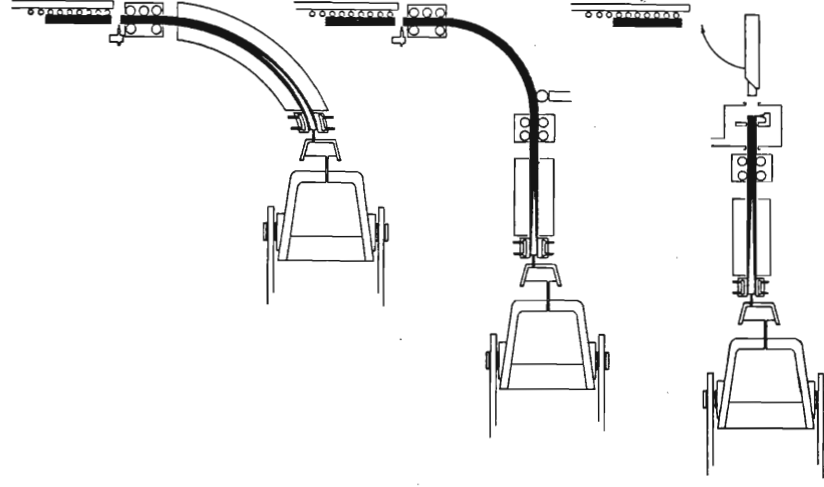


Fig. 8-11. Vertical, Bent-strand, and Curved-mold Continuous Casting Machines

Source: R. S. Wagstaff and G. E. Stock, "A Decade of Development in the Continuous Casting of Special Steels," Special Report No. 89, *Continuous Casting of Steel*, Iron and Steel Institute, London, 1965, p. 122.

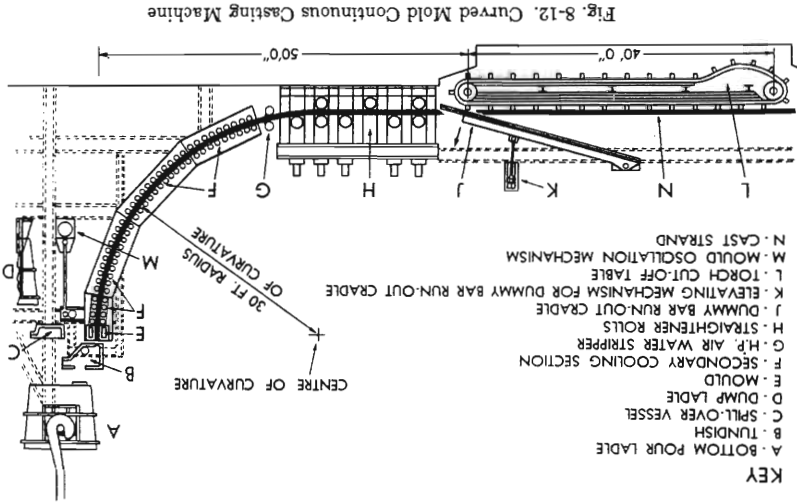


Fig. 8-12. Curved Mold Continuous Casting Machine

Source: *Iron and Steel Engineer*, July 1965, p. 147.

Most of the original continuous casting machines for steel were vertical machines. The vertical machine with bending and the curved mold machine, although more complicated in their construction, were developed to minimize the height of the machine and allow installation in present plants without modification of the crane height.

A primary factor influencing the casting rate is the rate of heat removal. The limiting casting rate is one which makes it just possible to remove the heat required for complete solidification prior to the time that the cast section is cut. Another more important limitation on casting rate involves the need to develop a solid shell within the water-cooled mold that can contain the liquid metal as the section leaves the mold. The governing factor is the thickness of the shell emerging from the mold, and this is determined largely by the rate at which heat is extracted in the mold. On this basis, then, the critical part of the continuous casting process is the removal of heat in the water-cooled mold. It is on this phase of the operation that the following analytical discussion will focus.

One of the earliest studies of solidification during continuous casting was made by Roth<sup>13</sup> who derived an expression showing that the freezing rate is proportional to the horizontal thickness already solidified, and predicting a parabolic-shaped freezing front. Ruddle<sup>14</sup> has reviewed this and other studies of the solidification of continuously cast metals.

<sup>13</sup> W. Roth, *Aluminum* 25, 283 (1943).

<sup>14</sup> R. W. Ruddle, *The Solidification of Castings*, Chap. 7, Institute of Metals Monograph and Report Series, 7, Institute of Metals, London, 1957.

Savage and Pritchard<sup>15</sup> investigated the rate of heat transfer in continuous casting of steel by measuring the heat transferred to a water stream passing through the cooled copper mold. Up to about 40 secs after casting, their results could be represented by the relation,

$$\frac{1}{A} \left[ \frac{\partial Q}{\partial t} \right] = 64 - 8\sqrt{t}, \text{ cal/cm}^2 - \text{sec.} \quad (8-14)$$

This equation may be integrated to give the average rate of heat transfer over a given period

$$\frac{1}{A} \left[ \frac{\partial Q}{\partial t_{av}} \right] = \frac{1}{t} \int_0^t \left[ \frac{\partial Q}{\partial t} \right] dt = 64 - \frac{16}{3} \sqrt{t}. \quad (8-15)$$

In the case of continuous casting with a withdrawal rate of  $v$  cm/sec and a mold length of  $L$  cm,  $t$  may be replaced by  $L/v$  so that Eq. (8-15) becomes

$$\frac{1}{A} \left[ \frac{\partial Q}{\partial t_{av}} \right] = 64 - \frac{16}{3} \sqrt{\frac{L}{v}}. \quad (8-16)$$

The prediction of this equation, e.g., that the average rate of heat transfer in the mold increases with the casting velocity, has been confirmed by experiment,<sup>16</sup> where it also was shown that the rate of freezing is proportional to the square root of  $t$ . The rate of freezing was found to be of the same order as that occurring in an ordinary chill casting during the first stage of cooling, about 0.65 in./ $(\text{min})^{1/2}$ . A large increase in the rate of freezing takes place during the second phase where the cooling is intensified by a water spray beneath the mold. In this stage the rate is equal to about 8.44 in./ $(\text{min})^{1/2}$ , a value much greater than that encountered in chill casting. For continuous casting, a plot of thickness frozen against the square root of  $t$  thus consists of two intersecting straight lines.

An investigation was carried out on the continuous casting of low carbon steel in which the thickness of the shell emerging from the water-cooled mold was estimated by measuring the outer slab temperature.<sup>17</sup> Using these temperatures, and assuming a constant temperature gradient across a uniform solidified shell, the thickness of the frozen outer skin was estimated at the time the casting emerged from a  $24 \times 6\frac{1}{2}$ -in. mold. The thickness of the emerging shell was found to decrease with increasing casting rate in qualitative agreement with the results of Savage and Pritchard.<sup>18</sup>

### 8-5 Other Casting Procedures

Several other casting processes of the continuous or semicontinuous type are either in use or under study in the basic metals industry.

<sup>15</sup> J. Savage and W. H. Pritchard, *J. Iron and Steel Inst.* 178, 269 (1954).

<sup>16</sup> D. M. Lewis and J. Savage, *Metallurgical Rev.* 1, 65 (1956).

<sup>17</sup> F. D. Jaicks, L. E. Kraay, and M. Tennenbaum, *AIME TRANS.*, 209, 1057 (1957).

<sup>18</sup> Savage and Pritchard, *op. cit.*

In the Hazelett process, liquid metal is poured between two water-cooled rolls or bands to produce a continuous strip, usually  $\frac{1}{4}$  to 2 in. in thickness. This process has been used to produce aluminum and attempts have been made to apply it to other nonferrous as well as ferrous materials.

The pressure pouring process developed by Griffin Wheel Company for casting steel freight car wheels has been adopted for casting steel billets and slabs. In this process, molten metal is forced from a closed ladle up through a refractory tube into a mold by compressed air. The molds are made up of an assembly of graphite blocks, and hence, are of adjustable size—lending flexibility to the process. The surface quality of the semifinished mill shapes cast using this method has been very good. The process is being used to cast high alloy and stainless steel slabs.

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### Discussion Questions

1. Discuss the factors to be evaluated in choosing a melting system for a large cast iron foundry.
2. What factors control the rate of scrap melting in a steelmaking operation using the basic open hearth process?
3. Discuss deoxidation practice on steel heats with respect to the advantages and disadvantages of carrying out the practice in the furnace, ladle, and ingot mold.
4. A steel mill has been encountering difficulties in its rimming steel ingots. The gas blowholes in the upper half of the ingot are too numerous and large giving rise to excessive croppage losses. It has been suggested that the steel be poured

5. Sketch a simplified flow diagram of a fully integrated steel mill. The diagram should include the size and number of operating units (typical of today's operation) for producing 3.5 million tons of sheet, strip and bar products, of which 0.5 million tons are high carbon, alloy, and stainless steels.
6. In the manufacture of steel sheets for deep drawing, the product of the hot strip mill is cold-reduced to slightly greater than final gauge, box annealed at 1400°F and temper-rolled to reduce its thickness approximately 3%. The susceptibility of rimming steel, thus treated, to strain aging is known to be due mainly to the presence of nitrogen in the steel.
- (a) Comment on the relative suitability of open hearth, basic Bessemer, and oxygen blown steels for this application.
- (b) A fully killed aluminum-deoxidized steel is not subject to strain aging. Explain.
- (c) It is claimed that the addition of vanadium to the mold does not interfere with the rimming action and produces a nonaging material. Discuss the physico-chemical background for this claim.
- (d) What other elements might be considered for use in producing rimmed or killed ingots for nonaging sheet?

## Problems

1. The production of a fine grain in low carbon rimming steels for deep drawing applications has been related to the formation of fine precipitates of carbides, oxides or nitrides in the solid which prevent grain coarsening during annealing. A slight excess of aluminum will ensure a fine grain, but other elements are often more desirable. Vanadium and titanium have both been proposed as additives to ensure a fine grain. One objection raised is that even if the addition is made after aluminum deoxidation, the residual oxygen (an average of about 0.03 wt%) will react with the additive and eliminate the rimming action. If it is necessary to retain 0.02 wt% of either V or Ti in the steel, which, if either, would you recommend as a ladle additive? Justify your answer with calculations. (Tempering Temperature—1550°C.)
2. It has been observed in vacuum melting of iron in magnesita crucibles that the oxygen content often increases markedly, sometimes approaching the saturation point. Demonstrate by calculation that decomposition of the magnesita refractory producing magnesium gas at a low pressure and oxygen in solution in liquid iron is a mechanism by which this phenomenon can occur.
3. Estimate the length of time liquid pig iron can be held in a torpedo ladle. Data: Blast furnace tap temperature—2700°F  
Pig iron liquidus—2100°F  
 $C_p$  of liquid pig iron—0.18 Btu/lb °F  
Metal weight—150 tons  
Ladle shell emissivity—0.8

- Ladle shell convection coefficient—0.3 Btu/hr °F ft<sup>2</sup>  
Ladle shell area—800 ft<sup>2</sup>  
Average ladle shell temperature—550°F  
Weight of ladle refractory—30 tons  
 $C_p$  of refractory—0.24 Btu/lb °F
4. A low carbon steel heat is bottom-poured into the tundish of a continuous casting machine. Estimate the maximum amount of nitrogen that could be absorbed by the pouring stream during the transfer to the tundish.  
 $D_N = 7.5 \times 10^{-4}$  cm<sup>2</sup>/sec.  
 $\delta = 0.003$  cm  
 $d$ , diameter of stream = 3 in. (7.6 cm)  
 $h$ , pouring height = 30 in. (76 cm)  
 $v$ , average velocity of stream during the pouring operation, 10 ft/sec (305 cm/sec)
  5. A 100-g sample of liquid iron-carbon alloy at its melting point is brought into equilibrium with CO gas at a partial pressure of 0.5 atm and then is allowed to solidify under a total pressure of 1 atm. The alloy contains 0.20% C. Estimate how much metal will solidify before bubbles can form. At this stage the concentration of carbon in the solid is 0.14 times that in the liquid. Assume that oxygen is insoluble in solid iron.
  6. A plant produces a full range of steels, including some by continuous casting, and also has finishing facilities for most products. One of the principal products of the mill is low carbon killed steel for sheet and plate applications. Two steels are used for this purpose, a silicon and an aluminum killed grade. The specifications are:

|           | C         | Mn            | P         | Si       | Al          | S        |
|-----------|-----------|---------------|-----------|----------|-------------|----------|
| Al killed | 0.03/0.10 | 0.25/0.40 max | 0.035 max | —        | 0.020/0.030 | 0.04 max |
| Si killed | 0.03/0.10 | 0.25/0.40 max | 0.035 max | 0.12 max | —           | 0.04 max |

7. Explain the limits on aluminum and silicon. Estimate the residual oxygen in each case as the metal is teemed into ingot molds. It is proposed to treat liquid "rimming" steel with 0.25 wt% vanadium. This practice would provide a deep drawing sheet material which is free from "stretcher strains" by virtue of tying up the dissolved nitrogen as vanadium nitride in the steel. However, in order to maintain surface quality of the steel the rimming action must not be impaired. It has been found in a given plant practice that at least 0.02 wt% oxygen is necessary to provide a satisfactory rim in low carbon steels. Can the vanadium addition be made without degrading surface quality?
8. A large plate is cast and slowly solidified. Assume the following conditions:
  - (1) The metal is a dilute solution of solute B in A.
  - (2) The segregation coefficient is a constant,  $k$ .

- (3) Equilibrium is obtained at the solidifying phase interface.
- (4) No diffusion occurs in the solid.
- (5) The liquid composition is homogeneous.

Derive an expression relating the concentration of solute B in the liquid or at the solidifying interface to the initial concentration of solute, the fraction solidified, and the segregation coefficient.

9. Low carbon steel is being continuously cast as a  $10 \times 52$ -in. slab. Using the result of Savage and Pritchard (Eq. 8-16), estimate the solidified thickness as the steel leaves the mold. The steel is cast  $70^\circ\text{F}$  above the liquidus. The mold is 30 in. long (27 in. are in contact with the solidifying steel). State your assumptions regarding heat transfer within the slab, particularly for the liquid core.
10. During continuous casting, cooling of the frozen outer shell results in a contraction which increases along the strand as further decreases in temperature take place. In the mold where the initial skin formation takes place, it is important that the frozen skin be supported by the water-cooled copper mold walls. Consequently, continuous casting molds are usually built with a slight taper to prevent the pressure of the ferrostatic head from stretching and tearing the frozen skin. Assume that the frozen thickness of a  $10 \times 48$ -in. low carbon steel slab is 0.6 inches as it leaves the mold and that the surface temperature is  $400^\circ\text{F}$  below the solidus temperature. The mold is 30 in. long and the liquid meniscus is 3 in. below the top of the mold. The thermal coefficient of expansion of the steel is  $1.2 \times 10^{-5}$  in./in.  $^\circ\text{F}$ . Estimate the taper required on the wide and narrow faces to compensate for 90% of the contraction in the mold during an average cast.
11. Estimate the local power costs to melt 200 lb of steel in an induction melting furnace. Compare the cost per pound with a 10 ton induction melting unit. Specify power supply, design of melting unit, charge, tapping temperature, etc.

## CHAPTER 9

### Computer Applications in Extractive Metallurgy

One of the major developments recently made in the scientific world has been the perfection of the electronic computer in both its analog and digital form. The utility of electronic computers in the engineering of metallurgical systems is now well established, and computers undoubtedly will take preeminence as a tool of the metallurgical process engineer. Computers are used presently in research and in operating practice for a variety of applications involving metallurgical calculations and data analysis. Computer applications involving simulation and control of metallurgical processes are rapidly expanding; furthermore, the storage and retrieval of metallurgical information is a subject of increasing import.

The purpose of the present chapter is to outline several computer applications that are particularly germane to extractive metallurgy, and to emphasize the potential applications and the increasing importance of this approach to the engineering of metallurgical processes. In the following chapter, a brief description is presented of digital and analog computers and their potential applications in process engineering. The techniques of operations research in the form of queueing theory and linear programming are introduced, along with a brief outline of metallurgical system simulation. Appendix B contains ten documented computer programs illustrating applications in extractive metallurgy.

#### 9-1 General Nature of Digital and Analog Computers

There are two basic types of large-scale calculating machines in use today, the analog, or continuous variable machine, and the digital, or discrete variable machine. An analog computer is a physical system, mechanical, electrical or optical which is designed in such a way that the variables of the system satisfy the same mathematical laws as do the variables of the problem of interest. The physical process of computation is replaced by a measurement of the physical quantities corresponding to the values of the unknown variables. Digital computers, in contrast, perform their operations by counting, in a manner similar to a desk calculator.

##### The Digital Computer

The large-scale digital calculator will perform only the simplest types of operations. First of all, it will read, i.e., assimilate information which is supplied to it on punched cards, punched paper tape, magnetic tape, or by other techniques. Secondly, it will remember what it has read. The memory cells of most digital computers consist of magnetic cores, mercury delay lines, cathode-ray tubes,

magnetic drums, banks of relays, or electrostatic storage tubes. A relay computer remembers information by having certain relays in an energized condition while others are in the unenergized condition. Information is stored in a similar manner by other basic electrical components. Thirdly, the digital machine will perform arithmetical operations. Most computers will add, subtract, multiply, and divide. By combination of these basic operations, subroutines may be developed to take roots, raise numbers to powers, or evaluate other commonly used functions. Fourth, the large-scale digital computer may exercise choice. It is able to follow a set of logical expressions, choosing between one set of operations and another on the basis of relative magnitudes of quantities stored within its memory. Finally, the computer can write. Based on instructions given to it, the computer may record on punched cards, tape, or other output devices, the values of quantities stored within its memory.

Figure 9-1 illustrates the performance of a digital computer. The computer reads instructions and data which are presented to it, and then performs the operations upon the data according to the instructions. In performing these operations, the computer may use any of the five facilities which it possesses. These facilities are indicated in the square of Fig. 9-1 which shows the computer as a black box.<sup>1</sup> The output of the computer is then the numerical results called for by the original machine instructions.

A simple example may serve to illustrate the way in which a digital computer may be used. Suppose one wishes to evaluate the polynomial,

$$R = a_0 + a_1x + a_2x^2 + a_3x^3 + \dots + a_nx^n, \quad (9-1)$$

at each integer value from 0 to 100.

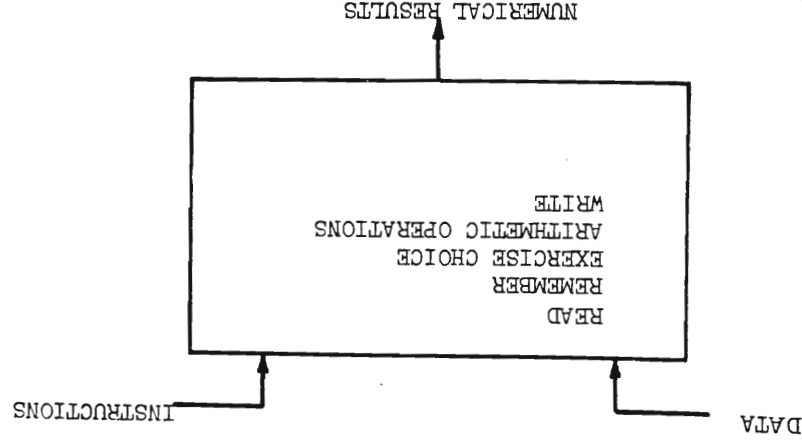


Fig. 9-1. Digital Computer Operation

<sup>1</sup> A detailed examination of the internal workings of a digital computer as well as a listing of references on the subject has been prepared: H. H. Goode and R. E. Machol, *System Engineering*, McGraw-Hill, New York, 1957.

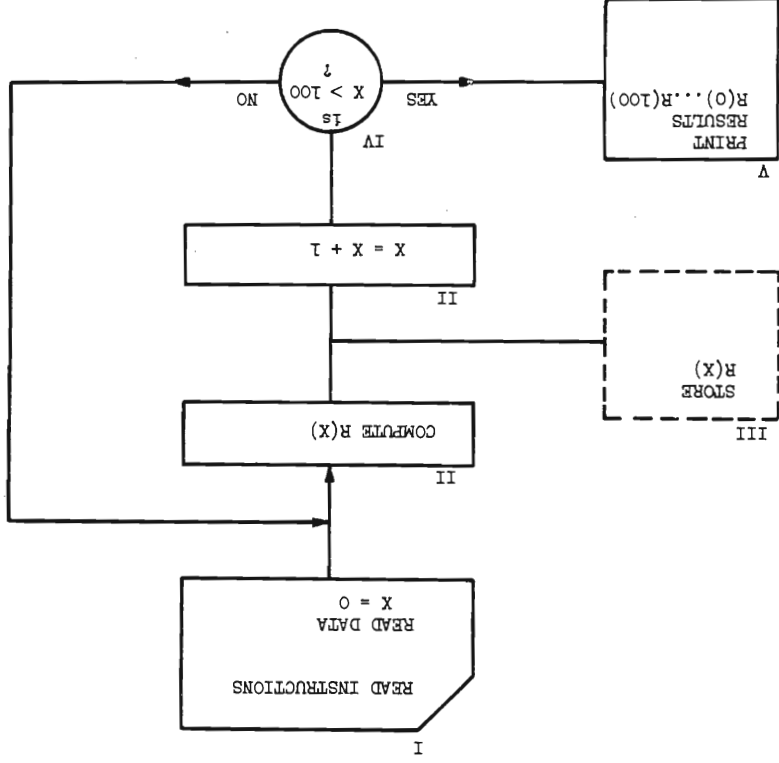


Fig. 9-2. Flow Diagram for Successive Evaluation of Polynomial

The overall organization of the computation is shown by a flow diagram in Fig. 9-2. The instructions and initial data are read into the machine in Input Box I. The machine has been instructed to compute the result,  $R$ , for the present value of  $x$ , which has been initialized at zero, Box II. The machine then stores the result,  $R(x)$ , in its memory, Box III. The value of  $x$  is then incremented by one and the computer is asked to exercise choice, Box IV. If the value of  $x$  exceeds 100, the limit of the range for calculation, the computer proceeds to print the results, Box V; if not, the loop containing instructions for computation and storage, II and III, is repeated, and the test at IV again imposed. When the value of  $x$  exceeds 100, the computer will call the values of  $R(0) \dots R(100)$  from memory and write them as Output V.

The flow diagram includes all of the operations which the digital computer is capable of performing: I Read, II Compute, III Remember, IV Exercise Choice, and V Write.

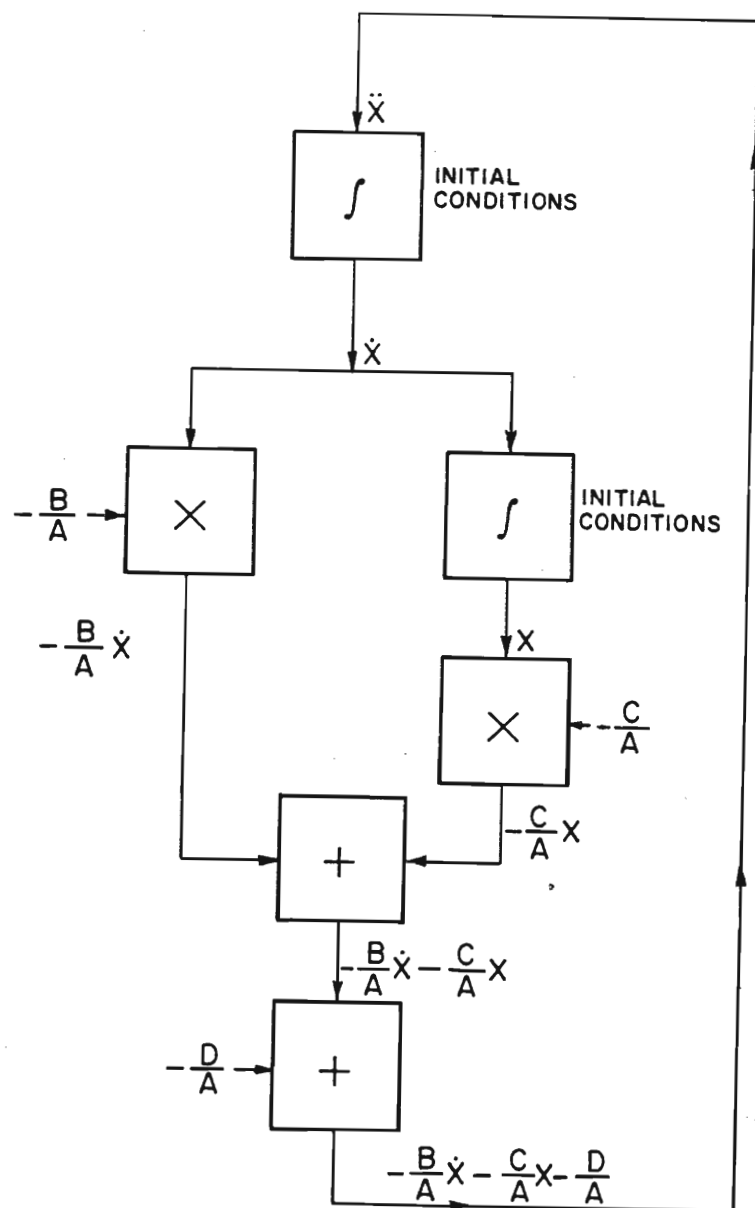


Fig. 9-3. Flow Diagram for Solution of Differential Equation with Analog Computer

### The Analog Computer

A particular form of the analog computer that is finding wide application in engineering is the electronic analog computer, or electronic differential analyzer. This device uses operational amplifiers to add, integrate, change sign, and multiply by constants greater than one. Linear potentiometers are used to multiply by constants less than one. Servo-driven potentiometers are used for general multiplication. Amplifier-servo combinations are used to divide one variable by another, and the device often includes special generators to provide certain types of functions. These components are connected to provide an electrical circuit with the same mathematical description as the problem to be solved. The circuit forms a complete loop, one variable being solved for in terms of the remaining variables and then fed back into itself.

Consider an elementary example, a second-order, linear, ordinary differential equation of the form,

$$A \frac{d^2x}{dt^2} + B \frac{dx}{dt} + Cx + D = 0. \quad (9-2)$$

Using dot notation and solving for the highest derivative,

$$\ddot{x} = -\frac{B}{A}\dot{x} - \frac{C}{A}x - \frac{D}{A}. \quad (9-3)$$

A flow diagram may be drawn indicating the solution to Eq. (9-3), as shown in Fig. 9-3. If  $\ddot{x}$  is known,  $\dot{x}$  and  $x$  may be found by integration. By performing the appropriate additions and multiplications indicated by the right side of Eq. (9-3),  $\ddot{x}$  is obtained and fed back into the input. The circuit behavior then corresponds to Eqs. (9-2) and (9-3). This type of feedback loop is basic to solutions of equations on analog computers. The initial conditions place constraints on the voltages in the loop in order to satisfy the conditions of the problem, and the results are obtained by output voltages in the circuit.

## 9-2 Applications of Electronic Computers

The applications of analog and digital computers have, in general, been in keeping with the characteristics of the two types of machines.<sup>2</sup> The analog machine is best suited to performing dynamic simulation of processes, particularly systems that are described in terms of differential relationships with respect to time. Consequently, applications of analog computers in process design have been primarily in process simulation<sup>3</sup> and in the solution of problems involving rate equations.<sup>4-6</sup>

<sup>2</sup> T. J. Williams, Systems Engineering for the Process Industries, Fourth E. P. Schoch Lecture at the University of Texas, Austin, Texas, October 16 and 17, 1959.

<sup>3</sup> H. W. Meyer, N. F. Simic, W. H. Ceckler and H. N. Lander, *Blast Furnace, Coke Oven, and Raw Materials Proc.* AIME 19, 580-93 (1960).

<sup>4</sup> R. M. Howe, *Application of Difference Technique to Heat Flow Problems Using the Electronic Analyzer*, Engineering Research Institute, University of Michigan, Ann Arbor, May, 1950.

<sup>5</sup> K. L. Chien, J. A. Hrones and J. B. Reswick, *Trans. ASME*, 74, 175 (1952).

<sup>6</sup> A. Acrivos and N. R. Amundson, *Ind. Eng. Chem.* 45, 467 (1953).

The digital computer is best suited to algebraic or logistic problems, as well as to data reduction and processing. Applications include the solution of linear programming models, statistical analysis, and process simulations that are too large or complex for the analog machine.<sup>7</sup> Several applications of a small electronic digital computer to problems in metallurgical research have been explored.<sup>8</sup>

#### Comparison of Analog and Digital Machines

The question as to whether analog or digital techniques should be employed to obtain a given problem solution often arises. The decision is not an easy one, since the theoretical advantages of one over the other may be essentially lost in practice. The decision should be based primarily on effectiveness and cost, but flexibility for use in other potential applications, ease of procurement, and considerations relative to the implementation of the machine should also be weighed.

In general, the analog machine is less expensive. But whereas both computers can solve any soluble mathematical problem, the digital machine is more suitable for problems which involve logic or massive sets of data. Other writers have discussed in some detail the relative desirability of analog or digital machines for use in solving particular classes of mathematical problems.<sup>9,10</sup> Table 9-1 presents a comparison of the two types of computers for use in process simulation, design, and analysis.

#### Extractive Metallurgy and System Engineering

The use of computers in metallurgical engineering applications is rapidly increasing, particularly in areas of extractive metallurgy, along with other engineering disciplines, accounting, production control, etc. These interdisciplinary activities are usually staffed by personnel with a variety of backgrounds and directed on a mission, often computer oriented, which requires a contribution from each of these areas. The metallurgist, as a viable and contributing member of such a team, should be prepared to consider his engineering problems in terms of the approach of other disciplines. In the following sections of this chapter, computer-oriented applications of system analysis techniques are introduced. The system optimization approaches considered are queueing theory, linear programming and simulation.

<sup>7</sup> A. L. Hodge, Predicting Effects of Oxygen, Moisture and Fuel Additions on Blast Furnace Operation with Electronic Computers, presented at the General Meeting of American Iron and Steel Institute, New York, May 25, 1960.

<sup>8</sup> R. J. Leary, R. W. Smith, Jr., and B. J. Mitchel, Applications of a Small Electronic Digital Computer to Pyrometallurgical Research, *Bureau of Mines Information Circular 7959*, U. S. Department of the Interior, 1960.

<sup>9</sup> M. Rubinoff, *Proc. IRE* **41**, 1254 (1953).

<sup>10</sup> J. Forrester and A. Vance, Institute of Radio Engineers Meeting, New York, 1951.

TABLE 9-1  
Comparison of Analog and Digital Computers<sup>a</sup>

| The advantages of analog computers relative to digital computers are:                                                                                                                                                                                                                                                                                                     |                                                                                                                               |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
| Analog computer                                                                                                                                                                                                                                                                                                                                                           | Digital computer                                                                                                              |
| Simulates behavior of any system by action of easily manipulated and measured variables                                                                                                                                                                                                                                                                                   | Performs arithmetic operations with numbers                                                                                   |
| Simulation is continuous, permits inclusion of concepts such as distance, velocity, acceleration                                                                                                                                                                                                                                                                          | Operates discontinuously; can only approximate higher order effects                                                           |
| Results presented as family of graphs of variation of dependent variable (same data obtained with recorder connected to process)                                                                                                                                                                                                                                          | Results presented as tables of numbers, although plotting subroutines are available for most systems                          |
| Speed of problem solving is direct function of actual speed of physical system, is independent of size or complexity of system                                                                                                                                                                                                                                            | Speed is direct function of problem complexity and size, relatively independent of operating speed of process                 |
| Programmed so that parameter magnitudes are entered as setting on variable potentiometers; parameter values can be changed at will                                                                                                                                                                                                                                        | Flexibility not present without special programming precautions                                                               |
| The disadvantages of the analog relative to the digital computer are:                                                                                                                                                                                                                                                                                                     |                                                                                                                               |
| Analog computer                                                                                                                                                                                                                                                                                                                                                           | Digital computer                                                                                                              |
| Size of computer (number of computing components) determines size of problem which can be solved; simplifying assumptions often made to reduce complexity                                                                                                                                                                                                                 | Problem size reflected in computing time; no limit to size of problem if time is available                                    |
| Specifically designed for solution of ordinary differential equations; other problems, e.g., solution of simultaneous algebraic equations, treated by trial and error. Less complex partial differential equations solved if converted to ordinary differential equations and one variable assumed constant; family of solutions for different values of variable results | Useful in nearly all types of problems, Complex partial differential equations more amenable to solution by digital equipment |

<sup>a</sup> T. J. Williams, *Ind. Eng. Chem.* **50**, 1632 (1958).

The relative advantages of the two types of computers for various applications are:

| Application                            | Analog computers                                                                                                                                      | Digital computers                                                                                                                    |
|----------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| Equipment and plant design             | Show great promise for working out relative sizes of plant equipment by solving dynamic equations of plant performance                                | Superior for details of mechanical design, e.g., stresses, sizing of members, costs, which are trial and error arithmetical problems |
| Instrumentation and data reduction     | Small, special purpose analogs, important in converting and plotting single variable and directly correlated multiple variable data in form of graphs |                                                                                                                                      |
| Process control simulations (research) | Best tool in existence for studying resulting phenomenon; limitation on system complexity imposed by computer size                                    |                                                                                                                                      |
| Plant control applications             | Definite promise as final control elements for units of highly automated plants                                                                       | Flexibility and accuracy of digital computers better for control of whole plants                                                     |
| Research in basic processes            | Well suited to simulation of reaction kinetics involved in process development                                                                        | Better for determination of kinetic parameters by statistical data reduction where necessary                                         |
| Research in unit operations            | Well suited for study of transient state such as heat transfer, distillation                                                                          | Better suited for steady-state studies which are usually arithmetical or statistical                                                 |
| Plant operations and management        |                                                                                                                                                       | Better here because statistics and arithmetical operations predominate                                                               |

### 9-3 Material Handling—A Queueing Theory Approach

The handling of materials between unit processes in a system plays an extremely important role in determining the overall efficiency of the operation. As a prime example of a computer application in metallurgy, a discussion will follow of a queueing theory approach to material handling. Although it is not an exhaustive treatment of the subject<sup>11</sup> it should lay a good foundation for the metallurgical

<sup>11</sup>A sound approach to plant design engineering (T. C. Vilbrands and C. E. Dryden, *Chemical Engineering Plant Design*, McGraw-Hill, New York, 1959.) and a discussion of some of the details involved in material handling [Session on materials handling, *Electric Furnace Steel Proceedings* 7, 5 (1949)] are available in the literature.

engineer in outlining some of the methods and procedures that are available to him when considering the design of systems that involve the transport of materials.

#### Queueing Theory

Queueing theory is used to describe the mathematical approaches to problems arising whenever delays occur or priorities must be arranged regarding the sequence of a given operation. The mathematical models and solutions of the problems are the same whether the individuals or things are waiting or whether a gate is moving around to the waiting persons or objects. Applications of queueing theory have been made to a large number of problems in which waiting time is involved, including the landing of aircraft, the loading and unloading of ore ships, the design of automobile parking, waiting and traffic facilities, the passage of travelers through customs, pedestrian movements, and servicing machine failures.<sup>12,13</sup>

In the development of a queueing model one must provide for (1) gate or service points, (2) an input process, (3) some queue discipline, and (4) some service mechanism. The model then describes the situation in which customers arrive at a gate or service point, are serviced, and then leave the service area. The arrival of customers is the input process, and may be described in terms of the distribution of arrivals at the service point. As the product of the input process arrives at the service point and joins a queue, it is termed a customer. The behavior of the customer is described in terms of a queue discipline that determines how the customer reacts to the existing condition of the queue. If the queue is too long, the customer may leave the service area and be lost to the system. In the case of a multiple channel servicing system, the customer may join the queue of shortest length. Or the customer may be required to remain in the queue, regardless of the apparent waiting time. The service mechanism is a description of the service provided in terms of the service time involved, which may be a constant or may decrease slightly with increase in queue length, or even be statistically distributed in some manner.

The elements of interest in an analysis of the queueing problem are: (1) waiting times for the customers, (2) the number of customers in the queue, (3) the ratio of waiting time to service time.

The purpose in seeking a model which describes the queueing problem is to provide for the servicing of as many customers with as few facilities as possible. Generally, one optimizes the economics of the situation by seeking the minimum cost involved for some balance of waiting time between servicing unit and customer.

#### Single Station Queueing Problem

Let us consider the problem of determining the probability of a given queue length and the expected queue length for the case of a single station for which both input and output are assumed to be random. (Specifically, a single channel queue system, having a Poisson input and a negative exponential service time distribution

<sup>12</sup> Marshall and Queueing, *Operational Res. Quart.* 3, No. 1 (1952).

<sup>13</sup> D. G. Kendall, *J. Roy. Stat. Soc. B* 13, 151 (1951).

in the steady state). A queue discipline is assumed such that each arriving unit takes the last position in the queue and that the units which make up the line are serviced in order of appearance in the line, i.e., first in, first out. It may be shown<sup>14</sup> that the probability of a waiting line of length  $n$  units  $P_n$  is given by

$$P_n = \left(\frac{\lambda}{\mu}\right)^n \left(\frac{1-\lambda}{\mu}\right), \quad (9-4)$$

if  $\lambda/\mu$  is less than one, where  $\lambda$  is the mean arrival rate, and  $\mu$  the mean service rate; (if  $\lambda/\mu$  were greater than one, the line would grow infinitely long). The ratio  $\lambda/\mu$  is sometimes called "traffic intensity" and is the average number of arrivals per unit of service.

Then the mean length of a waiting line is given by the expression,

$$\bar{n} = \frac{\lambda/\mu}{[1 - (\lambda/\mu)]} \quad (9-5)$$

if  $\lambda/\mu$  is less than one.

The expected waiting time of arrivals at a single station with random input can be formulated as follows:

Let  $\bar{t}_w$  = expected waiting time and  $\bar{t}_s$  = expected time spent in service; then  $\bar{t}_w + \bar{t}_s$  = total expected time consumed in both waiting and service. When the mean arrival rate is  $\lambda$ ,

$$\bar{n} = \lambda(\bar{t}_w + \bar{t}_s) \quad (9-6)$$

from which

$$\bar{t}_w = \frac{\bar{n}}{\lambda} - \bar{t}_s. \quad (9-7)$$

Since

$$\bar{t}_s = \frac{1}{\mu}. \quad (9-8)$$

By substitution in Eq. (9-5)

$$\bar{t}_w = \frac{1}{(\mu - \lambda)} - \frac{1}{\mu} \quad (9-9)$$

describes the expected waiting time at a single station.

In order that the real life situation be more closely approached by the queueing model, specific distributions for the probability of arrival often have been substituted in the model. In several cases data taken under actual operating conditions for a sufficiently large sample have been shown to be approximated very closely by exponential or Poisson distributions.

#### Example of Single Station Queueing Problem

Consider the case of a heat treating section consisting of a single furnace that provides service for the many areas of a manufacturing plant. The job requirements

<sup>14</sup> C. W. Churchman, R. L. Ackoff, and E. L. Arnoff, *Introduction to Operations Research*, John Wiley, New York, 1957.

vary in a random manner, as do the arrivals of parts for heat treating. The section is operated as a closed system, and parts arriving remain until they are treated with each job handled in the order in which it arrives. This hypothetical situation corresponds very closely with the queueing model derived above.

If the mean arrival rate  $\lambda$  is 5 jobs per day and the mean service rate  $\mu$  is 10 jobs per day, the traffic intensity  $\lambda/\mu = \frac{5}{10} = \frac{1}{2}$ . The probability of a waiting line of given length,  $n$ , is

$$P_n = \left(\frac{1}{2}\right)^n (1 - \frac{1}{2}) \quad (9-10)$$

and the average number of jobs waiting is

$$\bar{n} = \frac{\frac{1}{2}}{(1 - \frac{1}{2})} = 1. \quad (9-11)$$

If the traffic intensity  $\lambda/\mu$  increases, the average queue length increases, approaching infinity, as the service time approaches the arrival time, i.e.  $(1 - \lambda/\mu) \rightarrow 0$ .

The analysis above is important to the management of the manufacturing firm in determining the optimum heat treating facilities for handling a given distribution of job requests. In the simplified case just stated, an increase in the arrival rate to a level approaching 10 jobs per day would require that either the service times be decreased or that a multiple station arrangement be substituted, i.e., that the capacity of the facilities be increased.

#### Multistation Queueing Problem

Consider the case in which customers arrive at a service station and receive service from several units,  $S$ , under the assumptions made for the single station model. The probability of having to wait in line, which is the sum of all probabilities that all service facilities are being used or that  $S$  or more customers are in line, is given by the expression,

$$W = \sum_{n=S}^{\infty} P_n = \left(\frac{\lambda}{\mu}\right)^S \frac{P_0}{S!(1 - \lambda/\mu S)}, \quad (9-12)$$

where  $W$  is the probability that all service facilities are being used and  $P_0$  is the probability that zero customers are being served. The average waiting time for the case of multichannel servicing facilities is

$$\bar{t}_w = \frac{P_0}{\mu S (S!) [1 - (\lambda/\mu S)]^2} \left(\frac{\lambda}{\mu}\right)^S \quad (9-13)$$

and it may also be shown that the probability of no customers being served,  $P_0$ , is given by the expression,

$$P_0 = 1 / \left\{ \left[ \sum_{n=0}^{S-1} \frac{(\lambda/\mu)^n}{n!} \right] + \left[ \frac{(\lambda/\mu)^S}{S! [1 - (\lambda/\mu S)]} \right] \right\}. \quad (9-14)$$

## Example of Multistation Model

The crane facilities provided in an open-hearth shop for tapping, teeming, and other pouring floor service requirements may be optimized by application of the multistation queueing model described above.

While strictly speaking, the behavior of the handling system in a steelmaking plant does not follow the assumption of random input and output (in fact in most plants a large staff of people are engaged in preventing it from becoming so!), the model permits some examination of the problem and represents a situation more extreme than normal. It may be assumed that the facilities, one, two, three, or more cranes, are the service gates which provide service to the customers (the furnaces), and do so on a basis that permits any free crane to handle the service requirements of a furnace, the furnaces queueing until service may be provided. This last assumption also is not accurate, since the cranes usually operate on the same track and are not free to move around each other to change their relative position. However, the assumption may be justified on the basis that a crane that has received a ladle of metal may transfer that ladle to the next crane and then proceed to provide service to a furnace further down in the shop.

*Example Problem 9-1.* Consider an open hearth shop with twelve operating 200-ton furnaces which average 10 hr/heat. The service times for tapping, pouring, and removing the slag ladles average 1.0 hr/tap. Assuming a cost of \$300/hr for the furnaces and \$50/hr for the cranes, determine the optimum number of cranes.

*Solution.* The average time between arrivals is 0.833 hr, since in a 10-hr period, an average of 12 heats would require servicing. In a 24-hr period, an average of 28.8 arrivals would occur, requiring a total of 28.8 hr of service. This service requirement dictates that at least two cranes are necessary.

Evaluating the expected waiting times for the furnaces for two cranes may be done as follows. From Eq. (9-14), where the traffic intensity  $\lambda/\mu = 1/0.833/1.0 = 1.2$  heats per average service time

$$P_0 = 1 / \left\{ \left[ \sum_{n=0}^{\infty} \frac{(1.2)^n}{n!} \right] + \left[ \frac{(1.2)^2}{2! [1 - (1.2/2)]} \right] \right\} \quad (9-a)$$

$$= 1 / \left[ (1 + 1.2) + \frac{(1.2)^2}{0.8} \right] = 0.250. \quad (9-b)$$

$$\bar{L}_w = \frac{0.250}{(1)(2)(2)[1 - (1.2/2)]^2} (1.2)^2 = 0.561. \quad (9-c)$$

One may thus prepare a table, Table 9-2, indicating the waiting times for the furnaces in average service time units.

The idle hours of the furnaces and cranes are given in Table 9-3. The total waiting time for the furnaces is given by the average waiting time per heat times the number of heats per day, 28.8. The total waiting time of the cranes is given by the available hours, 24 times the number of cranes, minus the required hours of service, 28.8.

TABLE 9-2  
Summary of Calculations for Multistation Queueing Example

| Arrivals per service time | service time | No. of cranes, S | $P_0$ | Average furnace waiting time |       |
|---------------------------|--------------|------------------|-------|------------------------------|-------|
|                           |              |                  |       | Av. Ser. Time units          | Hours |
| 1.2                       | 1.0          | 2                | 0.250 | 0.561                        | 0.561 |
| 1.2                       | 1.0          | 3                | 0.294 | 0.078                        | 0.078 |
| 1.2                       | 1.0          | 4                | 0.300 | 0.013                        | 0.013 |

The total cost of idle time may be computed as shown in Table 9-3. The optimum service facilities are indicated by the minimum cost, and in this case are shown to be 3 cranes, a result in keeping with practice in the industry.

## Other Approaches to Queueing Problems

The analytical methods presented above are relatively straightforward and the examples used to illustrate them have been greatly simplified. Only a restricted number of cases can be validly treated by these methods. There are, however, techniques for determining the characteristics of a queueing system when the arrival and service distributions are not conveniently expressed mathematically. These methods are described in the literature and listed under several headings, which include Monte Carlo techniques, Theory of Games, and Stochastic Processes.

The problems involved in analyzing queueing situations which arise in actual integrated plant operations are extremely complex and often prohibitively difficult. However, advances are being rapidly made and new applications are being generated at a high rate. Consideration of these concepts is inherent to the system approach in

TABLE 9-3  
Cost Analysis for Service Facilities in Open Hearth Shop

| No. of cranes | Idle hr cranes | Cost of cranes | Idle hr furnaces | Cost of furnaces | Total cost per 24 hr |
|---------------|----------------|----------------|------------------|------------------|----------------------|
| 2             | 19.2           | \$ 960         | 16.2             | \$4860           | \$5820               |
| 3             | 43.2           | \$2160         | 2.25             | \$ 675           | \$2835               |
| 4             | 67.2           | \$3360         | 0.38             | \$ 114           | \$3474               |

metallurgical process design, and greater emphasis will undoubtedly be placed on the queueing theory approach to material transportation problems.<sup>15-23</sup>

### 9-4 Linear Programming

Linear programming is a mathematical procedure used for solving a general class of optimization problems that involve a combination of a number of interacting factors to produce a maximum or minimum result. In order to apply linear programming, the following criteria must be met: (1) There is some function that is to be made maximum or minimum; (2) There are a variety of solutions, each of which is subject to a set of well-defined restrictions that may be expressed as equalities or inequalities; and (3) Among the variables of the problem, the relationship between any two may be represented by a straight line or linear relationship at least to an acceptable degree of approximation.

The use of the linear programming model may be illustrated by the following example.

**Example Problem 9-2.** Consider a metallurgical firm that wishes to produce an alloy steel of the following specifications: vanadium—0.8% minimum; chromium—1.8% minimum; manganese—0.6% minimum. In addition, the firm possesses a supply of two alloying materials of the following compositions:

|     | Alloy 1 | Alloy 2 |
|-----|---------|---------|
| %V  | 40%     | 10%     |
| %Cr | 40%     | 30%     |
| %Mn | 10%     | 30%     |
| %Fe | Balance | Balance |

where Alloy 1 costs \$4/lb and Alloy 2 costs \$2/lb.

**Solution.** On the basis of the production of 100 lb of the desired alloy steel, let  $x_1$  equal the number of pounds of Alloy 1 used and  $x_2$  equal the number of pounds of Alloy 2 used, both as additives to molten low carbon steel scrap of negligible cost.

A combination of  $x_1$  and  $x_2$  will produce a solution to the problem if and only if that combination satisfies the specifications for the alloy steel. This may be expressed as

$$0.4x_1 + 0.1x_2 \geq 0.8 \quad \text{Vanadium balance,} \quad (9-a)$$

<sup>15</sup> J. F. McCloskey and F. N. Trefethen, Eds., *Operations Research for Management*, The Johns Hopkins Press, Baltimore, 1954.

<sup>16</sup> P. M. Morse, *Queues, Inventories, and Maintenance*, New York, John Wiley, New York, 1958.

<sup>17</sup> W. Feller, *An Introduction to Probability Theory and its Application*, John Wiley, New York, 1950.

<sup>18</sup> M. D. J. Brisby and R. T. Eddison, *J. Iron and Steel Inst.* **172**, 171 (1952).

<sup>19</sup> D. P. Gayer, *J. Operations Res. Soc. Amer.* **2**, No. 2 (1954).

<sup>20</sup> L. C. Eddie, *J. Operations Res. Soc. Amer.* **2**, 107 (1954).

<sup>21</sup> T. Fry, *Probability and Its Engineering Uses*, 2nd ed., D. Van Nostrand Co., Inc., Princeton, N.J., 1965.

<sup>22</sup> M. Sasiemi, A. Yaspan, and L. Friedman, *Operations Research*, John Wiley, New York, 1959.

<sup>23</sup> A. Charnes, W. Cooper, and A. E. Henderson, *An Introduction to Linear Programming*, John Wiley, New York, 1953.

$$0.4x_1 + 0.3x_2 \geq 1.8 \quad \text{Chromium balance,} \quad (9-b)$$

$$0.1x_1 + 0.3x_2 \geq 0.6 \quad \text{Manganese balance,} \quad (9-c)$$

where

$$x_1 \geq 0 \quad (9-d)$$

and

$$x_2 \geq 0 \quad (9-e)$$

It is possible to show graphically the feasible solutions which satisfy the set of inequalities presented above. The shaded region of Fig. 9-4 contains all the allowable solutions.

