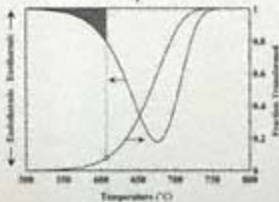


THERMAL ANALYSIS

OF MATERIALS



ROBERT F. SIEVER BOOK

THERMAL ANALYSIS OF MATERIALS

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Dedicated to my mother, June

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PREFACE

Technology changes so fast now, it must be frustrating for design engineers to see their products become out of date shortly after they hit the market. With the advent of inexpensive personal computers and microprocessors over the past decade, there has been a virtual explosion of new thermal analysis companies and products. The level of instrument sophistication has practically left the scientist/technician out of the loop; after popping the specimen in the machine, an elegant multi-colored printout completely describes a series of characteristics and properties of the material under investigation.

There is an inherent danger in trusting black boxes of this sort, and it is the intent of this monograph to elucidate their inner workings and provide some intuition into their operation. I have avoided being encyclopedic in enumerating pertinent journal and product literature. Rather, the narrative attempts to develop important underlying principles. The design and optimal use of thermal analysis instrumentation for materials' property measurements is emphasized, as necessary, based on atomistic models depicting the thermal behavior of materials.

This monograph, I believe, is unique in that it covers the broader topic of pyrometry; the latter chapters on infrared and optical temperature measurement, thermal conductivity, and glass viscosity are generally not treated in books on thermal analysis but are commercially and academically important. I have resisted the urge to elaborate on some topics by using ex-

tensive footnoting, in an attempt to maintain the larger picture in the flow of the main body of the text.

This should be a useful text for a junior or senior collegiate materials engineering student, endeavoring to learn about this topic for the first time, or corporate R & D personnel, attempting to decipher what all the bells and whistles of their new, quite expensive, instrument will do for them. By basing this treatment on the elementary physical chemistry, heat transfer, materials properties, and device engineering used in thermal analysis, it is my hope that what follows will be a useful textbook and handbook, and that the information presented will remain “current” well into the future.

I would like to acknowledge those who have assisted in the preparation of this work: Rita M. Slilaty and Kathleen C. Basile for copyediting of earlier versions of the manuscript, as well as Wendy Schechter and Andrew Berin for later versions. Dr. Jen Yan Hsu for figure preparation, and my colleagues at Georgia Tech: Drs. Joe K. Cochran, D. Norman Hill, and James F. Benzel for technical editing and helpful discussions. I am grateful to Professor Tracy A. Willmore for introducing me to the subject of pyrometry during my undergraduate years at the University of Illinois at Urbana-Champaign.

Robert F. Speyer

CONTENTS

PREFACE	v
1 INTRODUCTION	1
1.1 Heat, Energy, and Temperature	2
1.2 Instrumentation and Properties of Materials . .	5
2 FURNACES AND TEMPERATURE MEASUREMENT	9
2.1 Resistance Temperature Transducers	9
2.2 Thermocouples	12
2.3 Commercial Components	18
2.3.1 Thermocouples	18
2.3.2 Furnaces	19
2.4 Furnace Control	23
2.4.1 Semiconductor-Controlled Rectifiers . .	24
2.4.2 Power Transformers	26
2.4.3 Automatic Control Systems	28
3 DIFFERENTIAL THERMAL ANALYSIS	35
3.1 Instrument Design	35
3.2 An Introduction to DTA/DSC Applications . .	40
3.3 Thermodynamic Data from DTA	46
3.4 Calibration	49
3.5 Transformation Categories	49
3.5.1 Reversible Transformations	49
3.5.2 Irreversible Transformations	60
3.5.3 First and Higher Order Transitions . . .	63
3.6 An Example of Kinetic Modeling	66
3.7 Heat Capacity Effects	70

3.7.1	Minimization of Baseline Float	71
3.7.2	Heat Capacity Changes During Transformations	75
3.7.3	Experimental Determination of Specific Heat	79
3.8	Experimental Concerns	80
3.8.1	Reactions With Gases	80
3.8.2	Particle Packing, Mass, and Size Distri- bution	81
3.8.3	Effect of Heating Rate	85
4	MANIPULATION OF DATA	91
4.1	Methods of Numerical Integration	91
4.2	Taking Derivatives of Experimental Data . . .	95
4.3	Temperature Calibration	99
4.4	Data Subtraction	102
4.5	Data Acquisition	105
5	THERMOGRAVIMETRIC ANALYSIS	111
5.1	TG Design and Experimental Concerns	111
5.2	Simultaneous Thermal Analysis	120
5.3	A Case Study: Glass Batch Fusion	125
5.3.1	Background	126
5.3.2	Experimental Procedure	126
5.3.3	Results	128
5.3.4	Discussion	133
6	ADVANCED APPLICATIONS OF DTA AND TG	143
6.1	Deconvolution of Superimposed Endotherms . .	143
6.1.1	Background	143
6.1.2	Computer Algorithm	144
6.1.3	Models and Results	146
6.1.4	Remarks	151
6.1.5	Sample Program	152
6.2	Decomposition Kinetics Using TG	159