The solution to the problem is found in the optimum combination of alloying additions which minimize the cost function,

$$C = 4x_1 + 2x_2. \quad (9-f)$$

The cost function may be plotted as a family of parallel lines whose parameter is total cost. The family of parallel lines may be superimposed on the graph as shown in Fig. 9-4 from which it may be concluded that the optimum alloying addition will occur at the vertex of the line-bounded region of feasible additions. Since the firm seeks the lowest cost, the optimum alloying addition occurs at the point (0.75, 5) indicating that the optimum addition consists of

$$\left. \begin{array}{l} \frac{3}{4} \text{ lb of Alloy 1} \\ 5 \text{ lb of Alloy 2} \end{array} \right\} \text{ per 100 lb of steel}$$

$$\text{at a cost of } (\frac{3}{4})4 + (5)2 = \$13/100 \text{ lb of steel.}$$

As the number of variables in a linear programming problem increases, visualization of the region of feasible solutions is more difficult. In three dimensions, the region of feasible solutions is represented by a polyhedron bounded by planes corresponding to the problem restrictions. As in the two-dimensional case, the optimum solution will occur at a vertex of the polyhedron, and the cost function will define a family of planes. As the number of variables increases, the geometry becomes more and more complex. As a result, it is necessary to turn to an algebraic approach that may be applied to any number of variables and is most suitably carried out on a digital computer. The simplex technique is the most general linear programming model,<sup>24-31</sup> and permits a directed exploration of the extreme points of the problem. A documented computer program for executing the simplex tech-

<sup>24</sup> G. B. Dantzig, *Activity Analysis of Production and Allocation* (T. C. Koopmans, Ed.), Cowles Commission Monograph, Vol. 13, Chap. 21, John Wiley, New York, 1951.

<sup>25</sup> Churchman, Ackoff, and Arnoff, *op. cit.*

<sup>26</sup> *Operations Research for Management*, *op. cit.*

<sup>27</sup> A. Charnes, W. Cooper, and A. E. Henderson, *An Introduction to Linear Programming*, John Wiley, New York, 1953.

<sup>28</sup> An-Min Chung, *Linear Programming*, Charles E. Merrill Books, Inc., Columbus, Ohio, 1963.

<sup>29</sup> S. Gass, *Linear Programming*, McGraw-Hill, New York, 1964.

<sup>30</sup> M. Simonard, *Linear Programming*, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960.

<sup>31</sup> G. B. Dantzig, *Linear Programming and Extensions*, Princeton University Press, Princeton, N. J., 1963.

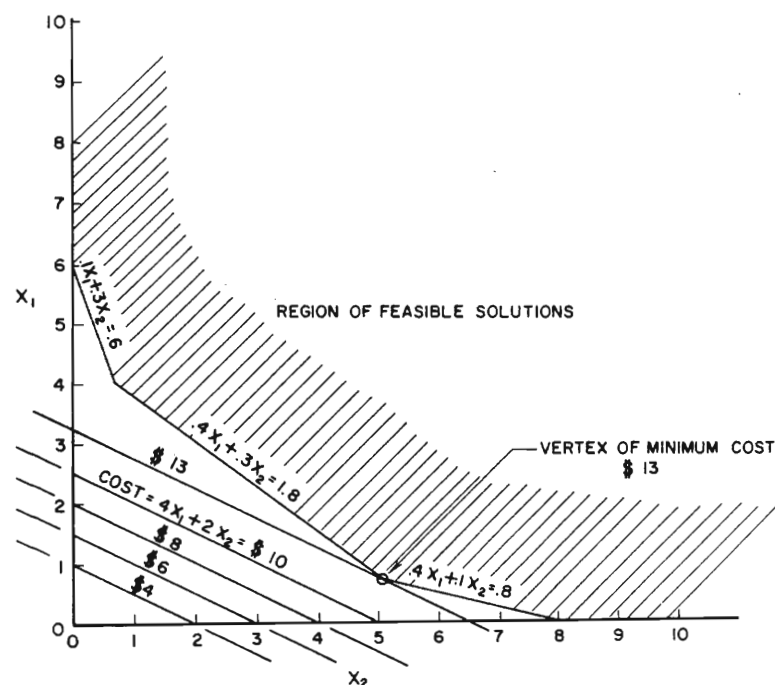


Fig. 9-4. Graphical Solution of Two-Dimensional Linear Programming Problem

nique has been presented.<sup>32,33</sup> (See Appendix B, Example Problem 10). In addition, most computing centers have linear programming models available as subroutines.

In certain special cases, the linear programming problem can be solved by the "transportation technique." Problems of this type also can be solved by the simplex method, but are solved more directly by the transportation technique. The general transportation problem involves a number of origins from which products are shipped to a given number of destinations, each requiring a given number of units of product. The cost of shipping is to be minimized. Techniques for treating this problem have been presented.<sup>34</sup>

#### Applications of Linear Programming

Linear programming has found considerable application in the field of business planning and operation. A few problems that have been solved by linear program-

ming techniques include the blending of aviation gases,<sup>35</sup> contract awards,<sup>36</sup> allocation of manufactured products,<sup>37,38</sup> optimum treatment of a natural resource,<sup>39</sup> and the long-range planning of coke oven replacements.<sup>40</sup>

The use of linear programming for control of technical processes has been developing rapidly in all areas of engineering, particularly for the chemical industry.<sup>41-43</sup> Fabian<sup>44</sup> has proposed the use of linear programming to determine the least cost rate of input of materials into an integrated steel mill. Although Fabian's treatment of the problem is limited, it clearly illustrates the potential of the method and represents an excellent approach to a relatively difficult problem. Linear programming has also been used to predict the minimum materials cost for melting stainless steels.<sup>45,46</sup>

It should be noted that the foregoing discussion is by no means complete. Optimization techniques extend beyond linear programming and include dynamic programming.<sup>47-50</sup> Dynamic programming has been applied to the optimization of stainless steel melting practice.<sup>51</sup> Other systematic techniques for determining optima have been reviewed.<sup>52</sup> The use of these optimization techniques, particularly in conjunction with large-scale digital computers, should offer an excellent means for utilizing the vast amount of data that is being produced in various areas of the process metallurgical industry. By combining these data with available operating and economic information in the form of optimization models, many problems—both economic and technical—that face the metallurgical process engineer may be greatly clarified and suitable solutions may be worked out using these techniques.<sup>53,54</sup>

<sup>35</sup> A. Charnes, W. W. Cooper, and B. Mellon, Blending Aviation Gasolines—A Study in Programming Interdependent Activities, Project SCOOP, Symposium of Linear Inequalities and Programming, Headquarters, U. S. Air Force, Washington, 1952.

<sup>36</sup> L. Goldstein, *The Theory of Gains and Economic Behavior*, Princeton University Press, Princeton, N.J., 1947.

<sup>37</sup> E. L. Arnoff, An application of linear programming, *Proceedings of the Conference on Operations Research in Production and Inventory Control*, Case Institute of Technology, Cleveland, Ohio, 1954.

<sup>38</sup> W. W. Cooper, A. Charnes and D. Farr, *Linear Programming Models for Scheduling Manufactured Products*, Carnegie Institute of Technology, Pittsburgh, September 1, 1952.

<sup>39</sup> R. Klimpel and M. Klein, *Symposium for the Use of Computers and Operations Research in the Mineral Industries*, University Park, Penn., April, 1966.

<sup>40</sup> T. D. Truan and D. A. Porco, *Management Sci.* **4**, 337 (1958).

<sup>41</sup> W. B. White, S. M. Johnson, and G. B. Dantzig, *J. Chem. Phys.* **28**, 751 (1958).

<sup>42</sup> P. Stillson, *Ind. Eng. Chem.* **48**, 402 (1956).

<sup>43</sup> J. M. Henderson, *Rev. Econ. Stat.* **37**, 336 (1955).

<sup>44</sup> T. Fabian, *Management Sci.* **4**, 415 (1958).

<sup>45</sup> D. C. Hilty, R. W. Taylor, and R. H. Gillespie, *J. Metals* **11**, 458 (1959).

<sup>46</sup> IBM: Data Processing Application, Paper No. B 20-0147-0.

<sup>47</sup> R. Bellman, *Dynamic Programming*, Princeton University Press, Princeton, N. J., 1957.

<sup>48</sup> G. Nemhauser, *Introduction to Dynamic Programming*, John Wiley, New York, 1966.

<sup>49</sup> D. F. Rudd and C. C. Watson, *Strategy of Process Engineering*, John Wiley, New York, 1968.

<sup>50</sup> R. Aris, *Discrete Dynamic Programming*, Blaisdell Publishing Company, New York, 1964.

<sup>51</sup> E. Calanog and G. H. Geiger, *J. Metals* **19**, No. 7, 96 (1967).

<sup>52</sup> B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods*, John Wiley, New York, 1969.

<sup>53</sup> J. J. Taborek, *Chem. Eng. Prog.* **56**, 37 (1960).

<sup>54</sup> C. Berg, *Chem. Eng. Prog.* **56**, 42 (1960).

<sup>32</sup> Simonnard, *op. cit.*

<sup>33</sup> B. Carnahan, Private Communication, University of Michigan, 1967.

<sup>34</sup> A. Charnes and W. W. Cooper, Appendix, *Management Sci.* **1**, No 1 (1954).

## 9-5 Process Simulation

One of the principal applications of computers to process engineering is in the area of simulation.<sup>55-62</sup> A detailed computer simulation of a process to determine the effect of all process parameters on yields and on by-product formation requires the derivation of a complete reaction model. An accurate simulation of a process permits optimum processing conditions to be specified and serves as a basis for control of a process or combination of processes.<sup>63</sup>

The derivation of an accurate dynamic model is often not an easy task, and one is faced with several alternatives.

1. The dynamics of the process may be described in terms of a series of differential equations that represent the mass and energy transfer processes which occur in the reactor.
2. The process dynamics may be described in terms of the operating results of similar reactors that are already in commercial use. A detailed description of the change in chemical concentrations, temperatures, flow rates, etc., as functions of time may be reduced to descriptive functions by numerical analysis with the assistance of a digital computer, or by trial and error techniques using an analog computer.
3. The system may be described in terms of the average operating characteristics for the particular type of reactor, based on the observations made on commercial-sized units. The particular reactor may present a characteristic concentration-time relationship, or may involve temperature dependences that are easily observable. In this case, the average operating results may be applied to the system which is in the design stage. This model is not entirely a dynamic one, but it is certainly highly descriptive of the process and may be used to some advantage.
4. In the case of metallurgical reactors in which the mechanisms of the processes being carried out are not completely understood, one may neglect the process dynamics and select a fixed process time for a batch unit or a suitable flow rate for a continuous unit on the basis of either previous experience or good engineering judgment. Although this final choice is far

<sup>55</sup> T. J. Williams, *Systems Engineering for the Process Industries*, The Fourth E. P. Schoch Lecture at the University of Texas, Austin, Texas, October 16 and 17, 1959.

<sup>56</sup> D. P. Campbell, *Process Dynamics*, John Wiley, New York, 1958.

<sup>57</sup> D. P. Eckman, *Automatic Process Control*, Chap. 2, John Wiley, New York, 1958.

<sup>58</sup> *Project Cyclone Symposium I on React Techniques*, Port Washington, N. Y., March 15 and 16, 1951, SDC, USN.

<sup>59</sup> *Project Cyclone Symposium II on Simulation and Computing Techniques*, Port Washington, N. Y., April 28-May 2, 1952, SDC, and BUAER, USN.

<sup>60</sup> *Symposium III on Simulation and Computing Techniques*, Port Washington, N. Y., October 12-14, 1953, BAUER and NADC, USN.

<sup>61</sup> *Proc. Natl. Simulation Conference*, Sponsored by Institute of Radio Engineers, Dallas, Texas, January 19-21, 1956.

<sup>62</sup> H. H. Goode, *Proc. IRE* 39, 1501 (1951).

<sup>63</sup> A. B. Chelyustkin, *The Application of Computing Technique to Automatic Control Systems in Metallurgical Plant*, Pergamon Press, New York, 1964.

from a satisfactory one, the reduction of the process model to a mass and energy balance does permit the evaluation of many of the process variables and furnishes a basis on which the dynamics of the process may be either estimated or evaluated after construction of the pilot plant or commercial-sized unit.

The set of simultaneous equations describing the process system includes one for each separate chemical species formed or utilized in the chemical reactions comprising the process. The mass and energy balances for each chemical species are interrelated in the form,

$$\frac{dQ}{dt} = -V \frac{dC}{dt} \Delta H, \quad (9-15)$$

where

$V$  = factor that converts concentration to weight units,

$C$  = concentration of product,

$\Delta H$  = change in thermal energy during the reaction for each weight unit formed,

$\frac{dQ}{dt}$  = rate of heat gain to the complete reactor system.

Heat transfer equations may then be set up to include:

1. The energy manifested as a temperature change in the reaction mass.
2. The energy representing that which appears as a temperature change in the reaction vessel.
3. The energy transferred to or from the surroundings.

Having expressed the process variables in such a set of simultaneous differential equations, the dynamics of the system may be included in the process model in the form of a differential equation involving the changes in concentration with respect to time as functions of process geometry and chemical driving forces.

Consider, for example, the reaction which takes place when a reactive gas is contacted with a liquid metal. The differential equation describing the rate of solution of gas is

$$\frac{dc}{dt} = k' \frac{A}{V} (c_s - c), \quad (9-16)$$

where

$\frac{dc}{dt}$  = rate of change of concentration, wt%/sec,

$k'$  = rate constant, cm/sec,

$A$  = area of gas-metal interface, cm<sup>2</sup>,

$V$  = volume of melt, cm<sup>3</sup>,

$c_s$  = equilibrium concentration of dissolved gas, wt%,

$c$  = instantaneous concentration of dissolved gas, wt%.

If the particular gas under consideration is nitrogen, and the melt is liquid pure iron, the mass and heat balances may be interrelated by the relationship,

$$\frac{dQ}{dt} = - \left[ \frac{dc}{dt} \right] \left[ \frac{W}{100} \right] \left[ \frac{860}{14} \right], \quad (9-17)$$

where

$\frac{dQ}{dt}$  = energy transferred to the system, cal/sec,

$W$  = weight of melt, g,

$\frac{860}{14}$  = heat of solution, cal/g.

The dynamics of the process may then be expressed in terms of Eqs. (9-16) and (9-17). These equations, when coupled with the mass and energy balances, may then form a process model suitable for simulation. The dynamics of this simple process are very well understood, and the computer simulation of such a process would yield highly accurate results. This particular model would correspond to the dynamic process Model 1 indicated above.

Process Model 2 would involve the observation of the behavior of the system with respect to mass changes, that is, gas going into solution in the metal and temperature changes along with the variation in those quantities entering into the mass and energy balances. Such data then could be reduced on a computer to a dynamic model that would yield a highly accurate simulation of the process, accuracy, of course, depending upon the reliability and extensiveness of the data taken.

Process Model 3 would involve the averaging of data observed on many systems involving gas-metal reactions, and the application of such generalized gas-metal behavior to the system under consideration. One might assume, for example, that the gas content of the metal varies linearly with time and that the average time of solution is given by a certain number of minutes. Such a model, of course, is not highly accurate, but does permit a reasonable prediction of the behavior of such a gas-metal equilibration process.

Process Model 4, which ignores the variations in process variables with respect to time and considers only the overall result, also can be applied to this particular process. If the equilibrium state of the system is known, and one has reason to believe that sufficient time will be allowed to approach this equilibrium condition, the mass and energy balances of the system may be written on this basis.

The example system selected above was a highly simplified one. In the general case, there are a large number of concentration variables as well as many thermal and geometrical parameters involved. In most metallurgical process operations, one is faced with the relatively difficult task of not only evaluating each of these variables, but also attempting to write a descriptive model that involves their interactions as well. Much of this data has become available in the last few years and considerable work is presently being expended in this direction. It is thus expected that Approach 1 will become more and more important as metallurgical process operations are better understood. In the present situation, the availability of high-

speed computing equipment as well as the installation of better instrumentation and control systems in metallurgical plants should permit very advantageous use to be made of Approach 2. The development of data processing techniques and the success with which simulation of processes has been used, particularly in the chemical industries, should be an indication to the practicing metallurgist that considerable clarification may be brought to bear on the operation of metallurgical processing plants.

In attempting to write descriptive models for the purpose of process simulation, one should bear in mind some of the basic elements of process dynamics. It may be noted that the dynamic behavior of a chemical process depends upon the kinetics of the reactions involved, the manner in which the environment variables change with time, and the geometry of the system. To relate these factors quantitatively requires that differential equations be formed to express the interrelation that exists between physical variables. As indicated above, these data generally are not available, or if available, the resulting equations are not solved easily by means of arithmetical methods because they are nonlinear. However, it often is unnecessary to make a precise study of the dynamics of the process in order to approximate sufficiently the reactor dynamics to a degree that may be useful in obtaining engineering results.

The rates of metallurgical reactions may range from very slow to very rapid. The relative speed of the reaction with respect to the residence time in the system determines whether the chemical reaction rates or the material handling steps have the dominant role in the process kinetics. When mixing lags are small and reaction rates are slow, the dynamic behavior of the system may be determined largely by the chemical kinetics.

However, when reaction rates are high and material handling lags large, the situation reverses. Instantaneous conversion of charge material into product can be assumed and the kinetics of the process treated on the basis of the material-handling dynamics of the product emerging from the system. If material handling is the rate-controlling step, static material balance equations may be used to describe the conversion of raw material into product in an "ideal system." These equations can be modified then by the appropriate functions to describe mixing and transportation of material.

In addition to the above concepts, a number of assumptions often are made to facilitate the formulation of a descriptive process mode. Batch and continuous stirred systems generally are considered to be perfectly mixed, i.e., there are no temperature or concentration gradients in the reacting materials. The heat transfer coefficients throughout the system are considered to be constant at the ambient operating temperatures of the system. The use of these assumptions, of course, involves their justification in each application for which they are used. One must often rely on engineering judgment, particularly where previous experience in the area is not available.

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### Discussion Questions

- Describe a general systematic approach to the development of a computer control system for an extractive metallurgical process. Include in addition to a philosophy, instrumentation, mathematical model building with special emphasis on the key links to kinetic descriptions of processes, open-loop versus closed loop control, integration of control system and process, and optimization of the individual process with the entire plant.
- Diagram and set up a flow chart describing the movement of all materials in and out of a three vessel basic oxygen steelmaking plant.
- Discuss computer control of the iron blast furnace. What variables should be monitored? What changes in operation can be effected to provide process control? Outline a means for developing the interrelationship between the monitored process variables and the control parameters.
- Prepare an algorithm for a computation procedure which would simulate the heat flow and temperature loss for steel between tapping from the steelmaking furnace and teeming into a continuous casting strand or ingot molds.
- Hybrid (analog-digital) computers have been developed to take advantage of combining the unique characteristics of both types of computers. Discuss possible applications of hybrid computers in simulation and control of metallurgical processes.

- Sintering plants for ore preparation represent a highly important portion of the process of steel production. A high rate of production and the need for presetting the mixture of material to be sintered with continuous regulation requires that sintering be done with a high degree of automation. Consider the feed to a sinter bed to consist of the following:

- (1) ore
- (2) mill scale
- (3) flue dust—from blast furnace and oxygen converter
- (4) sinter fines—recycled
- (5) coke fines

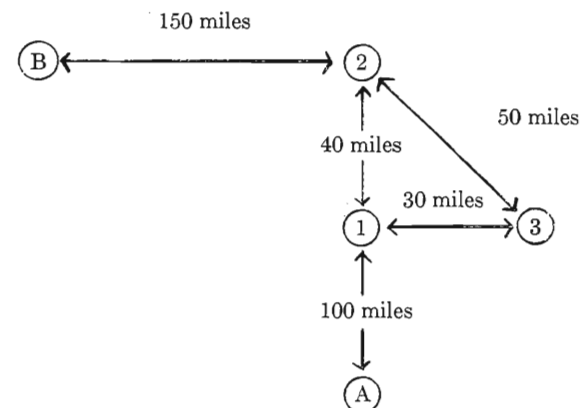
Draw a flow diagram for a process which would automatically control the proportions of these constituents. Indicate all instrumentation necessary to effect this control.

### Problems

- Available at plants A and B of American Steel Company are 5000 tons of steel for shipment to fill an order for 5000 tons at plants 1, 2, and 3 of United Auto Company. The distribution of material is:

| American Steel Company | United Auto Company |
|------------------------|---------------------|
| Supply                 | Demand              |
| Plant A—3000 tons      | Plant 1—1000 tons   |
| Plant B—2000 tons      | Plant 2—1500 tons   |
|                        | Plant 3—2500 tons   |

The cost of transportation is proportional to mileage. How should the steel be shipped?



2. The Bright Metal Company operates a general heat treating plant. A long-term contract has been written with two neighboring steel companies for the batch annealing of hot-band coils. The contract calls for the treating of 1500 coils/month in a random supply. The contract includes a penalty clause for delays in processing. The processing equipment to handle this contract, as well as the required storage and handling equipment, are to be purchased. The batch annealing units will handle 3 coils and the complete annealing cycle requires 28 hr. The annealing furnaces cost \$15/hr of actual operation including labor. The capital and installation costs can be amortized at \$6/day/unit. The cost of storing coils, including the delay penalty, will be \$20/day/coil. How many annealing units should Bright Metal Company purchase to supply the requirements of this contract?
3. A secondary brass and copper refiner produces an alloy which is guaranteed to contain a minimum of 90% copper and 5-8% nickel with the remainder other metallics. The refining company receives an order for 1000 lb of alloy at \$0.45/lb. Two scrap materials as well as pure copper and nickel are available. The analyses and costs for the materials are:

|              | Scrap I | Scrap II | Copper | Nickel |
|--------------|---------|----------|--------|--------|
| Cu           | 95      | 85       | 100    | —      |
| Ni           | 3       | 1        | —      | 100    |
| Other        | 2       | 14       | —      | —      |
| Cost (\$/lb) | 0.30    | 0.10     | 0.60   | 0.90   |

What is the optimum charge make-up?

4. A "mini-mill" operating one small electric arc furnace and a rolling mill to produce reinforcing rods has entered the low alloy bar market. The facility requirement and the relative profit for these two products are given below.

|                | Alloy Bar | Re-Rod |
|----------------|-----------|--------|
| Melting hr/ton | 3         | 5      |
| Rolling hr/ton | 4.5       | 3.5    |
| Profit \$/ton  | 15        | 12     |

How should the "mini-mill" utilize its facilities to maximize profit?

5. Evaluate and plot the relationship between  $\log (P_{\text{CO}}/P_{\text{CO}_2})$  versus temperature for the equilibrium  $\text{C}(\text{gr}) + \text{CO}_2(\text{g}) = 2\text{CO}(\text{g})$  with total pressure as a parameter. Compare this result with the equilibrium  $\text{Si} + 2\text{CO}_2(\text{g}) = \text{SiO}_2(\text{s}) + 2\text{CO}(\text{g})$  on the same plot with the activities of silicon and silica as parameters.
6. Write and test a computer program which will permit calculation of the volume of pure argon gas which must be bubbled through a ladle of liquid steel to reduce the hydrogen concentration from some initial value,  $c_0$ , to a final value,  $c$ . Assume the purging gas leaves the melt at 1 atm pressure and with a hydrogen gas pressure in equilibrium with various fractions of the residual hydrogen content of the liquid metal. Apply the results of this computer program to the following practical problem.

A steel company using 50-ton ladles has experienced hydrogen problems in the following three areas.

| Steel purpose        | Hydrogen analysis PPM |                   |
|----------------------|-----------------------|-------------------|
|                      | Ladle                 | Maximum tolerable |
| Rolling stock        | 14-15                 | 6                 |
| Light forging blanks | 7-8                   | 4                 |
| Heavy forging blanks | 4                     | 3                 |

Inert flush degassing in the ladle has been recommended in these three cases to solve the gas-metal problem. The equipment available will supply 250 ft<sup>3</sup>/min of purified argon, and the purging operation is limited to less than 30 min. Are you in accord with these recommendations?

7. Write and test a computer program which will provide design calculations for the mold of a continuous casting process for wide steel slabs. Calculate the thickness of solid skin building up in the mold, the rate of heat removal, and the temperatures of the mold and slab surfaces. Extend calculations to a skin thickness of 2 in. Assume that a one-dimensional analysis applied to the center of the wide face is adequate for design purposes. State all assumptions. Prepare a recommendation for the length of mold to be used in the installation for various casting speeds. What additional information is necessary to finalize your design?

8. The following solidification profile has been determined for a continuous casting installation:

| Time (min) | Thickness (in.) |
|------------|-----------------|
| 0.25       | 0.25            |
| 0.50       | 0.50            |
| 0.75       | 0.70            |
| 1.00       | 0.75            |
| 1.25       | 0.80            |
| 1.50       | 1.00            |
| 1.75       | 1.06            |
| 2.00       | 1.13            |
| 2.25       | 1.30            |
| 2.50       | 1.35            |
| 2.75       | 1.45            |
| 3.00       | 1.50            |
| 3.25       | 1.58            |
| 3.50       | 1.65            |
| 3.75       | 1.74            |
| 4.00       | 1.85            |
| 4.25       | 1.93            |
| 4.50       | 2.00            |
| 4.75       | 2.08            |
| 5.00       | 2.15            |

Evaluate the constants in a parabolic rate law describing the solidification process. With what quantitative accuracy can this parabolic law be applied to the given installation?

9. Current output from hot strip rolling mill facilities are to be increased. The heating and subsequent temperature control of slabs is a major factor in mill productivity. Slabs are delivered from a blooming mill to pusher-type slab heating facilities. Usually, the slabs have cooled after a substantial storage period in the slab yard. They are heated in gas-fired furnaces which are held at 2400°F. Experience has shown that the center of the slab must be at a temperature of 1700°F or higher for adequate sheet quality. The minimum heating time for 10" × 60" slabs must be known to determine whether another furnace will be required to optimize the mill.

Furthermore, delays on the rolling mill have resulted in edge cracks on the hot band. These cracks are caused when a slab is taken out of the furnace, and then is delayed on the table allowing the corners to reach temperatures below 1900°F. If a uniform temperature of 2250°F is assumed for the edge portion (e.g. outer 12" × 10" thick), how extensive a delay could be tolerated before the slab must be returned to the furnace?

## Appendix A

TABLE A-I  
Summary of Free Energy Equations<sup>a</sup>  
( $\Delta G^\circ = a + bT \log T + cT$ )

| Reaction                                                                                                         | a       | b     | c       | Range (°K)   | Accuracy |
|------------------------------------------------------------------------------------------------------------------|---------|-------|---------|--------------|----------|
| $\text{Ag}_2\text{SO}_4(l) = 2 \text{Ag}(c) + \text{SO}_2 + \text{O}_2$                                          | 96,640  | 30.49 | -162.44 | 930 to 1234  | 500      |
| $\frac{1}{2}\text{Al}_2(\text{SO}_4)_3 = \frac{1}{2}\text{Al}_2\text{O}_3(\alpha) + \text{SO}_3$                 | 47,090  | 9.25  | -73.51  | 600 to 1100  | 500      |
| $\frac{1}{2}\text{Al}_2(\text{SO}_4)_3 = \frac{1}{2}\text{Al}_2\text{O}_3(\gamma) + \text{SO}_3$                 | 48,670  | —     | -42.52  | 700 to 1100  | 2000     |
| $\text{BeSO}_4(\gamma) = \text{BeO} + \text{SO}_3$                                                               | 50,180  | 23.03 | -114.14 | 900 to 1100  | 500      |
| $\text{CaSO}_4 = \text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$                                               | 136,830 | 41.61 | -206.73 | 1100 to 1638 | 700      |
| $\frac{1}{2}\text{CdSO}_4 = \frac{1}{2}(\text{CdSO}_4 \cdot 2 \text{CdO}) + \text{SO}_3$                         | 38,700  | —     | -22.0   | 1100 to 1273 | 2000     |
| $\frac{1}{2}\text{Ce}_2(\text{SO}_4)_3 = \frac{1}{2}\text{Ce}_2\text{O}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2$ | 63,000  | —     | -50.97  | 900 to 1200  | 500      |
| $\text{CoSO}_4 = \text{CoO} + \text{SO}_3$                                                                       | 69,230  | 27.63 | -137.18 | 890 to 1250  | 500      |
| $\text{CoSO}_4 = \frac{1}{2}\text{Co}_3\text{O}_4 + \text{SO}_2 + \frac{1}{2}\text{O}_2$                         | 77,250  | 32.24 | -160.62 | 1000 to 1100 | 500      |
| $2 \text{CuSO}_4 = \text{CuO} \cdot \text{CuSO}_4 + \text{SO}_3$                                                 | 51,780  | 5.16  | -60.60  | 700 to 1100  | 500      |
| $\text{CuO} \cdot \text{CuSO}_4 = 2 \text{CuO} + \text{SO}_3$                                                    | 52,030  | 5.16  | -57.59  | 800 to 1200  | 500      |
| $\frac{1}{2}\text{Er}_2(\text{SO}_4)_3 = \frac{1}{2}(\text{Er}_2\text{O}_3 \cdot \text{SO}_3) + \text{SO}_3$     | 57,810  | —     | -38.56  | 1000 to 1300 | 500      |
| $\frac{1}{2}\text{Fe}_2(\text{SO}_4)_3 = \frac{1}{2}\text{Fe}_2\text{O}_3 + \text{SO}_3$                         | 48,590  | 8.151 | -71.03  | 700 to 1000  | 500      |
| $\frac{1}{2}\text{La}_2(\text{SO}_4)_3 = \frac{1}{2}(\text{La}_2\text{O}_3 \cdot \text{SO}_3) + \text{SO}_3$     | 60,480  | —     | -38.82  | 1000 to 1300 | 500      |
| $\frac{1}{2}\text{Lu}_2(\text{SO}_4)_3 = \frac{1}{2}(\text{Lu}_2\text{O}_3 \cdot \text{SO}_3) + \text{SO}_3$     | 57,840  | —     | -37.71  | 1000 to 1300 | 500      |
| $\text{MgSO}_4 = \text{MgO} + \text{SO}_3$                                                                       | 78,560  | 16.58 | -100.69 | 1000 to 1428 | 1000     |
| $\text{MnSO}_4 = \frac{1}{2}\text{Mn}_2\text{O}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2$                         | 75,890  | 14.90 | -106.69 | 700 to 1100  | 500      |
| $\text{MnSO}_4(c,l) = \frac{1}{2}\text{Mn}_2\text{O}_3(?) + \text{SO}_2 + \frac{1}{2}\text{O}_2$                 | 63,510  | —     | -47.25  | 1100 to 1300 | ?        |
| $\text{Na}_2\text{SO}_4(c,l) = \text{Na}_2\text{O} + \text{SO}_3$                                                | 137,480 | 14.90 | -83.76  | 600 to 1157  | 3000     |
| $\frac{1}{2}\text{Nd}_2(\text{SO}_4)_3 = \frac{1}{2}(\text{Nd}_2\text{O}_3 \cdot \text{SO}_3) + \text{SO}_3$     | 56,160  | —     | -38.03  | 1000 to 1300 | 500      |
| $\text{NiSO}_4 = \text{NiO} + \text{SO}_3$                                                                       | 59,290  | —     | -47.52  | 900 to 1200  | 500      |
| $2\text{PbSO}_4 = \text{PbSO}_4 \cdot \text{PbO} + \text{SO}_3$                                                  | 74,000  | 16.81 | -97.40  | 800 to 1139  | 500      |
| $3(\text{PbSO}_4 \cdot \text{PbO}) = 2(\text{PbSO}_4 \cdot 2\text{PbO}) + \text{SO}_3$                           | 87,920  | 16.81 | -104.08 | 889 to 1223  | 500      |
| $\frac{1}{2}(\text{PbSO}_4 \cdot \text{PbO}) = \frac{1}{2}(\text{PbSO}_4 \cdot 4\text{PbO}) + \text{SO}_3$       | 80,570  | 16.81 | -95.81  | 800 to 889   | 500      |
| $\frac{1}{2}(\text{PbSO}_4 \cdot 2\text{PbO}) = \frac{1}{2}(\text{PbSO}_4 \cdot 4\text{PbO}) + \text{SO}_3$      | 71,380  | 16.81 | -85.47  | 889 to 1168  | 500      |
| $\text{PbSO}_4 \cdot 4\text{PbO} = 5\text{PbO} + \text{SO}_3$                                                    | 72,870  | —     | -30.70  | 800 to 1108  | 500      |
| $\frac{1}{2}\text{Pr}_2(\text{SO}_4)_3 = \frac{1}{2}(\text{Pr}_2\text{O}_3 \cdot \text{SO}_3) + \text{SO}_3$     | 56,600  | —     | -37.99  | 1000 to 1300 | 500      |
| $\frac{1}{2}\text{Sc}_2(\text{SO}_4)_3 = \frac{1}{2}\text{Sc}_2\text{O}_3 + \text{SO}_3$                         | 60,980  | —     | -44.82  | 1000 to 1300 | 500      |
| $\frac{1}{2}\text{Sm}_2(\text{SO}_4)_3 = \frac{1}{2}(\text{Sm}_2\text{O}_3 \cdot \text{SO}_3) + \text{SO}_3$     | 56,190  | —     | -38.82  | 1000 to 1300 | 500      |
| $\frac{1}{2}\text{Th}(\text{SO}_4)_2 = \frac{1}{2}\text{ThO}_2 + \text{SO}_3$                                    | 70,290  | 25.33 | -133.60 | 700 to 1100  | 500      |
| $2 \text{VOSO}_4 = \text{V}_2\text{O}_5 + \text{SO}_2 + \text{SO}_3$                                             | 85,470  | 18.42 | -150.83 | 700 to 900   | 500      |
| $\frac{1}{2}\text{Y}_2(\text{SO}_4)_3 = \frac{1}{2}(\text{Y}_2\text{O}_3 \cdot \text{SO}_3) + \text{SO}_3$       | 60,070  | —     | -39.25  | 1000 to 1300 | 500      |
| $\frac{1}{2}\text{Yb}_2(\text{SO}_4)_3 = \frac{1}{2}(\text{Yb}_2\text{O}_3 \cdot \text{SO}_3) + \text{SO}_3$     | 57,150  | —     | -37.48  | 1000 to 1300 | 500      |

TABLE A-I (Continued)  
Summary of Free Energy Equations<sup>a</sup>  
( $\Delta G^\circ = a + bT \log T + cT$ )

| Reaction                                                                              | a      | b    | c      | Range(°K)    | Accuracy |
|---------------------------------------------------------------------------------------|--------|------|--------|--------------|----------|
| $3 \text{ZnSO}_4(\alpha) = \text{ZnO} \cdot 2 \text{ZnSO}_4 + \text{SO}_2$            | 53,730 | —    | -45.21 | 800 to 1007  | 500      |
| $3 \text{ZnSO}_4(\beta) = \text{ZnO} \cdot 2 \text{ZnSO}_4 + \text{SO}_2$             | 39,280 | —    | -30.87 | 1007 to 1200 | 500      |
| $\frac{1}{2}(\text{ZnO} \cdot 2 \text{ZnSO}_4) = \frac{1}{2}\text{ZnO} + \text{SO}_2$ | 57,190 | 7.60 | -65.63 | 800 to 1200  | 500      |

<sup>a</sup> The standard state for all sulfates and oxides is the normally stable crystal form unless otherwise indicated.

Note:  $\text{SO}_2 = \text{SO}_2 + \frac{1}{2}\text{O}_2$ ;  $\log K = 8.8557 - \frac{5465.5}{T} - 1.21572 \log T$ .

Source: H. H. Kellogg, *Trans. Met. Soc. AIME* 230, 1624 (1964). copyright AIME.

TABLE A-II  
Standard Free Energies of Formation of Compounds at Steelmaking Temperatures<sup>a,b,c</sup>  
( $\Delta G^\circ = A + BT$ )

| Reaction                                                                               | Temp (°K) | (A)      | (B)    |
|----------------------------------------------------------------------------------------|-----------|----------|--------|
| Elements Dissolved in Liquid Iron                                                      |           |          |        |
| $\text{CO}_2(g) + \text{C}(gr) = 2\text{CO}(g)$                                        | 1700-2000 | +38,400  | -40.40 |
| $\text{CO}_2(g) + \underline{\text{C}}(\%) = 2\text{CO}(g)$                            | 1700-2000 | +33,300  | -30.40 |
| $\text{CO}(g) + \underline{\text{O}}(\%) = \text{CO}_2(g)$                             | 1700-2000 | -38,700  | +20.9  |
| $\underline{\text{C}}(\%) + \underline{\text{O}}(\%) = \text{CO}(g)$                   | 1700-2000 | -5,350   | -9.48  |
| $\text{Cr}_2\text{O}_3(s) = 3\underline{\text{Cr}}(\%) + 4\underline{\text{O}}(\%)$    | 1700-2000 | +244,800 | -109.6 |
| $\text{H}_2\text{O}(g) = 2\underline{\text{H}}(\text{ppm}) + \underline{\text{O}}(\%)$ | 1700-2000 | +47,480  | -35.87 |
| $\text{Fe}(l) + \frac{1}{2}\text{O}_2(g) = \text{FeO}(l)$                              | 1700-2000 | -56,900  | +11.82 |
| $\text{MnO}(l \text{ in FeO}) = \underline{\text{Mn}}(\%) + \underline{\text{O}}(\%)$  | 1700-2000 | +58,400  | -25.98 |
| $\underline{\text{O}}(\%) + \text{H}_2(g) = \text{H}_2\text{O}(g)$                     | 1700-2000 | -32,200  | +14.63 |
| $\text{SiO}_2(s) = \underline{\text{Si}} + 2\underline{\text{O}}(\%)$                  | 1700-2000 | +142,000 | -55.0  |
| $\underline{\text{S}}(\%) + \text{H}_2(g) = \text{H}_2\text{S}(g)$                     | 1700-2000 | +9,980   | +6.46  |
| $\frac{1}{2}\text{S}_2(g) + 2\underline{\text{O}}(\%) = \text{SO}_2(g)$                | 1700-2000 | +1,390   | +13.40 |
| $\text{V}_2\text{O}_5(s) = 2\underline{\text{V}}(\%) + 3\underline{\text{O}}(\%)$      | (1600 C)  | +49,300  |        |
| Carbides (from graphite)                                                               |           |          |        |
| $4\text{Al}(l) + 3\text{C}(s) = \text{Al}_4\text{C}_3(s)$                              | 1500-2000 | -41,550  | +5.10  |
| $4\text{B}(s) + \text{C}(s) = \text{"B}_4\text{C"}(s)^c$                               | 1500-2000 | -16,700  | +4.48  |
| $\text{Ca}(l) + 2\text{C}(s) = \text{CaC}_2(\beta)$                                    | 1500-1765 | -14,900  | -5.87  |
| $\text{Ca}(g) + 2\text{C}(s) = \text{CaC}_2(\beta)$                                    | 1765-2000 | -50,900  | +14.58 |
| $23\text{Cr}(s) + 6\text{C}(s) = \text{"Cr}_{23}\text{C}_6"(s)$                        | 1500-2000 | -98,300  | -9.21  |
| $7\text{Cr}(s) + 3\text{C}(s) = \text{"Cr}_7\text{C}_3"(s)$                            | 1500-2000 | -45,100  | -4.43  |
| $3\text{Cr}(s) + 2\text{C}(s) = \text{"Cr}_3\text{C}_2"(s)$                            | 1500-2000 | -21,500  | -4.11  |
| $2\text{Co}(s) + \text{C}(s) = \text{Co}_2\text{C}(s)$                                 | 1500-1766 | +3,950   | -2.09  |
| $2\text{Co}(l) + \text{C}(s) = \text{Co}_2\text{C}(s)$                                 | 1766-2000 | -3,300   | +2.00  |

TABLE A-II (Continued)  
Standard Free Energies of Formation of Compounds at Steelmaking Temperatures<sup>a,b,c</sup>  
( $\Delta G^\circ = A + BT$ )

| Reaction                                                                             | Temp (°K) | (A)      | (B)     |
|--------------------------------------------------------------------------------------|-----------|----------|---------|
| Carbides (from graphite)—Continued                                                   |           |          |         |
| $2\text{C}(s) + \text{H}_2(g) = \text{C}_2\text{H}_2(g)$                             | 1500-2000 | +52,000  | -11.80  |
| $\text{C}(s) + 2\text{H}_2(g) = \text{CH}_4(g)$                                      | 1500-2000 | -22,100  | +26.45  |
| $3\text{Fe}(\gamma) + \text{C}(s) = \text{Fe}_3\text{C}(s)$                          | 1500-1665 | +2,900   | -2.73   |
| $\text{Mg}(g) + 2\text{C}(s) = \text{MgC}_2(s)$                                      | 1500-2000 | -11,900  | +24.45  |
| $7\text{Mn}(l) + 3\text{C}(s) = \text{Mn}_7\text{C}_3(s)$                            | 1516-2000 | -15,800  | -13.91  |
| $2\text{Mo}(s) + \text{C}(s) = \text{"Mo}_2\text{C"}(s)$                             | 1500-2000 | +15,800  | -26.00  |
| $\text{Mo}(s) + \text{C}(s) = \text{MoC}(s)$                                         | 1500-2000 | +9,700   | -14.01  |
| $3\text{Ni}(s) + \text{C}(s) = \text{Ni}_3\text{C}(s)$                               | 1500-1726 | +9,200   | -2.37   |
| $\text{Si}(s) + \text{C}(s) = \text{SiC}(s)$                                         | 1500-1686 | -12,800  | +1.68   |
| $\text{Si}(l) + \text{C}(s) = \text{SiC}(s)$                                         | 1686-2000 | -24,900  | +8.85   |
| $2\text{Ta}(s) + \text{C}(s) = \text{"Ta}_2\text{C"}(s)$                             | 1500-2000 | -34,000  | +1.32   |
| $\text{Ta}(s) + \text{C}(s) = \text{"TaC"}(s)$                                       | 1500-2000 | -38,500  | +1.32   |
| $\text{Ti}(\beta) + \text{C}(s) = \text{"TiC"}(s)$                                   | 1500-1940 | -44,400  | +3.41   |
| Nitrides                                                                             |           |          |         |
| $\text{Al}(l) + \frac{1}{2}\text{N}_2(g) = \text{AlN}(s)$                            | 1500-2000 | -77,700  | +26.80  |
| $\text{B}(s) + \frac{1}{2}\text{N}_2(g) = \text{BN}(s)$                              | 1500-2000 | -60,600  | +21.80  |
| $\text{B}(s) + \frac{1}{2}\text{N}_2(g) = \text{BN}(g)$                              | 1500-2000 | +155,500 | -26.85  |
| $3\text{Ca}(l) + \text{N}_2(g) = \text{Ca}_3\text{N}_2(l)$                           | 1500-1765 | -112,000 | +56.62  |
| $3\text{Ca}(g) + \text{N}_2(g) = \text{Ca}_3\text{N}_2(l)$                           | 1765-2000 | -219,500 | +117.55 |
| $2\text{Cr}(s) + \frac{1}{2}\text{N}_2(g) = \text{"Cr}_2\text{N"}(s)$                | 1500-2000 | -23,500  | +11.25  |
| $\text{Cr}(s) + \frac{1}{2}\text{N}_2(g) = \text{"CrN"}(s)$                          | 1500-2000 | -24,500  | +16.05  |
| $4\text{Fe}(\gamma) + \frac{1}{2}\text{N}_2(g) = \text{"Fe}_4\text{N"}(s)$           | 1500-1665 | -2,000   | +10.39  |
| $3\text{Mg}(g) + \text{N}_2(g) = \text{Mg}_3\text{N}_2(\gamma)$                      | 1500-2000 | -207,500 | +121.25 |
| $2\text{Mo}(s) + \frac{1}{2}\text{N}_2(g) = \text{"Mo}_2\text{N"}(s)$                | 1500-2000 | -17,100  | +13.83  |
| $3\text{Si}(s) + 2\text{N}_2(g) = \text{Si}_3\text{N}_4(s)$                          | 1500-1686 | -173,000 | +75.48  |
| $3\text{Si}(l) + 2\text{N}_2(g) = \text{Si}_3\text{N}_4(s)$                          | 1686-2000 | -209,000 | +96.78  |
| $\text{Ta}(s) + \frac{1}{2}\text{N}_2(g) = \text{TaN}(s)$                            | 1500-2000 | -56,150  | +18.87  |
| $\text{Ti}(\beta) + \frac{1}{2}\text{N}_2(g) = \text{"TiN"}(s)$                      | 1500-1940 | -80,000  | +22.21  |
| $\text{V}(s) + \frac{1}{2}\text{N}_2(g) = \text{"VN"}(s)$                            | 1500-2000 | -40,300  | +19.15  |
| $\text{Zr}(\beta) + \frac{1}{2}\text{N}_2(g) = \text{"ZrN"}(s)$                      | 1500-2000 | -86,300  | +21.67  |
| Oxides                                                                               |           |          |         |
| $2\text{Al}(l) + \frac{1}{2}\text{O}_2(g) = \text{Al}_2\text{O}(g)$                  | 1500-2000 | -47,000  | -13.06  |
| $\text{Al}(l) + \frac{1}{2}\text{O}_2(g) = \text{AlO}(g)$                            | 1500-2000 | +3,500   | -13.31  |
| $2\text{Al}(l) + \frac{1}{2}\text{O}_2(g) = \text{Al}_2\text{O}_3(s)$                | 1500-2000 | -401,500 | +76.91  |
| $\text{Ba}(l) + \frac{1}{2}\text{O}_2(g) = \text{BaO}(s)$                            | 1500-1910 | -132,000 | +22.10  |
| $\text{Ba}(g) + \frac{1}{2}\text{O}_2(g) = \text{BaO}(s)$                            | 1910-2000 | -167,250 | +40.60  |
| $\text{Be}(l) + \frac{1}{2}\text{O}_2(g) = \text{BeO}(s)$                            | 1555-2000 | -143,750 | +23.30  |
| $\text{B}(s) + \frac{1}{2}\text{O}_2(g) = \text{BO}(g)$                              | 1500-2000 | -16,500  | -19.43  |
| $2\text{B}(s) + \frac{1}{2}\text{O}_2(g) = \text{B}_2\text{O}_3(s) \text{ or } (gl)$ | 1500-2000 | -295,850 | +51.92  |

TABLE A-II (Continued)

Standard Free Energies of Formation of Compounds at Steelmaking Temperatures<sup>a,b,c</sup>

$$(\Delta G^\circ = A + BT)$$

| Reaction                                                                        | Temp (°K) | (A)      | (B)    |
|---------------------------------------------------------------------------------|-----------|----------|--------|
| Oxides—Continued                                                                |           |          |        |
| Ca (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = CaO (s)                             | 1500–1765 | –152,850 | +25.78 |
| Ca (g) + $\frac{1}{2}$ O <sub>2</sub> (g) = CaO (s)                             | 1765–2000 | –187,900 | +45.70 |
| C (s) + $\frac{1}{2}$ O <sub>2</sub> (g) = CO (g)                               | 1500–2000 | –28,200  | –20.16 |
| C (s) + O <sub>2</sub> (g) = CO <sub>2</sub> (g)                                | 1500–2000 | –94,755  | +0.02  |
| 2Cb (s) + 2O <sub>2</sub> (g) = Cb <sub>2</sub> O <sub>4</sub> (s)              | 1500–2000 | –374,500 | +80.56 |
| 2Cb (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = Cb <sub>2</sub> O <sub>3</sub> (s) | 1500–1785 | –446,200 | +97.56 |
| 2Cb (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = Cb <sub>2</sub> O <sub>5</sub> (l) | 1785–2000 | –417,500 | +81.42 |
| 2Ce (l) + $\frac{3}{2}$ O <sub>2</sub> (g) = Ce <sub>2</sub> O <sub>3</sub> (s) | 1500–2000 | –436,500 | +80.46 |
| Ce (l) + O <sub>2</sub> (g) = CeO <sub>2</sub> (s)                              | 1500–2000 | –246,000 | +51.20 |
| 2Cr (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = Cr <sub>2</sub> O <sub>3</sub> (s) | 1500–2000 | –270,550 | +61.35 |
| Co (γ) + $\frac{1}{2}$ O <sub>2</sub> (g) = CoO (s)                             | 1500–1766 | –56,900  | +17.50 |
| Co (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = CoO (s)                             | 1766–2000 | –60,500  | +19.53 |
| 3Co (γ) + 2O <sub>2</sub> = Co <sub>3</sub> O <sub>4</sub> (s)                  | 1500–1766 | –208,900 | +83.31 |
| 2Cu (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = Cu <sub>2</sub> O (l)              | 1502–2000 | –34,950  | +14.40 |
| Cu (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = CuO (s)                             | 1500–1720 | –40,000  | +23.06 |
| Cu (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = CuO (l)                             | 1720–2000 | –36,800  | +21.26 |
| H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) = H <sub>2</sub> O (g)    | 1500–2000 | –60,200  | +13.94 |
| Fe (γ) + $\frac{1}{2}$ O <sub>2</sub> (g) = "FeO" (s)                           | 1500–1650 | –62,600  | +15.18 |
| Fe (s) + $\frac{1}{2}$ O <sub>2</sub> (g) = "FeO" (l)                           | 1665–1809 | –54,850  | +10.47 |
| Fe (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = "FeO" (l)                           | 1809–2000 | –56,900  | +11.82 |
| 2Fe (γ) + $\frac{3}{2}$ O <sub>2</sub> (g) = Fe <sub>2</sub> O <sub>3</sub> (γ) | 1500–1665 | –191,300 | +57.60 |
| 2Fe (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = Fe <sub>2</sub> O <sub>3</sub> (γ) | 1665–1809 | –190,950 | +57.46 |
| 3Fe (γ) + 2O <sub>2</sub> (g) = Fe <sub>3</sub> O <sub>4</sub> (s)              | 1500–1665 | –259,450 | +70.84 |
| 3Fe (s) + 2O <sub>2</sub> (g) = Fe <sub>3</sub> O <sub>4</sub> (s)              | 1665–1809 | –259,550 | +70.91 |
| Mg (g) + $\frac{1}{2}$ O <sub>2</sub> (g) = MgO (s)                             | 1500–2000 | –174,750 | +49.09 |
| Mn (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = MnO (s)                             | 1516–2000 | –97,550  | +21.22 |
| 3Mn (l) + 2O <sub>2</sub> (g) = Mn <sub>3</sub> O <sub>4</sub> (s)              | 1516–1833 | –339,050 | +89.06 |
| Mo (s) + O <sub>2</sub> (g) = MoO <sub>2</sub> (s)                              | 1500–2000 | –130,800 | +34.17 |
| Mo (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = MoO <sub>3</sub> (g)                | 1553–2000 | –113,800 | +12.92 |
| Ni (s) + $\frac{1}{2}$ O <sub>2</sub> (g) = NiO (s)                             | 1500–1726 | –55,000  | +20.01 |
| Ni (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = NiO (s)                             | 1726–2000 | –60,350  | +22.61 |
| $\frac{1}{2}$ P <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) = PO (g)    | 1500–2000 | –27,000  | +2.28  |
| 2P <sub>2</sub> (g) + 5O <sub>2</sub> (g) = P <sub>2</sub> O <sub>10</sub> (g)  | 1500–2000 | –750,700 | +230.6 |
| Si (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = SiO (g)                             | 1686–2000 | –37,100  | –11.3  |
| Si (l) + O <sub>2</sub> (g) = SiO <sub>2</sub> (l)                              | 1883–2000 | –223,800 | +46.08 |
| Si (l) + O <sub>2</sub> (g) = SiO <sub>2</sub> (s-cryst.)                       | 1686–1986 | –226,500 | +47.50 |
| 2Ta (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = Ta <sub>2</sub> O <sub>5</sub> (s) | 1500–2000 | –475,450 | +94.08 |
| Sn (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = SnO (s)                             | 1500–2000 | –67,600  | +24.64 |
| Sn (l) + $\frac{1}{2}$ O <sub>2</sub> (g) = SnO (g)                             | 1500–2000 | –6,800   | –10.39 |
| Sn (l) + O <sub>2</sub> (g) = SnO <sub>2</sub> (s)                              | 1500–1898 | –135,500 | +47.15 |
| Sn (l) + O <sub>2</sub> (g) = SnO <sub>2</sub> (l)                              | 1898–2000 | –122,650 | +40.33 |
| Ti (s) + $\frac{1}{2}$ O <sub>2</sub> (g) = TiO (s)                             | 1500–1940 | –120,100 | +19.83 |
| Ti (s) + $\frac{1}{2}$ O <sub>2</sub> (g) = TiO (g)                             | 1500–1940 | +6,300   | –18.22 |
| 2Ti (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = Ti <sub>2</sub> O <sub>3</sub> (s) | 1500–1940 | –354,000 | +58.36 |

TABLE A-II (Continued)

Standard Free Energies of Formation of Compounds at Steelmaking Temperatures<sup>a,b,c</sup>

$$(\Delta G^\circ = A + BT)$$

| Reaction                                                                              | Temp (°K) | (A)      | (B)    |
|---------------------------------------------------------------------------------------|-----------|----------|--------|
| Oxides—Continued                                                                      |           |          |        |
| 3Ti (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = Ti <sub>3</sub> O <sub>5</sub> (s)       | 1500–1940 | –577,500 | +97.69 |
| Ti (s) + O <sub>2</sub> (g) = TiO <sub>2</sub> (s)                                    | 1500–1940 | –223,500 | +41.55 |
| W (s) + O <sub>2</sub> (g) = WO <sub>2</sub> (s)                                      | 1500–2000 | –134,800 | +38.92 |
| W (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = WO <sub>3</sub> (s)                        | 1500–1743 | –194,550 | +54.47 |
| W (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = WO <sub>3</sub> (l)                        | 1743–2000 | –177,750 | +44.85 |
| V (s) + $\frac{1}{2}$ O <sub>2</sub> (g) = VO (s)                                     | 1500–2000 | –96,000  | +17.78 |
| V (s) + $\frac{1}{2}$ O <sub>2</sub> (g) = VO (g)                                     | 1500–2000 | +47,000  | –17.78 |
| 2V (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = V <sub>2</sub> O <sub>3</sub> (s)         | 1500–2000 | –287,000 | +54.00 |
| 2V (s) + 2O <sub>2</sub> (g) = V <sub>2</sub> O <sub>4</sub> (s)                      | 1500–1818 | –331,000 | +70.80 |
| 2V (s) + 2O <sub>2</sub> (g) = V <sub>2</sub> O <sub>5</sub> (l)                      | 1818–2000 | –301,750 | +54.49 |
| 2V (s) + $\frac{3}{2}$ O <sub>2</sub> (g) = V <sub>2</sub> O <sub>5</sub> (l)         | 1500–2000 | –346,500 | +75.83 |
| Zr (s) + O <sub>2</sub> (g) = ZrO <sub>2</sub> (s)                                    | 1500–2000 | –258,000 | +42.50 |
| Sulfides                                                                              |           |          |        |
| Ca (l) + $\frac{1}{2}$ S <sub>2</sub> (g) = CaS (s)                                   | 1500–1765 | –132,060 | +25.91 |
| Ca (g) + $\frac{1}{2}$ S <sub>2</sub> (g) = CaS (s)                                   | 1765–2000 | –167,900 | +46.21 |
| C (s) + $\frac{1}{2}$ S <sub>2</sub> (g) = CS (s)                                     | 1500–2000 | +59,000  | –22.84 |
| C (s) + S <sub>2</sub> (g) = CS <sub>2</sub> (g)                                      | 1500–2000 | –3,250   | –1.61  |
| C (s) + $\frac{1}{2}$ O <sub>2</sub> (g) + $\frac{1}{2}$ S <sub>2</sub> (g) = COS (g) | 1500–2000 | –49,700  | –2.22  |
| H <sub>2</sub> (g) + $\frac{1}{2}$ S <sub>2</sub> (g) = H <sub>2</sub> S (g)          | 1500–2000 | –21,540  | +11.73 |
| Fe (γ) + $\frac{1}{2}$ S <sub>2</sub> (g) = "FeS" (l)                                 | 1500–1665 | –27,130  | +6.32  |
| Fe (s) + $\frac{1}{2}$ S <sub>2</sub> (g) = "FeS" (l)                                 | 1665–1809 | –26,700  | +6.06  |
| Fe (l) + $\frac{1}{2}$ S <sub>2</sub> (g) = "FeS" (l)                                 | 1809–2000 | –29,970  | +7.90  |
| Mg (g) + $\frac{1}{2}$ S <sub>2</sub> (g) = MgS (s)                                   | 1500–2000 | –132,540 | +47.24 |
| Mn (l) + $\frac{1}{2}$ S <sub>2</sub> (g) = MnS (s)                                   | 1516–1803 | –69,250  | +19.18 |
| Mn (l) + $\frac{1}{2}$ S <sub>2</sub> (g) = MnS (l)                                   | 1803–2000 | –63,100  | +15.77 |
| Mo (s) + S <sub>2</sub> (g) = MoS <sub>2</sub> (s)                                    | 1500–2000 | –86,650  | +46.36 |
| Pt (s) + $\frac{1}{2}$ S <sub>2</sub> (g) = "PtS" (s)                                 | 1500–1700 | –33,050  | +21.78 |
| $\frac{1}{2}$ S <sub>2</sub> (g) + O <sub>2</sub> (g) = SO <sub>2</sub> (g)           | 1500–2000 | –86,130  | +17.27 |
| $\frac{1}{2}$ S <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) = SO (g)          | 1500–2000 | –15,360  | –1.24  |

<sup>a</sup> The reference state of an element of compound is the form that is stable normally at 1 atm pressure and the temperature being considered, i.e., the pure stable solid, the pure stable liquid, and the equilibrium gas at 1 atm pressure. For elements dissolved in iron, the reference state is the hypothetical 1 per cent solution.

<sup>b</sup> See Elliott, J. F., and M. Gleiser: *Thermochemistry for Steelmaking, I*, Addison-Wesley (1960).

<sup>c</sup> Quotation marks indicate that compound is not necessarily of the stoichiometric composition.

Source: *Electric Furnace Steelmaking* (Clarence E. Sims, Ed.), Vol. 2, Chap. 16, pp. 134–137, Interscience Publishers, New York, 1963.

TABLE A-III  
Activity Coefficients at Infinite Dilution in Liquid Metals

| Solvent  | Solute | $\gamma^0$           | Temp, °C |
|----------|--------|----------------------|----------|
| Aluminum | Ag     | 0.38                 | 700      |
|          |        | 0.47                 | 900      |
|          |        | 0.53                 | 1000     |
| Antimony | Cd     | 0.25                 | 500      |
|          | Pb     | 0.72                 | 500      |
|          | Sn     | 0.40                 | 905      |
|          | Zn     | 0.30                 | 550      |
| Bismuth  | Au     | 0.78                 | 700      |
|          | Cd     | 1.0                  | 500      |
|          | Hg     | 0.39                 | 321      |
|          | Mg     | $5.5 \times 10^{-3}$ | 700      |
|          | Pb     | 0.44                 | 475      |
|          |        | 0.46                 | 500      |
|          |        | 0.48                 | 527      |
|          |        | 0.53                 | 665      |
|          |        | 1.12                 | 330      |
|          | Tl     | 0.04                 | 270      |
|          | Zn     | 0.14                 | 480      |
|          |        | 5.0                  | 352      |
|          |        | 3.5                  | 600      |
|          | U      | $1.6 \times 10^{-5}$ | 450      |
|          |        | $2.5 \times 10^{-5}$ | 507      |
|          |        | $4.6 \times 10^{-5}$ | 540      |
|          |        | $7.8 \times 10^{-5}$ | 570      |
| Cadmium  | Bi     | 0.85                 | 500      |
|          | Hg     | 0.10                 | 327      |
|          |        | 0.063                | 350      |
|          | Na     | 0.01                 | 350      |
|          |        | 0.01                 | 395      |
|          | Pb     | 6.3                  | 432      |
|          |        | 5.5                  | 480      |
|          |        | 5.1                  | 500      |
|          |        | 4.7                  | 544      |
|          |        | 4.3                  | 572      |
|          | Sb     | 0.27                 | 500      |
|          | Sn     | 2.2                  | 431      |
|          |        | 2.1                  | 483      |
|          |        | 1.9                  | 500      |
|          |        | 1.9                  | 544      |
|          |        | 1.8                  | 585      |
|          | U      | 6.58                 | 467      |
|          |        | 8.15                 | 507      |
|          | Zn     | 6.9                  | 435      |
|          |        | 6.3                  | 466      |
|          |        | 5.1                  | 540      |
|          |        | 2.8                  | 682      |

TABLE A-III (Continued)  
Activity Coefficients at Infinite Dilution in Liquid Metals

| Solvent | Solute | $\gamma^0$           | Temp, °C |
|---------|--------|----------------------|----------|
| Copper  | Zn     | 0.14                 | 604      |
|         |        | 0.17                 | 653      |
|         |        | 0.21                 | 727      |
|         |        | 0.24                 | 802      |
| Gold    | Bi     | 0.90                 | 700      |
|         | Pb     | 0.142                | 600      |
|         | Sn     | $1.0 \times 10^{-5}$ | 600      |
|         | Tl     | 0.49                 | 700      |
| Indium  | Zn     | 5.15                 | 352      |
| Iron    | Al     | 0.063                | 1600     |
|         | B      | 0.022                | 1600     |
|         | Cb     | 0.2                  | 1600     |
|         |        | 0.27                 | 1600     |
|         | Co     | 1                    | 1600     |
|         | Cr     | 1                    | 1600     |
|         | Cu     | 8.6                  | 1600     |
|         |        | 8.0                  | 1600     |
|         |        | 8.8                  | 1600     |
|         | Mn     | 1                    | 1600     |
|         | Mo     | 1                    | 1600     |
|         | Ni     | 0.47                 | 1510     |
|         |        | 0.66                 | 1600     |
|         | Si     | 0.66                 | 1600     |
|         |        | 0.0072               | 1600     |
|         | Ti     | 0.011                | 1627     |
|         | V      | 0.048                | 1600     |
|         |        | 0.12                 | 1600     |
|         | W      | 1                    | 1600     |
|         | Zr     | 0.0076               | 1600     |
| Lead    | Ag     | 2.3                  | 1000     |
|         |        | 1.5                  | 1085     |
|         | Au     | 0.25                 | 600      |
|         | Bi     | 0.52                 | 475      |
|         |        | 0.488                | 500      |
|         |        | 0.48                 | 527      |
|         |        | 0.43                 | 665      |
|         | Cd     | 3.7                  | 432      |
|         |        | 3.5                  | 480      |
|         |        | 3.22                 | 500      |
|         |        | 3.0                  | 544      |
|         |        | 2.9                  | 572      |
|         | Mg     | 0.066                | 560      |
|         |        | 0.064                | 560      |
|         | Mn     | 28.8                 | 750      |
|         |        | 20.5                 | 800      |
|         |        | 15.2                 | 850      |

TABLE A-III (Continued)  
Activity Coefficients at Infinite Dilution in Liquid Metals

| Solvent  | Solute | $\gamma^\circ$        | Temp, °C |
|----------|--------|-----------------------|----------|
| Mercury  |        | 11.4                  | 900      |
|          |        | 9.0                   | 950      |
|          |        | 7.7                   | 980      |
|          |        | 7.2                   | 1000     |
|          | Na     | 0.0022                | 400      |
|          | Sb     | 0.80                  | 500      |
|          | Sn     | 2.3                   | 500      |
|          | Tl     | 0.74                  | 450      |
|          | Zn     | 11.0                  | 653      |
|          | Ba     | $1.0 \times 10^{-15}$ | 25       |
|          | Ce     | $1.0 \times 10^{-15}$ | 25       |
|          |        | $2.2 \times 10^{-29}$ | 281      |
|          |        | $3.0 \times 10^{-27}$ | 301      |
|          |        | $1.8 \times 10^{-25}$ | 327      |
|          |        | $6.9 \times 10^{-23}$ | 378      |
|          | K      | $6.3 \times 10^{-22}$ | 0        |
|          |        | $4.0 \times 10^{-20}$ | 25       |
|          |        | $1.3 \times 10^{-18}$ | 50       |
|          |        | $2.5 \times 10^{-24}$ | 200      |
|          |        | $1.6 \times 10^{-22}$ | 250      |
|          |        | $4.0 \times 10^{-21}$ | 310      |
|          |        | $1.0 \times 10^{-19}$ | 390      |
|          | Na     | $1.0 \times 10^{-20}$ | 25       |
|          |        | $4.7 \times 10^{-14}$ | 335.5    |
|          |        | $5.6 \times 10^{-6}$  | 350      |
|          |        | $1.5 \times 10^{-13}$ | 375      |
|          |        | $1.2 \times 10^{-7}$  | 400      |
| Nickel   | Tl     | 0.12                  | 20       |
|          |        | 0.43                  | 325      |
|          | Fe     | 0.26                  | 1510     |
| Silver   |        | 0.39                  | 1600     |
|          |        | 0.40                  | 1600     |
|          | Al     | 0.022                 | 700      |
|          |        | 0.028                 | 800      |
|          |        | 0.039                 | 900      |
|          |        | 0.11                  | 1000     |
|          | Cd     | 0.18                  | 827      |
| Sodium   | Pb     | 2.0                   | 1000     |
|          | Hg     | $1.6 \times 10^{-3}$  | 350      |
| Thallium | Au     | 0.31                  | 700      |
|          | Bi     | 0.15                  | 480      |
|          | Hg     | 0.80                  | 325      |
|          | Sn     | 2.8                   | 352      |
|          |        | 2.4                   | 414      |
|          |        | 2.1                   | 478      |

TABLE A-III (Continued)  
Activity Coefficients at Infinite Dilution in Liquid Metals

| Solvent | Solute | $\gamma^\circ$ | Temp, °C |
|---------|--------|----------------|----------|
| Tin     | Au     | 0.006          | 600      |
|         | Cd     | 2.0            | 431      |
|         |        | 1.9            | 483      |
|         |        | 1.80           | 500      |
|         |        | 1.8            | 544      |
|         |        | 1.7            | 585      |
|         | Pb     | 2.33           | 500      |
|         | Sb     | 0.46           | 632      |
|         | Tl     | 2.9            | 352      |
|         |        | 2.4            | 414      |
|         |        | 1.8            | 478      |
|         | Zn     | 2.67           | 352      |
|         |        | 2.2            | 431      |
|         |        | 2.2            | 437      |
|         |        | 2.0            | 466      |
| Zinc    |        | 1.7            | 539      |
|         |        | 1.6            | 570      |
|         | Cd     | 3.7            | 435      |
|         |        | 3.5            | 466      |
|         |        | 3.1            | 540      |
|         |        | 3.5            | 682      |
|         | Sb     | 0.3            | 550      |
|         | Sn     | 5.8            | 431      |
|         |        | 5.3            | 466      |
|         |        | 4.0            | 539      |
|         |        | 3.5            | 570      |

Source: J. M. Dealy and R. D. Pehlke, *Trans. Met. Soc. AIME* **227**, 1031, 1032 (1963).

TABLE A-IV  
Standard Free Energy of Solution of Various Elements in Liquid Iron  
( $M$  (pure) =  $\underline{M}$  (1% solution, hypothetical))

| Element, state                                                       | $\gamma_{1873}^a$   | $\Delta G^\circ$               | Basis         |
|----------------------------------------------------------------------|---------------------|--------------------------------|---------------|
| Aluminum (l)                                                         | 0.063               | -10,300 - 7.71T                | —             |
| Carbon (graphite)                                                    | —                   | 5,100 - 10.00T                 | —             |
| Chromium (s)                                                         | 1                   | 5,000 - 11.31T                 | (Ideal soln.) |
| Cobalt (l)                                                           | 1                   | — 9.31T                        | (Ideal soln.) |
| Copper (l)                                                           | 8.5                 | 8,000 - 9.40T                  | —             |
| Hydrogen $\frac{1}{2}\text{H}_2$ (g) = $\underline{\text{H}}$ (ppm)  | —                   | 7,640 - 10.62T                 | —             |
| Manganese (l)                                                        | 1                   | — 9.11T                        | (Ideal soln.) |
| Molybdenum (s)                                                       | 1                   | 5,800 - 13.3T                  | (Ideal soln.) |
| Nickel (l)                                                           | 0.66                | -5,000 - 7.42T                 | —             |
| Nitrogen $\frac{1}{2}\text{N}_2$ (g) = $\underline{\text{N}}$ (%)    | —                   | 860 + 5.71T                    | —             |
| Oxygen $\frac{1}{2}\text{O}_2$ (g) = $\underline{\text{O}}$ (%)      | —                   | -28,000 - 0.69T                | —             |
| FeO (l) = $\underline{\text{O}}$ (%) + Fe (l)                        | —                   | +28,900 - 12.51T               | —             |
| Phosphorus, $\frac{1}{2}\text{P}_2$ (g) = $\underline{\text{P}}$ (%) | —                   | -29,200 - 4.6T                 | —             |
| Silicon (l)                                                          | 0.0072 <sup>d</sup> | -28,500 - 6.09T                | —             |
| Sulfur $\frac{1}{2}\text{S}_2$ (g) = $\underline{\text{S}}$ (%)      | —                   | -31,520 + 5.27T                | —             |
| Titanium (s)                                                         | 0.011               | -13,100 - 10.77 <sup>b,c</sup> | —             |
| Tungsten (s)                                                         | (1)                 | 8,000 - 13.4T <sup>c</sup>     | (Ideal soln.) |
| Vanadium (s)                                                         | 0.12                | -3,700 - 10.9T <sup>b,c</sup>  | —             |
| Zirconium (s)                                                        | 0.0076 <sup>d</sup> | -12,800 - 12.0T <sup>b</sup>   | —             |

<sup>a</sup>  $\gamma^\circ$  referred to pure liquid element.

<sup>b</sup> Calculated assuming regular solution behavior.

<sup>c</sup> Estimated on basis of heat and entropy of melting at 1600 C.

<sup>d</sup> Altered to agree with Table A-III.

Source: *Electric Furnace Steelmaking* (Clarence E. Sims, Ed.), Vol. 2, Chap. 16, p. 133, Interscience Publishers, New York, 1963

TABLE A-V  
Interaction Coefficients  $\epsilon_i^j \times 10^2$  for Elements Dissolved in Liquid Iron at 1600°C

| Dissolved element | Al  | As | Au | B | C    | Co   | Cr  | Cu   | H     | Mn   | Mo   | N     | Ni   | O     | P   | Pt  | S   | Sb | Se  | Si  | Sn | Ta | Ti | V    | W    |
|-------------------|-----|----|----|---|------|------|-----|------|-------|------|------|-------|------|-------|-----|-----|-----|----|-----|-----|----|----|----|------|------|
| Al                | 4.8 |    |    |   | 11   |      |     |      | 34    |      |      | 0.5   | 9.6  | -160  |     |     | 4.9 |    |     | 6.0 |    |    |    |      |      |
| As                |     |    |    |   |      |      |     |      |       |      |      |       |      | -4.5  |     |     |     |    |     |     |    |    |    |      |      |
| Au                |     |    |    |   |      |      |     |      |       |      |      |       |      |       |     |     |     |    |     |     |    |    |    |      |      |
| B                 |     |    |    |   |      |      |     |      |       |      |      |       |      |       |     |     |     |    |     |     |    |    |    |      |      |
| C                 | 4.8 |    |    |   | 22   | -6.0 | 1.2 | -2.4 | 1.6   | 72   | -0.9 | 11.1  | 1.2  | -9.7  |     |     | 9   | 10 | 280 |     |    |    |    | -3.8 | -3.3 |
| Co                |     |    |    |   | -46  | 8.3  |     |      |       | -81  |      | -44.4 |      | 82    |     |     |     |    |     |     |    |    |    |      |      |
| Cr                |     |    |    |   | 6    |      |     |      | 11    |      |      | 4.7   |      | 2.6   |     |     |     |    |     |     |    |    |    |      |      |
| Cu                |     |    |    |   | -10  |      |     |      | -11   |      |      | -16.6 |      | -13   |     |     |     |    |     |     |    |    |    |      |      |
| H                 |     |    |    |   | 8.5  |      |     |      | 3.1   |      |      | 4.1   |      | -3.8  |     |     |     |    |     |     |    |    |    |      |      |
| Mn                |     |    |    |   | 5    |      |     |      | -0.14 |      |      |       |      | 0     |     |     |     |    |     |     |    |    |    |      |      |
| Mo                |     |    |    |   | -7   |      |     |      | -7.7  |      |      | -7.8  |      | 0     | 1.1 |     |     |    |     |     |    |    |    |      |      |
| N                 |     |    |    |   | 13   |      |     |      |       |      |      |       |      | 2.1   |     |     |     |    |     |     |    |    |    |      |      |
| Ni                |     |    |    |   | 5.9  |      |     |      |       |      |      |       |      | 5.0   | 5.1 |     |     |    |     |     |    |    |    |      |      |
| O                 |     |    |    |   | -94  |      |     |      | 0     |      |      | 4.2   | -0.0 | 2.1   |     |     |     |    |     |     |    |    |    |      |      |
| P                 |     |    |    |   | -13  |      |     |      | 0     | 0.35 |      | 5.7   | 0.6  | -20   | 7.0 | 0.4 |     |    |     |     |    |    |    |      |      |
| Pt                |     |    |    |   |      |      |     |      | 34    |      |      | 11.3  |      | 13.5  |     |     |     |    |     |     |    |    |    |      |      |
| S                 |     |    |    |   | 24   |      |     |      |       |      |      |       |      | 5.5   |     |     |     |    |     |     |    |    |    |      |      |
| Sb                |     |    |    |   |      |      |     |      | 26    |      |      |       |      | -18   | 4.5 |     |     |    |     |     |    |    |    |      |      |
| Se                |     |    |    |   |      |      |     |      |       |      |      |       |      |       |     |     |     |    |     |     |    |    |    |      |      |
| Si                |     |    |    |   | 24   |      |     |      | 76    | 0    |      |       |      | 9.3   | 8.6 |     |     |    |     |     |    |    |    |      |      |
| Sn                |     |    |    |   | 28   |      |     |      |       |      |      |       |      | 0     |     |     |     |    |     |     |    |    |    |      |      |
| Ta                |     |    |    |   |      |      |     |      | -360  |      |      |       |      |       |     |     |     |    |     |     |    |    |    |      |      |
| Ti                |     |    |    |   |      |      |     |      | -385  |      |      |       |      | -56   |     |     |     |    |     |     |    |    |    |      |      |
| V                 |     |    |    |   | -16  |      |     |      |       |      |      |       |      | -86.4 |     |     |     |    |     |     |    |    |    |      |      |
| W                 |     |    |    |   | -4.7 |      |     |      |       |      |      |       |      | 9.7   |     |     |     |    |     |     |    |    |    |      |      |

<sup>a</sup>  $\epsilon_i^j = (\partial \log f_i / \partial (\%j)) = 0.2425 / (M_j - \epsilon_i^j)$ ; at infinite dilution of dissolved elements;  $f_i$  = activity coefficient;  $\%j$  = wt% of (j);  $M_j$  = atomic weight (of i or j). Plain numbers are obtained from values reported in the literature. Italicized numbers are obtained by calculation from the reciprocal relationship noted above. Author's Note: (These reciprocal relationships are only approximate—See Chapter 3, Equations 3-39 and 3-40).

Source: J. F. Elliott and M. Glaser, *Thermodynamics for Steelmaking*, II, p. 566-567, Addison Wesley Publishing Co., Inc., Reading, Mass. 1963.

TABLE A-VI  
Nonferrous Interaction Parameters

| Solvent  | <i>i</i> | <i>j</i> | $\epsilon^i_i$        | Temperature<br>(°C) | Basis |
|----------|----------|----------|-----------------------|---------------------|-------|
| Aluminum | Ag       | Ag       | -3.1                  | 1000                |       |
|          | Cu       | H        | see $\epsilon^{Cu_H}$ | 700-1000            | *     |
|          | H        | Cu       | 39.0                  | 700                 |       |
|          | H        | Cu       | 16.6                  | 800                 |       |
|          | H        | Cu       | 20.1                  | 900                 |       |
|          | H        | Cu       | 4.3                   | 1000                |       |
|          | H        | H        | 0                     | 700-1000            |       |
|          | H        | Si       | 11.5                  | 700                 |       |
|          | H        | Si       | 6.2                   | 800                 |       |
|          | H        | Si       | 4.2                   | 900                 |       |
|          | H        | Si       | 1.8                   | 1000                |       |
|          | Si       | H        | see $\epsilon^{Si_H}$ | 700-1000            | *     |
| Antimony | Cd       | Cd       | 1.5                   | 500                 |       |
|          | Cd       | Pb       | 2.8                   | 500                 |       |
|          | Pb       | Cd       | 2.8                   | 500                 | *     |
|          | Pb       | Pb       | 0.59                  | 500                 |       |
|          | Sn       | Sn       | 2.2                   | 905                 |       |
| Bismuth  | Au       | Au       | 2.1                   | 700                 |       |
|          | Cd       | Cd       | -1.22                 | 500                 |       |
|          | Cd       | Pb       | 1.62                  | 500                 |       |
|          | Hg       | Hg       | -0.33                 | 321                 |       |
|          | Mg       | Mg       | 0.85                  | 700                 |       |
|          | Pb       | Cd       | 1.62                  | 500                 | *     |
|          | Pb       | Pb       | 1.44                  | 500                 |       |
|          | Pb       | Pb       | 0.75                  | 665                 |       |
|          | Pb       | Pb       | 0.91                  | 475                 |       |
|          | Sn       | Sn       | -0.056                | 330                 |       |
|          | Tl       | Tl       | 3.22                  | 270                 |       |
|          | Tl       | Tl       | 2.14                  | 480                 |       |
|          | Zn       | Zn       | -3.3                  | 600                 |       |
| Cadmium  | Bi       | Bi       | -6.5                  | 500                 |       |
|          | Bi       | Pb       | -3.2                  | 500                 |       |
|          | Hg       | Hg       | 3.36                  | 327                 |       |
|          | Hg       | Hg       | 2.5                   | 350                 |       |
|          | Hg       | Na       | -6                    | 350                 |       |
|          | Na       | Hg       | -6                    | 350                 | *     |
|          | Na       | Na       | 17.8                  | 350                 |       |
|          | Na       | Na       | 15.8                  | 395                 |       |
|          | Pb       | Bi       | -3.2                  | 500                 | *     |
|          | Pb       | Pb       | -4.56                 | 500                 |       |
|          | Pb       | Sb       | 0                     | 500                 |       |
|          | Pb       | Sn       | 2.86                  | 500                 |       |
|          | Sb       | Pb       | 0                     | 500                 | *     |
|          | Sb       | Sb       | -6.5                  | 500                 |       |
|          | Sn       | Pb       | 2.86                  | 500                 | *     |

TABLE A-VI (Continued)  
Nonferrous Interaction Parameters

| Solvent | <i>i</i> | <i>j</i> | $\epsilon^i_i$ | Temperature<br>(°C) | Basis |
|---------|----------|----------|----------------|---------------------|-------|
| Cobalt  | Sn       | Sn       | -1.5           | 500                 |       |
|         | Zn       | Zn       | -1.78          | 682                 |       |
|         | Cr       | N        | -19.5          | 1600                | *     |
|         | Fe       | H        | 0.53           | 1600                | *     |
|         | H        | Fe       | 0.53           | 1600                |       |
|         | H        | Ni       | 0.09           | 1600                |       |
|         | N        | Cr       | -19.5          | 1600                |       |
|         | N        | Si       | 80             | 1600                |       |
|         | N        | V        | -72            | 1600                |       |
|         | Ni       | H        | 0.09           | 1600                | *     |
|         | Si       | N        | 80             | 1600                | *     |
|         | S        | Cu       | -4(±2)         | 1500                | **    |
|         | V        | N        | -72            | 1600                | *     |
| Copper  | H        | Sn       | 5 ± .3         | 1100-1300           |       |
|         | S        | Au       | 6.9(±1)        | 1115                | **    |
|         | S        | Co       | -4.8(±0.8)     | 1300                | **    |
|         | S        | Fe       | -7.4(±0.5)     | 1300                | **    |
|         | S        | Ni       | -6.6(±1)       | 1300                | **    |
|         | S        | Pt       | 9.2(±0.2)      | 1200                | **    |
|         | S        | Si       | 6.9(±2)        | 1200                | **    |
|         | Sn       | H        | 5 ± .3         | 1100-1300           | *     |
|         | Zn       | Zn       | 0.38           | 802                 |       |
|         | Zn       | Zn       | 0.72           | 727                 |       |
|         | Zn       | Zn       | 1.185          | 653                 |       |
|         | Zn       | Zn       | 1.40           | 604                 |       |
| Gold    | Bi       | Bi       | 0.1            | 700                 |       |
|         | Pb       | Pb       | 5              | 600                 |       |
|         | Sn       | Sn       | 38.9           | 600                 |       |
|         | Tl       | Tl       | 0.1            | 700                 |       |
| Lead    | Ag       | Ag       | -0.6           | 1085                |       |
|         | Ag       | Ag       | -0.92          | 1000                |       |
|         | Au       | Au       | 3.2            | 600                 |       |
|         | Bi       | Bi       | 2.6            | 500                 |       |
|         | Bi       | Cd       | -0.86          | 500                 |       |
|         | Cd       | Bi       | -0.86          | 500                 | *     |
|         | Cd       | Cd       | -2.6           | 500                 |       |
|         | Cd       | Sb       | -1.6           | 500                 |       |
|         | Cd       | Sn       | 1.35           | 500                 |       |
|         | Hg       | Na       | -5.25          | 400                 | *     |
|         | Mg       | Mg       | 0.6            | 833                 |       |
|         | Mn       | Mn       | 0              | 750-1000            |       |
|         | Na       | Hg       | -5.25          | 400                 |       |
|         | Na       | Na       | 3.6            | 400                 |       |
|         | Sb       | Cd       | -1.6           | 500                 | *     |

TABLE A-VI (Continued)  
Nonferrous Interaction Parameters

| Solvent | <i>i</i> | <i>j</i> | $\epsilon_i$ | Temperature<br>(°C) | Basis |
|---------|----------|----------|--------------|---------------------|-------|
| Mercury | Sb       | Sb       | 0.16         | 500                 |       |
|         | Sn       | Cd       | 1.35         | 500                 | *     |
|         | Sn       | Sn       | -1.17        | 500                 |       |
|         | Tl       | Tl       | 0.1          | 450                 |       |
|         | Zn       | Zn       | -5.3         | 653                 |       |
|         | Ba       | Ba       | 127          | 298                 |       |
|         | Cd       | Na       | 6.0          | 350                 | *     |
|         | Ce       | Ce       | 129.9        | 25                  |       |
|         |          |          | 66.0         | 281                 |       |
|         |          |          | 61.0         | 301                 |       |
|         |          |          | 57.0         | 327                 |       |
|         |          |          | 51.0         | 378                 |       |
|         | K        | K        | 73           | 0                   |       |
|         |          |          | 65.3         | 25                  |       |
|         |          |          | 61.6         | 50                  |       |
|         |          |          | 67           | ?                   |       |
|         |          |          | 54.4         | 200                 |       |
|         |          |          | 50.3         | 250                 |       |
|         |          |          | 47.0         | 310                 |       |
|         |          |          | 43.8         | 390                 |       |
|         | K        | Na       | 46.5         | ?                   | *     |
|         | K        | Tl       | 30.8         | ?                   |       |
|         | Li       | Li       | 26.5         | 25                  |       |
|         | Li       | Tl       | 17.5         | ?                   |       |
|         | Na       | Cd       | 6.0          | 350                 |       |
|         | Na       | K        | 46.5         | ?                   |       |
|         | Na       | Na       | 46.1         | 25                  |       |
|         |          |          | 30.7         | 335.5               |       |
|         |          |          | 29.6         | 375                 |       |
|         |          |          | 23.4         | 350                 |       |
|         |          |          | 36.0         | ?                   |       |
|         |          |          | 43.0         | 400                 |       |
|         | Na       | Pb       | 6            | 400                 |       |
|         | Na       | Tl       | 22.1         | ?                   |       |
|         | Pb       | Na       | 6            | 400                 | *     |
|         | Tl       | K        | 30.8         | ?                   | *     |
|         | Tl       | Li       | 17.5         | ?                   | *     |
|         | Tl       | Na       | 22.1         | ?                   | *     |
|         | Tl       | Tl       | 6.0          | 325                 |       |
|         | Tl       | Tl       | 13.1         | ?                   |       |
| Nickel  | Co       | H        | 2.58         | 1600                | *     |
|         | Cr       | N        | -23.6        | 1600                | *     |
|         | Fe       | H        | 0.009        | 1600                | *     |
|         | Fe       | N        | -3.25        | 1600                | *     |
|         | Fe       | O        | 132          | 1594                | *     |

TABLE A-VI (Continued)  
Nonferrous Interaction Parameters

| Solvent  | <i>i</i> | <i>j</i> | $\epsilon_i$         | Temperature<br>(°C) | Basis |
|----------|----------|----------|----------------------|---------------------|-------|
| Silver   | H        | Co       | 2.58                 | 1600                |       |
|          | H        | Fe       | 0.009                | 1600                |       |
|          | N        | Cr       | -23.6                | 1600                |       |
|          | N        | Fe       | -3.25                | 1600                |       |
|          | O        | Fe       | 132                  | 1594                |       |
|          | S        | Cu       | 0(±1)                | 1600                | **    |
|          | Al       | Al       | 6.4                  | 700                 |       |
|          |          |          | 5.6                  | 800                 |       |
|          |          |          | 4.6                  | 900                 |       |
|          |          |          | 4.22                 | 1000                |       |
| Sodium   | Cd       | Cd       | 1.47                 | 827                 |       |
|          | Pb       | Pb       | -0.4                 | 1000                |       |
|          | Cd       | Hg       | 4.2                  | 350                 | *     |
|          | Hg       | Cd       | 4.2                  | 350                 |       |
|          | Hg       | Hg       | 2.0                  | 350                 |       |
| Thallium | Au       | Au       | 2.6                  | 700                 |       |
|          | Hg       | Hg       | 0.091                | 325                 |       |
|          | Sn       | Sn       | -1.7                 | 352                 |       |
|          | Sn       | Sn       | -0.8                 | 414                 |       |
|          | Sn       | Sn       | 0                    | 478                 |       |
| Tin      | Au       | Au       | 5.8                  | 600                 |       |
|          | Cd       | Cd       | -1.05                | 500                 |       |
|          | Cd       | Cd       | -2.36                | 700                 |       |
|          | Cd       | Pb       | 0                    | 500                 |       |
|          | Cd       | Zn       | -1.65                | 700                 | *     |
|          | Cu       | H        | see $\epsilon_{CuH}$ | 1000-1300           | *     |
|          | H        | Cu       | -9.65                | 1000                |       |
|          | H        | Cu       | -8.05                | 1100                |       |
|          | H        | Cu       | -5.64                | 1200                |       |
|          | H        | Cu       | -4.45                | 1300                |       |
|          | Pb       | Cd       | 0                    | 500                 | *     |
|          | Pb       | Pb       | 0.65                 | 500                 |       |
|          | Tl       | Tl       | -3.2                 | 352                 |       |
|          | Tl       | Tl       | -1.78                | 414                 |       |
|          | Tl       | Tl       | -0.475               | 478                 |       |
|          | Zn       | Cd       | -1.65                | 700                 |       |
| Zinc     | Zn       | Zn       | -1.0                 | 437                 |       |
|          | Zn       | Zn       | -0.6                 | 684                 |       |
|          | Cd       | Cd       | -3.33                | 682                 |       |
|          |          |          |                      |                     |       |

\* Calculated from reciprocity relationship—See Chapter 3, Equation 3-36.

\*\* Values using data where  $z_i$  not approaching zero.

Source: J. M. Dealy and R. D. Pehlke, *Trans. Met. Soc. AIME* 227, 91, 92 (1963)

TABLE A-VII

Vapor Pressures of Liquid Metals

$$\log p = -A/T + B + C \log T \text{ (mm Hg)}$$

| Element | A      | B      | C      | Temp. Range (°K) |
|---------|--------|--------|--------|------------------|
| Ag      | 14,240 | 12.23  | -1.055 | 1234-2400        |
| Al      | 16,450 | 12.36  | -1.023 | 1200-2800        |
| Au      | 19,280 | 12.38  | -1.01  | 1336-3240        |
| Bi      | 10,400 | 12.35  | -1.26  | 544-1833         |
| Ca      | 9,600  | 12.55  | -1.21  | 1123-1765        |
| Cd      | 5,819  | 12.287 | -1.257 | 594-1050         |
| Cr      | 20,400 | 16.23  | -1.82  | 2171-2938        |
| Cu      | 17,650 | 13.39  | -1.273 | 1356-2870        |
| Hg      | 3,308  | 10.373 | -0.8   | 298-630          |
| Li      | 8,415  | 11.34  | -1.0   | 453-1603         |
| Mg      | 7,550  | 12.79  | -1.41  | 923-1390         |
| Mn      | 13,900 | 17.27  | -2.52  | 1520-2309        |
| Na      | 6,540  | 11.33  | -1.718 | 400-1200         |
| Ni      | 18,000 | 8.17   | —      | 1728-3000        |
| Pb      | 10,130 | 11.16  | -0.985 | 600-2030         |
| Pt      | 28,900 | 16.05  | -1.77  | 2042-4105        |
| Se      | 17,180 | 8.30   | —      | 1505-1748        |
| Si      | 20,900 | 10.84  | -0.565 | 1690-3000        |
| Sn      | 15,500 | 11.50  | -1.0   | 500-2960         |
| Ti      | 22,100 | 9.135  | —      | 2000-3300        |
| U       | 23,380 | 8.58   | —      | 1630-1970        |
| Zn      | 6,670  | 12.00  | -1.126 | 692-1000         |

Source: C. J. Smithells, *Metals Reference Book*, 3rd ed., Vol. 2, pp. 655, 656, Butterworth, Inc., Washington, 1962.

TABLE A-VIII

Standard Electrode Potentials at 25°C for Oxidation Reactions

| Electrode                                                               | Electrode Reaction                                                                         | $E^\circ$ (volts) |
|-------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|-------------------|
| Li   Li <sup>+</sup>                                                    | Li(s) = Li <sup>+</sup> + $\theta$                                                         | +3.024            |
| K   K <sup>+</sup>                                                      | K(s) = K <sup>+</sup> + $\theta$                                                           | +2.9241           |
| Ca   Ca <sup>++</sup>                                                   | Ca(s) = Ca <sup>++</sup> + 2 $\theta$                                                      | +2.763            |
| Na   Na <sup>+</sup>                                                    | Na(s) = Na <sup>+</sup> + $\theta$                                                         | +2.7146           |
| Zn   Zn <sup>++</sup>                                                   | Zn(s) = Zn <sup>++</sup> + 2 $\theta$                                                      | +0.7611           |
| Fe   Fe <sup>++</sup>                                                   | Fe(s) = Fe <sup>++</sup> + 2 $\theta$                                                      | +0.441            |
| Cd   Cd <sup>++</sup>                                                   | Cd(s) = Cd <sup>++</sup> + 2 $\theta$                                                      | +0.4021           |
| Pb   PbSO <sub>4</sub> (s), SO <sub>4</sub> <sup>--</sup>               | Pb(s) + SO <sub>4</sub> <sup>--</sup> = PbSO <sub>4</sub> (s) + 2 $\theta$                 | +0.3546           |
| Tl   Tl <sup>+</sup>                                                    | Tl(s) = Tl <sup>+</sup> + $\theta$                                                         | +0.3385           |
| Ni   Ni <sup>++</sup>                                                   | Ni(s) = Ni <sup>++</sup> + 2 $\theta$                                                      | +0.236            |
| Ag   AgI(s), I <sup>-</sup>                                             | Ag(s) + I <sup>-</sup> = AgI(s) + $\theta$                                                 | +0.1522           |
| Sn   Sn <sup>++</sup>                                                   | Sn(s) = Sn <sup>++</sup> + 2 $\theta$                                                      | +0.1406           |
| Pb   Pb <sup>++</sup>                                                   | Pb(s) = Pb <sup>++</sup> + 2 $\theta$                                                      | +0.1264           |
| H <sub>2</sub>   H <sup>+</sup>                                         | H <sub>2</sub> (g, 1 atm) = 2 H <sup>+</sup> + 2 $\theta$                                  | ±0.0000           |
| Ag   AgBr(s), Br <sup>-</sup>                                           | Ag(s) + Br <sup>-</sup> = AgBr(s) + $\theta$                                               | -0.0711           |
| Hg   Hg <sub>2</sub> Br <sub>2</sub> (s), Br <sup>-</sup>               | 2 Hg(l) + 2 Br <sup>-</sup> = Hg <sub>2</sub> Br <sub>2</sub> (s) + 2 $\theta$             | -0.1385           |
| Pt   Sn <sup>++</sup> , Sn <sup>++++</sup>                              | Sn <sup>++</sup> = Sn <sup>++++</sup> + 2 $\theta$                                         | -0.14             |
| Ag   AgCl(s), Cl <sup>-</sup>                                           | Ag(s) + Cl <sup>-</sup> = AgCl(s) + $\theta$                                               | -0.2225           |
| Hg   Hg <sub>2</sub> Cl <sub>2</sub> (s), Cl <sup>-</sup>               | 2 Hg(l) + 2 Cl <sup>-</sup> = Hg <sub>2</sub> Cl <sub>2</sub> (s) + 2 $\theta$             | -0.2680           |
| Cu   Cu <sup>++</sup>                                                   | Cu(s) = Cu <sup>++</sup> + 2 $\theta$                                                      | -0.3441           |
| I <sub>2</sub>   I <sup>-</sup>                                         | 2 I <sup>-</sup> = I <sub>2</sub> (s) + 2 $\theta$                                         | -0.5362           |
| Hg   Hg <sub>2</sub> SO <sub>4</sub> (s), SO <sub>4</sub> <sup>--</sup> | 2 Hg(l) + SO <sub>4</sub> <sup>--</sup> = Hg <sub>2</sub> SO <sub>4</sub> (s) + 2 $\theta$ | -0.6141           |
| Pt   Fe <sup>++</sup> , Fe <sup>+++</sup>                               | Fe <sup>++</sup> = Fe <sup>+++</sup> + $\theta$                                            | -0.7477           |
| Ag   Ag <sup>+</sup>                                                    | Ag(s) = Ag <sup>+</sup> + $\theta$                                                         | -0.7990           |
| Br <sub>2</sub>   Br <sup>-</sup>                                       | 2 Br <sup>-</sup> = Br <sub>2</sub> (l) + 2 $\theta$                                       | -1.0659           |
| Pt   Tl <sup>+</sup> , Tl <sup>+++</sup>                                | Tl <sup>+</sup> = Tl <sup>+++</sup> + 2 $\theta$                                           | -1.211            |
| Cl <sub>2</sub>   Cl <sup>-</sup>                                       | 2 Cl <sup>-</sup> = Cl <sub>2</sub> (g, 1 atm) + 2 $\theta$                                | -1.3583           |
| Pt   Ce <sup>+++</sup> , Ce <sup>++++</sup>                             | Ce <sup>+++</sup> = Ce <sup>++++</sup> + $\theta$                                          | -1.55             |
| Pt   Co <sup>++</sup> , Co <sup>+++</sup>                               | Co <sup>++</sup> = Co <sup>+++</sup> + $\theta$                                            | -1.817            |

Source: C. F. Prutton and S. H. Maron, *Fundamental Principles of Physical Chemistry*, p. 531, The MacMillan Company, New York, 1951.

TABLE A-IX  
Heat Content of Several Metals

| Temperature<br>°K              | H <sub>T</sub> - H° <sub>298.15</sub> cal/gm atom |            |                   |           |           |           |
|--------------------------------|---------------------------------------------------|------------|-------------------|-----------|-----------|-----------|
|                                | Aluminum                                          | Copper     | Iron <sup>a</sup> | Lead      | Magnesium | Zinc      |
| 298                            | 0                                                 | 0          | 0(α)              | 0         | 0         | 0         |
| 400                            | 600                                               | 600        | 642               | 656       | 620       | 630       |
| 500                            | 1230                                              | 1215       | 1318              | 1324      | 1256      | 1270      |
| 600                            | 1890                                              | 1845       | 2044              | 2014      | 1920      | 1940      |
| 700                            | 2580                                              | 2480       | 2832              | 3884(liq) | 2610      | 4400(liq) |
| 800                            | 3310                                              | 3130       | 3703              | 4605      | 3330      | 5150      |
| 900                            | 4060                                              | 3800       | 4682              | 5318      | 4095      | 5900      |
| 1000                           | 7330(liq)                                         | 4490       | 5819              | 6024      | 7010(liq) | 6650      |
| 1100                           | 8030                                              | 5190       | 7135              | 6723      | 7810      | 7400      |
| 1200                           | 8730                                              | 5895       | 8347(γ)           | 7415      | 8640      |           |
| 1300                           | 9430                                              | 6615       | 9203              | 8100      | 9490      |           |
| 1400                           | 10130                                             | 10480(liq) | 10059             | 8780      |           |           |
| 1500                           | 10830                                             | 11230      | 10915             | 9450      |           |           |
| 1600                           | 11530                                             | 11980      | 11771             | 10110     |           |           |
| 1700                           | 12230                                             | 12730      | 12939(δ)          | 10760     |           |           |
| 1800                           | 12930                                             | 13460      | 13914             | 11410     |           |           |
| 1900                           | 13630                                             | 14230      | 18658(liq)        | 12050     |           |           |
| 2000                           | 14330                                             | 14980      | 19714             | 12680     |           |           |
| 2100                           | 15030                                             | 15730      | 20774             |           |           |           |
| 2200                           | 15730                                             | 16480      | 21838             |           |           |           |
| 2300                           | 16430                                             | 17230      | 22906             |           |           |           |
| 2400                           | 17130                                             | 17980      | 23978             |           |           |           |
| 2500                           | 17830                                             | 18730      | 25054             |           |           |           |
| 2600                           | 18530                                             | 19480      | 26134             |           |           |           |
| 2700                           | 19230                                             | 20230      | 27218             |           |           |           |
| 2800                           |                                                   | 20980      | 28306             |           |           |           |
| 2900                           |                                                   |            | 29398             |           |           |           |
| 3000                           |                                                   |            | 30494             |           |           |           |
| Melting point<br>(°K)          | 932                                               | 1356       | 1809              | 606.6     | 923       | 692.7     |
| ΔH <sub>f</sub> cal/g-<br>atom | 2550                                              | 3120       | 3700              | 1141      | 2140      | 1765      |

<sup>a</sup> Phase changes: Curie pt 1042°K; α → γ 1184°K 215 cal/g-atom; γ → δ 1665°K 270 cal/g-atom.

Source: J. F. Elliott and M. Gleiser, *Thermochemistry for Steelmaking, I*, pp. 16, 48, 58, 61, 64, 118, Addison-Wesley Publishing Company, Inc., Reading, Mass., 1960.