7	DILATOMETRY AND INTERFEROMETRY	165
7.1	Linear vs. Volume Expansion Coefficient	166
7.2	Theoretical Origins of Thermal Expansion	168
7.3	Dilatometry: Instrument Design	169
7.4	Dilatometry: Calibration	173
7.5	Dilatometry: Experimental Concerns	175
7.6	Model Solid State Transformations	179
7.7	Interferometry	186
7.7.1	Principles	187
7.7.2	Instrument Design	191
8	HEAT TRANSFER AND PYROMETRY	199
8.1	Introduction to Heat Transfer	199
8.1.1	Background	199
8.1.2	Conduction	199
8.1.3	Convection	203
8.1.4	Radiation	205
8.2	Pyrometry	210
8.2.1	Disappearing Filament Pyrometry	211
8.2.2	Two Color Pyrometry	216
8.2.3	Total Radiation Pyrometry	218
8.2.4	Infrared Pyrometry	220
9	THERMAL CONDUCTIVITY	227
9.1	Radial Heat Flow Method	227
9.2	Calorimeter Method	231
9.3	Hot-Wire Method	234
9.4	Guarded Hot-Plate Method	240
9.5	Flash Method	242
10	VISCOSITY OF LIQUIDS AND GLASSES	251
10.1	Background	251
10.2	Margules Viscometer	255
10.3	Equation for the Rotational Viscometer	257
10.4	High Viscosity Measurement	262
10.4.1	Parallel Plate Viscometer	262

10.4.2 Beam Bending Viscometer	265
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APPENDIXES

A INSTRUMENTATION VENDORS	269
A.1 Thermoanalytical Instrumentation	269
A.2 Furnace Controllers and SCR's	270
A.3 Heating Elements	271
A.4 Optical Pyrometers	271
B SUPPLEMENTARY READING	273
B.1 Temperature Measurement, Furnaces, and Feedback Control	273
B.2 DTA, TG, and Related Materials Issues	274
B.3 Manipulation of Data	276
B.4 Dilatometry and Interferometry	276
B.5 Thermal Conductivity	277
B.6 Glass Viscosity	278
INDEX	279

THERMAL ANALYSIS OF MATERIALS

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Chapter 1

INTRODUCTION

This monograph provides an introduction to scanning thermoanalytical techniques such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), dilatometry, and thermogravimetric analysis (TG). Elevated temperature pyrometry, as well as thermal conductivity/diffusivity and glass viscosity measurement techniques, described in later chapters, round out the topics related to thermal analysis. Ceramic materials are used predominantly as examples, yet the principles developed should be general to all materials.

In differential thermal analysis, the temperature difference between a reactive sample and a non-reactive reference is determined as a function of time, providing useful information about the temperatures, thermodynamics and kinetics of reactions. Differential scanning calorimetry has a similar output, but the sample energy change during a transformation is more directly measured. Dilatometry measures the expansion or contraction behavior of solid materials with temperature, useful for studying sintering, expansion matching of constituents in composites of materials or glass-to-metal seals, and solid state transformations. Thermogravimetric analysis determines the weight gain or loss of a condensed phase due to gas release or absorption as a function of temperature.

We will begin by reviewing methods of temperature measurement, furnace design, and temperature control. The instruments, how they work, what they measure, potential pit-

falls to accurate measurements, and the application of theoretical models to experimental results will then be discussed in some detail. Voluminous information on the results of thermal analysis studies of specific materials resides in the literature, especially in the two journals specifically dedicated to the topic: *Journal of Thermal Analysis* and *Thermochimica Acta*.

1.1 Heat, Energy, and Temperature

To begin, it is helpful to formalize our understanding of some commonly used words: heat, thermal energy, and temperature.

It would be inappropriate to refer to an object as having “heat”. Rather it would be stated that it is at a certain temperature or has a certain thermal energy. Heat is thermal energy in transit; heat flows across a boundary. If two objects at different temperatures are placed in thermal contact, they will, with time, reach a third equal temperature as a result of heat flowing from the higher temperature object to the colder one.