## Appendix A-X: The Error Function

Diffusion of energy or mass often is described by differential equations that are solved by an integral of the form,

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\alpha^2} d\alpha,$$

which is referred to as the error function. The factor,  $\frac{2}{\sqrt{\pi}}$ , normalizes the function

such that it approaches 1 as  $x$  approaches  $\infty$ . The error function takes on values between 0 and 1 as  $x$  ranges from 0 to  $\infty$ , i.e.,  $\operatorname{erf}(0) = 0$ ,  $\operatorname{erf}(\infty) = 1$ . Differentiating the error function

$$\frac{d(\operatorname{erf} x)}{dx} = \frac{2}{\sqrt{\pi}} e^{-x^2}.$$

Then at  $x = 0$

$$\left( \frac{d(\operatorname{erf} x)}{dx} \right)_{x=0} = \frac{2}{\sqrt{\pi}}.$$

For small values of  $x$ , the first two terms of a Taylor series expansion of the function

TABLE A-X  
Values of the Error Function<sup>a</sup>

| $x$   | $\operatorname{erf} x$ | $x$  | $\operatorname{erf} x$ |
|-------|------------------------|------|------------------------|
| 0.000 | 0.00000                | 0.80 | 0.74210                |
| 0.05  | 0.05637                | 0.85 | 0.77067                |
| 0.10  | 0.11246                | 0.90 | 0.79691                |
| 0.15  | 0.16800                | 0.95 | 0.82089                |
| 0.20  | 0.22270                | 1.00 | 0.84270                |
| 0.25  | 0.27633                | 1.10 | 0.88021                |
| 0.30  | 0.32863                | 1.20 | 0.91031                |
| 0.35  | 0.37938                | 1.30 | 0.93401                |
| 0.40  | 0.42839                | 1.40 | 0.95229                |
| 0.45  | 0.47548                | 1.50 | 0.96611                |
| 0.50  | 0.52050                | 1.60 | 0.97635                |
| 0.55  | 0.56332                | 1.70 | 0.98379                |
| 0.60  | 0.60386                | 1.80 | 0.98909                |
| 0.65  | 0.64203                | 1.90 | 0.99279                |
| 0.70  | 0.67780                | 2.00 | 0.995322               |
| 0.75  | 0.71116                | 2.50 | 0.999593               |
|       |                        | 3.00 | 0.999978               |

<sup>a</sup> The values above are taken from the National Bureau of Standards tabulation, Applied Mathematics Series 41, *Tables of the Error Function and Its Derivatives*, 1954, 302 pages.

about zero yield

$$\operatorname{erf} x = \operatorname{erf}(0) + x \left( \frac{d(\operatorname{erf} x)}{dx} \right)_{x=0} = \frac{2}{\sqrt{\pi}} x,$$

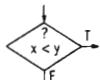
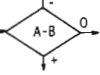
which is valid for  $x \ll 1$ .

Other special properties of the error function and application in diffusion problems are presented elsewhere.<sup>1-3</sup>

<sup>1</sup> R. M. Barrer, *Diffusion in and through Solids*, University Press, Cambridge, 1941.

<sup>2</sup> J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1955.

<sup>3</sup> W. Jost, *Diffusion*, Academic Press, New York, 1952.

| <u>SYMBOL</u>                                                                       | <u>USED FOR</u>                | <u>FORTRAN IMPLEMENTATION</u>                                 |
|-------------------------------------------------------------------------------------|--------------------------------|---------------------------------------------------------------|
|    | SUBSTITUTION STATEMENTS        | R = SQRT (X)                                                  |
|    | CONNECTORS OR LABELS           | STATEMENT LABEL 10                                            |
|    | TERMINAL OPERATIONS            | START & END IN A MAIN PROGRAM, ENTER & RETURN IN A SUBPROGRAM |
|    | LOGICAL CONDITIONAL CONTROL    | IF (X, LT, Y) GO TO 20                                        |
|   | ARITHMETIC CONDITIONAL CONTROL | IF (A-B) 20, 10, 5                                            |
|  | INPUT FROM CARDS               | READ (5, 500) N, A(3)                                         |
|                                                                                     |                                |                                                               |

Flow Charting Convention used for Example Problems in Appendix B.

## APPENDIX B Example Problems and Computer-facilitated Solutions

This appendix consists of ten example problems and their computer-facilitated solutions. The solutions are documented and include a flow diagram or other descriptive material of the solution algorithm, as well as a listing of the computer program and output. The programs were prepared in FORTRAN IV and were executed on the IBM 360/67 duplex computer at The University of Michigan, using the *Michigan Terminal System*, a multiprocessing facility. FORTRAN IV was chosen as the programming language to permit the most extensive direct use of these example programs.

A logic flowchart is presented for each computer program. The flowcharting convention used for the example problems in this appendix was designed to provide a system by which the *logic* of each computer program could be represented clearly, and concisely without sacrificing generality. Although the example problems have been solved using the FORTRAN language, the logic flow diagrams contained herein are language-independent.

The symbols and their interpretations follow. It should be noted that the larger example problems have only a system flow chart, i.e. each detailed step is not listed separately. A symbol table is provided for each program. Minor alterations to a few symbols shown below occur in some flowcharts.

### Example Problem No. 1: Thermochemical Data Calculation—Enthalpy Increments

#### Problem Statement

This problem requires that a computer program be written to integrate a specific heat equation over the temperature range 298.16 to 2500°K. Up to nine phase changes may be involved at various temperatures. The enthalpy increments are to be printed at 100°K intervals as well as for the primary phase at each transformation temperature and for the transformed phase at the same temperature.

The input data include in addition to the name of the material the coefficients,  $A$ ,  $B$ , and  $C$ , of a specific heat equation of the form:

$$C_p = A + BT + C/T^2,$$

for each phase; the temperature  $T$  of transformation; the first temperature  $X$  above  $T$  which is an integral multiple of 100; and  $H$ , the enthalpy of the transformation.

Symbol Table—Problem 1

| Algebraic Symbol           | Definition                                                        | FORTTRAN Symbol                  |
|----------------------------|-------------------------------------------------------------------|----------------------------------|
| $A_j$                      | Constant $A$ for phase $j$                                        | $A(J)$                           |
| $B_j$                      | Constant $B$ for phase $j$                                        | $B(J)$                           |
| $C_j$                      | Constant $C$ for phase $j$                                        | $C(J)$                           |
| $T_j$                      | Transition temperature between the $j$ -1st and $j$ th phases     | $T(J)$                           |
| $X_j$                      | Temperature just above $T_j$ which is an integral multiple of 100 | $X(J)$                           |
| $n$                        | Number of phase changes ( $N < 10$ )                              | $N$                              |
| $H_j$                      | Enthalpy change at phase transition temperature $T_j$             | $H(J)$                           |
| $j$                        | Counter on phases                                                 | $J$                              |
| $i$                        | Counter on 100° intervals                                         | $I$                              |
| $T_L$                      | Lower temperature limit for integration                           | $TL$                             |
| $\Delta T$                 | Temperature interval (in this case 100°)                          | $DELTA$                          |
| ...                        | Locations for storage of material names                           | $MA, TE, RI, AL, \text{ and } S$ |
| $(H_T - H_{298.16^\circ})$ | Enthalpy at $T$ above reference                                   | $E(J)$                           |

A flow diagram, tested program in the FORTRAN language and printed output for a few elements are to be presented.

#### Method of Solution—Problem 1

In regions where there is no phase change the increase in enthalpy between two temperatures is

$$\Delta H = \int_{T_1}^{T_2} \left( A_j + B_j T + \frac{C_j}{T^2} \right) dT. \quad (a)$$

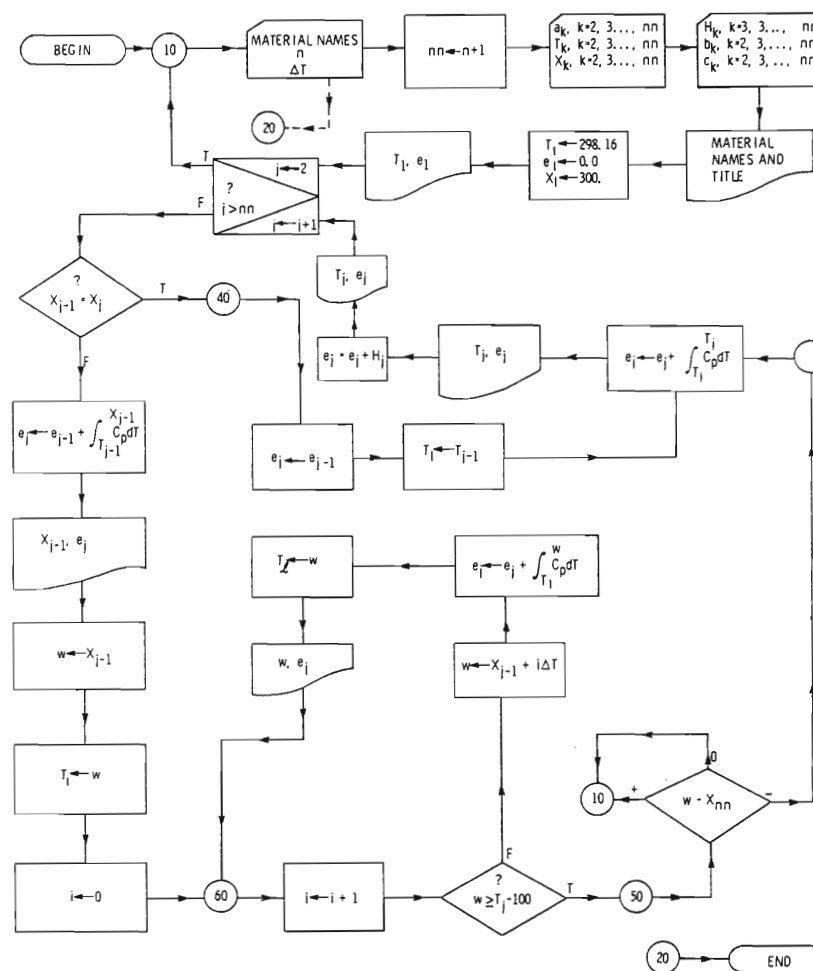
This may be integrated and  $(T_2 - T_1)$  factored out to give

$$\Delta H = \left[ A_j + \frac{B_j(T_2 + T_1)}{2} + \frac{C_j}{T_1 T_2} \right] (T_2 - T_1). \quad (b)$$

It is this form of the integral that is used in the computations.

At a phase transition point the increase in enthalpy will simply be that stipulated by input data. Since enthalpies are to be printed every 100°K and also at the beginning and end of each phase change, the program must be alert to the occurrence

of a transition at any given temperature between 298.16°K and 2500°K. The method by which this is done is to input not only the transition temperature, but also the next higher temperature above each transition that is an integral multiple of 100. Use of this integral multiple temperature  $X_j$ , is demonstrated in the following program.



Flow Chart—Problem 1. Flow diagram for computation of enthalpy increment.

## FORTRAN Listing—Problem 1

```

      REAL MA, I
      DIMENSION A(10), B(10), C(10), T(10), X(10), H(10), E(10)
10    READ (5, 500, END=20) MA, TE, RI, AL, S, N, DELT
      NN=N+1
      READ (5, 510) (A(K), K=2, NN)
      READ (5, 510) (T(K), K=2, NN)
      READ (5, 510) (X(K), K=2, NN)
      READ (5, 510) (H(K), K=2, NN)
      READ (5, 520) (B(K), K=2, NN)
      READ (5, 520) (C(K), K=2, NN)
      WRITE (6, 600) MA, TE, RI, AL, S
      T(1)=298.16
      E(1)=0.
      X(1)=300.
      WRITE (6, 610) T(1), E(1)
      DO 30 J=2, NN
      IF (X(J-1).EQ.X(J)) GO TO 40
      E(J)=E(J-1)+(A(J)+(B(J)*(X(J-1)+T(J-1))/2.)*C(J)/(X(J-1)*T(J-1)))*
1    (X(J-1)-T(J-1))
      WRITE (6, 610) X(J-1), E(J)
      TEMP=X(J-1)
      TL=TEMP
      I=0.
60    I=I+1.
      IF (TEMP.GE.(T(J)-100.)) GO TO 50
      TEMP=X(J-1)+I*DELT
      E(J)=E(J)+(A(J)+(B(J)*(TEMP+TL)/2.)*C(J)/(TEMP*TL))*(TEMP-TL)
      TL=TEMP
      WRITE (6, 610) TEMP, E(J)
      GO TO 60
50    IF (TEMP-X(NN)) 61, 10, 10
40    E(J)=E(J-1)
      TL=T(J-1)
61    E(J)=E(J)+(A(J)+(B(J)*(T(J)+TL)/2.)*C(J)/(T(J)*TL))*(T(J)-TL)
      WRITE (6, 610) T(J), E(J)
      E(J)=E(J)+H(J)
30    WRITE (6, 610) T(J), E(J)
      GO TO 10
20    CALL SYSTEM
500    FORMAT (5A4, 10X, 15, F5.0)
510    FORMAT (8F9.2)
520    FORMAT (8E9.2)
600    FORMAT (35H1HIGH TEMPERATURE HEAT CONTENT FOR 5A4/1H-, 12X, 16HT DEG
1    REES KELVIN, 9X, 16HH(T) - H(298.16)//1H-)
610    FORMAT (F20.0, F30.1)
      END

```

Consider a metal which has two transitions within a 100° interval, say one at 627°K which will be denoted  $T_1$  and the other at 685°K which will be denoted  $T_2$ . A comparison is first made between  $x_{j-1}$ , which for  $j = 1$  is  $X_0 = 300$  and  $X_j$ , which is  $X_1 = 700$ . The subscript  $j$  indicates the stable phase. Since 300 does not equal 700, the procedure is to calculate the increase in enthalpy between 298.16 and 300 using  $A_1$ ,  $B_1$ , and  $C_1$ . The temperature  $T$  is then incremented by 100 and the enthalpy increase between 300° and 400° computed and added to the value at 300. This process is repeated until  $T$  at the lower limit of the integral is equal to or greater than  $T_1 = 100$  or 527°. Thus, the last calculation will be between 500° and 600°, since 600° is greater than 527°, and the procedure will stop short of that. The next calculation is to integrate between 600° and  $T_1$  which is 627°, using still  $A_1$ ,  $B_1$ , and  $C_1$ , for so far we are dealing with only the first phase. At 627°,  $\Delta H$  of transi-

## Input (Data)—Problem 1

| IRON      | 5       | 100     | 1000    |
|-----------|---------|---------|---------|
| 337       | 1040    | 485     | 1030    |
| 103300    | 117900  | 167400  | 180300  |
| 110000    | 120000  | 170000  | 190000  |
| 41000     | 21000   | 11000   | 370000  |
| 7.10E-3   | 0.00E+0 | 3.00E-3 | 0.00E+0 |
| 0.43E+5   | 0.00E+0 | 0.00E+0 | 0.00E+0 |
| MANGANESE | 6       | 100     | 626     |
| 570       | 833     | 1070    | 1130    |
| 100000    | 137400  | 141000  | 151700  |
| 110000    | 140000  | 150000  | 160000  |
| 53500     | 54500   | 43000   | 350000  |
| 3.38E-3   | 0.66E-3 | 0.00E+0 | 0.00E+0 |
| 0.37E+5   | 0.00E+0 | 0.00E+0 | 0.00E+0 |
| CARBON    | 1       | 100     |         |
| 410       |         |         |         |
| 260000    |         |         |         |
| 250000    |         |         |         |
| 000       |         |         |         |
| 1.02E-3   |         |         |         |
| 2.10E+5   |         |         |         |
| SILICON   | 2       | 100     |         |
| 579       | 613     |         |         |
| 168600    | 260000  |         |         |
| 170000    | 250000  |         |         |
| 1210000   | 000     |         |         |
| 0.56E-3   | 0.00E+0 |         |         |
| 1.09E+5   | 0.00E+0 |         |         |

tion is added to the enthalpy to give the enthalpy of the transformed phase at 627°.

In considering phase 2, a comparison is made between  $X_1 = 700^\circ$  and  $X_2$ . Since the second transition is in the same 100° interval as the first,  $X_2$  also is 700°. Because these two are equal, the program transfers to a calculation of the integral between 627° and 685°. Then the  $\Delta H$  at 685° is added to give the enthalpy of the transformed or third phase at 685°. Continuing with the third phase the program determines the integral between 685° and 700° first, and then proceeds again by 100° intervals until a new transition temperature is reached.

## Discussion of Results—Problem 1

Examination of the computed enthalpies for iron shows how the calculation advanced by 100° intervals up to 1000°K. At this point the program proceeded to 1033°, the first transition temperature. There it added a  $\Delta H$  of 410, and then went on to 1100° etc.

The computed enthalpies ( $H$ ) are in calories per g-mole.

## Output (Results)—Problem 1

## HIGH TEMPERATURE HEAT CONTENT FOR IRON

| T DEGREES KELVIN | H(T) - H(298.16) |
|------------------|------------------|
| 298.             | 0.0              |
| 300.             | 11.0             |
| 400.             | 632.3            |
| 500.             | 1310.3           |
| 600.             | 2052.2           |
| 700.             | 2860.9           |

## Output (Results)—Problem 1

## HIGH TEMPERATURE HEAT CONTENT FOR IRON

| T DEGREES KELVIN | H(T) - H(298.16) |
|------------------|------------------|
| 800.             | 3738.1           |
| 900.             | 4684.5           |
| 1000.            | 5700.8           |
| 1033.            | 6051.6           |
| 1033.            | 6461.6           |
| 1100.            | 7158.4           |
| 1179.            | 7980.0           |
| 1179.            | 8190.0           |
| 1200.            | 8366.7           |
| 1300.            | 9226.7           |
| 1400.            | 10116.7          |
| 1500.            | 11036.7          |
| 1600.            | 11986.7          |
| 1674.            | 12709.0          |
| 1674.            | 12819.0          |
| 1700.            | 13086.8          |
| 1800.            | 14116.8          |
| 1803.            | 14147.7          |
| 1803.            | 17847.7          |
| 1900.            | 18817.7          |
| 2000.            | 19817.7          |
| 2100.            | 20817.7          |
| 2200.            | 21817.7          |
| 2300.            | 22817.7          |
| 2400.            | 23817.7          |
| 2500.            | 24817.7          |

## HIGH TEMPERATURE HEAT CONTENT FOR MANGANESE

| T DEGREES KELVIN | H(T) - H(298.16) |
|------------------|------------------|
| 298.             | 0.0              |
| 300.             | 13.1             |
| 400.             | 732.2            |
| 500.             | 1472.8           |
| 600.             | 2241.1           |
| 700.             | 3039.6           |
| 800.             | 3869.7           |
| 900.             | 4732.1           |
| 1000.            | 5627.3           |
| 1000.            | 6162.3           |
| 1100.            | 7064.6           |
| 1200.            | 7973.5           |
| 1300.            | 8889.0           |
| 1374.            | 9570.8           |
| 1374.            | 10115.7          |
| 1400.            | 10393.9          |
| 1410.            | 10500.9          |
| 1410.            | 10930.9          |
| 1500.            | 11947.9          |
| 1517.            | 12140.0          |
| 1517.            | 15640.0          |
| 1600.            | 16577.9          |
| 1700.            | 17707.9          |
| 1800.            | 18837.9          |
| 1900.            | 19967.9          |
| 2000.            | 21097.9          |
| 2100.            | 22227.9          |
| 2200.            | 23357.9          |
| 2300.            | 24487.9          |
| 2368.            | 25256.3          |
| 2368.            | 78956.3          |
| 2400.            | 79156.6          |
| 2500.            | 79782.5          |

## HIGH TEMPERATURE HEAT CONTENT FOR CARBON

| T DEGREES KELVIN | H(T) - H(298.16) |
|------------------|------------------|
| 298.             | 0.0              |
| 300.             | 12.4             |
| 400.             | 633.1            |
| 500.             | 1194.0           |
| 600.             | 1730.1           |
| 700.             | 2256.4           |
| 800.             | 2780.4           |
| 900.             | 3306.3           |
| 1000.            | 3836.5           |
| 1100.            | 4372.7           |
| 1200.            | 4915.9           |
| 1300.            | 5466.9           |
| 1400.            | 6026.1           |
| 1500.            | 6594.0           |
| 1600.            | 7170.9           |
| 1700.            | 7756.9           |
| 1800.            | 8352.2           |
| 1900.            | 8957.1           |
| 2000.            | 9571.5           |
| 2100.            | 10195.6          |
| 2200.            | 10829.4          |
| 2300.            | 11473.1          |
| 2400.            | 12126.6          |
| 2500.            | 12790.0          |

## HIGH TEMPERATURE HEAT CONTENT FOR SILICON

| T DEGREES KELVIN | H(T) - H(298.16) |
|------------------|------------------|
| 298.             | 0.0              |
| 300.             | 13.2             |
| 400.             | 702.6            |
| 500.             | 1361.3           |
| 600.             | 2007.5           |
| 700.             | 2648.8           |
| 800.             | 3289.3           |
| 900.             | 3931.0           |
| 1000.            | 4575.3           |
| 1100.            | 5223.0           |
| 1200.            | 5874.7           |
| 1300.            | 6530.7           |
| 1400.            | 7191.3           |
| 1500.            | 7856.7           |
| 1600.            | 8527.0           |
| 1686.            | 9107.5           |
| 1686.            | 21207.5          |
| 1700.            | 21293.4          |
| 1800.            | 21906.3          |
| 1900.            | 22519.3          |
| 2000.            | 23132.3          |
| 2100.            | 23745.3          |
| 2200.            | 24358.3          |
| 2300.            | 24971.3          |
| 2400.            | 25584.3          |
| 2500.            | 26197.3          |

### Example Problem No. 2: Calculation of Adiabatic Flame Temperatures at the Tuyeres of a Coke-Fueled Shaft Furnace

#### Problem Statement

One of the physical limitations placed on the coke-fueled shaft furnace (such as the cupola or iron-blast furnace) is the necessity for a specific temperature distribution to exist in the melting zone just above the tuyeres. A number of possibilities for coke reduction and increased production from the shaft furnace exist through the addition of blast injectants such as oxygen, natural gas, and fuel oil. In order to estimate the changes in blast composition and temperature required to maintain the desired temperature distribution about the tuyere zone, the concept of adiabatic flame temperature has been adopted.

The adiabatic flame temperature is assumed to relate to the combustion of the blast with the downwardly moving coke in the zone just in front of and above the tuyeres. If the furnace has been operating satisfactorily on a given burden and with a given blast composition and temperature, the adiabatic flame temperature for these conditions can be used as a required condition for smooth furnace operation.

Write and test a FORTRAN program to calculate the adiabatic flame temperature at the tuyeres of a coke-fueled shaft furnace (Problem 2A). Assume a temperature of 2800°F for the coke. Base the calculation on known values of blast temperature and composition (including moisture) and a mass balance based on the combustion gases nitrogen, hydrogen, and carbon monoxide. Changes in temperature of the metal and slag components as they move down through this zone can be assumed to be independent of the blast volume per unit of coke. Consider only oxygen enrichment and natural gas (methane) injection.

This calculation can be used to specify a balanced blast to maintain a desired flame temperature as blast operating conditions change. If the necessary flame temperature has been determined for a given furnace practice, the appropriate adjustments in composition and temperature of the blast to maintain this flame temperature also can be computed. One could, for example, enrich the blast in oxygen and compensate for the increased flame temperature by adding moisture or natural gas. Alternatively, one could increase the blast temperature, thereby increasing the flame temperature, and compensate for this by adding moisture or natural gas.

Write and test another program for calculating the required oxygen enrichment to maintain a specified flame temperature, given the other blast variables (Problem 2B).

#### Method of Solution—Problem 2

The carbon-oxygen reaction provides the thermal energy for operation of the coke-fueled shaft furnace. Oxygen may react with carbon to produce carbon monoxide or carbon dioxide. At the flame temperatures involved in the tuyere zone of

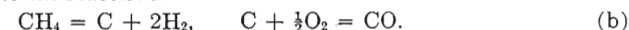
the cupola or blast furnace, the reaction product is essentially carbon monoxide. Nitrogen, the major constituent in air, acts as an inert material and passes through the furnace unchanged.

An important blast variable is the moisture content of the air. In the presence of graphite at high temperature, water vapor is decomposed into hydrogen and oxygen, with the oxygen immediately reacting to form carbon monoxide. This overall reaction,



is endothermic, and absorbs approximately 34,000 BTU per lb. mole. The flame temperature is thus highly dependent upon the moisture content of the blast, and decreases with increasing moisture content.

The enrichment of the blast with natural gas also will decrease the flame temperature. This is caused by the absorption of energy in decomposing methane (and other alkanes) into hydrogen and carbon, which will eventually react to form carbon monoxide according to the reactions:



The chemistry of tuyere zone reactions is illustrated in Fig. B-1. The reactants

#### COMBUSTION GAS

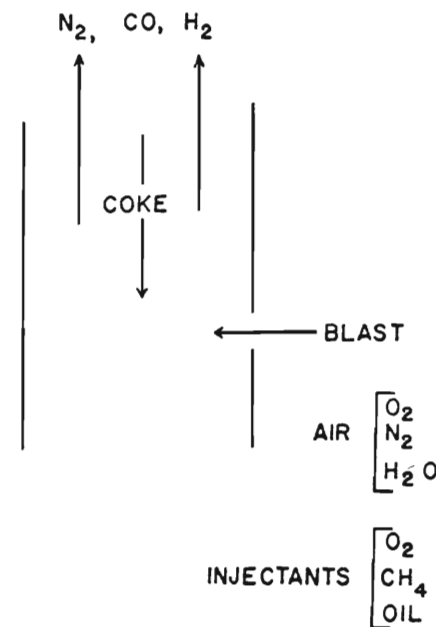


Fig. B-1. Components in Tuyere zone

are air, containing moisture, and in some cases added injectants such as oxygen or a fuel such as natural gas, oil, or powdered coal. The blast, sometimes preheated, reacts in the zone in front of the tuyeres with the coke, which has been preheated by the hot gases rising up the furnace stack. As discussed above, the products of combustion are hydrogen and carbon monoxide, which are essentially free of any moisture and carbon dioxide. The nitrogen passes through the furnace unchanged.

A mass and energy balance for combustion can be carried out taking into account the sensible heat of the reactants and the heats of reaction (including vaporization or decomposition reactions) and equating these energies to the sensible heat of the products. Usually this is accomplished by trial and error evaluation of the temperature of the reaction products.

Symbol Table—Problem 2A

| Algebraic Symbol              | Definition                                                                                                    | FORTRAN Symbol |
|-------------------------------|---------------------------------------------------------------------------------------------------------------|----------------|
| ...                           | Grains of moisture per ft <sup>3</sup> in blast                                                               | WIQH20         |
| ...                           | Per cent oxygen enrichment                                                                                    | WIQ2           |
| ...                           | Per cent carbon monoxide enrichment                                                                           | WICO           |
| ...                           | Per cent carbon dioxide enrichment                                                                            | WICO2          |
| ...                           | Per cent natural gas (methane) enrichment                                                                     | WICH4          |
| ...                           | Relative amount of moisture in the air blast, ft <sup>3</sup> moisture/ft <sup>3</sup> dry air                | RH20           |
| ...                           | Relative amount of oxygen in the air blast, ft <sup>3</sup> O <sub>2</sub> /ft <sup>3</sup> dry air           | RQ2            |
| ...                           | Relative amount of carbon monoxide in the air blast, ft <sup>3</sup> CO/ft <sup>3</sup> dry air               | RCO            |
| ...                           | Relative amount of carbon dioxide in the air blast, ft <sup>3</sup> CO <sub>2</sub> /ft <sup>3</sup> dry air  | RCO2           |
| ...                           | Relative amount of natural gas (methane) enrichment, ft <sup>3</sup> CH <sub>4</sub> /ft <sup>3</sup> dry air | RCH4           |
| X <sub>air</sub>              | Mole fraction of dry air in blast                                                                             | AR             |
| X <sub>O<sub>2</sub>(Q)</sub> | Mole fraction of (enriched) oxygen in blast                                                                   | XWIQ2          |
| X <sub>N<sub>2</sub></sub>    | Mole fraction of nitrogen in blast                                                                            | XWIN2          |
| X <sub>H<sub>2</sub>O</sub>   | Mole fraction of water in blast                                                                               | XWIH20         |
| X <sub>O<sub>2</sub></sub>    | Mole fraction of (air) oxygen in blast                                                                        | XWIO2          |
| X <sub>CO</sub>               | Mole fraction of carbon monoxide in blast                                                                     | XWICO          |
| X <sub>CO<sub>2</sub></sub>   | Mole fraction of carbon dioxide in blast                                                                      | XWICO2         |
| X <sub>CH<sub>4</sub></sub>   | Mole fraction of methane in blast                                                                             | XWICH4         |
| H <sub>O<sub>2</sub></sub>    | Enthalpy of (air) oxygen                                                                                      | HWO2           |
| H <sub>N<sub>2</sub></sub>    | Enthalpy of nitrogen                                                                                          | HWN2           |
| H <sub>H<sub>2</sub>O</sub>   | Enthalpy of water                                                                                             | HWH20          |
| H <sub>O<sub>2</sub>(g)</sub> | Enthalpy of (enriched) oxygen                                                                                 | HWQ2           |
| H <sub>CO</sub>               | Enthalpy of carbon monoxide                                                                                   | HWCO           |
| H <sub>CO<sub>2</sub></sub>   | Enthalpy of carbon dioxide                                                                                    | HWCO2          |
| H <sub>CO<sub>4</sub></sub>   | Enthalpy of methane                                                                                           | HWCH4          |

Symbol Table—Problem 2A—(Continued)

| Algebraic Symbol               | Definition                                                                  | FORTRAN Symbol |
|--------------------------------|-----------------------------------------------------------------------------|----------------|
| H <sub>C</sub>                 | Enthalpy of coke                                                            | HC             |
| H <sub>BL</sub>                | Enthalpy of blast                                                           | HBL            |
| H <sub>CO(CG)</sub>            | Enthalpy of carbon monoxide in combustion gases                             | HTGCO          |
| H <sub>H<sub>2</sub>(CG)</sub> | Enthalpy of hydrogen in combustion gases                                    | HTGH2          |
| H <sub>N<sub>2</sub>(CG)</sub> | Enthalpy of nitrogen in combustion gases                                    | HTGN2          |
| H <sub>CG</sub>                | Enthalpy of combustion products (total)                                     | HTG            |
| N <sub>CO(CG)</sub>            | Number of moles of carbon monoxide in combustion gases                      | NTGCO          |
| N <sub>H<sub>2</sub>(CG)</sub> | Number of moles of hydrogen in combustion gases                             | NTGH2          |
| N <sub>N<sub>2</sub>(CG)</sub> | Number of moles of nitrogen in combustion gases                             | NTGN2          |
| N <sub>C(tuyere)</sub>         | Moles of carbon burned in reaction per mole of blast in tuyere zone         | NBC            |
| T <sub>blast</sub>             | Temperature of the blast                                                    | TA             |
| T <sub>O<sub>2</sub>(Q)</sub>  | Temperature of oxygen added                                                 | TQ2            |
| T <sub>C</sub>                 | Temperature of coke                                                         | TC             |
| T <sub>CO</sub>                | Temperature of carbon monoxide                                              | TCO            |
| T <sub>CO<sub>2</sub></sub>    | Temperature of carbon dioxide                                               | TCO2           |
| T <sub>CH<sub>4</sub></sub>    | Temperature of methane                                                      | TCH4           |
| T <sub>f</sub>                 | Temperature of flame                                                        | TFL            |
| ΔT                             | Current increment in flame temperature                                      | TDELTA         |
| n                              | Iteration counter                                                           | N              |
| H <sub>err1</sub>              | (H <sub>products</sub> - H <sub>reactants</sub> ) for the last iteration    | ODIF           |
| H <sub>err2</sub>              | (H <sub>products</sub> - H <sub>reactants</sub> ) for the current iteration | NDIF           |

## Convergence by Half-Interval Method

The half-interval method is a technique for determining the root of an equation. In the present case, the sensible heat of the reaction products, expressed in terms of the adiabatic flame temperature, are set equal to the sensible heat of the reactants plus the energy released by reaction. The appropriate value of the flame temperature is the root of the energy balance equation. To determine this value, a flame temperature is assumed and the sensible heat of the products calculated. If this energy is less than the sensible heat of the reactants plus the energy of reaction, the flame temperature is incremented by a given amount and the process repeated. This technique is illustrated with a specific example in Fig. B-2.

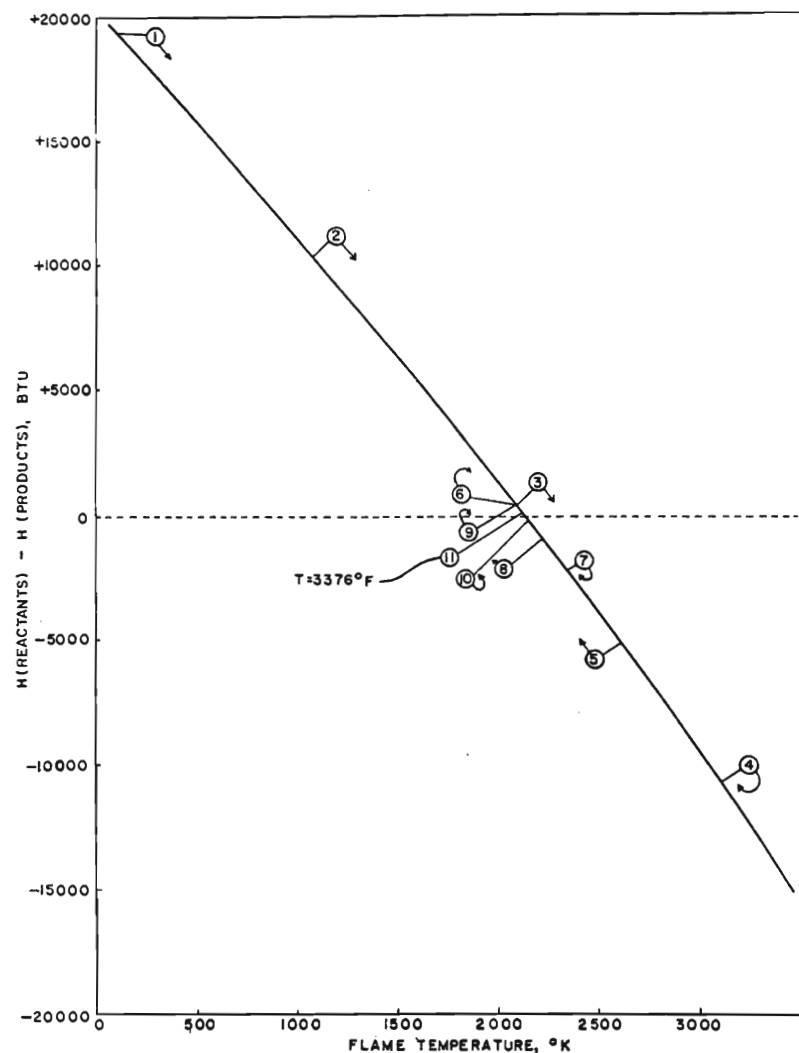
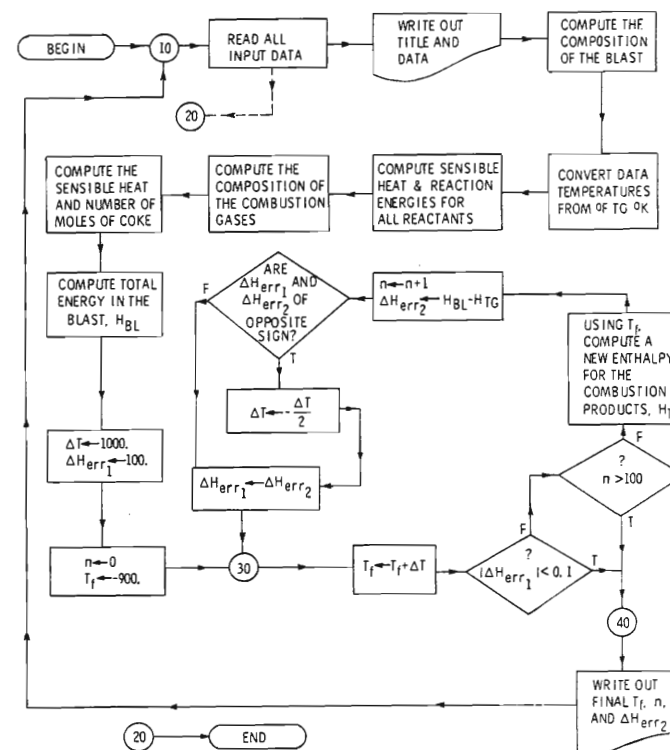


Fig. B-2. Flame temperature calculation by half-interval method.

The first point shown in Fig. B-2 is located at a temperature of 100°K, the first assumed value for the flame temperature. This value is obviously too low, and the difference between total energy for the reactants (the sensible heat and energy of reaction) and the products is quite large. The flame temperature then has been incremented by 1000°K to point 2. This assumed temperature also is too low, as is



Flow Chart—Problem 2A. Flow diagram for computation of flame temperature.

point 3. However, at point 4 the assumed flame temperature is too high, as evidenced by the fact that the sign of the difference between energy of reactants and products has changed from positive to negative. The increment to be added to the flame temperature has been decreased by a factor of one half and the sign changed. The next assumed flame temperature is at point 5. This assumed flame temperature is still too high, and an additional increment, in this case negative, has been added to the flame temperature, returning the assumed value to point 3 (also point 6). This value was too low, and the increment to the flame temperature is decreased by a factor of one half again and the sign changed, yielding point 7. This process continues until convergence is achieved at a flame temperature where the total enthalpy of the reactants is within an acceptable limit of difference from that of the products at point 11.

This routine procedure could be shortened somewhat by a person making a hand calculation. However, by cutting the interval in half each time the convergence point is passed, the maximum number of trials is well defined, and convergence is achieved rapidly. If the calculation were made by hand, the direction of imbalance in the total enthalpies for reactants and products readily would be observable.

## FORTRAN Listing—Problem 2A

```

10  REAL NTGCO,NTGH2,NTGN2,NBC,NDIF
    READ (5,500,END=20) WIGH20,WIQ2,WICO,WICO2,WCH4,TA,TQ2,TCO,TCO2,TC
    1H4,TC
    WRITE (6,600) TA,WCH4,TC,WICO,TCH4,WICO2,TCO,WIGH20,TCO2,WIQ2,TQ2
    RH20=379.*WIGH20/(7000.*18.)
    RQ2=WIQ2/100./(1.-RH20/(1.+RH20))
    RCO=WICO/100./(1.-RH20/(1.+RH20))
    RCO2=WICO2/100./(1.-RH20/(1.+RH20))
    RCH4=WCH4/100./(1.-RH20/(1.+RH20))
    AR=1./(1.+RH20*RQ2+RCO+RCO2+RCH4)
    XWIO2=.21*AR
    XWIN2=.79*AR
    XWIH20=RH20*AR
    XWIQ2=RQ2*AR
    XWICO=RCO*AR
    XWICO2=RCO2*AR
    XWICH4=RCH4*AR
    TA=(TA+460.)/1.8
    TQ2=(TQ2+460.)/1.8
    TCO=(TCO+460.)/1.8
    TCO2=(TCO2+460.)/1.8
    TCH4=(TCH4+460.)/1.8
    HWO2=7.16*TA+.5E-3*TA*TA+.4E5/TA-2313.
    HWN2=6.83*TA+.45E-3*TA*TA+.12E5/TA-2117.
    HWH20=7.3*TA+1.23E-3*TA*TA-2286.-57800.
    HWQ2=7.16*TQ2+.5E-3*TQ2*TQ2+.4E5/TQ2-2313.
    HWC0=6.79*TCO+.49E-3*TCO*TCO+.11E5/TCO-2105.-26620.
    HWC02=10.57*TCO2+1.05E-3*TCO2*TCO2+2.06E5/TCO2-3936.-94030.
    HWCH4=5.65*TCH4+.57E-3*TCH4*TCH4+.46E5/TCH4-2347.-17889.
    NTGCO=2.*XWIO2+XWIH20+2.*XWICO2+XWICO+2.*XWICO2+XWICH4
    NTGH2=XWIH20+2.*XWICH4
    NTGN2=XWIN2
    NBC=NTGCO-XWICO-XWICO2-XWICH4
    TC=(TC+460.)/1.8
    HC=4.03*TC+.57E-3*TC*TC+2.04E5/TC-1936.
    HBL=HWO2+XWIO2+HWN2+XWIN2+HWH20+XWIH20+HWQ2+XWIQ2+HWC0+XWICO+HWC02
    1 *XWICO2+HWCH4+XWICH4+NBC+HC
    TDELTA=1000.
    ODIF=100.
    N=0
    TFL=-900.
30  TFL=TFL+TDELTA
    IF (ABS(ODIF).LT..1.OR.N.GT.100) GO TO 40
    N=N+1
    HTGCO=6.79*TFL+.49E-3*TFL*TFL+.11E5/TFL-2105.-26620.
    HTGH2=6.52*TFL+.39E-3*TFL*TFL-.12E5/TFL-1938.
    HTGN2=6.83*TFL+.45E-3*TFL*TFL+.12E5/TFL-2117.
    HTG=NTGCO+HTGCO+NTGH2+HTGH2+NTGN2+HTGN2
    NDIF=HBL-HTG
    IF (ODIF*NDIF.LT.0.) TDELTA=-TDELTA/2.
    ODIF=NDIF
    GO TO 30
40  TFL=TFL-TDELTA
    TA=TA+1.8-460.
    TQ=TQ+1.8-460.
    TCO=TCO+1.8-460.
    TCO2=TCO2+1.8-460.
    TCH4=TCH4+1.8-460.
    WRITE (6,610) TFL,NDIF,N
    WRITE (6,611) HBL,HWH20,ODIF,HC,HWN2,TC,HTG,HWO2,XWICH4,HTGCO,HWQ2
    1,XWICO,HTGH2,NBC,XWICO2,HTGN2,NDIF,XWIH20,HWCH4,NTGCO,XWIN2,HWC0,
    2,NTGH2,XWIO2,HWC02,NTGN2,XWIQ2
    GO TO 10
20  CALL SYSTEM
500  FORMAT (5F6.2,6F5.0)
600  FORMAT (30H1FLAME TEMPERATURE CALCULATION/5H0DATA/1H0,1X,3HTA=F6.0
    1,11X,5HWCH4=F6.2/2X,3HTC=F6.0,11X,5HWICO=F6.2/2X,5HTCH4=F6.0,9X,6H
    2,WICO2=F6.2/2X,4HTCO=F6.0,10X,7HWICH20=F6.2/2X,5HTCO2=F6.0,9X,5HWI
    32=F6.2/2X,4HTQ2=F6.0)

```

```

610  FORMAT (8H-RESULTS/32H0FLAME TEMPERATURE, DEGREES F. =F6.0/ 58H0
    1ENTHALPY DIFFERENCE BETWEEN REACTANTS AND PRODUCTS, CAL =F8.0/41H0
    2ITERATIONS REQUIRED TO ATTAIN SOLUTION =13)
611  FORMAT (1H-,1X,4HHBL=F8.0,8X,6HWH20=F8.0,6X,5HODIF=F6.0/2X,3HHC=F
    18.0,9X,5HHWN2=F8.0,7X,3HTC=F6.0/2X,4HHTG=F8.0,8X,5HHWO2=F8.0,7X,7H
    2XWICH4=F5.2/2X,6HHTGCO=F8.0,6X,5HHWO2=F9.0,6X,6HXWICO=F5.2/2X,6HHT
    3GH2=F8.0,6X,4HNBC=F6.1,10X,7HXWICO2=F5.2/2X,6HHTGN2=F8.0,6X,5HNDIF
    4=F6.1,9X,7HXWIH20=F5.2/2X,6HHWCH4=F8.0,6X,6HNTGCO=F6.1,8X,6HXWIN2=
    5F5.2/2X,5HHWCO=F8.0,7X,6HNTGH2=F6.1,8X,6HXWIO2=F5.2/2X,6HHWCO2=F8.
    60,6X,6HNTGN2=F6.1,8X,6HXWIQ2=F5.0)
    END

```

Input (Data)—Problem 2A

```

300 00 00 00 00 1000 1000 77 77 77 2800
Output (Results)—Problem 2A
FLAME TEMPERATURE CALCULATION
DATA

```

```

TA= 1000.      WCH4= 0.0
TC= 2800.      WICO= 0.0
TCH4= 77.      WICO2= 0.0
TCO= 77.       WICH20= 3.00
TCO2= 77.      WIO2= 0.0
TQ2= 1000.

```

## RESULTS

FLAME TEMPERATURE, DEGREES F. = 3380.

ENTHALPY DIFFERENCE BETWEEN REACTANTS AND PRODUCTS, CAL = 0.

ITERATIONS REQUIRED TO ATTAIN SOLUTION = 28

```

HBL= 6375.      HWH20= -53356.      ODIF= 0.
HC= 7345.       HWN2= 3734.         TC= 1811.
HTG= 6375.      HWO2= 3873.         XWICH4= 0.0
HTGCO= -12006.  HWQ2= 6833.         XWICO= 0.0
HTGH2= 13739.   NBC= 0.4           XWICO2= 0.0
HTGN2= 14506.   NDIF= 0.0          XWIH20= 0.01
HWCH4= -17887.  NTGCO= 0.4         XWIN2= 0.78
HWC0= -26619.   NTGH2= 0.0         XWIO2= 0.21
HWC02= -94029.  NTGN2= 0.8         XWIQ2= 0.

```

However, in machine computation, and particularly for use of the technique in other applications, a direct and simple way to indicate that the convergence point has been overshoot is to multiply the difference between the calculated quantities, in this case the enthalpies of the reactants and products, by the difference on the previous iteration. If the convergence point has been passed, the sign of this product will be negative (a negative quantity times a positive quantity) and the direction of search is reversed and the increment is decreased to one half of its former magnitude. If, however, the product is positive (the product of two positive or of two negative quantities), the procedure is continued in the same direction and the magnitude of the increment is maintained at the same level.

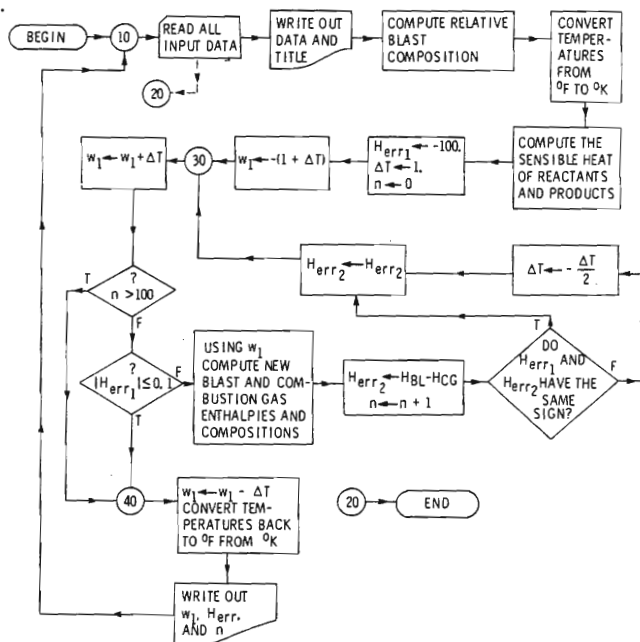
It is necessary, of course, to set some criterion for convergence or the iterative procedure would continue indefinitely. Two criteria can be adopted, and either should prove successful. One is to set an acceptable limiting maximum increment for the flame temperature, whereas the second (and the one used in this particular case) is to set the acceptable maximum increment on the difference between the enthalpy values for the reactants and products.

## ✓ Problem 2B—Calculation of Oxygen Enrichment Level

In precisely the same manner outlined above, a blast variable (such as per cent oxygen enrichment, per cent natural gas, moisture content, blast temperature, etc.) can be calculated to provide a given adiabatic flame temperature. The iterative technique employed involves incremental changes in the particular blast variable of interest, until the enthalpy balance for reactants and products converges. A flow chart showing how this calculation is carried out for enrichment of the blast with oxygen is presented below. Parallel programs can be developed for other blast variables. Results of calculations are discussed in later paragraphs.

## Symbol Table—Problem 2B

The symbols used in the program are the same as those for the flame temperature program. *QDEL*T is used to indicate the current increment in oxygen enrichment.



Flow Chart—Problem 2B. Flow diagram for computation of oxygen enrichment of blast.

## FORTRAN Listing—Problem 2B

```

REAL NTGCO,NTGH2,NTGN2,NBC,NDIF
10 READ (5,500,END=20) WIGH20,WICO,WICO2,WCH4,TA,TQ2,TCO,TCO2,TCH4,TC
1,TFL
WRITE (6,600) TA,TQ2,TC,WCH4,TCH4,WICO,TCO,WICO2,TCO2,WIGH20,TFL
RH20=379.*WIGH20/(7000.*18.)
RCO=WICO/100./(1.-RH20/(1.+RH20))
RCO2=WICO2/100./(1.-RH20/(1.+RH20))
RCH4=WCH4/100./(1.-RH20/(1.+RH20))

```

```

TA=(TA+460.)/1.8
TQ2=(TQ2+460.)/1.8
TCO=(TCO+460.)/1.8
TCO2=(TCO2+460.)/1.8
TCH4=(TCH4+460.)/1.8
TFL=(TFL+460.)/1.8
HWO2=7.16*TA+.5E-3*TA*TA+.4E5/TA-2313.
HWN2=6.83*TA+.45E-3*TA*TA+.12E5/TA-2117.
HWH2O=7.3*TA+1.23E-3*TA*TA-2286-57800.
HWO2=7.16*TQ2+.50E-3*TQ2*TQ2+.4E5/TQ2-2313.
HWC0=6.79*TCO+.49E-3*TCO*TCO+.11E5/TCO-2105.-26620.
HWC02=10.57*TCO2+1.05E-3*TCO2*TCO2+.20E5/TCO2-3936.-94030.
HWCH4=5.65*TCH4+5.72E-3*TCH4*TCH4+.46E5/TCH4-2347.-17889.
TC=(TC+460.)/1.8
HC=4.03*TC+.57E-3*TC*TC+2.04E5/TC-1936.
HTGCO=6.79*TFL+.49E-3*TFL*TFL+.11E5/TFL-2105.-26620.
HTGH2=6.52*TFL+.39E-3*TFL*TFL+.12E5/TFL-1938.
HTGN2=6.83*TFL+.45E-3*TFL*TFL+.12E5/TFL-2117.
ODIF=-100.
QDEL T=1.
N=0
WIO2=-1.-QDEL T
WIO2=WIO2+QDEL T
IF (ABS(ODIF).LT..1.OR.N.GT.100) GO TO 40
N=N+1
RQ2=WIO2/100./(1.-RH20/(1.+RH20))
AR=1./(1.+RH20*RQ2+RCO+RCO2+RCH4)
XWIO2=.21*AR
XWIN2=.79*AR
XWIH2O=RH20*AR
XWIO2=RQ2*AR
XWICO=RCO*AR
XWICO2=RCO2*AR
XWICH4=RCH4*AR
NTGCO=2.*XWIO2+XWIH2O+2.*XWIO2+XWICO+2.*XWICO2+XWICH4
NTGH2=XWIH2O+2.*XWICH4
NTGN2=XWIN2
NBC=NTGCO-XWICO-XWICO2-XWICH4
HBL=HWO2*XWIO2+HWN2*XWIN2+HWH2O*XWIH2O+HWO2*XWIO2+HWC0*XWICO+HWC02
1 *XWICO2+HWCH4*XWICH4+NBC*HC
HTG=NTGCO*HTGCO+NTGH2*HTGH2+NTGN2*HTGN2
NDIF=HBL-HTG
IF (ODIF*NDIF.LT.0.) QDEL T=-QDEL T/2.
ODIF=NDIF
GO TO 30
40 WIO2=WIO2-QDEL T
TA=TA+1.8-460.
TQ=TQ+1.8-460.
TCO=TCO+1.8-460.
TCO2=TCO2+1.8-460.
TCH4=TCH4+1.8-460.
TFL=TFL+1.8-460.
WRITE (6,610) WIO2,NDIF,N
WRITE (6,611) HBL,HWH2O,ODIF,HC,HWN2,TC,HTG,HWO2,XWICH4,HTGCO,HWO2
1,XWICO,HTGH2,NBC,XWICO2,HTGN2,NDIF,XWIH2O,HWCH4,NTGCO,XWIN2,HWC0,N
2TGH2,XWIO2,HWC02,NTGN2,XWIO2
GO TO 10
20 CALL SYSTEM
500 FORMAT (4F5.2,7F6.0)

```

```

600  FORMAT (30H1OXYGEN ENRICHMENT CALCULATION/5H0DATA/1H0,1X,3HTA=F6.0
1,11X,4HTQ2=F6.0/2X,3HTC=F6.0,11X,5HWCH4=F6.2/2X,5HTCH4=F6.0,9X,5HW
2ICO=F6.2/2X,4HTCO=F6.0,10X,6HWICO2=F6.2/2X,5HTCO2=F6.0,9X,7HWICH2O
3=F6.2/2X,4HTFL=F6.0)
610  FORMAT (8H-RESULTS/26H0OXYGEN ENRICHMENT LEVEL =F5.2/58H0ENTHALPY
10DIFFERENCE BETWEEN REACTANTS AND PRODUCTS, CAL =F4.0/41H0ITERATION
2S REQUIRED TO ATTAIN SOLUTION =I3)
611  FORMAT (1H-,1X,4HHBL=F8.0,8X,6HHWH2O=F8.0,6X,5HODIF=F6.0/2X,3HHC=F
18.0,9X,5HHWN2=F8.0,7X,3HTC=F6.0/2X,4HHTG=F8.0,8X,5HHWQ2=F8.0,7X,7H
2XWICH4=F5.2/2X,6HHTGCO=F8.0,6X,5HHWQ2=F9.0,6X,6HXWICO=F5.2/2X,6HHT
3GH2=F8.0,6X,4HNBC=F6.1,10X,7HXWICO2=F5.2/2X,6HHTGN2=F8.0,6X,5HNDIF
4=F6.1,9X,7HXWIH2O=F5.2/2X,6HHWCH4=F8.0,6X,6HNTGCO=F6.1,8X,6HXWIN2=
5F5.2/2X,5HHWCO=F8.0,7X,6HNTGH2=F6.1,8X,6HXWIO2=F5.2/2X,6HHWCO2=F8.
60,6X,6HNTGN2=F6.1,8X,6HXWIQ2=F5.0)
END

```

## Input (Data)—Problem 2B

```

300  00  00  800 1000 1000  77  77  77 2800 3380

```

## Output (Results)—Problem 2B

## OXYGEN ENRICHMENT CALCULATION

## DATA

|            |              |
|------------|--------------|
| TA= 1000.  | TQ2= 1000.   |
| TC= 2800.  | WCH4= 8.00   |
| TCH4= 77.  | WICO= 0.0    |
| TCO= 77.   | WICO2= 0.0   |
| TCO2= 77.  | WICH2O= 3.00 |
| TFL= 3380. |              |

## RESULTS

OXYGEN ENRICHMENT LEVEL = 6.27

ENTHALPY DIFFERENCE BETWEEN REACTANTS AND PRODUCTS, CAL = -0.

ITERATIONS REQUIRED TO ATTAIN SOLUTION = 26

|                |                |              |
|----------------|----------------|--------------|
| HL= 5346.      | HHW2O= -53356. | ODIF= -0.    |
| HC= 7345.      | HHWN2= 3734.   | TC= 1811.    |
| HTG= 5346.     | HWQ2= 3873.    | XWICH4= 0.07 |
| HTGCO= -12004. | HWQ2= 3873.    | XWICO= 0.0   |
| HTGH2= 13741.  | NBC= 0.5       | XWICO2= 0.0  |
| HTGN2= 14507.  | HDIF= -0.0     | XWIH2O= 0.01 |
| HWCH4= -17887. | NTGCO= 0.6     | XWIN2= 0.69  |
| HWCO= -26619.  | NTGH2= 0.1     | XWIO2= 0.18  |
| HWC02= -94029. | HTGN2= 0.7     | XWIQ2= 0.    |

## Discussion of Results—Problem 2

Calculation of the adiabatic flame temperature for air preheated to temperatures ranging up to 1200°F and containing 5.5 grains of moisture per cubic foot are

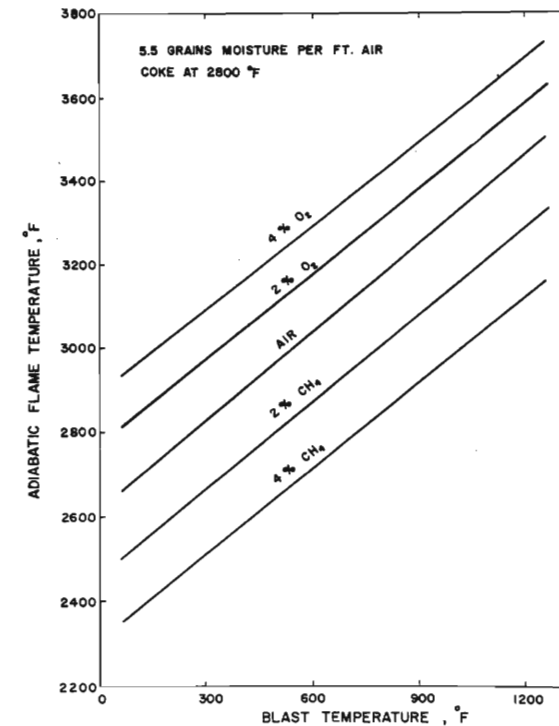


Fig. B-3. Calculated adiabatic flame temperature in tuyere zone for various levels of blast enrichment.

presented in Fig. B-3. These calculations have been extended to include various levels of enrichment of oxygen and natural gas. The injection of cold natural gas at the tuyeres decreases the temperature in the melting zone because of the decomposition of methane to carbon and hydrogen. The ensuing combustion in the presence of hot coke does not proceed beyond carbon monoxide and hydrogen, and the overall result is that less energy is developed in the melting zone with injection. Consequently, natural gas injection should be accompanied by oxygen enrichment or an increased blast temperature to maintain a given flame temperature in the melting zone. The enrichment with oxygen shows an increase in flame temperature since the oxygen reacts with hot coke to form carbon monoxide, releasing energy in the combustion zone.

The most useful part of this approach to developing guidelines for operating practice is that adjustments in blast variables can be made to maintain a constant flame temperature at the tuyeres and provide smooth furnace operation for a given charge and blowing practice. Several examples of simultaneous enrichment with

TABLE B-1\*

| Blast temp<br>(°F)                      | Moisture<br>(gr/ft <sup>3</sup> ) | %CH <sub>4</sub> | %O <sub>2</sub> | Flame temp<br>(°F) (calculated) |
|-----------------------------------------|-----------------------------------|------------------|-----------------|---------------------------------|
| Calculated Adiabatic Flame Temperatures |                                   |                  |                 |                                 |
| 1000                                    | 3                                 | 0                | 0               | 3380                            |
| 1000                                    | 5                                 | 0                | 0               | 3332                            |
| 1000                                    | 3                                 | 3                | 0               | 3222                            |
| 1800                                    | 3                                 | 0                | 0               | 3957                            |
| 1800                                    | 5                                 | 0                | 0               | 3910                            |
| 1800                                    | 3                                 | 3                | 0               | 3766                            |

| Flame temp<br>(°F)           | Moisture<br>(gr/ft <sup>3</sup> ) | %CH <sub>4</sub> | %O <sub>2</sub><br>(calculated) | Blast temp<br>(°F) |
|------------------------------|-----------------------------------|------------------|---------------------------------|--------------------|
| Calculated Oxygen Enrichment |                                   |                  |                                 |                    |
| 3380                         | 3.0                               | 8.0              | 6.27                            | 1000               |
| 3766                         | 3.0                               | 3.0              | 0.01                            | 1800               |
| 3957                         | 3.0                               | 3.0              | 3.09                            | 1800               |
| 3957                         | 5.0                               | 3.0              | 3.81                            | 1800               |
| 3957                         | 3.0                               | 8.0              | 8.24                            | 1800               |

\* Table based on 2800°F coke, 77°F CH<sub>4</sub>, with O<sub>2</sub> enrichment at blast temperature.

natural gas and oxygen injection are presented in Table B-1. The blast variables have been adjusted to provide the same flame temperature.

Several assumptions are involved in this approach, and place a limitation on the accuracy and potential usefulness of this technique. It should be recognized that the adiabatic flame temperature is an idealized concept, and that actual flame temperatures would be lower than those calculated on the basis of adiabatic conditions. This limitation should not prove to be particularly serious, however, since the actual combustion temperatures should be proportional or directly related to the theoretical flame temperatures. The application of this approach should be limited to blast volume rates within the same range, since heat transfer and temperature distribution undoubtedly are related to gas flowing through this zone of the furnace. Another assumption which goes to the very heart of the analysis is whether or not the reactions taking place in this particular zone are accurately represented by the calculated equilibria. There has been some indication that carbon dioxide may be formed at low blast temperatures, such as found in the cupola, but that this carbon dioxide is reduced to carbon monoxide within a very short distance from the tuyere. Consequently, the kinetics of combustion are a major factor in the validity of this equilibrium assumption, and conditions may vary markedly with the level of enrichment in the blast. Indications from operating practice are that the adiabatic flame temperature concept is quite useful in predicting a required blast condition to provide smooth furnace operation, particularly

when combined with operating experience on various sizes of furnaces, tuyere designs, blast conditions, and other related operating factors.<sup>1-3</sup>

<sup>1</sup> J. A. Cordier, Injection of different materials in the blast, *Blast Furnace, Coke Oven, and Raw Materials Proceedings, AIME* 19, 238 (1960).  
<sup>2</sup> H. N. Lander, H. W. Meyer, and F. D. Delve, Prediction of blast furnace performance from operating and thermal data, *Blast Furnace, Coke Oven, and Raw Materials Proceedings, AIME* 19, 219 (1960).  
<sup>3</sup> R. D. Pehlke, Computer prediction of cupola performance utilizing oxygen and natural gas in the blast, *AFS Trans.* 72, 806 (1964).

### Example Problem No. 3: Cooling of Pig Iron in a Transfer Ladle

#### Problem Statement

The pig iron produced in a blast furnace is transferred to steelmaking facilities in a ladle mounted on a railroad car. Several types of ladles are used, the most prominent one being the Pugh-type which is a cigar-shaped tilting ladle. The pig iron is tapped from the blast furnace into the ladle and then transferred to the steelmaking facilities which may be some distance from the blast furnace. It is of interest to know the time which one can allow the metal to remain in the ladle before solidification begins.

Write and test a FORTRAN program which will calculate the temperature drop of liquid pig iron held in a closed transport ladle of the Pugh-type (see Fig. B-4). Using the test data, extend the computations to either the initial solidification temperature or to an elapsed time of 24 hr.

*Suggested Approach.* Assume the following:

1. The temperature of the liquid metal is uniform and equal to the internal wall temperature of the refractory lining of the ladle car.
2. The heat losses may be computed by determining the rate of loss over short intervals of time and approximating the heat loss as the rate-time product.
3. The thermal resistance of the thin steel shell which surrounds the ladle may be neglected.

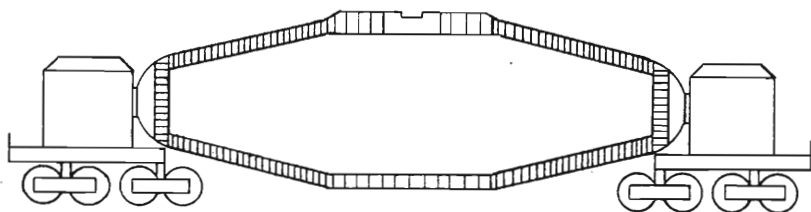


Fig. B-4. 150 Ton transfer ladle car.

#### Method of Solution—Problem 3

Heat is transferred to the surroundings by conduction through the refractory and then by radiation and convection to the ambient surroundings at temperature  $T_a$ . The conduction heat transfer during a unit time is

$$q_c = \frac{k \cdot A_{lm}}{l} (T_0 - T_s), \quad (a)$$

where the cylindrical wall is being considered; the log mean area for the heat con-

duction calculation is given by the relationship,

$$A_{lm} = \frac{A_0 - A_i}{\ln(A_0/A_i)}. \quad (b)$$

The radiation loss during a unit time period of one hour is

$$q_{rad} = 0.173 \times 10^{-8} (\epsilon) (T_s^4 - T_a^4) A_0. \quad (c)$$

The convection loss is

$$q_{conv} = h A_0 (T_s - T_a). \quad (d)$$

The convection coefficient  $h$  is a function of the temperature difference to the one-quarter power,  $(T_s - T_a)^{0.25}$ . Therefore, one may write

$$q_{conv} = h_c A_0 (T_s - T_a)^{1.25}. \quad (e)$$

The combined convection and radiation loss is

$$q_r = q_{rad} + q_{conv}. \quad (f)$$

The heat loss from the metal results in a decrease in its temperature. This decrease in energy is

$$\Delta H = 2000 w_m C_p F (T_0 - T_n). \quad (g)$$

By energy balance

$$q_c = q_r. \quad (h)$$

If either of these is multiplied by a short time interval,  $\Delta t$ , a quantity of heat is computed which determines the decrease in metal temperature during the interval. Thus,

$$\Delta t \cdot q_c = 2000 w \cdot C_p \cdot F (T_0 - T_n) = CPM (T_0 - T_n), \quad (i)$$

where  $CPM$  is the combination of factors given.

At the start of any time interval the metal temperature  $T_0$  and the ambient temperature  $T_a$  are known. The surface temperature  $T_s$  is not known, so an initial estimate is made. This allows  $q_c$  and  $q_r$  to be calculated. If  $T_s$  has been estimated correctly,  $q_c$  is equal to  $q_r$ , and the temperature of the metal at the end of the time interval can be calculated as

$$T_n = T_0 - \frac{\Delta t \cdot q_c}{CPM}. \quad (j)$$

If  $T_s$  has not been determined within a small limit of error, it is necessary to correct the assumed temperature. The magnitude of the change to be made in  $T_s$  depends upon how different  $q_c$  and  $q_r$  turn out to be for a given  $T_s$ . In this solution it was

Symbol Table—Problem 3

| Algebraic Symbol | Definition                                                    | FORTTRAN Symbol |
|------------------|---------------------------------------------------------------|-----------------|
| $T_m$            | Temperature of charged metal                                  | <i>TM</i>       |
| $T_a$            | Temperature of surroundings                                   | <i>TA</i>       |
| $T_{sol}$        | Temperature of initial solidification, °F                     | <i>TLOW</i>     |
| $T_0$            | Temperature of metal at time $t$ , °R                         | <i>TO</i>       |
| $T_s$            | Temperature of outside surface, °R                            | <i>TS</i>       |
| $T_{s1}$         | Most recent value of $T_s$ during iteration, °R               | <i>TI</i>       |
| $T_n$            | Metal temperature after latest iteration, °R                  | <i>TN</i>       |
| $T_z$            | $T_n$ in °F                                                   | <i>TX</i>       |
| $T_y$            | $T_{s1}$ in °F                                                | <i>TY</i>       |
| $\Delta T$       | Tolerable error in surface temperature, °R                    | <i>EPS</i>      |
| $r$              | Radiation from surroundings to the ladle                      | <i>R</i>        |
| $q_c$            | Conductive heat transfer, BTU/hr                              | <i>QC</i>       |
| $q_r$            | Radiative and convective heat transfer, BTU/hr                | <i>QR</i>       |
| $h$              | Convective heat transfer coefficient                          | —               |
| $h_c$            | Coefficient for $h$                                           | <i>HC</i>       |
| $\epsilon$       | Emissivity of steel shell                                     | <i>E</i>        |
| $C_p$            | Specific heat of metal, BTU/lb°F                              | <i>CP</i>       |
| <i>CPM</i>       | Gross heat capacity for ladle and metal, BTU/lb °F            | <i>CPM</i>      |
| $k$              | Thermal conductivity of refractory                            | <i>K</i>        |
| $w_m$            | Weight of metal charged                                       | <i>W</i>        |
| $F$              | Factor to account for specific heat of ladle                  | <i>F</i>        |
| $A_0$            | Area of external surface                                      | <i>AO</i>       |
| $A_i$            | Area of internal surface                                      | <i>AI</i>       |
| $A_{lm}$         | Log mean area for heat transfer through the refractory        | <i>AM</i>       |
| $l$              | Thickness of refractory                                       | <i>L</i>        |
| $t$              | Elapsed time from charging of ladle, hours                    | <i>P</i>        |
| $\Delta t$       | Time interval, hours                                          | <i>I</i>        |
| $j$              | Number of time intervals                                      | <i>J</i>        |
| $i_{max}$        | Maximum time of holding, hours                                | <i>IMAX</i>     |
| $n_{max}$        | Maximum number of iterations to determine surface temperature | <i>NMAX</i>     |
| $n$              | Number of iterations required for temperature convergence     | <i>N</i>        |

decided that if

$$|T_{s1} - T_s| \geq \Delta T, \quad (k)$$

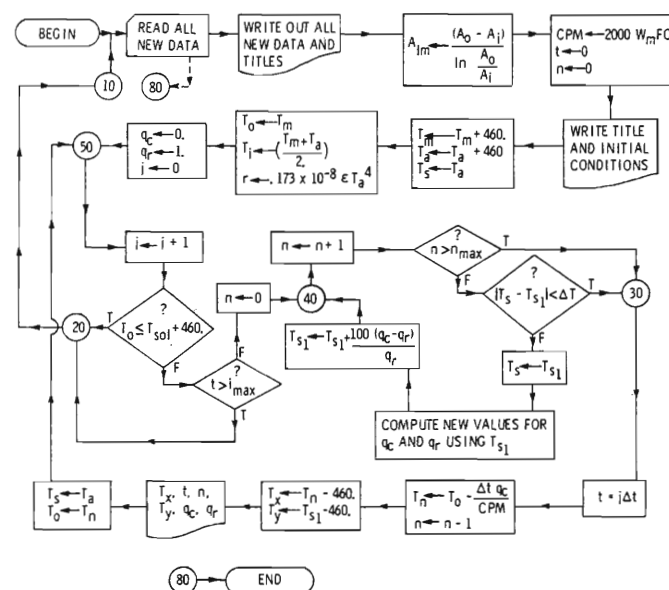
where  $\Delta T$  is 0.1°R, the surface temperature would be changed to

$$T_s = T_{s1} + (100) \cdot \left( \frac{q_c - q_r}{q_r} \right). \quad (l)$$

It is clear that a higher order approximation might be made in the heat transfer equations by putting in the average metal or average surface temperatures during the time interval. Thus, for conduction, one might write

$$q_c = \frac{k \cdot A_{lm}}{l} \left( \frac{T_0 + T_n}{2} - \frac{T_s + T_{s1}}{2} \right). \quad (m)$$

The anticipated change in temperature, however, does not merit this refinement, so it is assumed for the heat transfer calculations that  $T_0$  and  $T_s$  remain constant during each time step.



Flow Chart—Problem 3. Flow diagram for computation of cooling of pig iron.

## FORTRAN Listing—Problem 3

```

      REAL K,L,I,J,IMAX
10  READ (5,500,END=80) TM,TA,AL,AO,K,L,HC,E,W,CP,F,EPS,I,IMAX,NMAX,TL
      LOW
      WRITE (6,600) TM,TA,AL,AO,K,L,HC,E,W,CP
      WRITE (6,601) F,EPS,I,IMAX,NMAX,TLOW
      AM=(AO-AL)/ALOG(AO/AL)
      CPM=W*2000.*CP*F
      P=0.
      N=0
      WRITE (6,610) TM,P,N
      TM=TM+460.
      TA=TA+460.
      R=.173E-8*E*TA**4
      TS=TA
      TO=TM
      TI=(TM+TA)/2.
      QC=0.
      QR=1.
      J=0.
50  J=J+1.
      IF (TO.LE.(TLOW+460.)).OR.P.GE.IMAX) GO TO 20
      N=0
40  N=N+1
      IF (N.GT.NMAX.OR.ABS(TS-TI).LT.EPS) GO TO 30
      TS=TI
      QR=AO*(HC*(TI-TA)**1.25+.173E-8*E*TI**4-R)
      QC=K*AM*(TO-TI)/L
      TI=TI+100.*(QC-QR)/QR
      GO TO 40
30  P=I*J
      TN=TO-QC*I/CPM
      TX=TN-460.
      TY=TI-460.
      N=N-1
      WRITE (6,620) TX,P,N,TY,QC,QR
      TS=TA
      TO=TN
      GO TO 50
20  GO TO 10
80  CALL SYSTEM
500  FORMAT (4F5.0,4F5.2,F4.0,4F4.2,F4.0,I3,F5.0)
600  FORMAT (48HTEMPERATURE DROP OF LIQUID METAL IN A LADLE CAR//5H-DA
1TA//1H-.1X,27HINITIAL METAL TEMPERATURE =F6.0/2X,17HHAIR TEMPERATUR
2E =F4.0/2X,20HINSIDE AREA, SQ FT =F5.0/2X,21HOUTSIDE AREA, SQ FT =
3F5.0/2X,22HTHERMAL CONDUCTIVITY =F4.1/2X,26HREFRACTORY THICKNESS,
4FT =F4.1/2X,24HCONVECTION COEFFICIENT =F3.1/2X,18HSEMI EMISSIVITY
5 =F3.1/2X,20HMETAL WEIGHT, TONS =F5.0/2X,36HSPECIFIC HEAT OF THE M
6ETAL, BTU/LB =F3.1)
601  FORMAT (2X,13HHEAT FACTOR =F4.1/2X,23HTEMPERATURE DEVIATION =F4.2/
12X,20HTIME INCREMENT, HR =F3.1/2X,30HMAXIMUM NUMBER OF INCREMENTS
2=F4.0/2X,26HMAXIMUM NUMBER OF TRIALS =I4/2X,16HFREEZING POINT =F6.
30/40H-METAL TEMPERATURE AS A FUNCTION OF TIME)
610  FORMAT (6H-METAL,5X,4HTIME,4X,10HITERATIONS,4X,7HSURFACE,4X,10HCON
1DUCTION,4X,8HRAD-CONV/1X,6HTEMP F,5X,2HHR,19X,6HTEMP F,4X,11HLOSS
3BTU/HR,3X,11HLOSS BTU/HR/1H0,F6.1,4X,F4.1,8X,12)
620  FORMAT (1H9,F6.1,4X,F4.1,8X,12,8X,F5.1,7X,F8.0,5X,F8.0)
      END

```

## Input (Data)—Problem 3

2700 80 530 800 240 150 30 80 150 20 140 10 50 48100 2100

## Output (Results)—Problem 3

## TEMPERATURE DROP OF LIQUID METAL IN A LADLE CAR

## DATA

INITIAL METAL TEMPERATURE = 2700.  
 AIR TEMPERATURE = 80.  
 INSIDE AREA, SQ FT = 530.  
 OUTSIDE AREA, SQ FT = 300.  
 THERMAL CONDUCTIVITY = 2.4  
 REFRACTORY THICKNESS, FT = 1.5  
 CONVECTION COEFFICIENT = 0.3  
 SHELL EMISSIVITY = 0.8  
 METAL WEIGHT, TONS = 150.  
 SPECIFIC HEAT OF THE METAL, BTU/LB = 0.2  
 HEAT FACTOR = 1.4  
 TEMPERATURE DEVIATION = 0.10  
 TIME INCREMENT, HR = 0.5  
 MAXIMUM NUMBER OF INCREMENTS = 48.  
 MAXIMUM NUMBER OF TRIALS = 100  
 FREEZING POINT = 2100.

## METAL TEMPERATURE AS A FUNCTION OF TIME

| METAL<br>TEMP F | TIME<br>HR | ITERATIONS | SURFACE<br>TEMP F | CONDUCTION<br>LOSS BTU/HR | RAD-CONV<br>LOSS BTU/HR |
|-----------------|------------|------------|-------------------|---------------------------|-------------------------|
| 2700.0          | 0.0        | 0          |                   |                           |                         |
| 2687.1          | 0.5        | 24         | 637.8             | 2163620.                  | 2165121.                |
| 2674.3          | 1.0        | 5          | 636.2             | 2151737.                  | 2153777.                |
| 2661.6          | 1.5        | 5          | 634.6             | 2139988.                  | 2142052.                |
| 2648.9          | 2.0        | 5          | 633.0             | 2128315.                  | 2130358.                |
| 2636.3          | 2.5        | 5          | 631.4             | 2116711.                  | 2118731.                |
| 2623.8          | 3.0        | 5          | 629.8             | 2105176.                  | 2107169.                |
| 2611.3          | 3.5        | 5          | 628.2             | 2093709.                  | 2095679.                |
| 2598.9          | 4.0        | 5          | 626.6             | 2082310.                  | 2084257.                |
| 2586.6          | 4.5        | 5          | 625.0             | 2070978.                  | 2072902.                |
| 2574.3          | 5.0        | 5          | 623.4             | 2059713.                  | 2061616.                |
| 2562.1          | 5.5        | 5          | 621.8             | 2048515.                  | 2050392.                |
| 2550.0          | 6.0        | 5          | 620.2             | 2037383.                  | 2039239.                |
| 2537.9          | 6.5        | 5          | 618.7             | 2026316.                  | 2028153.                |
| 2526.0          | 7.0        | 5          | 617.1             | 2015316.                  | 2017127.                |
| 2514.0          | 7.5        | 5          | 615.5             | 2004379.                  | 2006170.                |
| 2502.2          | 8.0        | 5          | 613.9             | 1993508.                  | 1995274.                |
| 2490.4          | 8.5        | 5          | 612.4             | 1982700.                  | 1984447.                |
| 2478.6          | 9.0        | 5          | 610.8             | 1971956.                  | 1973679.                |
| 2466.9          | 9.5        | 5          | 609.3             | 1961276.                  | 1962982.                |
| 2455.3          | 10.0       | 5          | 607.7             | 1950658.                  | 1952341.                |
| 2443.8          | 10.5       | 5          | 606.2             | 1940103.                  | 1941763.                |
| 2432.3          | 11.0       | 5          | 604.6             | 1929610.                  | 1931252.                |
| 2420.9          | 11.5       | 5          | 603.1             | 1919179.                  | 1920799.                |
| 2409.5          | 12.0       | 5          | 601.5             | 1908809.                  | 1910410.                |
| 2398.2          | 12.5       | 5          | 600.0             | 1898500.                  | 1900081.                |
| 2387.0          | 13.0       | 5          | 598.5             | 1888252.                  | 1889814.                |
| 2375.3          | 13.5       | 5          | 596.9             | 1878064.                  | 1879607.                |
| 2364.7          | 14.0       | 5          | 595.4             | 1867936.                  | 1869460.                |
| 2353.6          | 14.5       | 5          | 593.9             | 1857868.                  | 1859373.                |
| 2342.6          | 15.0       | 5          | 592.4             | 1847858.                  | 1849346.                |
| 2331.7          | 15.5       | 5          | 590.8             | 1837908.                  | 1839375.                |
| 2320.8          | 16.0       | 5          | 589.3             | 1828016.                  | 1829464.                |
| 2310.0          | 16.5       | 5          | 587.8             | 1818182.                  | 1819612.                |
| 2299.2          | 17.0       | 5          | 586.3             | 1808406.                  | 1809816.                |
| 2288.5          | 17.5       | 5          | 584.8             | 1798686.                  | 1800080.                |
| 2277.8          | 18.0       | 5          | 583.3             | 1789024.                  | 1790399.                |
| 2267.3          | 18.5       | 5          | 581.8             | 1779418.                  | 1780776.                |

|        |      |   |       |          |          |
|--------|------|---|-------|----------|----------|
| 2256.7 | 19.0 | 5 | 580.3 | 1769860. | 1771208. |
| 2246.2 | 19.5 | 5 | 578.0 | 1760376. | 1761700. |
| 2235.8 | 20.0 | 5 | 577.6 | 1750938. | 1752246. |
| 2225.5 | 20.5 | 5 | 575.9 | 1741556. | 1742849. |
| 2215.1 | 21.0 | 5 | 574.4 | 1732228. | 1733501. |
| 2204.9 | 21.5 | 5 | 572.9 | 1722955. | 1724212. |
| 2194.7 | 22.0 | 5 | 571.5 | 1713736. | 1714976. |
| 2184.5 | 22.5 | 5 | 570.0 | 1704571. | 1705795. |
| 2174.4 | 23.0 | 5 | 568.5 | 1695460. | 1696668. |
| 2164.4 | 23.5 | 5 | 567.1 | 1686402. | 1687594. |
| 2154.4 | 24.0 | 5 | 565.6 | 1677300. | 1678573. |
| 2144.5 | 24.5 | 5 | 564.2 | 1668444. | 1669606. |
| 2134.6 | 25.0 | 5 | 562.7 | 1659543. | 1660691. |
| 2124.8 | 25.5 | 5 | 561.3 | 1650695. | 1651826. |
| 2115.0 | 26.0 | 5 | 559.8 | 1641898. | 1643015. |
| 2105.3 | 26.5 | 5 | 558.4 | 1633152. | 1634254. |
| 2095.6 | 27.0 | 5 | 557.0 | 1624458. | 1625544. |

## Discussion of Results—Problem 3

The computed result indicates that liquid pig iron can be held in a transfer ladle for periods of about 24 hours prior to the start of solidification. The exact time is dependent upon the initial hot metal temperature and the condition of the ladle lining.

### Example Problem No. 4: Predicting the Scrap Requirement for the Oxygen Steelmaking Process

#### Problem Statement

The computer analysis of oxygen steel converting has become operational at most steel companies. The computer programs consider many process variables which include hot metal analysis, temperature, oxygen flow rate, process geometries, and several others which influence the control of the converting process. Most commercial computer programs are highly empirical, and although of limited accuracy, have produced marked improvement in control of the operation.

In an effort to present the magnitude of some of the thermochemical interactions which play a role in design and operation of oxygen converters, a problem was selected for computer analysis which requires a mass and thermal balance for the oxygen steelmaking process. The relationship selected for investigation is the influence of silicon content of the hot metal on the required scrap addition. Computation of the mass balance involves an iterative calculation. The thermal balance requires lengthy calculations of the heat effect of each reaction, a task suitable for the digital computer.

Write and test a FORTRAN program which will permit a calculation of the scrap requirement for an oxygen steelmaking converter. Use the program to determine the influence of silicon content of the hot metal on scrap consumption for production of a 250 ton heat.

The following thermodynamic data may be used.

- Heats of reaction at 77°F  $\Delta H$  (Btu/lb-mole)
 

|                                                              |            |
|--------------------------------------------------------------|------------|
| $P_2(g) + 3 CaO + \frac{1}{2} C_2(g) \rightarrow Ca_3P_2O_8$ | -1,016,000 |
| $2 Fe + \frac{1}{2} O_2(g) \rightarrow Fe_2O_3$              | -354,000   |
| $Fe + \frac{1}{2} O_2 \rightarrow FeO$                       | -114,800   |
| $Si + O_2(g) \rightarrow SiO_2$                              | -369,700   |
| $Mn + \frac{1}{2} O_2(g) \rightarrow MnO$                    | -165,600   |
| $2 CaO + SiO_2 \rightarrow 2 CaO \cdot SiO_2$                | -53,640    |
| $FeO + SiO_2 \rightarrow FeSiO_3$                            | -8,100     |
| $MnO + SiO_2 \rightarrow MnSiO_3$                            | -10,600    |
| $C(gr) + \frac{1}{2} O_2(g) \rightarrow CO(g)$               | -47,600    |
| $C(gr) + O_2(g) \rightarrow CO_2(g)$                         | -169,000   |
- Heats of solution (Btu/lb-mole)  $T$  in °F
 

|                                             |                              |
|---------------------------------------------|------------------------------|
| $Si_{77°F} \rightarrow Si_T$                | $\Delta H = 6.7 T - 34,150$  |
| $Mn_{77°F} \rightarrow Mn_T$                | $\Delta H = 11.0 T + 2,900$  |
| $\frac{1}{2} P_2(g)_{77°F} \rightarrow P_T$ | $\Delta H = 4.45 T - 92,500$ |
| $C(gr)_{77°F} \rightarrow C_T$              | $\Delta H = 5.23 T + 10,020$ |
- Sensible heats (Btu/lb mole)—Reference temperature 77°F ( $T$  in °F)
 

|                          |                                                           |
|--------------------------|-----------------------------------------------------------|
| Iron-Base metal (liquid) | $\Delta H = 0.184 T + 63$ Btu/lb.                         |
| Slag (liquid)            | $\Delta H = 875 + (T - 2820) \times 0.3$ Btu/lb.          |
| CO                       | $\Delta H = 23,200 + (T - 3000) \times 8.5$ Btu/lb.-mole  |
| CO <sub>2</sub>          | $\Delta H = 37,400 + (T - 3000) \times 14.4$ Btu/lb.-mole |
| N <sub>2</sub>           | $\Delta H = 23,000 + (T - 3000) \times 8.6$ Btu/lb.-mole  |

## Method of Solution—Problem 4

The diagramming of a sequence to solve this problem involves a relatively complete presentation of the steelmaking process. The oxygen converting process for producing steel is presented in Chapter 4. The detailed examination of the process in terms of its mass and energy requirements is presented here, and one of the principal process variables is explored in detail.

The solution requires that a mass balance be completed which satisfies the production rate to which the heat losses are tied. Upon completion of the mass balance, excess thermal energy is calculated to determine the amount of scrap which is required to achieve the desired final process temperature. This scrap plus the refined steel produced by oxidizing the impurities from the blast furnace hot metal charged to the converter must satisfy the specified production tonnage.

The mass balance involves an iterative computation sequence because the burnt lime added depends upon both the silicon which is oxidized from the hot metal and the basicity ratio of the slag. Mill scale, added to supply additional oxygen to the process, is defined in terms of the lime added. The thread which runs through the several input and output streams of the converting process is the requirement that the charged iron, a constituent of all of the condensed phase streams (i.e., all except the oxygen lanced into the converter and the combustion gases exiting from the process) must be equal to the iron removed. The mass balance then is defined in terms of an iron balance.

Symbol Table—Problem 4

| FORTTRAN<br>Symbol | Definition and/or Purpose                                                                                           |
|--------------------|---------------------------------------------------------------------------------------------------------------------|
| <i>A</i>           | Percent available base in the charged lime                                                                          |
| <i>BLMTID</i>      | Holds the 14-character identification for the blown metal                                                           |
| <i>BLOTIM</i>      | Time of oxygen blow in minutes                                                                                      |
| <i>BTIME</i>       | <i>BTIME</i> (1) has the number of whole minutes for the oxygen blow;<br><i>BTIME</i> (2) has the number of seconds |
| <i>BR</i>          | Basicity ratio expressed as moles CaO/mole SiO <sub>2</sub>                                                         |
| <i>CORFAC</i>      | Correction factor applied to hot metal and scrap weight after each energy balance iteration                         |
| <i>CSCPF</i>       | Weight—% carbon in the scrap whose weight is fixed                                                                  |
| <i>DANAL</i>       | Holds the long version of the date and time of analysis                                                             |
| <i>DELT</i>        | Maximum allowable error for the ore balance and the slag FeO balance                                                |
| <i>EPS</i>         | Maximum allowable error for the blown metal production balance                                                      |
| <i>EXIT</i>        | Called when there is no more data; A subprogram which terminates execution of the calling program                   |
| <i>FDLOSS</i>      | Flue dust loss, as a percentage of the charged hot metal                                                            |
| <i>FESCPF</i>      | Weight—% iron in the scrap whose weight is fixed                                                                    |

Symbol Table—Problem 4—(Continued)

| FORTTRAN<br>Symbol | Definition and/or Purpose                                                                                                                                                                                                                                                  |
|--------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <i>FSCRAP</i>      | Basic material matrix for the two possible fixed scraps; 2 rows by 7 columns, where the first row is for the first fixed scrap and the second row is for the second fixed scrap (if used). The column definitions are the same as those for <i>HM</i>                      |
| <i>FSC17</i>       | Used to store the weight in pounds of the first fixed scrap                                                                                                                                                                                                                |
| <i>FSC27</i>       | Used to store the weight in pounds of the second fixed scrap                                                                                                                                                                                                               |
| <i>FV23RS</i>      | Ratio of iron valence 2 (FeO) to iron valence 3 (Fe <sub>2</sub> O <sub>3</sub> ) in the slag                                                                                                                                                                              |
| <i>HCG</i>         | Energy content of the combustion gases, BTU                                                                                                                                                                                                                                |
| <i>HHM</i>         | Energy content of the charged hot metal, BTU                                                                                                                                                                                                                               |
| <i>HL</i>          | Total of all energy losses per heat, BTU                                                                                                                                                                                                                                   |
| <i>HM</i>          | Basic material vector for the charged hot metal. <i>HM</i> (1) is wt-% Si, <i>HM</i> (2) is wt-% Mn, <i>HM</i> (3) is wt-% C, <i>HM</i> (4) is wt-% P, <i>HM</i> (5) is wt-% S, <i>HM</i> (6) is temperature in degrees Fahrenheit, and <i>HM</i> (7) is weight in pounds. |
| <i>HO2</i>         | Energy content of the total oxygen blown, BTU                                                                                                                                                                                                                              |
| <i>HS</i>          | Energy content of the final slag, BTU                                                                                                                                                                                                                                      |
| <i>HSCRAP</i>      | Energy available for melting scrap, BTU                                                                                                                                                                                                                                    |
| <i>HST</i>         | Energy content of the final blown metal minus the scrap, BTU                                                                                                                                                                                                               |
| <i>HTMLID</i>      | Holds the 14-character identification for the hot metal charged                                                                                                                                                                                                            |
| <i>I, J, K</i>     | Iteration variables, used as needed                                                                                                                                                                                                                                        |
| <i>IHL</i>         | Energy loss in BTU's per heat (same as <i>HL</i> ) used for output                                                                                                                                                                                                         |
| <i>MNSCPF</i>      | Weight-% manganese in the scrap whose weight is fixed                                                                                                                                                                                                                      |
| <i>NBMC</i>        | Number of moles of carbon in the blown metal                                                                                                                                                                                                                               |
| <i>NBMMN</i>       | Number of moles of manganese in the blown metal                                                                                                                                                                                                                            |
| <i>NBMP</i>        | Number of moles of phosphorus in the blown metal                                                                                                                                                                                                                           |
| <i>NBMSI</i>       | Number of moles of silicon in the blown metal                                                                                                                                                                                                                              |
| <i>NCCG</i>        | Number of moles of carbon in the combustion gases                                                                                                                                                                                                                          |
| <i>NCGC</i>        | Number of moles of carbon in the total charge                                                                                                                                                                                                                              |
| <i>NCGMN</i>       | Number of moles of manganese in the total charge                                                                                                                                                                                                                           |
| <i>NCGP</i>        | Number of moles of phosphorus in the total charge                                                                                                                                                                                                                          |
| <i>NCGSI</i>       | Number of moles of silicon in the total charge                                                                                                                                                                                                                             |
| <i>NFE2SI</i>      | Number of moles of 2FeO·SiO <sub>2</sub> in the slag, zero in basic slag                                                                                                                                                                                                   |
| <i>NMNSI</i>       | Number of moles of MnO·SiO <sub>2</sub> in the slag, zero in basic slag                                                                                                                                                                                                    |
| <i>NOXYO</i>       | Number of moles of O required for the charge                                                                                                                                                                                                                               |
| <i>NSCAO</i>       | Number of moles of lime in the slag                                                                                                                                                                                                                                        |
| <i>NSCRPS</i>      | Number of scraps to be used                                                                                                                                                                                                                                                |
| <i>NSFEO</i>       | Number of moles of FeO in the slag                                                                                                                                                                                                                                         |
| <i>NSFEOX</i>      | Number of moles of iron oxides (FeO and Fe <sub>2</sub> O <sub>3</sub> ) in the slag                                                                                                                                                                                       |
| <i>NSF2O3</i>      | Number of moles of Fe <sub>2</sub> O <sub>3</sub> in the slag                                                                                                                                                                                                              |
| <i>NSMNO</i>       | Number of moles of MnO in the slag                                                                                                                                                                                                                                         |
| <i>NSP2O5</i>      | Number of moles of P <sub>2</sub> O <sub>5</sub> in the slag                                                                                                                                                                                                               |

Symbol Table—Problem 4—(Continued)

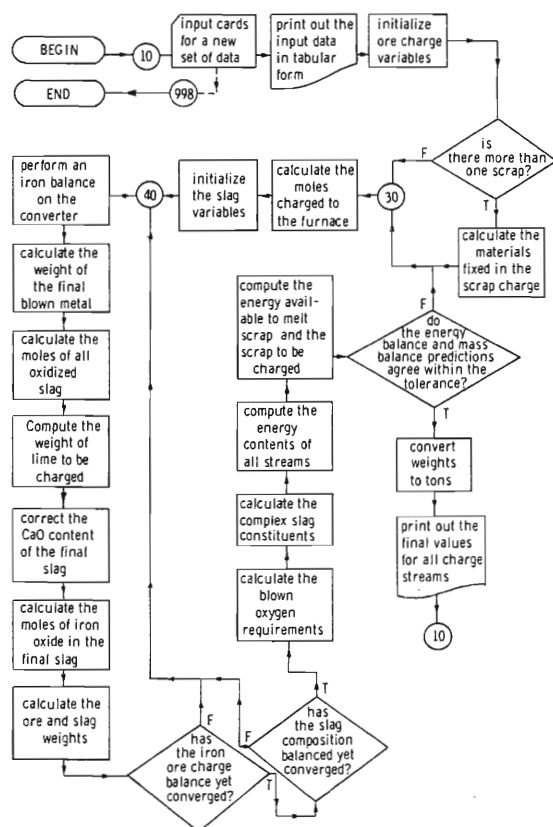
| FORTTRAN<br>Symbol | Definition and/or Purpose                                                                                                                                                   |
|--------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <i>NSSIOT</i>      | Number of moles of $\text{SiO}_2$ (total) in the slag                                                                                                                       |
| <i>NSSIO2</i>      | Number of moles of $\text{SiO}_2$ in the slag which came from oxidation of charged materials                                                                                |
| <i>N2CS</i>        | Number of moles of $2\text{CaO} \cdot \text{SiO}_2$ in the slag                                                                                                             |
| <i>ONE</i>         | The integer 1, used in output                                                                                                                                               |
| <i>ORE</i>         | Pounds of ore charged                                                                                                                                                       |
| <i>OREFRC</i>      | Weight ratio of ore charge to lime charge                                                                                                                                   |
| <i>OXYFLO</i>      | Oxygen flow rate in standard cubic feet per minute                                                                                                                          |
| <i>PCSIOR</i>      | Weight percent $\text{SiO}_2$ in the iron ore                                                                                                                               |
| <i>PORFEO</i>      | Weight percent $\text{FeO}$ in the iron ore                                                                                                                                 |
| <i>POXYO2</i>      | Purity of oxygen blown, in volume percent                                                                                                                                   |
| <i>PSC</i>         | Weight percent scrap in the total charge                                                                                                                                    |
| <i>PSCPF</i>       | Weight-% phosphorus in the scrap whose weight is fixed                                                                                                                      |
| <i>QNSFEO</i>      | Temporary location for comparison with <i>NSFEO</i> to check for slag composition convergence                                                                               |
| <i>RCO2</i>        | Ratio of $\text{CO}_2/\text{CO}$ in the combustion gases                                                                                                                    |
| <i>RSTM</i>        | Used for storage of the results of the call to the <i>TIME</i> subprogram                                                                                                   |
| <i>SCFOX</i>       | Standard cubic feet of oxygen (as $\text{O}_2$ ) required for the blow                                                                                                      |
| <i>SCRAP</i>       | Basic material vector for the variable (first) scrap charge; the column definitions are the same as those for <i>HM</i>                                                     |
| <i>SCRPID</i>      | Array for storage of the identifications of the three scraps; 3 rows by 2 columns; each row corresponds one of three possible scraps and the two columns hold the <i>ID</i> |
| <i>SISCPF</i>      | Weight-% silicon in the scrap whose weight is fixed                                                                                                                         |
| <i>SSCPF</i>       | Weight-% sulfur in the scrap whose weight is fixed                                                                                                                          |
| <i>STEEL</i>       | Basic material vector for the blown metal to be produced; the column definitions are the same as those for <i>HM</i> (see program symbol <i>HM</i> )                        |
| <i>TCG</i>         | Temperature of the combustion gases, degrees Fahrenheit                                                                                                                     |
| <i>THMCG</i>       | Tons of hot metal charged                                                                                                                                                   |
| <i>TIME</i>        | A subprogram called to obtain the current date and time of analysis                                                                                                         |
| <i>TLIME</i>       | Tons of lime charged                                                                                                                                                        |
| <i>TORE</i>        | Tons of ore charged                                                                                                                                                         |
| <i>TO2</i>         | Temperature at the nozzle of the incoming oxygen jet, degrees Fahrenheit                                                                                                    |
| <i>TS</i>          | Temperature of the slag, degrees Fahrenheit                                                                                                                                 |
| <i>TSC</i>         | Temperature of the total scrap charge                                                                                                                                       |
| <i>TSCP</i>        | Tons of scrap charged                                                                                                                                                       |
| <i>TSCPF</i>       | Temperature of the scrap whose weight is fixed, degrees Fahrenheit                                                                                                          |
| <i>TVSCP</i>       | Tons of the variable (first) scrap charged                                                                                                                                  |
| <i>WBM</i>         | Weight of blown metal, pounds                                                                                                                                               |
| <i>WFENET</i>      | Weight of iron in the charge which goes into the final blown metal                                                                                                          |

Symbol Table—Problem 4—(Continued)

| FORTTRAN<br>Symbol | Definition and/or Purpose                                                                              |
|--------------------|--------------------------------------------------------------------------------------------------------|
| <i>WFESCF</i>      | Weight percent iron in the scrap whose weight is fixed                                                 |
| <i>WFESCP</i>      | Pounds of iron in the total scrap charge                                                               |
| <i>WHMFE</i>       | Pounds of iron in the hot metal, corrected for flue dust loss                                          |
| <i>WTHM</i>        | Pounds of hot metal charged, identical to <i>HM</i> (7) (see program symbol <i>HM</i> )                |
| <i>WTLIME</i>      | Pounds of lime charged                                                                                 |
| <i>WTORE</i>       | Pounds of ore charged                                                                                  |
| <i>WTSCP</i>       | Pounds of total scrap charged                                                                          |
| <i>WTSCPF</i>      | Pounds of fixed scrap charged                                                                          |
| <i>WTSCP1</i>      | Pounds of the variable (first) scrap, identical to <i>SCRAP</i> (7) (see program symbol <i>SCRAP</i> ) |
| <i>WTSLAG</i>      | Pounds of slag                                                                                         |
| <i>XSFE0</i>       | Mole fraction of iron oxides in the slag, expressed as $\text{FeO}$                                    |

The method of calculation is as follows.

1. Read the input data and calculate the combined weights and components in any fixed scrap charged.
2. Calculate the moles of silicon, manganese, carbon, and phosphorous in the hot metal which is assumed to be charged, after correcting for flue-dust losses.
3. Initialize the weight of ore added, and the moles of iron in the slag stream at zero.
4. Determine the value for the net weight of iron from the hot metal and scrap by adding the weight of iron in the ore and subtracting the weight of iron in the slag.
5. Calculate the weight of blown metal produced from the hot metal charged on the basis of an iron balance.
6. Calculate the moles of silicon, manganese, carbon, and phosphorous which remain in the blown metal, subtracting them from the results of steps 1 and 2 to determine the moles which are oxidized.
7. Calculate the weight of burnt lime added to provide the correct basicity ratio in the slag, based on silica as the only acidic slag component ( $\text{P}_2\text{O}_5$  could be included).
8. Calculate the weight of ore added on the basis of the result of step 7, and calculate the weight of slag produced.
9. Compare the weight of ore calculated with that used in Step 4. If they agree within a limit of error continue on; otherwise, return to step 4, substituting the result of step 8. Repeat for  $\text{FeO}$  in slag.
10. Calculate the oxygen gas required and determine blowing time.
11. Calculate the composition of the slag in terms of the compounds which form, assuming a preferred order to the reactions.



Flow Chart—Problem 4. Flow diagram for computation of BOF charge.