The first law of thermodynamics, which is simply a statement of the law of conservation of energy, relates energy to heat:

$$dU = dQ - dW$$

where U is the internal energy, Q is heat, and W is work. This equation states that the change in energy of a system is dependent on the heat that flows in or out of the system and how much work the system does or has done on it.

Often, slashes are put through the d 's of the differentials on the right hand side of the expression to emphasize a distinction between derivatives of energy and heat (and work): If we wish to know the (potential) energy change due to re-positioning an object from a higher to a lower position above the ground, we know it to be entirely a function of the difference in height, multiplied by mass and gravitational acceleration. The path the object traversed in going from its higher to lower position

is irrelevant to the calculation. Functions showing such path independence, such as energy, are referred to as state functions, and their derivatives are exact differentials. This concept does not hold for heat and work. The heat released by an individual, or the work done by an individual in going from one place to another would certainly depend on the path taken (e.g. a direct path versus a more scenic route). Thus, these derivatives are inexact differentials, and heat and work are path dependent functions. There is no such thing as a change in heat or a change in work, hence, the integrated form of the first law is:

$$\Delta U = Q - W$$

Under conditions where no work is done on/by the system, the change in internal energy of the system is equal to the heat flowing in or out of it.

Joule's experiments on the free expansion of an ideal gas showed that the internal energy of such a system is a function of temperature alone. For a real gas, this is only approximately true. For condensed phases, which are effectively incompressible, the volume dependence on the change in internal energy is negligible. As a result, the internal energies of liquids and solids are also considered a function of temperature alone. For this reason, the internal energy of a system may loosely be referred to as the "thermal energy".

The thermal energy of a gas is manifested as the translational motion of individual atoms or molecules. Energy is also stored in gaseous molecules by rotation and vibrations of the atoms of the molecule, with respect to one another. Solids sustain their thermal energy by the vibration of atoms about their mean lattice positions, while atoms in a liquid translate, rotate (albeit more sluggishly than gases), and vibrate. As temperature increases, these processes become more fervent.

Temperature is a constructed, rather than fundamental, entity with arbitrary units, which indicates the thermal energy of a system. A thermometer measuring the outside tempera-

ture functions via a series of materials' properties: Atoms in the air impact against the glass of the thermometer, propagating phonons (lattice vibrations) through the glass to the mercury. The increased motion and vibration of the mercury atoms, causing a net expansion of the fluid up the graduated capillary, is an indicator of the thermal energy of the gas on an arbitrary scale: degrees Fahrenheit, degrees Celsius, Kelvin, or degrees Rankine (the Kelvin analog on the Fahrenheit scale).

In the early 1700's, the Dutch scientist Gabriel Fahrenheit designed what was generally considered the first accurate mercury thermometer where 0°F was the freezing point of saturated salt solution, presumably since this condition was more reproducibly met than absolutely pure water, and 96°F was its highest value (apparently related to body temperature) [1]. Mercury was used in place of its predecessor, spirits of wine, due to its more linear thermal expansion behavior [2]. In 1742, Anders Celsius designed a scale in which the value of zero was assigned to the boiling point of pure water, and 100 was assigned to the freezing point. Later, the centigrade (the term meaning divided into 100 parts) scale used the same divisions but with the extreme values reversed. In 1948, this more familiar reversed scale was officially renamed the Celsius scale. In the early 1800's, William Thompson (Lord Kelvin) established the thermodynamic temperature scale, whereby it was proven that for a Carnot engine to be perfectly efficient, the cold reservoir must be at a specific *absolute zero* (-273.15°C) temperature.¹ Measuring the properties of ideal gases used as thermometers allows extrapolation to experimentally deter-

¹It can be shown [3] that the efficiency of a Carnot engine doing work via heat provided by a hot reservoir and rejecting waste heat into a cold reservoir, is $\eta = 1 - (Q_{\text{cold}}/Q_{\text{hot}}) = 1 - (T_{\text{cold}}/T_{\text{hot}})$. Thus for $\eta = 1$, perfect efficiency, T_{cold} must be at an absolute zero in temperature. Negative temperatures are not possible since an efficiency greater than unity is not possible. This relation can be derived explicitly using the ideal gas law, and it follows that the temperature used in the ideal gas law is based on this scale. By trapping an ideal gas (real gases at low pressures behave as ideal gases) in a capillary with mercury above it, the gas is at constant pressure. The volume of the gas can be measured at various temperatures, the latter measured on an arbitrary scale such as $^{\circ}\text{C}$. Extrapolating to zero volume establishes the absolute zero of temperature (-273.15°C).

mine the absolute zero in temperature.