## FORTRAN Listing—Problem 4

```

IMPLICIT REAL(N)
REAL*8 HTMLID(2),SCRPID(3,2),BLMTID(2)
REAL MNSCPF
INTEGER NSCRPS,ONE(1),BTIME(2)
LOGICAL*1 DANAL(20)
DIMENSION HM(7),SCRAP(7),FSCRAP(2,7),STEEL(7),RSTM(5)
EQUIVALENCE(DANAL(1),RSTM(1))

C
C READ THE DATA AND PRINT IT OUT IN TABULAR FORM
C
10 READ(5,500,END=998) HTMLID,HM,BLMTID,STEEL,NSCRPS,SCRPID(1,1),
1SCRPID(1,2),SCRAP,((SCRPID(K+1,1),I=1,2),(FSCRAP(K,J),J=1,7),K=1,2),
2),POXYO2,A,PORFEO,BR,RCO2,TO2,TS,TCG,HL,FDLOSS,DELT,EPS,OREFRC,
3XSFEQ,FV23RS,PCSIOR,OXYFLO
CALL TIME(6,0,RSTM)
IHL=HL
PRINT 501,RSTM(1),RSTM(2),DANAL(13),DANAL(14),RSTM(3),RSTM(5),
1HTMLID,HM,SCRPID(1,1),SCRPID(1,2),ONE,SCRAP
IF(NSCRPS-1)10,14,11

```

```

11 DO 13 I=2,NSCRPS
13 PRINT 502,SCRPID(1,1),SCRPID(1,2),I,(FSCRAP(I-1,J),J=1,7)
14 PRINT 503,BLMTID,STEEL,POXYO2,TO2,OXYFLO,FDLOSS,TCG,RCO2,IHL,BR,
1TS,XSFEQ,FV23RS,PORFEO,PCSIOR,OREFRC,A,DELT,EPS
C
C INITIALIZE THE FIXED SCRAP AND ITERATION VARIABLES
C
WTORE=0.
WTSCPF=0.
WFESCF=0.
WTSCP=SCRAP(7)+FSCRAP(1,7)+FSCRAP(2,7)
C
C IF THERE IS MORE THAN ONE SCRAP, CALCULATE THE MATERIALS FIXED IN THE CHARGE
C
16 IF(NSCRPS-1)10,24,16
FSC17=FSCRAP(1,7)
FSC27=FSCRAP(2,7)
WTSCPF=FSC17+FSC27
SISCPF=(FSCRAP(1,1)*FSC17+FSCRAP(2,1)*FSC27)/WTSCPF
MNSCPF=(FSCRAP(1,2)*FSC17+FSCRAP(2,2)*FSC27)/WTSCPF
CSCPF=(FSCRAP(1,3)*FSC17+FSCRAP(2,3)*FSC27)/WTSCPF
PSCPF=(FSCRAP(1,4)*FSC17+FSCRAP(2,4)*FSC27)/WTSCPF
SSCPF=(FSCRAP(1,5)*FSC17+FSCRAP(2,5)*FSC27)/WTSCPF
IF(NSCRPS.EQ.3)GOTO21
TSCPF=FSCRAP(1,6)
FESCPF=100.-(FSCRAP(1,1)+FSCRAP(1,2)+FSCRAP(1,3)+FSCRAP(1,4)+FSCR
1AP(1,5))
GO TO 23
21 TSCPF=(FSCRAP(1,6)*FSC17+FSCRAP(2,6)*FSC27)/WTSCPF
FESCPF=100.-(SISCPF+MNSCPF+CSCPF+PSCPF+SSCPF)
23 WFESCF=(WTSCPF+FESCPF)/100.
GO TO 25
24 TSCPF=SCRAP(6)
C
C STORE THE COMMONLY USED WEIGHTS IN SINGLE VARIABLE LOCATIONS FOR REFERENCE
C
25 WTHM=HM(7)
30 WTSCP1=SCRAP(7)
C
C CALCULATE MOLES OF PRIMARY CONSTITUENTS CHARGED TO THE FURNACE
C
NCGSI=(WTHM*HM(1)+WTSCP1*SCRAP(1)+SISCPF*WTSCPF)/2806.
NCGRN=(WTHM*HM(2)+WTSCP1*SCRAP(2)+MNSCPF*WTSCPF)/5494.
NCGC=(WTHM*HM(3)+WTSCP1*SCRAP(3)+CSCPF*WTSCPF)/1201.
NCGP=(WTHM*HM(4)+WTSCP1*SCRAP(4)+PSCPF*WTSCPF)/3098.
WFESCF=WFESCF+WTSCP1*(100.-(SCRAP(1)+SCRAP(2)+SCRAP(3)+SCRAP(4)+
1SCRAP(5)))/100.
WWMFE=(100.-FDLOSS)/100.*WTHM*(100.-(HM(1)+HM(2)+HM(3)+HM(4)+HM(5)
1))/100.
C
C INITIALIZE THE ORE CHARGE VARIABLES
C
NSF203=0.
NSFEO=0.
C
C BEGIN THE INNER ITERATIVE MASS BALANCE
C
40 ORE=WTORE
WFENET=WWMFE+WFESCF+WTORE*PORFEO*55.85/7185.+WTORE*(100.-PORFEO-P
1CSIOR)*111.7/15970.-NSFEO*55.85-NSF203*111.7
C
C CALCULATE THE WEIGHT OF BLOWN METAL FROM THE IRON CHARGED AND CALCULATE
C THE MOLES OF THE PRIMARY OTHER CONSTITUENTS IN THE FINAL BLOWN METAL
C
WBM=100.*WFENET/(100.-(STEEL(1)+STEEL(2)+STEEL(3)+STEEL(4)+STEEL(
15)))
NBMSI=WBM*STEEL(1)/2806.
NBMMN=WBM*STEEL(2)/5494.
NBMC=WBM*STEEL(3)/1201.
NBMP=WBM*STEEL(4)/3098.
C
C CALCULATE THE MOLES OF OXIDIZED CONSTITUENTS IN THE SLAG
C

```

```

NSSI02=NCGSI-NBMSI
NSMNO=NCGMN-NBMMN
NSP205=(NCGP-NBMP)/2.
NCCG=NCGC-NBMC

C
C COMPUTE THE WEIGHTS OF LIME AND ORE TO BE ADDED
C
NCAO=(NSSI02+PCSIOR*WTORE/6006.)*BR
WTIME=NCAO*5608./A

C
C COMPUTE THE CORRECTION OF THE SLAG CAO FOR AVAILABILITY OF LIME
C
NCAO=NCAO*(WTIME*(100.-A)/100.)*(BR/(BR+1.))/56.08

C
C COMPUTE THE MOLES OF FEO AND FE2O3 IN THE SLAG, THE REQUIRED
C CHARGE OF ORE, AND THE TOTAL WEIGHT OF THE FINAL SLAG
C
NSSIOT=NCAO/BR
NSFEOX=(NSSIOT+NSMNO+NSP205+NCAO)*XSFE0/(1.-XSFE0)
QNSFEO=NSFEO
NSFEO=NSFEOX*FV23RS/(FV23RS+1.)
NSF2O3=NSFEOX-NSFEO
WTORE=OREFRC*WTIME
WTSLAG=NSSIOT*60.06+NSMNO*70.94+NSP205*141.96+NSFEO*71.85+
1NSF2O3*159.7+NCAO*56.08

C
C IF THE ORE CHARGE ITERATIVE CALCULATION HAS CONVERGED, PROCEED; IF
C NOT, CONTINUE THE ITERATION BY GOING BACK TO THE IRON BALANCE
C
C IF THE ORE CHARGE ITERATIVE CALCULATION HAS CONVERGED, PROCEED; IF
C NOT, CONTINUE THE ITERATION BY GOING BACK TO THE IRON BALANCE
C
IF(ABS(ORE-WTORE).LT.DELT)GO TO 45
GO TO 40

C
C IF THE SLAG COMPOSITION ITERATIVE CALCULATION HAS CONVERGED, PROCEED;
C IF NOT, CONTINUE THE ITERATION BY GOING BACK TO THE IRON BALANCE
C
45 IF(ABS(QNSFEO-NSFEO).LT.DELT/71.85)GO TO 50
GO TO 40

C
C CALCULATION OF BLOWN OXYGEN REQUIREMENT
C
50 NOXYO=NSSI02*2.+NSMNO+NSP205*5.+NSFEO+NCCG*(1.+2.*RCO2)/(1.+RCO2)
1-WTORE*PORFEO/7185.-WTORE*(100.-PORFEO-PCSIOR)*3./15970.+3.*NSF2O3
2*WHMFE*FDLOSS/(100.-FDLOSS)/55.85
SCFOX=NOXYO/2.*37900./POXYO
BLOTIM=SCFOX/OXYFLO

C
C CALCULATION OF SLAG CONSTITUENTS
C
N2CS=NSSIOT
IF(NCAO.GT.2.*NSSIOT+3.*NSP205)GO TO 80
N2CS=(NCAO-3.*NSP205)/2.
NMNSI=NSSIOT-N2CS
IF(NMNSI.GT.NSMNO)GO TO 70
NFE2SI=0.
GO TO 90
70 NFE2SI=NSSIOT-N2CS-NSMNO
NMNSI=NSMNO
GO TO 90
80 NMNSI=0.
NFE2SI=0.

C
C BEGIN ENERGY BALANCE ON ENTIRE OXYGEN CONVERTER SYSTEM
C
90 HHM=(.184*HM(6)+63.)*WHMFE+(6.7*HM(6)-34150.)*NSSI02+(11.*HM(6)+29
100.)*NSMNO+(4.45*HM(6)-92500.)*NSP205*2.+(5.23*HM(6)+10020.)*NCCG
HS=(875.+(TS-2820.)*.3)*WTSLAG-1016000.*NSP205-114800.*(NSFEO+WHMFE
1E+FDLOSS/100./55.85-WTORE*PORFEO/7185.)*369700.*NSSI02-105600.*NSM
2NO-53640.*N2CS-10600.*NMNSI-8100.*NFE2SI-353160.*(NSF2O3-WTORE*(10
30.-PORFEO-PCSIOR)/15970.))
HCG=(23200.+(TCG-3000.)*8.5-47600.)*NCCG/(1.+RCO2)+(37400.+(TCG-30
100.)*14.4-169000.)*NCCG*RCO2/(1.+RCO2)

```

```

HST=(.184*STEEL(6)+63.)*(WBM-WTSCP)
HO2=7.+(NOXYO/2.)*(TO2-77.)
HSCRAP=HHM-HST-HS-HCG-HL+HO2
TSC=(SCRAP(7)*SCRAP(6)+WTSCPF*TSCPF)/(SCRAP(7)+WTSCPF)
WTSCP=HSCRAP/(.184*(STEEL(6)-TSC)+63.+14.2)
SCRAP(7)=WTSCP-WTSCPF

C
C IF THE RESULTS OF THE ITERATIVE ENERGY BALANCE AGREE WITH THE TARGET
C BLOWN METAL PRODUCTION, CALCULATE THE FINAL RESULTS; IF NOT, GO BACK
C TO THE INITIAL STAGES OF THE CHARGE CALCULATION
C
IF(ABS(WBM-STEEL(7)).LT.EPS)GOTO100
CORFAC=STEEL(7)/WBM
WTHM=WTHM*CORFAC
HM(7)=WTHM
SCRAP(7)=(SCRAP(7)+WTSCPF)*CORFAC-WTSCPF
GO TO 30

C
C CONVERT WEIGHTS TO TONS AND PRINT OUT THE RESULTS FOR THIS DATA SET
C
100 TVSCP=SCRAP(7)/2000.
TSCP=WTSCP/2000.
THMCG=HM(7)/2000.
TORE=WTORE/2000.
TLIME=WTIME/2000.
BTIME(1)=BLOTIM
BTIME(2)=INT(60.*(BLOTIM-BTIME(1)))
PSC=100.*WTSCP/(WTSCP+WTHM)
PRINT 504,PSC,TSCP,TVSCP,THMCG,TORE,TLIME,BTIME
GO TO 10

500 OFORMAT(2(A8,A6,7F8.0/),12/3(A8,A6,7F8.0/),10F7.0/9F7.0)
501 OFORMAT('1CHARGE CALCULATION FOR A BASIC OXYGEN STEELMAKING CONTROL
2 SYSTEM, /' /'-THIS ANALYSIS IS BEING RUN AT ',2A4,2X,2A1,1X,
3A3,2H, ,A4/'- BASIC PROCESS COMPOSITIONS, IN WEIGHT PERCENT
4 TEMPER- WEIGHT' / ' MATERIALS MATRIX:',37X,'ATURE, IN LBS' /
5 22X,2HSI,5X,2HMN,6X,1HC,6X,1HP,6X, 'S' DEG. F (==EST.)/' HOT
6METAL' / 2X,A8,A6,F10.3,4F7.3,F7.0,F9.0,2H *' / 'OSCRAP' / 2X,A8,A6,
72H (,11,1H),F6.3,4F7.3,F7.0,F9.0,2H *)
502 OFORMAT(2X,A8,A6,2H (,11,1H),F6.3,4F7.3,F7.0,F9.0)
503 OFORMAT('OBLOWN METAL' / 2X,A8,A6,F10.3,4F7.3,F7.0,F9.0 / '-% OXYGE
1N IN BLAST ='F6.2,' % OXYGEN TEMPERATURE ='F6.0,' DEG. F
2.' / ' FLUE DUST LOSS, AS',15X,'BLOWN O2 FLOW RATE ='F7.0,' SCF
3M' / ' PERCENT OF HOT METAL='F6.2,' % COMBUSTION GAS TEMP ='
4F7.0,' DEG. F. / 'CO2/CO, COMBUST GAS ='F6.3,6X,'ENERGY LOSS EST
5IMATE ='18,' BTU/HT' / ' SLAG MOLE FRACTION',15X,'SLAG BASICITY R
6ATIO ='F5.1 / 'OF IRON OXIDES',18X,'TEMPERATURE OF SLAG ='F6.
70,' DEG. F. / 'EXPRESSED AS FEO ='F5.2,7X,'SLAG FEO/FE2O3 RA
8TIO ='F5.2 / ' PERCENT FEO IN ORE ='F6.2,' % PERCENT SIO2 IN
9 ORE ='F5.2,' % / ' ORE-TO-LIME RATIO ='F6.2,6X,'PERCENT BA
1SE IN LIME ='F6.2,' % / 'MAX ERROR, CHARGE WT='F5.1,' LB MAX
2 ERROR, METAL OUT ='F6.0,' POUNDS' / '0')
504 OFORMAT('1-RESULTS FOLLOW:' / 'OPERCENT SCRAP CHARGED ='F6.2,5X
1.'TONS SCRAP CHARGED ='F7.2 / 'OTONS VARIABLE SCRAP (1) ='
2F6.2,5X,'TONS HOT METAL CHARGED ='F7.2 / 'OTONS IRON ORE CHARGED
3 ='F6.3,5X,'TONS OF LIME CHARGED ='F7.3 / '002 BLOW TIME (MIN
4:SEC) ='13,1H:,12 / '-')
998 CALL EXIT
END

```

## Input (Data)—Problem 4

|              |        |     |       |       |       |        |       |            |        |
|--------------|--------|-----|-------|-------|-------|--------|-------|------------|--------|
| BOTTLE       | 701632 | 0.8 | 0.72  | 4.5   | 0.229 | 0.1    | 2445. | 400000.BOF | DATA 1 |
| TARGET STEEL |        | 0.0 | 0.11  | 0.052 | 0.013 | 0.005  | 2920. | 500000.BOF | DATA 2 |
| YARD SCRAP   |        | 0.0 | 0.45  | 0.15  | 0.015 | 0.015  | 77.   | 130000.BOD | DATA 4 |
| 99.8         | 92.    | 0.  | 3.    | 0.111 | -200. | 2920.  | 3000. | 6000000    | 2.     |
| 5.0          | 500.   | 0.0 | 0.128 | 4.0   | 4.0   | 22000. |       |            |        |

## Output (Results)—Problem 4

## CHARGE CALCULATION FOR A BASIC OXYGEN STEELMAKING CONTROL SYSTEM,

THIS ANALYSIS IS BEING RUN AT

| BASIC PROCESS<br>MATERIALS MATRIX:       | COMPOSITIONS, IN WEIGHT PERCENT |       |       |       |       | TEMPER-<br>ATURE, IN LBS<br>DEG. F                   | WEIGHT<br>IN LBS<br>(**EST.) |
|------------------------------------------|---------------------------------|-------|-------|-------|-------|------------------------------------------------------|------------------------------|
|                                          | SI                              | MN    | C     | P     | S     |                                                      |                              |
| HOT METAL<br>BOTTLE 701632               | 0.800                           | 0.720 | 4.500 | 0.229 | 0.100 | 2445.                                                | 400000. *                    |
| SCRAP<br>YARD SCRAP                      | (1) 0.0                         | 0.450 | 0.150 | 0.015 | 0.015 | 77.                                                  | 130000. *                    |
| BLOWN METAL<br>TARGET STEEL              | 0.0                             | 0.110 | 0.052 | 0.013 | 0.005 | 2920.                                                | 500000.                      |
| % OXYGEN IN BLAST = 99.80 %              |                                 |       |       |       |       | OXYGEN TEMPERATURE = -200. DEG. F.                   |                              |
| FLUE DUST LOSS, AS                       |                                 |       |       |       |       | BLOWN O <sub>2</sub> FLOW RATE = 22000. SCFM         |                              |
| PERCENT OF HOT METAL = 2.00 %            |                                 |       |       |       |       | COMBUSTION GAS TEMP = 3000. DEG. F.                  |                              |
| CO <sub>2</sub> /CO, COMBUST GAS = 0.111 |                                 |       |       |       |       | ENERGY LOSS ESTIMATE = 6000000 BTU/HT                |                              |
| SLAG MOLE FRACTION                       |                                 |       |       |       |       | SLAG BASICITY RATIO = 3.0                            |                              |
| OF IRON OXIDES,                          |                                 |       |       |       |       | TEMPERATURE OF SLAG = 2920. DEG. F.                  |                              |
| EXPRESSED AS FEO = 0.13                  |                                 |       |       |       |       | SLAG FEO/FE <sub>2</sub> O <sub>3</sub> RATIO = 4.00 |                              |
| PERCENT FEO IN ORE = 0.0 %               |                                 |       |       |       |       | PERCENT SiO <sub>2</sub> IN ORE = 4.00 %             |                              |
| ORE-TO-LIME RATIO = 0.0                  |                                 |       |       |       |       | PERCENT BASE IN LIME = 92.00 %                       |                              |
| MAX ERROR, CHARGE WT = 5.0 LB            |                                 |       |       |       |       | MAX ERROR, METAL OUT = 500. POUNDS                   |                              |

## RESULTS FOLLOW:

|                                            |                                 |
|--------------------------------------------|---------------------------------|
| PERCENT SCRAP CHARGED = 31.45              | TONS SCRAP CHARGED = 84.20      |
| TONS VARIABLE SCRAP (1) = 84.20            | TONS HOT METAL CHARGED = 183.52 |
| TONS IRON ORE CHARGED = 0.0                | TONS OF LIME CHARGED = 9.568    |
| O <sub>2</sub> BLOW TIME (MIN:SEC) = 17:49 |                                 |

12. Compute the enthalpy of each of the streams, the hot metal charge, the slag, combustion gases, and blown metal produced. The inlet enthalpy of the hot metal (including the oxidizing reactions which occur) minus the enthalpy of the slag, combustion gases, blown metal (minus scrap) and heat lost from the vessel will yield the excess energy which is available to melt scrap.

13. Calculate the scrap which can be melted, and the metal produced which is the scrap plus the blown metal (minus the scrap).

14. Compare the metal produced with that specified for the heat. If they do not agree, correct the assumed hot metal and scrap charge proportionally and return to step 2.

## Discussion of Results—Problem 4

As the silicon content of the hot metal increases, the excess heat available for melting scrap increases resulting in a higher scrap percentage in the charge as shown in Figure B-5.

The structure of the computer program is such that other variables may be investigated, including the influences of changing the temperatures of the process. One commercial proposal for increasing the ability of the process to handle scrap involves scrap preheating, which decreases the energy required to accomplish melting. This program can be used to study the effect of preheating to various temperature levels. Other compositional variables also can be studied.

### Example Problem No. 5: Digital Computer Analysis of Heat Flow and Temperature Distribution Around a Copper Converter Tuyere

## Problem Statement

Write and test a FORTRAN program which will perform the relaxation calculations outlined by Krivsky and Schuhmann<sup>1</sup> for determining the heat flow and temperature distribution around a copper converter tuyere.

The cross section of a copper converter through a tuyere center line is shown schematically in Fig. B-6. A relaxation technique was employed to obtain a solution. This involves dividing a solid into volume elements represented by grid points, specifying boundary conditions, and assuming a steady-state temperature distribution which dictates that the heat flow into each grid point shall be zero. The heat flow is evaluated in a two-dimensional matrix with radial symmetry about the center line of the tuyere, through which the blast air is supplied. The equations for heat flow into each type of grid point, including the interior points, interior or exterior surface points, tuyere surface points, and the points at the tuyere source and tuyere mouth have been derived.<sup>1</sup> These heat flow equations are solved in terms of the steady state temperatures of each grid point, where the calculation of the steady state temperature at each grid point is a function of the temperatures of the surrounding grid points or boundary temperatures. It should be noted that in Fig. 5

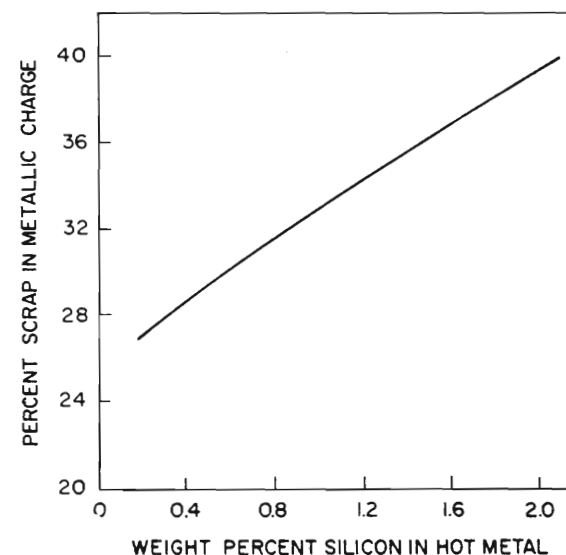


Fig. B-5. Effect of silicon content of hot metal on percent scrap in metallic charge to BOF.

<sup>1</sup> Krivsky, W. A., and R. Schuhmann, Jr., Heat flow and temperature distribution around a copper converter tuyere, *AIME Trans.* 215, 82 (1959).

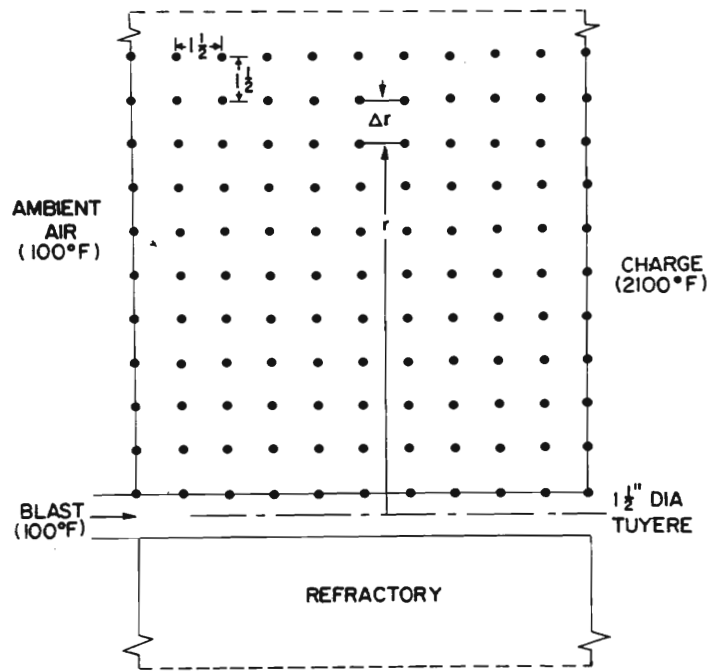


Fig. B-6. Idealized cross section of single  $1\frac{1}{2}$  in. tuyere in 15 in. wall, showing grid of points for temperature distribution calculation.<sup>1</sup>

of reference 1, the equation which appeared in print as

$$\frac{\Sigma Q}{\pi r k} = 2B_1 T_1 + \left(1 + \frac{\Delta r}{4r}\right) (T_2 + T_4 + 2T_3) - \left(2B_1 + 4 + \frac{\Delta r}{r}\right) T_0 = 0$$

should read

$$\frac{\Sigma Q}{\pi r k} = 2B_1 T_1 + \left(1 + \frac{\Delta r}{4r}\right) (T_2 + T_4) + 2 \left(1 + \frac{\Delta r}{2r}\right) T_3 - \left(2B_1 + 4 + \frac{3\Delta r}{2r}\right) T_0 = 0$$

and in Fig. 6 of reference 1, the equation which appeared as

$$Q_{4 \rightarrow 0} = h_4 \pi \left(r + \frac{\Delta r}{4}\right) (T_4 - T_0)$$

should read

$$Q_{4 \rightarrow 0} = h_4 \Delta r \pi \left(r + \frac{\Delta r}{4}\right) (T_4 - T_0)$$

#### Method of Solution—Problem 5

1. Initialize the temperature distribution using an estimate of the temperature at each grid point.
2. Make a point by point calculation of the steady state temperature by systematically moving through the grid, utilizing the surrounding temperatures and heat flow equations at each grid point.
3. After calculating the temperature at each grid point, make a comparison of the calculated temperature with the temperature which existed on the previous pass through the grid. When there are no temperature adjustments which are greater than a specified temperature increment  $\Delta T_{err}$  for any of the points in the grid from one pass to the next, the calculation is considered complete and the temperature distribution is printed out.

#### Symbol Table—Problem 5

| Algebraic Symbol | Definition                                                            | FORTRAN Symbol |
|------------------|-----------------------------------------------------------------------|----------------|
| $T_{i,j}$        | Temperature array (grid)                                              | $T$            |
| $d_{max}$        | Maximum number of grid points up from the tuyere/refractory interface | $DIST$         |
| $w_{max}$        | Maximum number of grid points across the tuyere                       | $THICK$        |
| $s$              | Grid spaces, per foot                                                 | $SCALE$        |
| $r_z$            | Tuyere radius                                                         | $RADIUS$       |
| $T_n$            | Current new temperature at a point                                    | $TN$           |
| $T_m$            | Melt temperature                                                      | $TMELT$        |
| $T_{bl}$         | Blast temperature                                                     | $TBLAST$       |
| $T_{air}$        | Air temperature                                                       | $TAIR$         |
| $n$              | Iteration counter                                                     | $N$            |
| $n_{max}$        | Maximum number of iterations                                          | $NMAX$         |
| —                | Heat transfer coefficient for outside surface                         | $HAIR$         |
| —                | Heat transfer coefficient for blast/tuyere interface                  | $HBLAST$       |
| —                | Heat transfer coefficient for melt/refractory interface               | $HMELT$        |
| $k$              | Thermal conductivity of refractory                                    | $KCOND$        |
| $\Delta T_{err}$ | Maximum error for each point at convergence                           | $ERR$          |
| $c$              | Check digit to test convergence                                       | $C$            |
| $r$              | Radial distance from tuyere centerline                                | $R$            |
| $a$              | Iteration counter for distance across the refractory                  | $A$            |



Symbol Table—Problem 5 —(Continued)

| Algebraic<br>Symbol | Definition                                          | FORTRAN<br>Symbol |
|---------------------|-----------------------------------------------------|-------------------|
| $u$                 | Iteration counter for distance $up$ from the tuyere | $U$               |
| $B_{air}$           | Biot number for outside surface                     | $BAIR$            |
| $B_{bl}$            | Biot number for blast                               | $BBLAST$          |
| $B_m$               | Biot number for melt                                | $BMELT$           |

FORTRAN Listing—Problem 5

```

      INTEGER A,U,THICK,DIST,C
      REAL KCOND
      DIMENSION T(50,50)
      READ (5,500,END=10) DIST,THICK,NMAX,SCALE,RADIUS,TMELT,TBLAST,TAIR
      1,HBLAST,HMELT,HAIR,KCOND,ERR
      WRITE (6,600)
      WRITE (6,610) DIST,THICK,NMAX,SCALE,RADIUS,TMELT,TBLAST,TAIR,HBLAS
      1T,HMELT,HAIR,KCOND,ERR
      DO 30 A=1,THICK
      DO 30 U=1,DIST
      30  T(A,U)=TAIR+(TMELT-TAIR)*(A-L.)/(THICK-1.)
      BBLAST=HBLAST/(KCOND*SCALE)
      BMELT=HMELT/(KCOND*SCALE)
      BAIR=HAIR/(KCOND*SCALE)
      N=0
      C=0
      40  DO 50 A=1,THICK
      DO 50 U=1,DIST
      R=RADIUS+(U-1.)/SCALE
      IF (U.EQ.1.AND.A.GT.1.AND.A.LT.THICK) GO TO 60
      IF (U.GT.1.AND.A.EQ.1) GO TO 61
      IF (U.GT.1.AND.A.EQ.THICK) GO TO 62
      IF (U.EQ.1.AND.A.EQ.THICK) GO TO 63
      IF (U.EQ.1.AND.A.EQ.1) GO TO 64
      IF (U.EQ.DIST.AND.A.GT.1.AND.A.LT.THICK) GO TO 65
      TN=(T(A-1,U)+T(A+1,U)+T(A,U+1)+T(A,U-1)+(T(A,U+1)-T(A,U-1))/(2.*R
      1*SCALE))/4.
      52  IF (ABS(TN-T(A,U)).GT.ERR) C=C+1
      GO TO 50
      60  TN=((2.*BBLAST*TBLAST)+(1.+(1./(4.*R*SCALE)))*(T(A-1,U)+T(A+1,U))
      2+2.*(1.+(1./(2.*R*SCALE))*T(A,U+1))/(2.*BBLAST+4.+(3./(2.*R*SCALE))
      3)
      GO TO 52
      61  TN=(T(1,U-1)+T(1,U+1)+(2.*T(2,U))+(2.*BAIR*
      1TAIR)+(T(1,U+1)-T(1,U-1))*((1./(2.*R*SCALE))))/(4.+2.*BAIR)
      GO TO 52
      62  TN=(T(A,U-1)+T(A,U+1)+(2.*T(A-1,U))+(2.
      1BMELT*TMELT)+(T(A,U+1)-T(A,U-1))*((1./(2.*R*SCALE))))/(4.+2.*BMELT)
      GO TO 52
      63  TN=((BBLAST*TBLAST)+(T(A-1,1)*(1.+(1./(4.
      14.*R*SCALE)))+(T(A,2)*(1.+(1./(2.*R*SCALE)))+(TMELT*BMELT*(1.+(1.
      2/(4.*R*SCALE)))/(2.+BBLAST+(1./(4.*R*SCALE))+1./(2.*R*SCALE)
      3+(BMELT*(1.+(1./(4.*R*SCALE))))))
      GO TO 52
      64  TN=((BBLAST*TBLAST)+(T(2,1)*(1.+(1./(4.*R*
      1SCALE)))+(T(1,2)*(1.+(1./(2.*R*SCALE)))+(TAIR*BAIR*(SCALE+(1./(4.
      3R))))/(2.+BBLAST+(1./(4.*R*SCALE)))+(1./(2.*R*SCALE)))+(BAIR*(SCAL
      4E+(1./(4.*R))))))
      GO TO 52

```

```

      65  TN=T(1,U)+(T(THICK,U)-T(1,U))*(A-1.)/(THICK-1.)
      GO TO 52
      50  T(A,U)=TN
      N=N+1
      IF (N.LT.NMAX.AND.C.NE.0) GO TO 40
      WRITE (6,620) N,C

```

Input (Data)—Problem 5

```

      11  11  100 8000 0625210000 10000 10000 20000 50000 600 200 50
      11  11  100 8000 0625210000 10000 10000 1000 50000 600 200 50

```

Output (Results)—Problem 5

## TEMPERATURE DISTRIBUTION AROUND A COPPER CONVERTER TUYERE

## DATA

```

      DISTANCE FROM TUYERE, SPACES = 11
      REFRACTORY THICKNESS, SPACES = 11
      MAXIMUM NUMBER OF ITERATIONS = 100
      SCALE, SPACES/FT = 8.0
      TUYERE RADIUS, FT =0.0625
      MELT TEMPERATURE, DEGREES F. = 2100.
      BLAST TEMPERATURE, DEGREES F. = 100.
      AIR TEMPERATURE, DEGREES F. = 100.
      HBLAST, BTU/HR/SQ FT/DEGREE F. = 200.
      HMELT, BTU/HR/SQ FT/DEGREE F. = 500.
      HAIR, BTU/HR/SQ FT/DEGREE F. = 6.
      THERMAL CONDUCTIVITY OF REFRACTORY,
      BTU-FT/HR/SQ FT/DEGREE F. = 2.
      ALLOWABLE ERROR, DEGREES F. =.50

```

## RESULTS

```

      N = 37
      C = 0

```

## TEMPERATURE DISTRIBUTION

```

      285.7  463.1  640.6  818.1  995.5  1173.0  1350.4  1527.9  1705.4  1882.8  2060.3
      373.5  507.1  662.7  827.7  997.9  1171.6  1347.9  1526.9  1708.8  1895.5  2093.1
      406.1  532.8  677.3  833.2  997.2  1167.2  1342.4  1522.6  1707.7  1898.0  2093.7
      417.7  543.2  681.8  831.3  990.1  1156.9  1331.2  1512.6  1700.9  1895.2  2093.6
      418.0  541.7  675.7  819.9  973.9  1137.6  1311.0  1494.2  1686.8  1887.6  2093.4
      409.8  529.6  658.1  796.5  945.3  1105.2  1277.4  1462.8  1661.8  1873.4  2093.0
      393.1  506.2  627.3  757.9  899.4  1053.7  1223.0  1410.4  1618.4  1847.5  2092.2
      366.3  469.0  579.1  698.3  828.7  973.0  1135.5  1322.1  1540.5  1797.9  2090.6
      325.0  412.1  505.5  607.0  719.1  845.3  991.4  1167.7  1391.6  1690.7  2087.2
      258.0  319.8  386.0  458.1  538.2  629.6  738.4  877.0  1074.8  1408.0  2074.5
      117.6  130.1  139.4  149.4  160.5  173.1  188.2  207.7  238.3  343.1  1659.7

```

## TEMPERATURE DISTRIBUTION AROUND A COPPER CONVERTER TUYERE

## DATA

DISTANCE FROM TUYERE, SPACES = 11  
 REFRACTORY THICKNESS, SPACES = 11  
 MAXIMUM NUMBER OF ITERATIONS = 100  
 SCALE, SPACES/FT = 8.0  
 TUYERE RADIUS, FT = 0.0625  
 MELT TEMPERATURE, DEGREES F. = 2100.  
 BLAST TEMPERATURE, DEGREES F. = 100.  
 AIR TEMPERATURE, DEGREES F. = 100.  
 HBLAST, BTU/HR/SQ FT/DEGREE F. = 10.  
 HMELT, BTU/HR/SQ FT/DEGREE F. = 500.  
 HAIR, BTU/HR/SQ FT/DEGREE F. = 6.  
 THERMAL CONDUCTIVITY OF REFRACTORY,  
 BTU-FT/HR/SQ FT/DEGREE F. = 2.  
 ALLOWABLE ERROR, DEGREES F. = .50

## RESULTS

N = 52  
 C = 0

## TEMPERATURE DISTRIBUTION

287.5 464.7 642.0 819.3 996.6 1173.9 1351.2 1528.4 1705.7 1883.0 2060.3  
 379.0 514.3 671.1 837.1 1007.7 1181.1 1356.7 1534.3 1714.2 1898.4 2093.2  
 416.3 546.6 693.9 852.0 1017.1 1187.0 1360.9 1538.3 1719.2 1904.2 2093.9  
 433.9 565.1 708.4 861.7 1022.6 1189.7 1362.1 1539.1 1720.5 1905.8 2094.0  
 441.5 573.6 714.8 864.8 1022.7 1187.5 1358.6 1535.6 1718.0 1904.6 2093.9  
 442.5 574.1 713.4 860.6 1015.7 1178.5 1348.7 1526.1 1710.4 1900.4 2093.8  
 437.5 567.0 703.5 847.7 999.7 1160.1 1329.3 1507.6 1695.4 1891.7 2093.5  
 425.6 551.1 683.6 823.4 971.3 1128.1 1295.2 1474.4 1667.4 1874.7 2093.0  
 403.2 522.7 649.4 782.8 923.8 1074.3 1236.6 1414.6 1613.5 1839.3 2091.9  
 356.3 472.0 591.2 713.7 842.2 979.7 1130.0 1299.4 1499.6 1752.8 2089.0  
 205.7 366.9 471.5 567.9 667.0 772.9 889.5 1023.6 1192.9 1455.7 2056.1

## Discussion of Results—Problem 5

The corner temperature at the tuyere mouth is particularly critical in copper converter operation. A low temperature at this point permits precipitation of magnetite from the slag, which blocks the tuyere and requires that the operation be stopped and the tuyere punched out. Tuyere punching is presently one of the limiting steps in copper production rates and adds to the expense and difficulty of the operation. The results of the calculation show that a more highly insulating refractory at the tuyere wall, which in effect decreases the rate of heat transfer to the incoming air, would increase the theoretical temperature at the tuyere mouth and prevent the precipitation of magnetite from the slag, thus eliminating the necessity of punching the tuyeres.

The accuracy of the result which is obtained depends upon the number of grid points selected. The solution of Krivsky and Schuhmann was carried out by hand

TABLE B-2

Computed Corner Temperatures for Various Grid Spacings  
 (Allowable temperature change at grid point, 0.5°F)

| Tuyere heat<br>transfer coefficient<br>(Btu/hr-ft <sup>2</sup> -°F) | Matrix size | Grid spacing<br>(in.) | Iterations | Corner<br>temperature<br>(°F) |
|---------------------------------------------------------------------|-------------|-----------------------|------------|-------------------------------|
| 10                                                                  | 4 × 4       | 5                     | 11         | 2076                          |
| 10                                                                  | 6 × 6       | 3                     | 21         | 2068                          |
| 10                                                                  | 11 × 11     | 1.5                   | 52         | 2056                          |
| 10                                                                  | 16 × 16     | 1                     | 78         | 2049                          |
| 200                                                                 | 4 × 4       | 5                     | 9          | 1830                          |
| 200                                                                 | 6 × 6       | 3                     | 17         | 1754                          |
| 200                                                                 | 11 × 11     | 1.5                   | 37         | 1660                          |
| 200                                                                 | 16 × 16     | 1                     | 52         | 1614                          |

calculation and involved first selecting a five inch grid spacing (4 × 4 matrix). Then, utilizing this calculated temperature distribution, they estimated a temperature distribution for the temperature calculation at the tuyere mouth based on a finer grid spacing in the lower right-hand corner of the grid shown in Figure B-6.

The calculated result is influenced markedly by the grid spacing, as shown by the results presented in Table B-2. The calculations carried out for presentation of the example problem were not extended to extremely fine grid sizes because of time and cost requirements on the computer. One of the major factors in the time requirement (in addition to the number of matrix points) is the accuracy of the initial temperature distribution. In the present problem a linear distribution was assumed between the melt and the outside or ambient air temperature. This assumption would be true for temperature independent thermal properties in the case of a perfectly insulated tuyere, but is far from precise in the case considered in the example problem.

**Example Problem No. 6: Heat Loss Through a Furnace Roof****Problem Statement**

Write and test a FORTRAN program for evaluating the heat loss through the roof of a reverberatory furnace.

Suggested conditions for the furnace operation are:

Furnace temperature—2800°F

Temperature of surroundings—70°F

Roof size—50 × 22, i.e. 1100 ft<sup>2</sup>

Refractory thickness—1 ft.

Convective heat transfer coefficient—.38  $\Delta T^{.25}$

Thermal conductivity of refractory—.27 -  $5 \times 10^{-4} t_{avg}$

Emissivity of refractory—0.85

Method of Solution—Problem 6

Under steady state operation, the temperature distribution through the refractory roof of a reverberatory furnace is constant. The mechanism of heat loss consists of conduction through the refractory roof and convection and radiation from the outer surface of the roof. Since the temperature distribution in a roof is constant, the heat flux is constant at all points and the rate of energy transmission through the roof by conduction must be equal to the heat loss from the outer surface of the roof by convection and radiation.

Thus,

$$q_{\text{conduction}} = q_{\text{convection}} + q_{\text{radiation}}. \quad (a)$$

The thermal loss by conduction through the refractory is given by the expression

$$q_{\text{conduction}} = k_{av} A_r \frac{\Delta T}{\Delta X} = k_{av} A_r (T_f - T_r) / w_r. \quad (b)$$

The thermal loss from the outer surface of the roof by radiation is

$$q_{\text{radiation}} = (0.173) (\epsilon) \left[ \frac{(T_r + 460)^4}{100} - \frac{(T_s + 460)^4}{100} \right] (A_r) \quad (c)$$

and by convection is

$$q_{\text{convection}} = C' (T_r - T_s)^{1.25} (A_r), \quad (d)$$

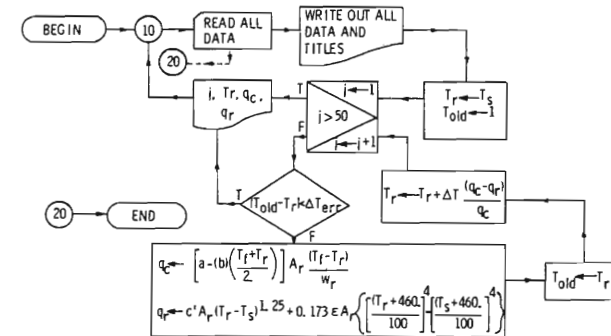
$$h_c = C' (T_r - T_s)^{0.25}. \quad (e)$$

The steady state condition is defined by a given surface temperature for the refractory,  $T_r$ , which satisfies Eq. a. Since  $T_r$  appears in the equations in a non-linear manner, this problem is best solved by an iterative procedure.

Symbol Table—Problem 6

| Algebraic Symbol | Definition                           | FORTTRAN Symbol |
|------------------|--------------------------------------|-----------------|
| $T_r$            | Exterior surface temperature of roof | TREFR           |
| $T_f$            | Temperature of furnace               | TFCE            |
| $T_s$            | Temperature of surroundings          | TSURR           |

|                  |                                                         |        |
|------------------|---------------------------------------------------------|--------|
| $T_{old}$        | Previously computed value of roof temperature           | TOLD   |
| $\Delta T$       | Initial temperature increment in iteration              | INC    |
| $\Delta T_{err}$ | Acceptable temperature difference for convergence       | EPS    |
| $\epsilon$       | Emissivity of refractory                                | EMIS   |
| $C'$             | Convection coefficient for horizontal surface facing up | CPRIME |
| $a$              | Intercept in equation for average thermal conductivity  | TCONDA |
| $b$              | Slope in equation for average thermal conductivity      | TCONDB |
| $A_r$            | Area of furnace roof                                    | AREA   |
| $w_r$            | Thickness of refractory roof                            | THICK  |
| $q_c$            | Conductive energy loss                                  | QC     |
| $q_r$            | Convective and radiative energy loss                    | QR     |



Flow Chart—Problem 6. Flow diagram for computation of heat loss from furnace roof.

**FORTTRAN Listing—Problem 6**

```

C      HEAT LOSS THROUGH FURNACE ROOF
      REAL INC
10     READ (5,500,END=20) TFCE,TSURR,CPRIME,TCONDA,TCONDB,EMIS,AREA,THIC
      1K, EPS, INC
      WRITE (6,600) AREA,TCONDA,CPRIME,TCONDB,EMIS,TFCE, EPS, THICK, INC, TS
      1URR
      TREFR=TSURR
      TOLD=1.
      DO 30 J=1,50
      IF (ABS(TOLD-TREFR).LT.EPS) GO TO 40
      QC=(TCONDA-TCONDB*(TFCE+TREFR)/2.)*AREA*(TFCE-TREFR)/THICK
      QR=CPRIME*AREA*(TREFR-TSURR)**1.25+.173*EMIS*(((TREFR+460.)/100.)*
      1*4-(((TSURR+460.)/100.))**4)*AREA
      TOLD=TREFR
30     TREFR=TREFR+INC*(QC-QR)/QC
40     WRITE (6,610) J,TREFR, QC, QR
      GO TO 10

```

```

20 CALL SYSTEM
500 FORMAT (F5.0,F4.0,F4.2,F4.1,F6.4,F4.2,F5.0,F4.2,F3.1,F4.0)
600 FORMAT('HEAT LOSS THROUGH FURNACE ROOF','0DATA','0AREA =',F5.0,13
1X,'TCONDA =',F4.1,'CPRIME =',F4.2,12X,'TCONDB =',F6.4,'EMIS ',
2F4.2,15X,'TFCE =',F5.0,'EPS =',F3.1,16X,'THICK =',F4.2,'INC =',
3F4.0,15X,'TSURR =',F4.0)
610 FORMAT ('0RESULTS','0ITERATIONS REQUIRED TO ATTAIN SOLUTION =',13/
1'0EXTERIOR SURFACE TEMPERATURE OF ROOF, DEGREES F. =',F6.1,'0THERM
2AL LOSS BY CONDUCTION, BTU/HR =',F8.0,'0THERMAL LOSS BY CONVECTION
3AND RADIATION, BTU/HR =',F8.0)
END

```

## Input (Data)—Problem 6

2800 70 38 2.7 5 85 1100 100 1 100

## Output (Results)—Problem 6

## HEAT LOSS THROUGH FURNACE ROOF

## DATA

|              |                |
|--------------|----------------|
| AREA =1100.  | TCONDA = 2.7   |
| CPRIME =0.38 | TCONDB =0.0005 |
| EMIS 0.85    | TFCE =2800.    |
| EPS =0.1     | THICK =1.00    |
| INC =100.    | TSURR = 70.    |

## RESULTS

ITERATIONS REQUIRED TO ATTAIN SOLUTION = 23

EXTERIOR SURFACE TEMPERATURE OF ROOF, DEGREES F. = 706.1

THERMAL LOSS BY CONDUCTION, BTU/HR =4200313.

THERMAL LOSS BY CONVECTION AND RADIATION, BTU/HR =4196966.

## Discussion of Results—Problem 6

A computer calculation of the steady state temperature was achieved using a "sledge-hammer" approach. This technique involved selection of an initial value for  $T_r$  and incrementing it depending upon how far away the estimated value is from the correct value, and also whether it is too high or too low. One such correction might be given by the expression

$$T_r = T_r + \Delta T * (QC - QR) / QC,$$

where  $QC = q_c$  and  $QR = q_{\text{convection}} + q_{\text{radiation}}$

Classical trial and error solutions also can be achieved graphically. An initial series of surface temperatures are assumed in this approach. At each selected value of surface temperature, the heat loss by conduction through the refractory and the heat loss by convection and radiation from the roof surface is calculated. The two heat losses are plotted against surface temperature yielding the curves shown in Fig. B-7. The steady state temperature is that temperature at which the same heat flux is calculated for the two consecutive transfer processes, i.e., the surface temperature corresponding to the intersection of the two curves in Fig. B-7.

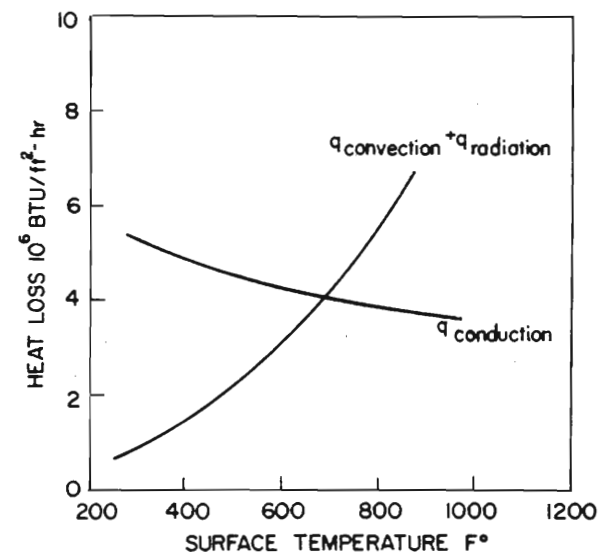


Fig. B-7. Heat loss by radiation and convection from a furnace roof.

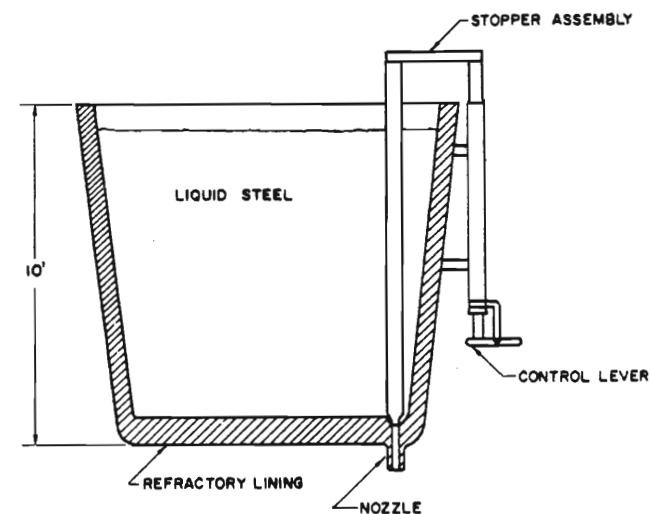


Fig. B-8. 200 Ton bottom-pour ladle.

### Example Problem No. 7: Digital Computer Simulation of a Bottom-Pouring Ladle

#### Problem Statement

Write and test a FORTRAN program which will permit the calculation of pouring rates as a function of time, as well as the total pouring time, for a ladle which is teeming liquid steel as shown in Fig. B-8. The metal flows out of a nozzle in the bottom of the ladle into the ingot mold. The ladle also may be used to vacuum pour into a low pressure chamber.