Finally, the relationship between heat and temperature follows an Ohm's law form²:

$$\frac{dQ}{dt} = k'(T_2 - T_1)$$

where heat flows in response to a temperature gradient (k' being the proportionality constant), analogous to electrical current flow (dQ/dt) through a resistive medium ($1/k'$) as a result of a potential difference ($T_2 - T_1$). Perhaps the most useful definition of temperature is as a thermal potential for heat flow, just as voltage is an electrical potential for current flow. The relationship between heat flow and temperature becomes more complex than that above when non-steady state heat flow, geometries, surfaces, convection, radiation, etc., are considered. However, the general principle is still the same; heat flows as a result of a temperature difference between two regions in thermal contact.

1.2 Instrumentation and Properties of Materials

Pyrometric cones (Figure 1.1) have been in common use over the past century in the manufacture of ceramic ware. They are a series of fired mixtures of ceramic materials pointing 8° from vertical, which “droop” after exposure to elevated temperatures for a period of time. The manufacturer [4] provides a series of sixty-four cone numbers ranging from 022 (deformation at 576°C at a heating rate of 1°C/min) to 42 (over 1800°C).³ By placing a series of cones near the firing ware in a kiln, the operator can determine when firing of the ware is complete, even when the furnace temperature is only loosely controlled. The refractories industry has made cone shapes out

²This equation is valid for steady-state one-dimensional conductive heat flow.

³The lower temperature cones tend to have a high percentage of glassy phase of rapidly decreasing viscosity with increasing temperature.



Figure 1.1: Orton pyrometric cones [4].

of their materials and correlated the points of collapse under thermal processing to pyrometric cones, in order to designate their products with “pyrometric cone equivalents”. Pyrometric cones are a prime example of the use of well characterized materials for the investigation and optimization of other materials. While seeming more elegant, thermoanalytical instruments are based on the same principle.

The accurate measurement of thermal properties, e.g. heat flow through a material, energy released during a transformation, expansion upon heating, all require an underlying understanding of the instrumentation of thermal analysis. The functionality of the devices themselves, however, require calibration based on the exploitation of material properties, e.g. the thermoelectric behavior of thermocouples, or the melting points of calibration standards. The meticulous scientist must never permit accuracy of measurement to rely on elegant, computer-interfaced instrumentation, without the prior blessing of the reproducible properties of well characterized materials.

References

- [1] *The Temperature Handbook*, Volume 27, Omega Corp., Stamford, CT (1991).
- [2] T. D. McGee, *Principles and Methods of Temperature Measurement*, Wiley-Interscience, NY (1988).
- [3] W. J. Moore, *Physical Chemistry*, Fourth Ed., Prentice Hall, Englewood Cliffs, NJ, pp. 81-83 (1972).
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Chapter 2

FURNACES AND TEMPERATURE MEASUREMENT

Although there are a myriad of devices used to measure the temperature of an object, thermal analysis instruments predominantly use thermocouples, platinum resistance thermometers, and thermistors. Thus, only these items, with special emphasis on thermocouples, will be discussed.

2.1 Resistance Temperature Transducers

A sketch of the behavior of two resistance temperature transducers with increasing temperature is shown in Figure 2.1. The electrical resistance of a metal increases with temperature, since electrons in a metal, similar in behavior to the molecules in a gas, are more agitated at higher temperatures. This greater kinetic motion decreases individual electron mobility. Thus, under an applied electric field, net electron drift in response to the field is diminished. For platinum, this increase in resistivity with temperature is remarkably linear. Platinum resistance temperature detectors often consist of spirals of a very thin wire, designed to maximize the measured resistance (commonly 100Ω at 0°C). They are fragile but considered quite accurate. The Perkin-Elmer differential scanning calorimeter uses this

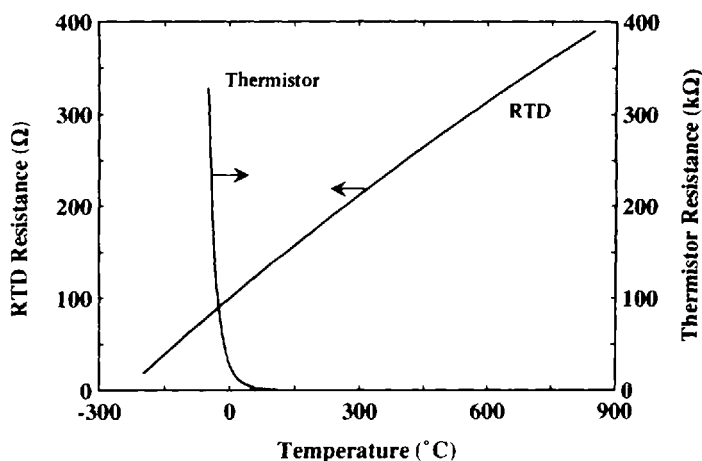


Figure 2.1: Thermal behavior of a thermistor [1] and a platinum resistance temperature detector (RTD) [2].

device as a sample and reference temperature transducer.