The ladle contains 200 tons of liquid metal. The initial diameter of the nozzle is 2 inches and its length is 18 in. The nozzle erodes during pouring, however, and the eroded diameter is given by the relationship,

$$D_N = 2 + \epsilon N, \quad (a)$$

where  $D_N$  is the diameter in inches,  $\epsilon$  is the linear erosion coefficient, 0.006 in./ton, and  $N$  is the number of tons of metal which have passed through the nozzle. The flow of liquid metal through the nozzle is characterized by the friction factor of the nozzle and the entrance coefficient which may be assumed independent of flow rate and assigned the values, 0.04 and 0.20, respectively. The initial depth of metal in the ladle is 10 ft. Liquid steel has a density of 450 lb/ft<sup>3</sup>.

#### Method of Solution—Problem 7

The flow velocity can be calculated at any stage of the pouring operation by the generalized flow equation, expressed for any two locations in the system as

$$\frac{g}{g_c}(z_2 - z_1) + \frac{(V_2^2 - V_1^2)}{2g_c} + \frac{(P_2 - P_1)}{\rho} = -lw - w, \quad (b)$$

where  $g$  is the acceleration due to gravity, 32.17 ft/sec<sup>2</sup>,  $g_c$  is a conversion factor, numerically equal to  $g$  but with the units lb-mass ft/lb-force sec<sup>2</sup>,  $z$  is the height above a reference plane in ft,  $V$  is the velocity of the liquid steel in ft/sec,  $P$  is the pressure of the system in lb/ft<sup>2</sup>,  $\rho$  is the density of the liquid in lb-mass/ft<sup>3</sup>,  $-w$  is the work done by the system which is zero in the case under consideration, and  $-lw$  is the lost work in ft lb<sub>f</sub>/lb<sub>m</sub> and is given by the relationship,

$$lw = \frac{f_N V_N^2 L}{2g_c D_N} + \frac{\phi_N V_N^2}{2g_c}, \quad (c)$$

where  $L$  is the length of the nozzle in inches,  $D_N$  is the diameter of the nozzle in inches,  $V_N$  is the fluid velocity in the nozzle, and  $f_N$  and  $\phi_N$  are dimensionless coefficients, the friction factor of the nozzle and the entrance coefficient, respectively.

For purposes of illustrating the approach to programming the problem for the computer, the flow velocity and pouring rate at the onset of the operation are calculated below.

Selecting point 1 at the upper surface of the metal in the ladle and point 2 just above the nozzle exit the pressure drop ( $P_1 - P_2$ ) is zero.  $V_1$ , the velocity of the surface of the metal in the ladle, is negligibly small in comparison to the exiting velocity from the nozzle. Then,

$$-\frac{g}{g_c} \left[ 10 \left( \frac{200 - N}{200} \right) + L \right] + \frac{V_2^2}{2g_c} = \frac{-V_2^2}{2g_c} \left( f_N \frac{L}{D_N} + \phi_N \right) \quad (d)$$

$$V_2 = \left[ (2g_c) \frac{10[(200 - N)/200] + L}{(1 + f_N L/D_N + \phi_N)} \right]^{1/2} \quad (e)$$

$V_2$ , the exiting flow velocity in ft/sec can be converted to a flow rate by the relationship,

$$\dot{N} \text{ (flow rate in tons per minute)} = \frac{V_2(60) D_N^2 \pi \rho}{(2000)(4)} \quad (f)$$

Then

$$\dot{N} = \left\{ (2g_c) \frac{10[(200 - N)/200] + L}{(1 + f_N L/D_N + \phi_N)} \right\}^{1/2} \cdot \frac{60 D_N^2 \pi \rho}{(2000)(4)}, \quad (g)$$

where  $D_N = 2 + 0.006 N$ .

Evaluating the last two expressions at the start of pouring:

$$D_N = 2 + 0.006 \times 0 = 2 \text{ in.} \quad (h)$$

$$\begin{aligned} \dot{N} &= \left\{ (2)(32.2) \frac{10[(200 - 0)/200] + 18}{1 + (0.04) \frac{18}{2} + 0.2} \right\}^{1/2} \cdot \frac{(60)(2)^2 \pi 450}{(2000)(144)} \\ &= \left[ (64.4) \frac{11.5}{2.56} \right]^{1/2} \cdot \frac{240\pi(450)}{(2000)(576)} = 6.41 \text{ tons/min.} \end{aligned} \quad (i)$$

In addition to the stream velocity and the pouring rate, a principal variable in the design of the operation is the time required for pouring. The total pouring time may be estimated by breaking the operation down into short intervals in which the average pouring rate and the number of tons poured are determined. The total time is given by the expression,

$$t = \sum_1^m \frac{(\text{Tons poured in interval } m)}{(\text{Average rate})} \quad (j)$$

The Basic Approach Involves the Steps:

1. Calculate the stream velocity at the nozzle and the flow rate at the initial conditions.
2. Assume the flow rate remains constant over a short interval of time, and calculate the tons of steel poured during the interval.

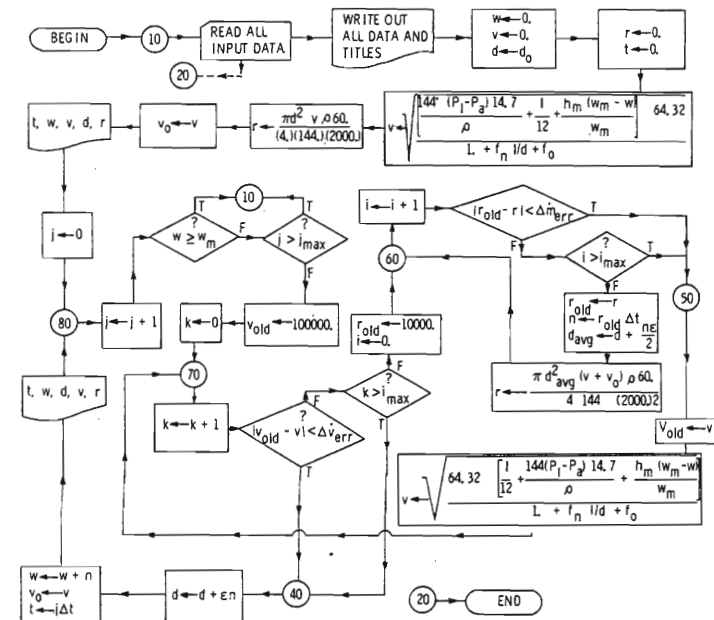
Symbol Table—Problem 7

| Algebraic Symbol       | Definition                                          | FORTTRAN Symbol |
|------------------------|-----------------------------------------------------|-----------------|
| $P_1$                  | Ladle pressure, atm absolute                        | PL              |
| $P_a$                  | Mold pressure, atm absolute                         | PA              |
| $\rho$                 | Metal density, lb/ft <sup>3</sup>                   | RHO             |
| $w_m$                  | Weight of metal, tons                               | WT              |
| $n$                    | Tons of metal poured during this increment          | N               |
| $w$                    | Tons of metal poured (total)                        | W               |
| $r$                    | Pouring rate, tons/min                              | R               |
| $r_{old}$              | Previous estimate for $r$                           | RL              |
| $h_m$                  | Height of metal, feet                               | HI              |
| $l$                    | Length of nozzle, inches                            | L               |
| $d_0$                  | Initial diameter of nozzle, inches                  | DI              |
| $d$                    | Current diameter of nozzle, inches                  | D               |
| $d_{avg}$              | Average diameter over current time interval, inches | DAVG            |
| $i_{max}$              | Maximum number of iterations                        | IMAX            |
| $j_{max}$              | Maximum number of intervals                         | JMAX            |
| $f_n$                  | Nozzle friction factor                              | F               |
| $f_0$                  | Nozzle entrance loss factor                         | ENT             |
| $\epsilon$             | Erosion coefficient, inches/ton                     | EROS            |
| $v$                    | Liquid velocity, ft/sec                             | V               |
| $v_{old}$              | Previous estimate for $v$                           | VL              |
| $\Delta t$             | Time increment, minutes                             | INC             |
| $t$                    | Current elapsed time, minutes                       | T               |
| $\Delta \dot{m}_{err}$ | Maximum allowable error in rate, tons/min           | RERR            |
| $\Delta \dot{V}_{err}$ | Maximum allowable error in velocity, ft/min         | VERR            |
| $i$                    | Number of iterations                                | J               |

3. Calculate a new metal depth in the ladle, and a new nozzle diameter based on the tons poured during the last interval.
4. Return to 1 and perform the calculation using the Results of 3 until the entire 200 tons of metal has been poured from the ladle.

One should be aware of the fact that more accurate results could be obtained by using shorter time intervals. In the solution presented below, an average flow rate for each time interval is used to calculate the amount of metal poured during each interval.

1. Calculate the stream velocity at the nozzle exit and the flow rate at the initial conditions.
2. Calculate the number of tons poured during the next interval by multiplying the last calculated pouring rate by the length of the time interval.
3. Calculate an average diameter for the interval based on the diameter at the end of the last interval and the predicted eroded diameter at the end of the present interval.
4. Calculate an average pouring rate based on the average diameter calculated in 3 and the last calculated flow velocity.
5. Return to 2 until the pouring rate calculated in 4 agrees with the previous one to within a given error tolerance.
6. Calculate an average stream velocity based on the average diameter calculated in 3.
7. Return to 2 until the stream velocity calculated in 6 compares with the previous one within a given limit of error.
8. Calculate the total time, the tons poured at the end of the interval, and the eroded diameter. Print these results.
9. Return to 2 to evaluate the next interval. Keep doing so until the entire heat of metal has been poured from the ladle.



Flow Chart—Problem 7. Flow diagram for computation of flow rate from bottom-pour ladle.

FORTTRAN Listing—Problem 7

```
10  REAL L,INC,N,JJ
    READ (5,500,END=20) DI,L,HI,WT,RHO,F,ENT,EROS,PL,PA,INC,RERR,VERR,
    1JMAX,IMAX
    WRITE (6,600) DI,L,HI,WT,RHO,F,ENT,EROS,PL,PA
    WRITE (6,601) INC,RERR,VERR,JMAX,IMAX
    W=0.
    V=0.
    D=DI
    R=0.
    T=0.
    V=SQRT(((PL-PA)*14.7*144./RHO+L/12.+HI*(WT-W)/WT)*64.32/(1.+F*L/D+
    1ENT))
    R=D**2*3.1416/(4.*144.)*V*RHO*60./2000.
    VO=V
    WRITE (6,610) T,W,D,V,R
    J=0
    J=J+1
    IF (W.GE.WT.OR.J.GT.JMAX) GO TO 30
    VL=100000.
    K=0
    K=K+1
    IF (ABS(VL-V).LT.VERR.OR.K.GT.IMAX) GO TO 40
    RL=10000.
    I=0
    I=I+1
    IF (ABS(RL-R).LT.RERR.OR.I.GT.IMAX) GO TO 50
    RL=R
    N=RL*INC
    DAVG=D+EROS*N/2.
    R=DAVG**2*3.1416*(V+VO)*RHO*60./(4.*144.*2000.*2.)
    GO TO 60
    VL=V
    V=SQRT(((PL-PA)*14.7*144./RHO+L/12.+HI*(WT-W)/WT)*64.32/(1.+F*L/D+
    1VG+ENT))
    GO TO 70
    D=D+EROS*N
    VO=V
    W=W+N
    T=J*INC
    WRITE (6,610) T,W,D,V,R
    GO TO 80
    GO TO 10
    20  CALL SYSTEM
    500  FORMAT (8F9.3/5F9.3,2I4)
    600  FORMAT (21H1BOTTOM POURING LADLE/1H-,1X,26HINITIAL DIAMETER, INCHE
    1S =F5.1/2X,26HLENGTH OF NOZZLE, INCHES =F5.1/2X,31HINITIAL HEIGHT
    2OF METAL, FEET =F5.1/2X,23HWEIGHT OF METAL, TONS =F5.1/2X,38HDENSI
    3TY OF METAL IN LB PER CUBIC FT. =F5.1/2X,38HFRICITION FACTOR OF NOZ
    4ZLE, FT PER FT =F5.3/2X,29HNOZZLE ENTRANCE LOSS FACTOR =F5.2/2X,37
    5HEROSION COEFFICIENT, INCHES PER TON =F6.3/2X,38HLADLE PRESSURE, A
    6TMSOPHERES ABSOLUTE =F5.1/2X,37HMOLD PRESSURE, ATMOSPHERES ABSOLUT
    7E =F5.1)
    601  FORMAT (2X,27HTIME INCREMENT IN MINUTES =F5.1/2X,29HERROR IN RATE,
    1 TONS PER MIN =F7.3/2X,41HERROR IN STREAM VELOCITY, FT PER MINUTE
    2=F7.3/2X,29HMAXIMUM NUMBER OF INTERVALS =I5/2X,30HMAXIMUM NUMBER O
    3F ITERATIONS =I5/1H-,1X,4HTIME,4X,6HPOURED,3X,3HDIA,5X,15HSTREAM V
    4ELOCIY,3X,12HPOURING RATE/2X,3HMIN,6X,4HTONS,3X,6HINCHES,5X,10HFT
    5 PER SEC,6X,12HTONS PER MIN/1H0,/)
    610  FORMAT (F6.2,F9.2,F8.2,F13.2,F17.2)
    END
```

Input (Data)—Problem 7

|      |       |       |        |        |     |     |     |
|------|-------|-------|--------|--------|-----|-----|-----|
| 2000 | 18000 | 10000 | 200000 | 450000 | 040 | 200 | 006 |
| 1000 | 1000  | 1000  | 010    | 010    | 100 | 100 |     |
| 2000 | 18000 | 10000 | 200000 | 450000 | 040 | 200 | 006 |
| 1000 | 000   | 1000  | 010    | 010    | 100 | 100 |     |

Output (Results)—Problem 7

Results—Standard Pouring Practice

| BOTTOM POURING LADLE                            |                |               |                               |                              |
|-------------------------------------------------|----------------|---------------|-------------------------------|------------------------------|
| INITIAL DIAMETER, INCHES = 2.0                  |                |               |                               |                              |
| LENGTH OF NOZZLE, INCHES = 18.0                 |                |               |                               |                              |
| INITIAL HEIGHT OF METAL, FEET = 10.0            |                |               |                               |                              |
| WEIGHT OF METAL, TONS =200.0                    |                |               |                               |                              |
| DENSITY OF METAL IN LB PER CUBIC FT. =450.0     |                |               |                               |                              |
| FRICTION FACTOR OF NOZZLE, FT PER FT =0.040     |                |               |                               |                              |
| NOZZLE ENTRANCE LOSS FACTOR = 0.20              |                |               |                               |                              |
| EROSION COEFFICIENT, INCHES PER TON = 0.006     |                |               |                               |                              |
| LADLE PRESSURE, ATMOSPHERES ABSOLUTE = 1.0      |                |               |                               |                              |
| MOLD PRESSURE, ATMOSPHERES ABSOLUTE = 1.0       |                |               |                               |                              |
| TIME INCREMENT IN MINUTES = 1.0                 |                |               |                               |                              |
| ERROR IN RATE, TONS PER MIN = 0.010             |                |               |                               |                              |
| ERROR IN STREAM VELOCITY, FT PER MINUTE = 0.010 |                |               |                               |                              |
| MAXIMUM NUMBER OF INTERVALS = 100               |                |               |                               |                              |
| MAXIMUM NUMBER OF ITERATIONS = 100              |                |               |                               |                              |
| TIME<br>MIN                                     | POURED<br>TONS | DIA<br>INCHES | STREAM VELOCITY<br>FT PER SEC | POURING RATE<br>TONS PER MIN |
| 0.0                                             | 0.0            | 2.00          | 21.78                         | 6.41                         |
| 1.00                                            | 6.54           | 2.04          | 21.80                         | 6.54                         |
| 2.00                                            | 13.31          | 2.08          | 21.54                         | 6.77                         |
| 3.00                                            | 20.26          | 2.12          | 21.25                         | 6.95                         |
| 4.00                                            | 27.40          | 2.16          | 20.96                         | 7.14                         |
| 5.00                                            | 34.72          | 2.21          | 20.64                         | 7.32                         |
| 6.00                                            | 42.22          | 2.25          | 20.31                         | 7.50                         |
| 7.00                                            | 49.91          | 2.30          | 19.96                         | 7.68                         |
| 8.00                                            | 57.76          | 2.35          | 19.59                         | 7.86                         |
| 9.00                                            | 65.79          | 2.39          | 19.19                         | 8.02                         |
| 10.00                                           | 73.97          | 2.44          | 18.78                         | 8.18                         |
| 11.00                                           | 82.30          | 2.49          | 18.34                         | 8.33                         |
| 12.00                                           | 90.77          | 2.54          | 17.88                         | 8.46                         |
| 13.00                                           | 99.35          | 2.60          | 17.39                         | 8.58                         |
| 14.00                                           | 108.03         | 2.65          | 16.88                         | 8.68                         |
| 15.00                                           | 116.78         | 2.70          | 16.34                         | 8.75                         |
| 16.00                                           | 125.57         | 2.75          | 15.77                         | 8.79                         |
| 17.00                                           | 134.38         | 2.81          | 15.17                         | 8.80                         |
| 18.00                                           | 143.16         | 2.86          | 14.54                         | 8.78                         |
| 19.00                                           | 151.87         | 2.91          | 13.88                         | 8.71                         |
| 20.00                                           | 160.47         | 2.96          | 13.19                         | 8.60                         |
| 21.00                                           | 168.91         | 3.01          | 12.46                         | 8.43                         |
| 22.00                                           | 177.12         | 3.06          | 11.69                         | 8.21                         |
| 23.00                                           | 185.04         | 3.11          | 10.89                         | 7.92                         |
| 24.00                                           | 192.62         | 3.16          | 10.06                         | 7.57                         |
| 25.00                                           | 199.77         | 3.20          | 9.18                          | 7.15                         |
| 26.00                                           | 206.43         | 3.24          | 8.26                          | 6.65                         |

Results—Vacuum Pouring Practice

| BOTTOM POURING LADLE                            |  |  |  |  |
|-------------------------------------------------|--|--|--|--|
| INITIAL DIAMETER, INCHES = 2.0                  |  |  |  |  |
| LENGTH OF NOZZLE, INCHES = 18.0                 |  |  |  |  |
| INITIAL HEIGHT OF METAL, FEET = 10.0            |  |  |  |  |
| WEIGHT OF METAL, TONS =200.0                    |  |  |  |  |
| DENSITY OF METAL IN LB PER CUBIC FT. =450.0     |  |  |  |  |
| FRICTION FACTOR OF NOZZLE, FT PER FT =0.040     |  |  |  |  |
| NOZZLE ENTRANCE LOSS FACTOR = 0.20              |  |  |  |  |
| EROSION COEFFICIENT, INCHES PER TON = 0.006     |  |  |  |  |
| LADLE PRESSURE, ATMOSPHERES ABSOLUTE = 1.0      |  |  |  |  |
| MOLD PRESSURE, ATMOSPHERES ABSOLUTE = 0.0       |  |  |  |  |
| TIME INCREMENT IN MINUTES = 1.0                 |  |  |  |  |
| ERROR IN RATE, TONS PER MIN = 0.010             |  |  |  |  |
| ERROR IN STREAM VELOCITY, FT PER MINUTE = 0.010 |  |  |  |  |
| MAXIMUM NUMBER OF INTERVALS = 100               |  |  |  |  |
| MAXIMUM NUMBER OF ITERATIONS = 100              |  |  |  |  |

| TIME<br>MIN | POURED<br>TONS | DIA<br>INCHES | STREAM VELOCITY<br>FT PER SEC | POURING RATE<br>TONS PER MIN |
|-------------|----------------|---------------|-------------------------------|------------------------------|
| 0.0         | 0.0            | 2.00          | 25.85                         | 7.61                         |
| 1.00        | 7.79           | 2.05          | 25.88                         | 7.80                         |
| 2.00        | 15.93          | 2.10          | 25.64                         | 8.14                         |
| 3.00        | 24.38          | 2.15          | 25.37                         | 8.45                         |
| 4.00        | 33.15          | 2.20          | 25.09                         | 8.77                         |
| 5.00        | 42.25          | 2.25          | 24.78                         | 9.10                         |
| 6.00        | 51.69          | 2.31          | 24.46                         | 9.44                         |
| 7.00        | 61.47          | 2.37          | 24.10                         | 9.78                         |
| 8.00        | 71.61          | 2.43          | 23.73                         | 10.14                        |
| 9.00        | 82.11          | 2.49          | 23.32                         | 10.49                        |
| 10.00       | 92.96          | 2.56          | 22.89                         | 10.85                        |
| 11.00       | 104.17         | 2.62          | 22.43                         | 11.20                        |
| 12.00       | 115.72         | 2.69          | 21.95                         | 11.55                        |
| 13.00       | 127.61         | 2.77          | 21.40                         | 11.89                        |
| 14.00       | 139.82         | 2.84          | 20.82                         | 12.21                        |
| 15.00       | 152.33         | 2.91          | 20.21                         | 12.50                        |
| 16.00       | 165.10         | 2.99          | 19.56                         | 12.76                        |
| 17.00       | 178.08         | 3.07          | 18.86                         | 12.98                        |
| 18.00       | 191.24         | 3.15          | 18.11                         | 13.15                        |
| 19.00       | 204.49         | 3.23          | 17.31                         | 13.25                        |

## Discussion of Results—Problem 7

The results printed out by the computer program include the pouring time at intervals of one minute, the total number of tons of steel poured up to that time, the current diameter of the pouring nozzle in inches, the stream velocity in feet per second, and pouring rate in tons per minute as averaged for the time increment. Results are presented for a standard pouring practice and for vacuum pouring into an evacuated chamber, a practice which is increasing in importance in steel processing.

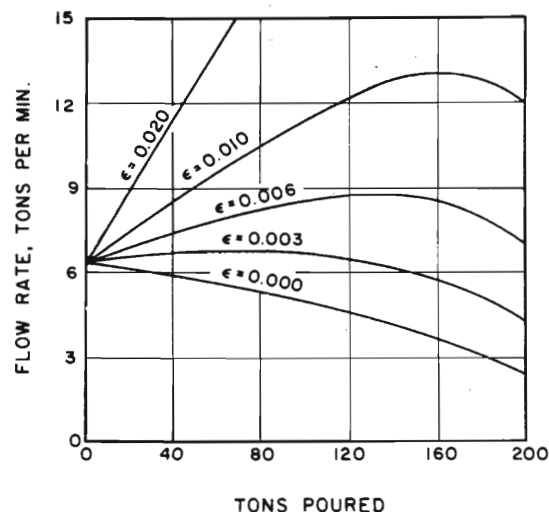


Fig. B-9. Flow rates from bottom-pour ladle for various nozzle materials with erosion coefficient,  $\epsilon$ . (Standard pouring conditions.)

The nozzle gradually enlarges during pouring, an effect which is desirable since the rate of pouring does not decline continuously with the ferrostatic head in the ladle as it would if the nozzle diameter remained constant. While the head of metal decreases, the diameter of the orifice increases, and the pouring rate can remain nearly constant or even increase slightly. The rate of pouring is an important variable in ingot quality, and a reasonably constant pouring rate is desired throughout the entire pouring operation. Knowing the erosion coefficients for various nozzle materials, a process engineer can select the optimum nozzle material for a given pouring operation, based on the above analysis. The pouring practice as given in the problem statement is presented in Fig. B-9.

The pouring rate continually increases throughout the vacuum pouring operation. The result indicates that a more stable material (lower erosion coefficient) would better suit those operating conditions, such that the pouring rate would undergo a minimum change during the pouring operation.

**Example Problem No. 8: Unsteady State Heat Flow—Cooling of a Slab**

**Problem Statement**

Heat conduction in one dimension in a solid semi-infinite plate can be represented by the second order partial differential equation,

$$\left(\frac{\partial \theta}{\partial t}\right)_x = \frac{k}{C_p \rho} \left(\frac{\partial^2 \theta}{\partial x^2}\right), \tag{a}$$

where  $k$  is the thermal conductivity of the solid,  $C_p$  is its specific heat,  $\rho$  is its density,  $x$  is distance,  $\theta$  is temperature, and  $t$  is time. The quantity  $k/C_p \rho$  is the thermal diffusivity,  $\alpha$ .

The solution of Eq. (a) can be developed by finite difference techniques which involve a network of grid points in terms of the independent variables. The grid spacings are small increments of the independent variables, e.g., in Eq. (a),  $\Delta t$  and  $\Delta x$ .

Write and test a FORTRAN program which will calculate the temperature distribution after thirty minutes in a large slab (semi-infinite in length  $\times$  12 inches thick) which is removed from a preheating furnace at a uniform temperature of 1600°F and set on its edge in the slab yard. Assume constant thermal properties.

**Method of Solution—Problem 8**

**Finite Difference Approximation**

The derivatives in the conduction equation with respect to distance may be

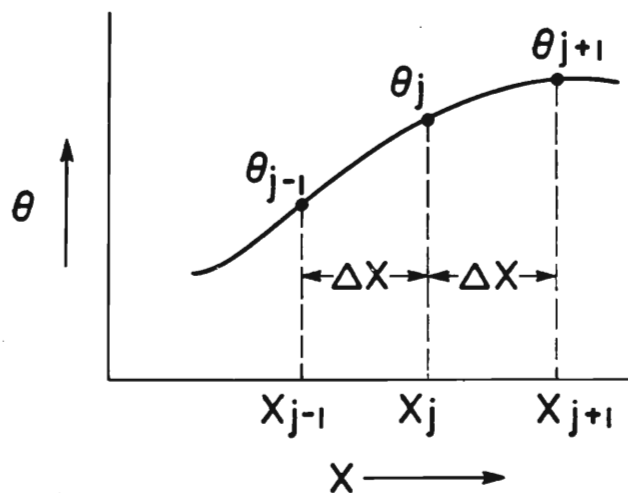


Fig. B-10. Temperature distribution in solid.

represented by numerical approximations which are computed from a temperature distribution for a network of space points within the conducting medium.

Consider a temperature distribution as given in Fig. B-10.

The variations of temperature,  $\theta$ , with distance,  $x$ , can be expressed by a Taylor Series expansion of the form,

$$\theta_{j+1} = \theta_j + \frac{(\Delta x)^1}{1!} \frac{\partial \theta_j}{\partial x} + \frac{(\Delta x)^2}{2!} \frac{\partial^2 \theta_j}{\partial x^2} + \frac{(\Delta x)^3}{3!} \frac{\partial^3 \theta_j}{\partial x^3} + \dots, \tag{b}$$

$$\theta_{j-1} = \theta_j - \Delta x \frac{\partial \theta_j}{\partial x} + \frac{(\Delta x)^2}{2!} \frac{\partial^2 \theta_j}{\partial x^2} - \frac{(\Delta x)^3}{3!} \frac{\partial^3 \theta_j}{\partial x^3} + \dots, \tag{c}$$

where  $\theta_{j+1}$  and  $\theta_{j-1}$  are points on either side of  $\theta_j$ ,  $\Delta x$  units away. Subtracting Eq. (c) from Eq. (b)

$$\theta_{j+1} - \theta_{j-1} = 2\Delta x \frac{\partial \theta_j}{\partial x} + \frac{2(\Delta x)^3}{3!} \frac{\partial^3 \theta_j}{\partial x^3} + \dots \tag{d}$$

Neglecting terms of third order or higher, and solving for the first approximation to the first derivative:

$$\frac{\partial \theta_j}{\partial x} = \frac{\theta_{j+1} - \theta_{j-1}}{2\Delta x}. \tag{e}$$

Adding Eqs. (b) and (c), the second derivative can be solved for in a similar manner.

$$\theta_{j+1} + \theta_{j-1} = 2\theta_j + (\Delta x)^2 \frac{\partial^2 \theta_j}{\partial x^2} + \frac{2(\Delta x)^4}{4!} \frac{\partial^4 \theta_j}{\partial x^4} + \dots \tag{f}$$

Then, neglecting terms of 4th order or higher, rearrangement yields:

$$\frac{\partial^2 \theta_j}{\partial x^2} = \frac{\theta_{j+1} + \theta_{j-1} - 2\theta_j}{(\Delta x)^2}. \tag{g}$$

The derivative with respect to time is first order and is given by the forward difference relationship:

$$\frac{\partial \theta}{\partial t} = \frac{(\theta_j)_{t+\Delta t} - (\theta_j)_t}{\Delta t}, \tag{h}$$

where  $(\theta_j)_{t+\Delta t}$  is the value of  $\theta_j$  after a time interval  $\Delta t$  and  $(\theta_j)_t$  is the temperature at time,  $t$ .

**Explicit Form of the Difference Equation**

Substituting Eqs. (g) and (h) into Eq. (a) yields

$$(\theta_j)_{t+\Delta t} = (\theta_j)_t + \alpha \frac{\Delta t}{(\Delta x)^2} [(\theta_{j+1})_t + (\theta_{j-1})_t - 2(\theta_j)_t]. \tag{i}$$

It is often more convenient to work with dimensionless variables, and if the

thermal properties of the conducting medium can be assumed constant, the variables  $t$  and  $x$  can be replaced by

$$X = \frac{x}{L}, \quad (j)$$

and

$$\tau = \frac{\alpha t}{L^2}, \quad (k)$$

where  $X$  is a dimensionless space variable ranging from 0 to 1, and defined by the ratio of  $x$ , the variable distance to  $L$  the total distance;  $\tau$  is a dimensionless time variable which is related to real time by the thermal diffusivity,  $\alpha$ , and total distance,  $L$ . Equation (i) then becomes

$$(\theta_j)_{\tau+\Delta\tau} = (\theta_j)_\tau + \frac{\Delta\tau}{(\Delta X)^2} [\theta_{j+1} + \theta_{j-1} - 2\theta_j]_\tau. \quad (l)$$

If  $\Delta\tau/(\Delta X)^2 = \lambda$ , then

$$(\theta_j)_{\tau+\Delta\tau} = [\lambda(\theta_{j+1} + \theta_{j-1}) + (1 - 2\lambda)\theta_j]_\tau. \quad (m)$$

The temperature at point  $j$  at dimensionless time,  $\tau + \Delta\tau$ , is defined in terms of the temperature at points  $j$  and neighboring points,  $j + 1$  and  $j - 1$ , at dimensionless time,  $\tau$ . An iterative procedure, advancing  $\Delta\tau$  units and calculating temperatures at each space point,  $X_j$ , yields the time-dependent temperature distribution.

#### Stability of the Explicit Form

It can be shown that a sufficient condition for stability of the explicit form is that  $0 < \lambda \leq \frac{1}{2}$ .<sup>1</sup>

#### Boundary Conditions

The temperature at any point,  $X_j$ , has been defined in terms of temperatures at neighboring points. The solution also requires that boundary conditions be defined at the end points of the space interval.

Heat transfer from the surface of an object can be by the transport processes convection, radiation, conduction, or some combination of these. For radiation and/or convection the heat transfer can be defined by a heat transfer coefficient,  $h$ , where continuity at the boundary (in this case, a left-hand boundary where  $X$  increases to the right) requires

$$-q = k \left( \frac{\partial \theta}{\partial x} \right)_{x=0} = h(\theta_{x=0} - \theta_s), \quad (n)$$

where  $\theta_s$  is the temperature of the surroundings.

Several conditions for heat flow may be considered.

<sup>1</sup> B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods*, John Wiley, New York, 1969.

*Case A— $h$  very large, relative to  $k$ .* If the heat transfer coefficient is very large,  $\theta_{x=0} \approx \theta_s$ , and the surface of the conducting medium can be assumed to be maintained at  $\theta_s$ . If this is the case and the conducting medium is initially at a temperature  $\theta_0$ , it is often helpful to define a dimensionless temperature  $T$  where

$$T = \frac{\theta_j - \theta_0}{\theta_s - \theta_0}. \quad (o)$$

Equation (a) then is simplified to

$$\frac{\partial T}{\partial \tau} = \frac{\partial^2 T}{\partial X^2}. \quad (p)$$

Equation (p), applied to an infinite parallel sided slab with the boundary conditions,

$$T = 0 \text{ at } \tau = 0 \text{ for } 0 \leq X \leq 1,$$

$$T = 1 \text{ at } X = 0 \text{ and } X = 1 \text{ for } \tau > 0,$$

has been solved by finite difference approximation using the computer, and the calculated results compared with the analytical solution.<sup>2</sup>

*Case B— $k$  very large, relative to  $h$ .* In this case, all the resistance to heat flow is at the surface of the conducting medium, and all interior temperatures are equal (Newton's Law of Cooling). Then

$$\text{Heat Loss} = -V\rho C_p \left( \frac{d\theta}{dt} \right) = hA(\theta - \theta_s), \quad (q)$$

where  $V$  and  $A$  are the volume and surface area of the conducting medium, respectively, and  $\theta$  is the uniform temperature of the body at any time  $t$ . Equation (q) integrates to

$$\log_{10} \left[ \frac{\theta - \theta_s}{\theta_{t=0} - \theta_s} \right] = - \frac{hA}{2.3 V\rho C_p} t. \quad (r)$$

*Case C—General values of  $h$  and  $k$ .* For values of  $h$  and  $k$  which are intermediate between Cases A and B, the heat transfer at the surface is given by Eq. (n). Rearranging at  $x = 0$ :

$$\left( \frac{\partial \theta}{\partial x} \right)_{x=0} = \frac{h}{k} (\theta_j - \theta_s). \quad (s)$$

Substituting Eq. (s) in Eq. (b), dropping terms of higher order, and solving for the second-order partial differential:

$$\left( \frac{\partial^2 \theta}{\partial x^2} \right) = \frac{2}{(\Delta x)^2} \left\{ \theta_{j+1} + \frac{h(\Delta x)}{k} \theta_s - \theta_j \left( 1 + \frac{h(\Delta x)}{k} \right) \right\}. \quad (t)$$

Substituting Eqs. (h) and (t) into Eq. (a) yields

$$\frac{(\theta_j)_{t+\Delta t} - (\theta_j)_t}{\Delta t} = \frac{2\alpha}{(\Delta x)^2} \left\{ \theta_{j+1} + \frac{h(\Delta x)}{k} \theta_s - \theta_j \left( 1 + \frac{h(\Delta x)}{k} \right) \right\}_t. \quad (u)$$

<sup>2</sup> Ibid.

$$(\theta_j)_{\tau+\Delta\tau} = \left\{ 2\lambda \left[ \theta_{j+1} + \left( \frac{h(\Delta X)L}{k} \right) \theta_s \right] + \theta_j \left[ 1 - 2\lambda \left( 1 + \frac{h(\Delta X)L}{k} \right) \right] \right\}_{\tau}. \quad (\text{v})$$

### Central Point Approximation

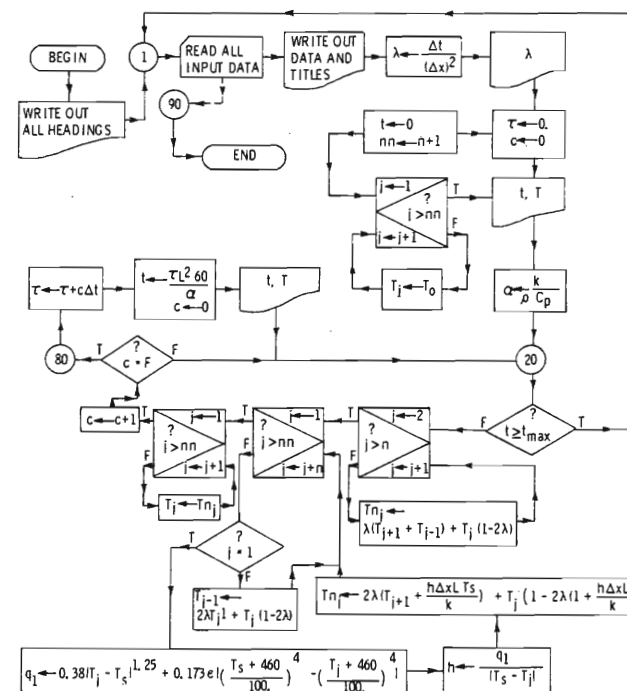
$$(\theta_i)_{r+\Delta r} = \lceil \theta_i + 2\lambda(\theta_{i-1} - \theta_i) \rceil_r. \quad (\text{w})$$

Symbol Table—Problem 8

| Algebraic<br>Symbol | Definition                                                                | FORTRAN<br>Symbol |
|---------------------|---------------------------------------------------------------------------|-------------------|
| $n$                 | Number of grid spaces                                                     | $N$               |
| $t_{\max}$          | Maximum time of simulation, minutes                                       | $TMAX$            |
| $\Delta t$          | Time Increment                                                            | $DEL T$           |
| $T_j$               | Temperature array for the last time step                                  | $T$               |
| $T_{n_j}$           | Temperature array for the current time step                               | $TN$              |
| $T_0$               | Initial uniform temperature of slab                                       | $TINIT$           |
| $T_s$               | Temperature of surroundings                                               | $TSURR$           |
| $\tau$              | Dimensionless Time                                                        | $TAU$             |
| $t$                 | Real time                                                                 | $TIME$            |
| $k$                 | Thermal Conductivity, BTU-ft/(hr-ft <sup>2</sup> -°F)                     | $K$               |
| $C_p$               | Specific Heat, BTU/°F-lb.                                                 | $CP$              |
| $\rho$              | Density, 490 lb./ft <sup>3</sup>                                          | $RHO$             |
| $\alpha$            | Thermal Diffusivity                                                       | $ALPH$            |
| $\epsilon$          | Emissivity of slab surface                                                | $EMIS$            |
| $h$                 | Linear Heat Transfer coefficient combining radiation and convection terms | $H$               |
| $j$                 | Subscript for grid points                                                 | $J$               |
| $\lambda$           | Combination of terms                                                      | $LAMBDA$          |
| $\Delta x$          | Grid Spacing                                                              | $DEL X$           |
| $L$                 | Half width of slab, ft.                                                   | $L$               |
| $F$                 | Number of time steps between printouts of temperature distribution        | $FREQ$            |
| $c$                 | Counter for output frequency                                              | $COUNT$           |
| $q_1$               | Convective and radiative flux term                                        | $Q1$              |

Verification of convergence can be made by using ever decreasing increments of  $\tau$  and  $X$ , until the solution does not change, within some acceptable tolerance limit.

In an implicit method, the finite difference approximations are written in terms of a series of simultaneous equations involving the temperature terms at the next time step. The computational procedure is slightly more complex, but offers the advantage of not being limited to small time increments as in the explicit method where  $0 < \Delta\tau/(\Delta X)^2 \leq \frac{1}{2}$ . In many problems the advantage of a larger time step far outweighs the added programming complexity. A detailed development of some implicit methods and several example problems using this form have been presented.<sup>3</sup>



Flow Chart—Problem 8. Flow diagram for computation of cooling of slab.

<sup>3</sup> Ibid

## FORTRAN Listing—Problem 8

```

      REAL LAMBDA,L,K
      DIMENSION T(100),TN(100)
      WRITE (6,600)
      READ (5,500,END=90) H,TMAX,DELX,L,FREQ,TINIT,TSURR,K,CP,RHO,E
      IMIS
      WRITE (6,610) H,TINIT,TMAX,TSURR,DELX,K,DELX,CP,L,RHO,FREQ,EMIS
      LAMBDA=DELX/DELX**2
      WRITE (6,620) LAMBDA
      TAU=0.
      COUNT=0.
      TIME=0.
      NN=N+1
      DO 10 J=1, NN
      10 T(J)=TINIT
      WRITE (6,630)
      WRITE (6,640) TIME, (T(J), J=1, NN)
      ALPH=K/(CP*RHO)
      20 IF (TIME.GE.TMAX) GO TO 30
      DO 40 J=2, H
      40 TN(J)=LAMBDA*(T(J+1)+T(J-1))+T(J)*(1.-2.*LAMBDA)
      DO 50 J=1, NN, N
      IF (J.EQ.1) GO TO 60
      TN(J)=2.*LAMBDA*T(J-1)+T(J)*(1.-2.*LAMBDA)
      GO TO 50
      60 Q1=.38*ABS(T(J)-TSURR)**1.25+.173*EMIS*ABS(((TSURR+460.)/100.))**.4
      1-((T(J)+460.)/100.))**.4)
      H=Q1/ABS(TSURR-T(J))
      TN(J)=2.*LAMBDA*(T(J+1)+H*DELX*L/K*TSURR)+T(J)*(1.-2.*LAMBDA*(1.+H
      1*DELX*L/K))
      50 CONTINUE
      DO 70 J=1, NN
      70 T(J)=TN(J)
      COUNT=COUNT+1.
      IF (COUNT.EQ.FREQ) GO TO 80
      GO TO 20
      80 TAU=TAU+COUNT*DELX
      TIME=TAU+L**2*60./ALPH
      COUNT=0.
      WRITE (6,640) TIME, (T(J), J=1, NN)
      GO TO 20
      30 GO TO 1
      90 CALL SYSTEM
      500 FORMAT (I3,F4.1,F6.4,3F4.1,F6.1,F6.2,F4.1,F4.2,F5.1,F3.1)
      600 FORMAT (30H1COOLING OF SEMI-INFINITE SLAB)
      610 FORMAT (1H-,4X,2HN=I3,15X,6HTINIT=F7.1/5X,5HTMAX=F5.1,10X,
      16HTSURR=F6.1/5X,5HDELX=F7.4,8X,2HK=F5.1/5X,5HDELX=F4.1,
      211X,3HCP=F5.2/5X,2HL=F4.1,14X,4HHRHO=F6.1/5X,
      35HFREQ=F5.1,10X,5HEMIS=F4.1)
      620 FORMAT (1H-,5X,7HLAMBDA=F6.3)
      630 FORMAT (1H-,1X,5HTIME,,20X,24HTEMPERATURE DISTRIBUTION/2X,3HMIN///
      1)
      640 FORMAT (1X,F5.2,11F7.1)
      END

```

## Input (Data)—Problem 8

10 30 25 1 5 100 16000 10000 250 11 4900 8

## Output (Results)—Problem 8

## COOLING OF SEMI-INFINITE SLAB

```

N= 10          TINIT= 1600.0
TMAX= 30.0     TSURR= 100.0
DELX= 0.0025   K= 25.0
DELX= 0.1      CP= 0.11
L= 0.5         RHO= 490.0
FREQ= 10.0     EMIS= 0.8

```

LAMBDA= 0.250

| TIME,<br>MIN | TEMPERATURE DISTRIBUTION |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
|--------------|--------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 0.0          | 1600.0                   | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 |
| 0.81         | 1511.5                   | 1551.9 | 1577.3 | 1590.9 | 1597.0 | 1599.2 | 1599.8 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 | 1600.0 |
| 1.62         | 1480.3                   | 1520.6 | 1550.7 | 1571.6 | 1584.8 | 1592.5 | 1596.6 | 1598.6 | 1599.5 | 1599.8 | 1599.9 | 1599.9 | 1599.9 | 1599.9 | 1599.9 |
| 2.43         | 1458.2                   | 1497.9 | 1529.5 | 1553.6 | 1570.9 | 1582.6 | 1590.2 | 1594.7 | 1597.3 | 1598.5 | 1598.9 | 1599.3 | 1599.5 | 1599.6 | 1599.7 |
| 3.23         | 1440.7                   | 1479.6 | 1511.8 | 1537.6 | 1557.4 | 1571.9 | 1582.2 | 1589.0 | 1593.3 | 1595.5 | 1596.3 | 1596.8 | 1597.1 | 1597.3 | 1597.5 |
| 4.04         | 1426.0                   | 1464.1 | 1496.6 | 1523.3 | 1544.7 | 1561.2 | 1573.4 | 1582.1 | 1587.7 | 1590.9 | 1592.0 | 1592.8 | 1593.2 | 1593.5 | 1593.7 |
| 4.85         | 1413.2                   | 1450.7 | 1483.1 | 1510.4 | 1532.8 | 1550.7 | 1564.3 | 1574.3 | 1581.1 | 1585.0 | 1586.2 | 1586.8 | 1587.1 | 1587.3 | 1587.5 |
| 5.66         | 1401.9                   | 1438.7 | 1470.9 | 1498.6 | 1521.6 | 1540.4 | 1555.1 | 1566.0 | 1573.6 | 1578.0 | 1579.5 | 1580.1 | 1580.4 | 1580.6 | 1580.8 |
| 6.47         | 1391.6                   | 1427.8 | 1459.8 | 1487.5 | 1511.0 | 1530.4 | 1545.7 | 1557.4 | 1565.5 | 1570.3 | 1571.9 | 1572.6 | 1572.9 | 1573.1 | 1573.3 |
| 7.28         | 1382.1                   | 1417.7 | 1449.4 | 1477.1 | 1500.8 | 1520.6 | 1536.4 | 1548.5 | 1557.0 | 1562.1 | 1563.7 | 1564.3 | 1564.6 | 1564.8 | 1565.0 |
| 8.08         | 1373.2                   | 1408.3 | 1439.7 | 1467.3 | 1491.0 | 1511.0 | 1527.1 | 1539.5 | 1548.3 | 1553.5 | 1555.2 | 1555.8 | 1556.1 | 1556.3 | 1556.5 |
| 8.89         | 1364.8                   | 1399.3 | 1430.4 | 1457.8 | 1481.5 | 1501.5 | 1517.8 | 1530.4 | 1539.3 | 1544.7 | 1546.4 | 1547.0 | 1547.3 | 1547.5 | 1547.7 |
| 9.70         | 1356.8                   | 1390.8 | 1421.5 | 1448.7 | 1472.3 | 1492.3 | 1508.6 | 1521.3 | 1530.3 | 1535.7 | 1537.5 | 1538.1 | 1538.4 | 1538.6 | 1538.8 |
| 10.51        | 1349.1                   | 1382.6 | 1412.9 | 1439.9 | 1463.3 | 1483.2 | 1499.5 | 1512.2 | 1521.2 | 1526.7 | 1528.5 | 1529.1 | 1529.4 | 1529.6 | 1529.8 |
| 11.32        | 1341.7                   | 1374.7 | 1404.6 | 1431.3 | 1454.5 | 1474.3 | 1490.5 | 1503.1 | 1512.2 | 1517.6 | 1519.4 | 1520.0 | 1520.3 | 1520.5 | 1520.7 |
| 12.13        | 1334.4                   | 1367.0 | 1396.5 | 1422.9 | 1445.9 | 1465.5 | 1481.6 | 1494.2 | 1503.2 | 1508.6 | 1510.4 | 1511.0 | 1511.3 | 1511.5 | 1511.7 |
| 12.94        | 1327.4                   | 1359.5 | 1388.6 | 1414.6 | 1437.4 | 1456.8 | 1472.8 | 1485.3 | 1494.2 | 1499.6 | 1501.4 | 1502.0 | 1502.3 | 1502.5 | 1502.7 |
| 13.74        | 1320.5                   | 1352.1 | 1380.9 | 1406.6 | 1429.1 | 1448.3 | 1464.1 | 1476.5 | 1485.3 | 1490.7 | 1492.4 | 1493.0 | 1493.3 | 1493.5 | 1493.7 |
| 14.55        | 1313.7                   | 1344.9 | 1373.3 | 1398.7 | 1420.9 | 1439.9 | 1455.5 | 1467.8 | 1476.5 | 1481.8 | 1483.6 | 1484.2 | 1484.5 | 1484.7 | 1484.9 |
| 15.36        | 1307.0                   | 1337.8 | 1365.8 | 1390.9 | 1412.8 | 1431.6 | 1447.0 | 1459.2 | 1467.8 | 1473.1 | 1474.8 | 1475.4 | 1475.7 | 1475.9 | 1476.1 |
| 16.17        | 1300.5                   | 1330.9 | 1358.5 | 1383.2 | 1404.9 | 1423.4 | 1438.7 | 1450.6 | 1459.2 | 1464.4 | 1466.1 | 1466.7 | 1466.9 | 1467.1 | 1467.3 |
| 16.98        | 1294.0                   | 1324.0 | 1351.3 | 1375.7 | 1397.1 | 1415.3 | 1430.4 | 1442.3 | 1450.7 | 1455.8 | 1457.5 | 1458.1 | 1458.3 | 1458.5 | 1458.7 |
| 17.79        | 1287.7                   | 1317.2 | 1344.1 | 1368.2 | 1389.3 | 1407.4 | 1422.3 | 1434.0 | 1442.3 | 1447.4 | 1449.1 | 1449.7 | 1449.9 | 1450.1 | 1450.3 |
| 18.60        | 1281.4                   | 1310.6 | 1337.1 | 1360.9 | 1381.7 | 1399.5 | 1414.3 | 1425.8 | 1434.0 | 1439.0 | 1440.7 | 1441.3 | 1441.5 | 1441.7 | 1441.9 |
| 19.40        | 1275.2                   | 1304.0 | 1330.2 | 1353.6 | 1374.2 | 1391.8 | 1406.3 | 1417.7 | 1425.9 | 1430.8 | 1432.4 | 1433.0 | 1433.2 | 1433.4 | 1433.6 |
| 20.21        | 1269.0                   | 1297.5 | 1323.3 | 1346.5 | 1366.8 | 1384.2 | 1398.5 | 1409.7 | 1417.8 | 1422.6 | 1424.3 | 1424.9 | 1425.1 | 1425.3 | 1425.5 |
| 21.02        | 1263.0                   | 1291.1 | 1316.6 | 1339.4 | 1359.5 | 1376.6 | 1390.8 | 1401.9 | 1409.8 | 1414.6 | 1416.2 | 1416.8 | 1417.0 | 1417.2 | 1417.4 |
| 21.83        | 1257.0                   | 1284.7 | 1309.9 | 1332.5 | 1352.3 | 1369.2 | 1383.1 | 1394.1 | 1401.9 | 1406.7 | 1408.2 | 1408.8 | 1409.0 | 1409.2 | 1409.4 |
| 22.64        | 1251.1                   | 1278.4 | 1303.3 | 1325.6 | 1345.1 | 1361.8 | 1375.6 | 1386.4 | 1394.2 | 1398.8 | 1400.4 | 1401.0 | 1401.2 | 1401.4 | 1401.6 |
| 23.45        | 1245.2                   | 1272.3 | 1296.8 | 1318.8 | 1338.1 | 1354.6 | 1368.2 | 1378.8 | 1386.5 | 1391.1 | 1392.6 | 1393.2 | 1393.4 | 1393.6 | 1393.8 |
| 24.25        | 1239.4                   | 1266.1 | 1290.4 | 1312.1 | 1331.1 | 1347.4 | 1360.9 | 1371.4 | 1378.9 | 1383.5 | 1385.0 | 1385.6 | 1385.8 | 1386.0 | 1386.2 |
| 25.06        | 1233.7                   | 1260.1 | 1284.0 | 1305.5 | 1324.3 | 1340.3 | 1353.6 | 1364.0 | 1371.5 | 1375.9 | 1377.4 | 1377.9 | 1378.1 | 1378.3 | 1378.5 |
| 25.87        | 1228.0                   | 1254.1 | 1277.7 | 1298.9 | 1317.5 | 1333.4 | 1346.5 | 1356.7 | 1364.1 | 1368.5 | 1370.0 | 1370.5 | 1370.7 | 1370.9 | 1371.1 |
| 26.68        | 1222.4                   | 1248.2 | 1271.5 | 1292.4 | 1310.8 | 1326.5 | 1339.4 | 1349.5 | 1356.8 | 1361.2 | 1362.6 | 1363.1 | 1363.3 | 1363.5 | 1363.7 |
| 27.49        | 1216.9                   | 1242.3 | 1265.4 | 1286.1 | 1304.2 | 1319.6 | 1332.4 | 1342.4 | 1349.6 | 1353.9 | 1355.4 | 1355.9 | 1356.1 | 1356.3 | 1356.5 |
| 28.30        | 1211.4                   | 1236.5 | 1259.3 | 1279.7 | 1297.6 | 1312.9 | 1325.5 | 1335.4 | 1342.5 | 1346.8 | 1348.2 | 1348.7 | 1348.9 | 1349.1 | 1349.3 |
| 29.11        | 1206.0                   | 1230.8 | 1253.3 | 1273.5 | 1291.2 | 1306.3 | 1318.7 | 1328.5 | 1335.5 | 1339.7 | 1341.1 | 1341.6 | 1341.8 | 1342.0 | 1342.2 |
| 29.91        | 1200.6                   | 1225.1 | 1247.4 | 1267.3 | 1284.8 | 1299.7 | 1312.0 | 1321.6 | 1328.5 | 1332.7 | 1334.1 | 1334.6 | 1334.8 | 1335.0 | 1335.2 |
| 30.72        | 1195.3                   | 1219.5 | 1241.5 | 1261.2 | 1278.4 | 1293.2 | 1305.3 | 1314.9 | 1321.7 | 1325.8 | 1327.2 | 1327.7 | 1327.9 | 1328.1 | 1328.3 |

## Discussion of Results—Problem 8

The results present the temperature profile developing across the half-thickness of the slab. They show that the rate of temperature decrease at the surface of the slab decreases with time. The program also can be used to investigate heating rates.

### Example Problem No. 9: Linear Regression Analysis—BOF Steel Chemistry

#### Problem Statement

The oxygen content of an oxygen-blown heat of steel is very important in that it determines the quantity of deoxidizing elements which must be added to control the oxygen content of the steel. The oxygen content of the liquid steel bath is proportional to the reciprocal of the carbon content according to the reaction,



where the equilibrium constant for reaction (a) is

$$K_a = \frac{P_{\text{CO}}}{a_C a_O}. \quad (b)$$

At equilibrium with one atmosphere carbon monoxide pressure and at 1600°C, and neglecting the small influence of solute elements on the oxygen and carbon activity

$$(a_O) = \frac{P_{\text{CO}}}{(K_a)(a_C)} = \%O = \frac{0.00203}{(\%C)}. \quad (c)$$

At the end of a BOF heat, the bath oxygen content will be greater than for equilibrium with one atmosphere carbon monoxide pressure. Nevertheless, it is expected that the oxygen content will be related to the carbon content, perhaps by an expression of the form

$$\%O = A + B/(\%C), \quad (d)$$

where  $A$  is the intercept and  $B$  the slope for a postulated linear relationship for percent oxygen versus the reciprocal of percent carbon.

Prepare a computer program which will fit a linear relationship of the form given in Eq. (d) to  $N$  data sets of the form  $[(\%O), (\%C)], \dots, [(\%O)_i, (\%C)_i], \dots, [(\%O)_N, (\%C)_N]$ . The least-square criterion should be of the form given in equation (d) to  $N$  data sets of the form  $[(\%O)_i, (\%C)_i], i = 1, 2, \dots, N-1, N$ . A least squares method can be used as the criterion for "best" fit of the data. The program also should provide a measure of the "goodness of fit." To provide generality for the program (which might be used for fitting a linear relationship to any set of data), the regression analysis should be written as a subprogram for a general program which reads data, modifies it (e.g. takes the reciprocal, squares, etc.), calls on the subprogram, and prints both data and results.

#### Method of Solution—Problem 9

The purpose of regression analysis is to fit a curve to a set of data points. This curve will best represent the data according to some criterion. If the criterion adopted is that the sum of the squares of the point deviations from the regression curve is a minimum, the technique is called a "least squares" regression. If the regression curve is first order, the technique is called "linear regression."

Assume a relationship of the form

$$Y = A + BX \quad (e)$$

To minimize the sum of the squares of the deviations of the measured values of the independent variable from the values predicted by equation (e),

$$\frac{\partial \left( \sum_{i=1}^N (Y_i - A - BX_i)^2 \right)}{\partial B} = 0 \quad (f)$$

and

$$\frac{\partial \left( \sum_{i=1}^N (Y_i - A - BX_i)^2 \right)}{\partial A} = 0 \quad (g)$$

Taking the indicated derivatives and setting them equal to zero we have:

$$-2 \sum_{i=1}^N (Y_i - A - BX_i) = 0 \quad (h)$$

$$-2 \sum_{i=1}^N X_i (Y_i - A - BX_i) = 0 \quad (i)$$

Dividing each of these equations by  $-2$ , and realizing that  $\sum_{i=1}^N A = NA$

$$NA + B \sum_{i=1}^N X_i = \sum_{i=1}^N Y_i \quad (j)$$

$$A \sum_{i=1}^N X_i + B \sum_{i=1}^N (X_i)^2 = \sum_{i=1}^N X_i Y_i \quad (k)$$

Solving equations (j) and (k), usually called the *normal equations*, simultaneously for the coefficients  $A$  and  $B$

$$B = \frac{N \sum_{i=1}^N X_i Y_i - \sum_{i=1}^N X_i \sum_{i=1}^N Y_i}{N \sum_{i=1}^N (X_i)^2 - \left( \sum_{i=1}^N X_i \right)^2} \quad (l)$$

$$A = \frac{\sum_{i=1}^N Y_i - B \sum_{i=1}^N X_i}{N} \quad (m)$$

The average squared error, known as the *variance* of the data points about the regression line, is estimated from the data as

$$s_{y,x}^2 = \frac{\sum_{i=1}^N Y_i^2 - A \sum_{i=1}^N Y_i - B \sum_{i=1}^N X_i Y_i}{N - 2} \quad (n)$$

A measurement of how well we can predict a value of  $Y$ , given a value of  $X$ , is a *product moment correlation coefficient*, usually denoted  $r$ . It ranges in value from  $-1$  to  $1$ , where a value of  $1$  represents perfect correlation,  $0$  represents no correlation, and  $-1$  represents perfect inverse correlation. The value of  $r$  is estimated from data by:

$$r = \frac{N \sum_{i=1}^N X_i Y_i - \sum_{i=1}^N Y_i \sum_{i=1}^N X_i}{\sqrt{N \sum_{i=1}^N X_i^2 - (\sum_{i=1}^N X_i)^2} \sqrt{N \sum_{i=1}^N Y_i^2 - (\sum_{i=1}^N Y_i)^2}} \quad (o)$$

For statistical reasons, linear regression results usually are presented with the regression constants, the standard deviation (square root of the variance), and product moment correlation coefficient.

Two cautions on the use of linear regression must be observed. First, the correlation coefficient is a measure of how much uncertainty in the prediction of a value of  $Y$  is removed by using the regression equation. Values of  $r > 0.8$  usually indicate a strong deterministic association, i.e. a chosen form of equation appears to be the correct one. In other fields, such as the social sciences,  $r > 0.3$  often is considered a significant correlation because stochastic (probabilistic) processes continually affect each measurement in unknown ways. This example problem is deterministic because we have sound thermodynamic knowledge on which to base our chosen form of the regression equation.

Second, this type of analysis is rigorous only under the assumption that the absolute errors of measurement are the same over the entire range of the data. Here this is not the case, since the  $X$  values are reciprocals of the %C analysis. The "standard deviation" as computed is actually the *minimum* standard deviation at a value of  $X$  equal to the average of all the data values of  $X$ . A final determination of the appropriateness of a computed regression line always must be based on a visual comparison of the computed regression line with the original data points.

#### Computer Solution

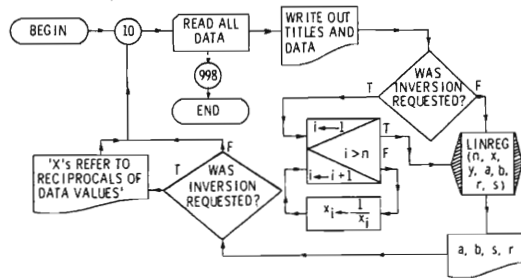
The computer program to solve the problem of correlating BOF turndown oxygen and carbon analyses consists of a main program which handles the data and a subroutine which performs the actual regression calculation.

Symbol Table—Problem 9 Main Program

| Algebraic Symbol | Definition                                                     | FORTTRAN Symbol |
|------------------|----------------------------------------------------------------|-----------------|
| $x$              | Measured values of the independent variable                    | $X$             |
| $y$              | Measured values of the dependent variable                      | $Y$             |
| $n$              | Number of data points                                          | $N$             |
| $inv$            | Logical check variable to test for inversion of $X$ values     | $INVERT$        |
| $a$              | Best estimate of the intercept of the regression line          | $A$             |
| $b$              | Best estimate of the regression line slope                     | $B$             |
| $s$              | Best estimate of the standard deviation of the regression line | $STDDEV$        |
| $r$              | Best estimate of the correlation coefficient                   | $R$             |

Symbol Table—Problem 9 Subroutine LINREG

| Algebraic Symbol | Definition                                   | FORTTRAN Symbol |
|------------------|----------------------------------------------|-----------------|
| $n, x, y, a$     | Defined the same as for the calling program, | $N, X, Y, A,$   |
| $b, r, s$        | above                                        | $B, R, STDDEV$  |
| $sx$             | Sum of $x_i$ values                          | $SX$            |
| $sy$             | Sum of $y_i$ values                          | $SY$            |
| $sx^2$           | Sum of $x_i^2$ values                        | $SX2$           |
| $sy^2$           | Sum of $y_i^2$ values                        | $SY2$           |
| $sxy$            | Sum of $x_i y_i$ products                    | $SXY$           |
| $xi$             | Temporary storage for current $x_i$          | $XI$            |
| $yi$             | Temporary storage for current $y_i$          | $YI$            |
| $s_{2y_x}$       | Common term (variance)                       | $S2YX$          |



Flow Chart—Problem 9. Flow diagram of main program for linear regression analysis.

## FORTRAN Listing—Problem 9

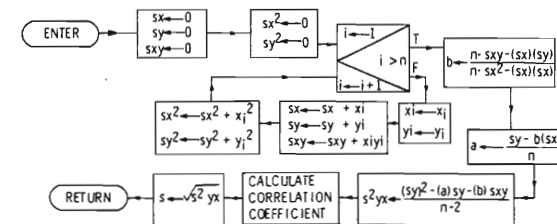
## FORTRAN Listing—Main Program

```

LOGICAL INVERT
DIMENSION X(200),Y(200)
10  READ(5,500,END=998) N,INVERT,(X(I),I=1,N)
    READ(5,501) (Y(I),I=1,N)
    WRITE(6,502) N,(X(I),Y(I),I=1,N)
    IF(.NOT.INVERT) GO TO 30
    DO 20 I=1,N
      X(I)=1./X(I)
20  CALL LINREG(N,X,Y,A,B,R,STDDEV)
    WRITE(6,503) A,B,STDDEV,R
    IF(INVERT) WRITE(6,504)
    GO TO 10
500  FORMAT(15,L2/(10F8.0))
501  FORMAT(10F8.0)
502  FORMAT('1LEAST SQUARES LINEAR REGRESSION'/'-THE',I3,' DATA POINTS
1 ARE:','0 X Y'/(F7.3,F9.4))
503  FORMAT('1-RESULTS: Y =',F9.5,' + (',F8.5,') * X'/
1'0ESTIMATE OF STANDARD DEVIATION =',F9.5/'0ESTIMATE OF CORRELATION
2 COEFFICIENT =',F7.3)
504  FORMAT('0WHERE THE X'S ABOVE REFER TO THE'/' RECIPROCAL OF THE D
1ATA VALUES FOR X.')
998  CALL EXIT
    END
  
```

## Main Program

The main program consists of input and output statements which handle the data and results.  $N$  is the number of data points, stored in  $X$  and  $Y$  as number pairs. The  $X$ 's are turndown carbon contents and the  $Y$ 's are turndown oxygen contents. The program provides a logical variable *INVERT* which may be set to a value of *.TRUE.* or *.FALSE.* by the data and which provides for possible inversion of the  $X$  values prior to regression. After calling on the regression subprogram, the main program prints out the resulting equation and two statistical measures for "goodness of fit," namely the standard deviation and the correlation coefficient.



Flow Chart—Problem 9. Flow diagram of subroutine LINREG for linear regression analysis.

## FORTRAN Listing—Subroutine LINREG

```

SUBROUTINE LINREG(N,X,Y,A,B,R,STDDEV)
DIMENSION X(N),Y(N)
SX=0.
SY=0.
SX2=0.
SY2=0.
SXY=0.
DO 20 I=1,N
  X1=X(I)
  Y1=Y(I)
  SX=SX+X1
  SY=SY+Y1
  SX2=SX2+X1*X1
  SY2=SY2+Y1*Y1
  SXY=SXY+X1*Y1
20  B=(N*SXY-SX*SY)/(N*SX2-SX*SX)
    A=(SY-B*SX)/N
    S2YX=(SY2-A*SY-B*SXY)/(N-2)
    R=(N*SXY-SX*SY)/(SQRT(N*SX2-SX*SX)*SQRT(N*SY2-SY*SY))
    STDDEV=SQRT(S2YX)
    RETURN
  END
  
```

## Subroutine LINREG

The subroutine LINREG is a subprogram which operates on a given set of  $N$  values stored in the vectors  $X$  and  $Y$  and computes the regression constants  $A$  and  $B$  as well as the standard deviation and correlation coefficient.

## Input (Data)—Problem 9

| 30 T   | 0.06   | 0.04   | 0.05   | 0.066  | 0.07   | 0.055 | 0.04  | 0.15   | 0.06   | 0.066 |
|--------|--------|--------|--------|--------|--------|-------|-------|--------|--------|-------|
| 0.042  | 0.04   | 0.03   | 0.04   | 0.24   | 0.03   | 0.06  | 0.05  | 0.045  | 0.06   |       |
| 0.05   | 0.06   | 0.06   | 0.035  | 0.05   | 0.07   | 0.12  | 0.18  | 0.055  | 0.2    |       |
| 0.068  | 0.08   | 0.095  | 0.074  | 0.069  | 0.075  | 0.108 | 0.037 | 0.0714 | 0.0698 |       |
| 0.1070 | 0.082  | 0.114  | 0.095  | 0.019  | 0.136  | 0.065 | 0.084 | 0.105  | 0.0675 |       |
| 0.078  | 0.0686 | 0.0728 | 0.1140 | 0.0835 | 0.0560 | 0.036 | 0.025 | 0.0626 | 0.024  |       |

## Output (Results)—Problem 9

## LEAST SQUARES LINEAR REGRESSION

THE 30 DATA POINTS ARE:

| X     | Y      |
|-------|--------|
| 0.060 | 0.0680 |
| 0.040 | 0.0830 |
| 0.050 | 0.0950 |
| 0.066 | 0.0740 |
| 0.070 | 0.0690 |
| 0.055 | 0.0750 |
| 0.040 | 0.1080 |
| 0.150 | 0.0370 |
| 0.060 | 0.0714 |
| 0.066 | 0.0698 |
| 0.042 | 0.1070 |
| 0.040 | 0.0820 |
| 0.030 | 0.1140 |
| 0.040 | 0.0950 |
| 0.240 | 0.0190 |
| 0.030 | 0.1360 |
| 0.060 | 0.0650 |
| 0.050 | 0.0840 |
| 0.045 | 0.1050 |
| 0.060 | 0.0675 |
| 0.050 | 0.0780 |
| 0.050 | 0.0686 |
| 0.060 | 0.0728 |
| 0.035 | 0.1140 |
| 0.050 | 0.0835 |
| 0.070 | 0.0560 |
| 0.120 | 0.0360 |
| 0.180 | 0.0250 |
| 0.055 | 0.0626 |
| 0.200 | 0.0240 |

RESULTS:  $Y = 0.00983 + (0.00357) \cdot X$ 

ESTIMATE OF STANDARD DEVIATION = 0.00854

ESTIMATE OF CORRELATION COEFFICIENT = 0.954

WHERE THE X'S ABOVE REFER TO THE  
RECIPROCAL OF THE DATA VALUES FOR X.

## Discussion of Results—Problem 9

The turndown oxygen content of the BOF heats used in the regression analysis can be predicted by the relationship,

$$\%O = 0.0098 + \frac{0.00357}{(\%C)}, \quad (o)$$

with a standard deviation of 0.00854% O. The correlation coefficient of 0.954 indicates that a good fit is obtained with this linear relationship.

The data are plotted in Fig. B-11 together with the regression line and the equilibrium relationship for 1 atm CO pressure at 1600°C. The data in the vicinity of 0.06% carbon, a typical turndown analysis for low carbon steel heats, indicate average oxygen concentrations corresponding to an equilibrium CO pressure of about 1.8 atm.

## Example Problem No. 10: Linear Programming—Optimization of Cupola Charge

## Problem Statement

A problem which often arises in melting operations is the calculation of a charge to meet specific composition limits. This calculation is relatively easy if one is concerned only with the composition and is not seeking the absolute minimum cost of meeting the charge requirements. Rule of thumb techniques can usually produce a charge that is low in cost, but there is no guarantee that the estimated mix is the most economical. Linear Programming techniques can produce the most economical solution which lies within the required composition limits. The following problem illustrates the application of linear programming to optimize the charge to a cupola melting furnace producing a specified cast iron composition.

## Available Materials

| Material        | Compositions (w/o) <sup>a</sup> |      |      |      | Cost<br>(\$)/Ton |
|-----------------|---------------------------------|------|------|------|------------------|
|                 | C                               | Si   | Mn   | Cr   |                  |
| Pig iron        | 4.2                             | 2.25 | 0.8  | —    | 58               |
| Silvery pig     | —                               | 15.0 | 4.5  | 10.0 | 120              |
| Ferrosilicon #1 | —                               | 45.0 | —    | —    | 128              |
| Ferrosilicon #2 | —                               | 42.0 | —    | —    | 120              |
| Master alloy #1 | —                               | 18.0 | 60.0 | —    | 200              |
| Master alloy #2 | —                               | 30.0 | 9.0  | 20.0 | 260              |
| Master alloy #3 | —                               | 25.0 | 33.0 | 8.0  | 238              |
| Silicon carbide | 15.0                            | 30.0 | —    | —    | 160              |
| Steel scrap #1  | 0.4                             | —    | 0.9  | —    | 39               |
| Steel scrap #2  | 0.1                             | —    | 0.3  | —    | 30               |
| Steel scrap #3  | 0.1                             | —    | 0.3  | —    | 33               |

<sup>a</sup> Balance Fe.

## Composition Limits and Other Constraints

- $3.2 \leq \text{w/o C} \leq 3.5$
- $2.7 \leq \text{w/o Si} \leq 3.0$
- $1.4 \leq \text{w/o Mn} \leq 1.6$
- $0.3 \leq \text{w/o Cr} \leq 0.45$
- SiC  $\leq 0.01$  ton
- Steel scrap #1  $\leq 0.3$  ton
- Steel scrap #2  $\leq 0.3$  ton
- Steel scrap #3  $\leq 0.3$  ton
- Total steel scrap  $\leq 0.3$  ton
- Total weight of charge is to be one ton.

Write a computer program which will minimize the cost per ton of charge while maintaining the above constraints.

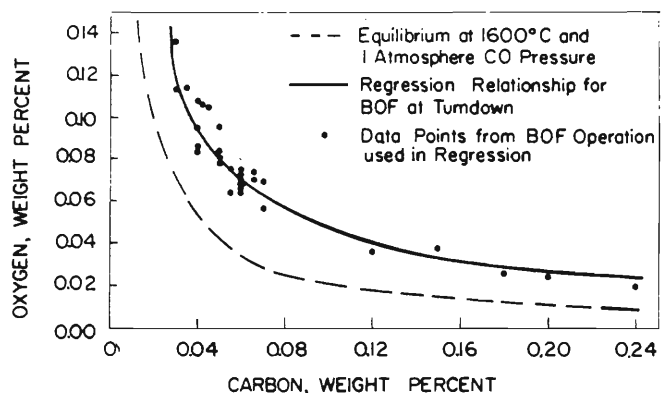


Fig. B-11. Carbon-Oxygen relationship in BOF steelmaking.

## Method of Solution—Problem 10

This problem can be solved using a Simplex routine. A computer program could consist of a Main Program which calls on a Subroutine to carry out matrix manipulations according to the Simplex technique. A computer program using this approach is presented, as adopted from Carnahan et al.<sup>1</sup> and including modifications suggested by Simonnard.<sup>2</sup>

The following notation is used to represent the mass of each material in the charge, expressed in tons:

- $X(1)$  = Pig iron,
- $X(2)$  = Silvery pig,
- $X(3)$  = Ferrosilicon #1,
- $X(4)$  = Ferrosilicon #2,
- $X(5)$  = Master alloy #1,
- $X(6)$  = Master alloy #2,
- $X(7)$  = Master alloy #3,
- $X(8)$  = Silicon carbide,
- $X(9)$  = Steel scrap #1,
- $X(10)$  = Steel scrap #2,
- $X(11)$  = Steel scrap #3.

Converting the real variables to those of the program and setting up the constraints, one obtains:

## Carbon balance.

$$4.2X(1) + 15X(8) + 0.4X(9) + 0.1X(10) + 0.1X(11) \geq 3.2.$$

$$4.2X(1) + 15X(8) + 0.4X(9) + 0.1X(10) + 0.1X(11) \leq 3.5.$$

<sup>1</sup> B. Carnahan, private communication, University of Michigan, 1967.

<sup>2</sup> M. Simonnard, *Linear Programming*, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1960.

## Silicon balance.

$$2.25X(1) + 15X(2) + 45X(3) + 42X(4) + 18X(5) + 30X(6) + 25X(7) + 30X(8) \geq 2.7.$$

$$2.25X(1) + 15X(2) + 45X(3) + 42X(4) + 18X(5) + 30X(6) + 25X(7) + 30X(8) \leq 3.0.$$

## Manganese balance.

$$0.8X(1) + 4.5X(2) + 60X(5) + 9X(6) + 33X(7) + 0.9X(9) + 0.3X(10) + 0.3X(11) \geq 1.4.$$

$$0.8X(1) + 4.5X(2) + 60X(5) + 9X(6) + 33X(7) + 0.9X(9) + 0.3X(10) + 0.3X(11) \leq 1.6.$$

## Chromium balance.

$$10X(2) + 20X(6) + 8X(7) \geq 0.3.$$

$$10X(2) + 20X(6) + 8X(7) \leq 0.45.$$

## Other constraints.

$$X(8) \leq 0.01,$$

$$X(9) \leq 0.3,$$

$$X(10) \leq 0.3,$$

$$X(11) \leq 0.3,$$

$$X(9) + X(10) + X(11) \leq 0.3,$$

$$X(1) + X(2) + \dots + X(11) = 1.0.$$

This approach is designed to handle only the " $\leq$ " and " $=$ " type constraints, so a slack variable must be subtracted from each of the " $\geq$ " type constraints. The method automatically adds a slack variable to the " $\leq$ " type constraints and an artificial variable to the " $=$ " type constraints. This results in the following constraints:

$$4.2X(1) + 15X(8) + 0.4X(9) + 0.1X(10) + 0.1X(11) - X(12) + X(16) = 3.2.$$

$$4.2X(1) + 15X(8) + 0.4X(9) + 0.1X(10) + 0.1X(11) + X(17) = 3.5.$$

$$2.25X(1) + 15X(2) + 45X(3) + 42X(4) + 18X(5) + 30X(6) + 25X(7) + 30X(8) - X(13) + X(18) = 2.7.$$

$$2.25X(1) + 15X(2) + 45X(3) + 42X(4) + 18X(5) + 30X(6) + 25X(7) + 30X(8) + X(19) = 3.0.$$

$$0.8X(1) + 4.5X(2) + 60X(5) + 9X(6) + 33X(7) + 0.9X(9) + 0.3X(10) + 0.3X(11) - X(14) + X(20) = 1.4.$$

$$0.8X(1) + 4.5X(2) + 60X(5) + 9X(6) + 33X(7) + 0.9X(9) + 0.3X(10) + 0.3X(11) + X(21) = 1.6.$$

$$10X(2) + 20X(6) + 8X(7) - X(15) + X(22) = 0.3$$

$$10X(2) + 20X(6) + 8X(7) + X(23) = 0.45,$$

$$X(8) + X(24) = 0.01,$$

$$X(9) + X(25) = 0.3,$$

$$X(10) + X(26) = 0.3,$$

$$X(11) + X(27) = 0.3,$$

$$X(9) + X(10) + X(11) + X(28) = 0.3,$$

$$X(1) + X(2) + \dots + X(11) + X(29) = 1.0,$$

where  $X(1), X(2), \dots, X(29) \geq 0$ ;  $X(16), X(18), X(20), X(22)$ , and  $X(29)$  are artificial variables;  $X(12), \dots, X(15), X(17), X(19), X(21), X(23), \dots, X(28)$  are slack variables.

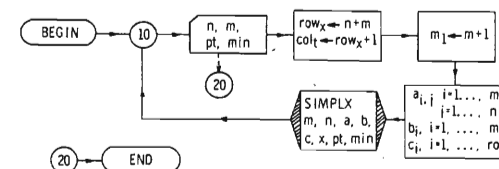
The objective function to be minimized is

$$P = 58X(1) + 120X(2) + 128X(3) + 120X(4) + 200X(5) + 260X(6) \\ + 238X(7) + 160X(8) + 39X(9) + 30X(10) + 33X(11) \\ + M(X(16) + X(18) + X(20) + X(22) + X(29)).$$

where  $M$  is some arbitrarily large value so as to force the artificial variables out of the solution. The cost coefficients of the slack variables are 0, as it costs nothing to not use part of a stockpile.

Symbol Table—Problem 10

| Algebraic Symbol | Definition                                                                                     | FORTRAN Symbol |
|------------------|------------------------------------------------------------------------------------------------|----------------|
| $n$              | Number of variables in the original problem                                                    | $N$            |
| $m$              | Number of constraints                                                                          | $M$            |
| $a$              | The $m \times n$ matrix of constraint coefficients                                             | $A$            |
| $b$              | The $m$ -element vector which contains the right-hand side of the constraint equations         | $B$            |
| $c$              | The $n + m$ vector of cost coefficients                                                        | $C$            |
| $x$              | The $n + m$ vector of solutions                                                                | $X$            |
| $row_x$          | $n + m_1$ used for the maximum length of $c$                                                   | $ROWX$         |
| $col_i$          | $n + m + 1$ , used by the subprogram for the number of columns in the full (augmented) tableau | $COLT$         |
| $m_1$            | $m + 1$ , used by the subprogram for the number of rows in the full (augmented) tableau        | $M1$           |
| $pt$             | A logical variable used to determine if all intermediate results are to be printed             | $PT$           |
| $min$            | A logical variable used to determine if this is a minimization or maximization problem         | $MIN$          |



Flow Chart—Problem 10. Flow diagram for computation of linear programming optimization.

The program requires as data the  $X$  coefficients, the composition limits, the other constraining limits, and the cost coefficients.

#### FORTRAN Listing—Problem 10

#### FORTRAN Listing—Main Program

```

DIMENSION A(30,80),B(30),C(30),X(30)
COMMON M1,COLT,ROWX
INTEGER ROWX,COLT
LOGICAL PT,MIN
10 READ (5,500,END=20) N,M,PT,MIN
   ROWX=N+M
   COLT=ROWX+1
   M1=M+1
   READ (5,510) ((A(I,J),J=1,N),I=1,M),(B(I),I=1,M),(C(I),I=1,ROWX)
   CALL SIMPLX(M,N,A,B,C,X,PT,MIN)
   GO TO 10
20 CALL SYSTEM
500 FORMAT (2I4,2L3)
510  FORMAT ((12F6.2))
999  FORMAT (1H0)
END

```

#### FORTRAN Listing—Subroutine SIMPLX

```

SUBROUTINE SIMPLX(M,N,A,B,C,X,PT,MIN)
REAL LIMIT
INTEGER ROWS,COLT,ROWX,BASIS,BAS
DIMENSION BASIS(30),A(30,80),B(30),C(30),X(30),TABLO(30,80)
COMMON M1,COLT,ROWX
LOGICAL PT,MIN
IF (M.GT.30.OR.ROWX.GT.80) WRITE (6,600)
DO 10 I=1,M1
DO 10 J=1,COLT
DO 20 I=1,M
DO 30 J=1,N
10 TABLO(I,J)=0.
TABLO(I,N+1)=1.
TABLO(I,COLT)=B(I)
20 TABLO(M1,COLT)=TABLO(M1,COLT)+B(I)*C(N+1)
BASIS(I)=N+1
DO 40 J=1,N
TABLO(M1,J)=-C(J)
DO 40 I=1,M

```



## Output (Results)—Problem 10

THE RESULTS AND FINAL TABLEAU ARE:

ITERATIONS REQUIRED TO ATTAIN SOLUTION = 10

THE INDICES OF THE CURRENT BASIS VECTOR ARE:

1  
17  
4  
19  
5  
21  
2  
23  
8  
25  
26  
27  
28  
10

THE OPTIMUM SOLUTION IS: 56.240

THE FINAL MIXTURE IS: X( 1) = 0.721  
X( 2) = 0.030  
X( 3) = 0.0  
X( 4) = 0.003  
X( 5) = 0.010  
X( 6) = 0.0  
X( 7) = 0.0  
X( 8) = 0.010  
X( 9) = 0.0  
X(10) = 0.225  
X(11) = 0.0  
X(12) = 0.0  
X(13) = 0.0  
X(14) = 0.0  
X(15) = 0.0  
X(16) = 0.0  
X(17) = 0.300  
X(18) = 0.0  
X(19) = 0.300  
X(20) = 0.0  
X(21) = 0.200  
X(22) = 0.0  
X(23) = 0.150  
X(24) = 0.0  
X(25) = 0.300  
X(26) = 0.075  
X(27) = 0.300  
X(28) = 0.075  
X(29) = 0.0

## Discussion of Results—Problem 10

$M$ , the cost of the artificial variables, was chosen as \$1000 for this problem. All of these variables were driven from the final tableau, i.e. took on zero values. As the calculation approached an optimum, in this case, minimum cost, the total cost of raw materials to produce a ton of cast iron decreased.

The computer output is not shown, as the matrix is very large ( $30 \times 15$ ). Con-

verted to the original variables, the solution is:

| Material        | w/o    |
|-----------------|--------|
| Pig iron        | = 72.1 |
| Silvery pig     | = 3.0  |
| Ferrosilicon #1 | = 0    |
| Ferrosilicon #2 | = 0.3  |
| Master alloy #1 | = 1.0  |
| Master alloy #2 | = 0    |
| Master alloy #3 | = 0    |
| Silicon carbide | = 1.0  |
| Steel scrap #1  | = 0    |
| Steel scrap #2  | = 22.5 |
| Steel scrap #3  | = 0    |

Cost per ton of charge = \$56.24.

This program computes the optimum charge to a melting unit on the basis of cost of raw materials. Electric arc and induction melting operations can be monitored similarly. The use of continually up-dated cost information in conjunction with an optimization program of this type can be a valuable operator guide in charge control of melting furnaces.

## INDEX

- Activity, 39
- Activity Coefficients, Table A-III, 292-295
  - Henrian, 42
  - in metal salt solutions, 182
- Adiabatic flame temperature, 314-327
- Agglomeration, 7
- Agitation
  - in leaching of slimes, 178
- Aluminum, 3
  - carbothermic reduction, 50
  - deoxidation of steel, 106-109
  - hydrometallurgy (see Bayer Process)
  - minerals, 3
  - nitride, 147-148
  - production, 5, 207-211
  - source, 2
- Analog computer, 261, 265-268
- Anglesite, 3
- Anode
  - copper, 217, 222
  - effect, 211
  - inert, in electrowinning, 224-225
  - mud, 221
  - preparation, 215
- Antimony, 4, 122, 215, 225
  - minerals, 4
- Arc melting, 230-231
- Argentite, 3
- Argon degassing, 149, 153
- Arsenic, 122, 218, 225
- Autogenous smelting, 82
  
- Baddeleyite, 3
- Bauxite, 2
- Bayer Process, 195-196
- Beneficiated materials, 79-80
- Beryllium, 4, 207
  - minerals, 4
- Bessemer
  - copper converting, 83
  - steelmaking, 88-92, 233
- Betterton process, 123-124
- Betts process, 224
- Biot number, 350
- Bismuth, 135
- Blast furnace
  - energy balance, 79
  - iron, 72-80, 314
  - lead, 71-72
  - smelting, 71-80
  - stoichiometry, 78-79
- Blister copper, 83, 87
  - analysis, 222
- Boudouard Reaction, 32-33
- Boundary layer model, 151-152
  
- Cadmium, 4, 55, 135, 225
  - minerals, 4
- Calaverite, 3
- Calcination, 22-24
- Calcium, 208
- Carbides, Table A-II, 288-289
  - stability, 38
- Carbon-oxygen equilibrium in steel furnaces, 146-147, 374-381
- Carbothermic reduction, 30-33, 50, 52-55
- Carnotite, 3
- Cassiterite, 3
- Castner cell, 214
- Cathode
  - analysis of copper, 222
  - refining of copper, 223-224
  - starting sheets, 218-219
- Cell potential, 203-204
- Cell voltage, 204-207
- Cementation, 179, 224
  - copper, 175, 187-189
- Cerargyrite, 3
- Cerium, 208
- Cerussite, 3
- Chalcocite, 3
- Chalcopyrite, 3
- Checkers, 232-233
- Chill zone, 246-247, 252
- Chlorides
  - reducibility, 35-38
- Chromite, 3
- Chromium, 3
  - chloride reduction, 35-38
  - minerals, 3
- Clausius-Clapeyron Equation, 131-133
- Cobalt, 4, 215, 225
  - hydrogen reduction, 184-187

- hydrometallurgy, 195
- minerals, 4
- roasting, 10-11
- Columnar zone, 247-248, 252
- Compound gases, 146-147
- Computer applications, 261-286
- Continuous casting, 254-257
- Cooling
  - of pig iron, 328-334
  - of slab, 366-373
- Copper, 1, 3
  - activity in liquid iron, 41, 43
  - anodes, 217
  - converter tuyere, heat flow, 345-353
  - converting, 82-87
  - electrowinning, 224
  - hydrometallurgy, 191
  - leaching, 177
  - minerals, 3
  - native, 3
  - production, 5
  - refining, 215-224
  - roasting, 10-11
  - smelting, 67-71
  - solidification of, 252-253
  - source, 2
- Correlation coefficient, product moment, 376, 378-380
- Counter current decantation (C.C.D.), 178
- Covellite, 3
- Cropped ingot, 250
- Cupola, 233-236, 237-241
  - energy balance, 237-241
  - optimization of charge, 381-389
  - reference period data, 238-239
- Cuprite, 3
- Degassing, 141-167
  - inert flush, 148-155
  - methods, 162
  - vacuum, 155-166
- Deoxidation, 105-109
- Desulfurization
  - by vacuum treatment, 156-157, 159
  - of molten pig iron, 109-111
- Diaspore, 3
- Diatomic gases, 141-142
- Digital computer, 261-268
- Dilute solution behavior, 40
- Dissolved gasses, 141-148
  - effect on ingot structure, 250-253
- Distillation, 130-141
  - equilibrium, 135-137
  - molecular, 137-139
- Dolomite, 3
- Dore furnace, 221
- Dortmund-Hörder Degassing Process, 162-165
- Dow Magnesium Cell, 211-214
- Downs Cell, 214
- Drag coefficient, 154
- Drossing of liquid lead, 116-119, 122
- Dwight Lloyd sintering, 71
- Dynamic programming, 277
- Electric furnace steelmaking, 98-99
- Electrochemical equivalent, 202
- Electrode arc melting, 230-231
- Electrode potentials, 180-185, 303
  - metal-metal ion, 181
  - oxidation reactions, Table A-VIII, 303
- Electrolysis
  - of fused salts, 207-214
  - principles, 201-207
- Electrolytic refining, 214-224
  - treatment of insolubles, 221
- Electrometallurgy, 5-6, 201-227
- Electrowinning, 224-225
- Ellingham diagram, 27-28
- Engineering relationships for design of
  - sintering operations, 19
- Enthalpy increments, 307-313
  - (see heat content)
- Equilibrium process for degassing, 148-151
- Error function, Table A-X, 305-306
- Extractive metallurgy
  - definition, 4-5
- Faraday's Laws, 202-203
- Finite difference approximation, 366-371
  - explicit form, 367-371
  - implicit form, 371
- FIOR (fluid-iron-ore-reduction) process, 60
- Flash smelting, 81-82
- Flotation of separating phase, 115-116
- Flow equation, 358
- Franklinite, 3
- Free energy, 39
  - equations for sulfation reactions, Table A-I, 287-288
  - of formation of compounds, Table A-II, 288-291
  - of nucleus formation, 113-114
  - of solution of elements in iron, Table A-IV, 296
  - of solution of gas forming solutes, 146
- Fuel requirements, 18
- Fume, 94
- Fuming, 55

- Furnace roof
  - heat loss, 354-357
- Fused salt electrolysis, 207-214
- Galena, 3, 72
- Gangue, 1
- Garnierite, 3
- Gas cleaning, 94-96, 239
  - oxygen converter gas recovery process, O-G Process, 95
- Gas over-voltage, 207
- Gaseous reduction
  - kinetics, 185-187
- Gibbsite, 3
- Gold, 1, 3, 215, 221-223, 225
  - amalgamation, 191
  - hydrometallurgy, 191-193
  - leaching, 177
  - minerals, 3
  - native, 3
  - recovery from leaching solutions, 187
- Growth of separating phase, 115-116
- H-Iron Process, 60
- Half cell reactions, 201-202
- Half-Interval Method, 317-321
- Hall cell, 208-211
- Hazelett process, 257
- Heap leaching, 177-178
- Heat
  - of reaction, 335
  - of solution, 335
- Heat content, of several metals, Table A-IV, 304
- Heat flow, unsteady state, 366-373
- Heat losses, 236-237
  - from furnace roof, 354-357
- Heat removal
  - effect on ingot structure, 246-247
- Hematite, 3, 19-20, 57, 74
- Henrian activity, 41-42
- Henry's Law, 40-42, 136
- Heroult Process (see Hall Cell)
- Hoeganaes Process, 60
- Hot top, 250
- Hydrogen
  - electrode, 180-181
  - reduction of metal ions, 182-185
- Hydrometallurgy, 5-6, 175-199
  - of cobalt, 195
  - of copper, 195
  - of nickel, 195
- HyL Process, 60
- Ilmenite, 3
- Imperial Smelting Process, 52, 54, 72, 116, 120, 121
- Inclusions
  - exogenous, 253
  - indigenous, 253
- Induction melting, 229-230
- Indurating, 19
- Ingot
  - defects, 253
  - structure, 246-253
- Ingotism, 253
- Interaction
  - coefficients in iron, Table A-V, 297
  - non ferrous parameters, Table A-VI, 298-301
  - parameters, 46-47
- Ion exchange, 190-191
- Iron, 3, 218, 225
  - minerals, 3
  - ores, 1
  - production, 5
  - source, 1-2
- Iron blast furnace, 72-80, 314
  - chemistry, 74-78
  - operation improvements, 79-80
  - stoichiometry, 78-79
- Kaldo Process, 95-97
- Kaolinite, 3
- Killed steel, 248-250
- Knapsack sodium cell, 213
- Kroll Process, 47-48
- Krupp-Renn Process, 60
- Ladle
  - bottom pouring, 358-365
  - transfer (Pugh-type), 328-334
- Langmuir Equation, 137-138, 140
- Langmuir-Knudsen Equation, 138-139
- Leaching, 176-179
  - of sulfides, 178-179
- Lead, 3, 135
  - blast furnace smelting, 71-72
  - minerals, 3
  - production, 5
  - refining, 111-113, 116-117, 119-121, 224
  - roasting reactions, 7-8, 11
  - source, 2
- Lead-copper system, 116, 118
- Lead-silver system, 116-117
- Least squares
  - (see linear regression)
- Lime boil, 91
- Limonite, 3

- Linear programming, 274-277, 381-389
- Linear regression, 374-380
  - normal equations, 375
  - product moment correlation coefficient, 376
  - variance, 376
- Liquid phase separation, 116-122
- Lithium, 208
- Logic flowchart, 306-307
- Magnesite, 3
- Magnesium, 3, 29-30, 49-50
  - carbothermic reduction, 50
  - chloride reduction, 38
  - chlorination, 12
  - minerals, 3
  - production, 5, 207, 211-214
  - source, 1
- Magnetite, 3, 19-20, 57-58, 67, 84, 352
- Manganese, 3
  - electrowinning, 225
  - minerals, 3
  - source, 4
- Mass-energy balance, 237-241
- Matte, 67-71
- Melting, 229-241
  - thermal requirements, 229
- Melting units, 229-235
- Mercury, 4, 55
  - minerals, 4
- Metal composition
  - effect on ingot structure, 247-248
- Michigan Terminal System (MTS), 307
- Millerite, 3
- Mineral engineering
  - definition, 4
- Minerals, 3-4
- Moebius cell, 222-223
- Molybdenite, 3
- Molybdenum, 3
  - minerals, 3
- Molybdate, 3
- Mond(Carbonyl) Process, 55-56
- Monte Carlo Technique, 273
- Native copper, gold, silver, 3
  - form, 1
- Nernst Equation, 204, (also 180)
- Newton's Law of Cooling, 369
- Nickel, 3, 218
  - hydrogen reduction, 184-187
  - hydrometallurgy, 195
  - minerals, 3
  - Mond (carbonyl) Process, 55-56
  - refining, 224
  - roasting, 9-10
  - smelting, 70-71
- Nitrides, Table A-II, 289
  - stability, 38
- Nitrogen
  - in iron, 142-145
- Nonideal solutions, 39
- Normal equations, 375
- Nozzle
  - laval, 93-94
  - pouring, 242-243, 358-365
- Nucleation, 113-115
- Nu-iron Process, 60
- Ohmic resistance, 205
- Open hearth, basic, 232-233
  - process, 88, 91-92
  - shop, 272-273
- Optimization, 274-277, 381-389
- Ore boil, 91
- Ores, 1
- Orford Process, 70
- Over-voltage, 207
- Oxides, Table A-II, 289-291
  - thermodynamic stability, 27-33
- Oxygen converter gas recovery process, 95
- Oxygen enrichment, 79-80, 322-327
- Oxygen steelmaking, 91-98, 335-345
- Palladium, 215, 221, 223
- Parkes Process, 111-113, 225
- Patronite, 3
- Pattinson Process, 116
- Pelletizing, 7, 19-23
- Pellets, 20-21, 80
- Pentlandite, 3
- Percolation, 178
- pH, equilibrium values, 184
- Pidgeon Process, 29-30, 49-50
- Pierce-Smith Converter, 83-85
- Pipe, 249-251
- Platinum, 215, 221, 223
- Poisson distribution, 270
- Polarization, 205-207
- Potassium, 208
- Pourbaix Diagram, 29-30
- Pourbaix-Ellingham Diagram, 30-32
- Pouring
  - of metal, 242-244
  - pressure, 257
  - simulation, 357-365
  - vacuum, 364-365
- Precipitation stoichiometry, 108-109
- Predominance Area Diagram, 9-11
- Pressure leaching, 178
- Processing operations
  - lead-silver system, 116

- Production of metals, 5
- Pyrolusite, 3
- Pyrometallurgy, 5-6, 7-173
- Queueing theory, 268-274
- R-N Process, 60
- Raoult's Law, 39
- Rayleigh Equation, 135-137
- Reduction
  - direct, of iron ore, 56-60
  - from aqueous solution, 179-180
- Refining
  - of copper-cathodes, 223-224
  - of tin, 123
- Refining systems
  - parallel, 215-216
  - series, 215-216
- Relaxation calculation, 345-353
- Residence time, 152-155
- Resistance melting, 232
- Reverberatory smelting, 67-71
- Reversible cell potential, 205
- Rhodochrosite, 3
- Rhodonite, 3
- Rimmed steel, 252
- Roasting, 7-16
  - chloridizing roast, 12
  - dead roast, 8
  - flash, 13-14
  - fluid bed, 14-15
  - hearth, 12-13
  - processes, 12-16
  - sinter roast, 16
  - sweet roast, 8
  - thermodynamics, 7-11
  - volatilization, 12-13
- Rotor Process, 95-97
- Ruhrstahl-Heraus Process, 162, 165-166
- Rutile, 3
- Scheelite, 3, 49
- Scrap requirement for oxygen steelmaking, 335-345
- Secondary metal refining, 130
- Seeding, 115
- Selenium, 221-222
- Semikilled ingot, 252
- Sensible heat, 236, 237, 335
  - (see enthalpy increment)
- Shrinkage
  - effect on ingot structure, 249-250
- Siderite, 3
- Sieverts' Law, 141-143
- Silicon
  - activity in liquid iron, 40, 42
- Silver, 1, 3, 215, 221-223, 225
  - hydrometallurgy, 191
  - leaching, 177
  - minerals, 3
  - native, 3
  - removed from zinc, 111-113
- Simplex technique
  - (see linear programming)
- Simulation, 278-281
- Sintering, 16-19
  - Dwight Lloyd Sintering Machine, 16-19
  - self-fluxing sinter, 17, 74
- Slab, cooling of, 366-373
- Slag
  - blast furnace smelting, 71-80
  - copper converting, 82-87
  - reverberatory smelting, 67-71
  - steelmaking, 87-99
- Slime
  - copper cell analysis, 222
- Smelting
  - autogenous, 81-82
  - blast furnace, 71-80
  - copper, 70
  - copper-nickel ores, 70-71
  - reverberatory, 67-71
  - tin, 70
- Sodium production, 208, 213-214
- Softening of lead, 122-123
- Solidification, 244-257
  - rate of, 244-246
- Solute
  - interactions, 46-47
- Solutions
  - conversion of standard states, 43-47
  - dilute solution behavior, 40-42
  - free energy and activity, 39
  - metallic, 38-47
  - non ideal, 39-40
  - thermodynamics of metallic, 39
- Solvent extraction, 189-190
- Specific heat, 307
- Speiss, 72
- Sphalerite, 3
- Splash condenser, 116, 121
- Spray steelmaking, 97-98
- Standard deviation, 94, 376-380
- Standard state conversion, 43-45
- Stannite, 3
- Starter button, 230
- Starting sheets, 217
- Strategic-Udy Process, 60
- Steelmaking, 87-99

- Stochastic processes, 273, 376
- Streamlined flow model, 157-161, 163
- Sulfates, 8; Table A-I, 287-288
- Sulfides, Table A-II, 291
  - thermodynamic stability, 33-35
- Sylvanite, 3
- System engineering, 266
  
- Taconite, 2, 80
- Tank house
  - log, 222
  - practice, 218-220
- Tantalum, 30-32
- Taylor series expansion, 46, 367
- Tellurium, 221-222
- Temperature drop
  - during degassing, 167
  - in pouring, 243-244
- Theory of games, 273
- Thermodynamics of Reduction
  - of metals from aqueous solution, 179-180
- Thomas process, 88, 90-91
- Thum cell, 222-223
- Tin, 3, 215
  - minerals, 3
  - production, 2-4
  - refining of, 123
  - removal from lead, 122-123
  - smelting, 70
  - source, 2-4
- Titanium, 3, 47-48
  - melting, 230
  - minerals, 3
  - source, 4
- Transportation technique, 276
- Tungsten, 3
  - minerals, 3
  - production, 48-49
- Tuyere, 71, 77, 83-85, 314-327, 345-353
  - zone, 315
  
- Uranium, 4
  - anionic removal, 193
  
- hydrometallurgy, 193
- minerals, 4
  
- Vacuum
  - degassing, 155-166
  - dezincing, 140
  - pouring, 363-365
- Vanadinite, 3
- Vanadium, 3
  - minerals, 3
- Vapor pressure of liquid metals, 132; Table A-VII, 302
- Variance, 376
- Volatility, relative, 133-135
- Volatilization, during roasting, 12
  
- Waelz Process, 55
- Walker Casting Machine, 215, 218
- Weatheril Process, 55
- White metal, 82
- Wiberg Process, 60
- Williams continuous process, 111
- Wohlwill Process, 223
- Wolframite, 3, 48-49
- Wüstite, 57-58
  
- Zinc, 3, 30-31, 51-55, 218, 225
  - blende, 2
  - electrothermic process, 53
  - electrowinning, 224-225
  - fuming, 55
  - hydrometallurgy, 194-195
  - leaching, 177
  - minerals, 3
  - production, 5
  - recovery, 72, 116-117, 121
  - retort process, 51-55
  - roasting, 8, 11
  - source, 2
- Zincite, 3
- Zircon, 3
- Zirconium, 3, 48
  - melting, 230
  - minerals, 3
- Zone refining, 124-130