A thermistor is a semiconducting device which has a negative coefficient of resistance with temperature, e.g. its resistance decreases with increasing temperature. The principles behind its operation follows.

The (quantum mechanically) permissible energies of electrons in a solid lattice are constrained by the Pauli exclusion principle, which states that no two interacting electrons can be in the same quantum state. Envisioning atoms approaching from infinite separation to form a solid, their electrons begin to interact, and the permissible electron levels split into a multitude of states with a multitude of energies (Figure 2.2). These energy levels become so closely spaced in certain regions of the energy spectrum that they are treated as being continuous and referred to as “bands”. Other regions of energy become devoid of permissible states; the region marked E_g in the figure is the “band gap”. As atoms assemble to their equilibrium lattice positions, the energy spectrum for semiconducting materials can be represented by the simplified drawing on the left in Fig-

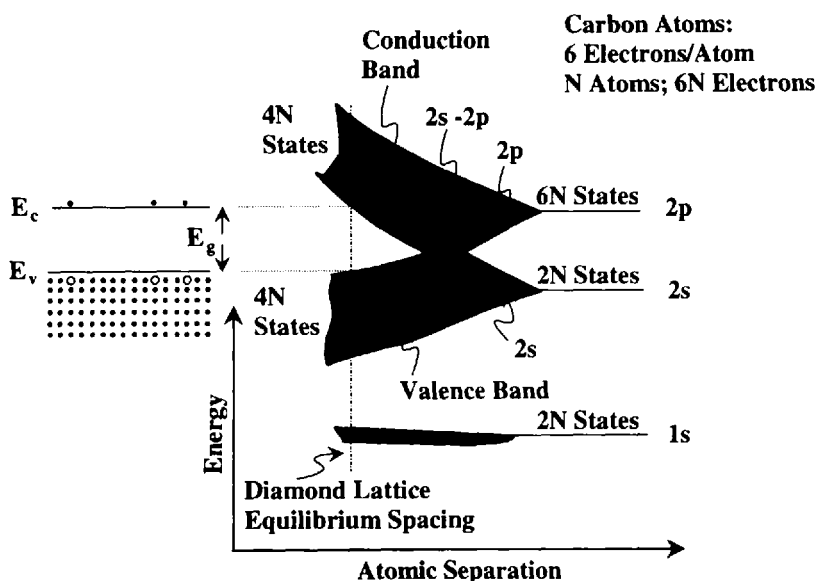


Figure 2.2: Band diagram in a semiconductor, diamond-structured carbon used as an example. In the left-hand drawing, the bottom line refers to the top of the valence band and the top line refers to the bottom of the conduction band [3].

ure 2.2. The low-energy portion of the spectrum, referred to as the “valence band”, is predominantly filled with electrons, all bound to atoms. Above the band gap is the “conduction band”, which consists of a series of permissible energy states which are predominantly empty. Electrons with energies in the conduction band are unbound, similar to electrons in a metal. The important property of a semiconductor is that with increasing temperature, adequate thermal energy is provided to excite more electrons from the valence band to the conduction band, increasing the material’s electrical conductivity.¹

¹Insulators (e.g. Al_2O_3) are characterized by large band gaps; thermal excitation of electrons is not adequate to permit electrons to assume a state in the conduction band, hence the electrical conductivity of such a material is very low. Conversely, conductive substances, such as metals, have ground state electrons occupying states in the conduction band. Hence, thermal excitation is not required for such a material to be conductive.

In the sharply dropping region of their resistance-temperature characteristic, thermistors show a significant sensitivity to small temperature changes (Figure 2.1). However, since much of their characteristic is essentially flat, they have a limited useful temperature range. Thermistor-based devices are commonly used for room temperature compensation of thermocouples, which will be treated in the following discussion.

2.2 Thermocouples

Thermocouples are the most commonly used temperature measuring device in elevated temperature thermal analysis. Thermocouples are made up of two dissimilar metals. If the welded junctions between the two materials are at different temperatures, a current through the loop is generated. This phenomenon can be explained by visualizing electrons in a solid as analogous to a gas in a tube (Figure 2.3).

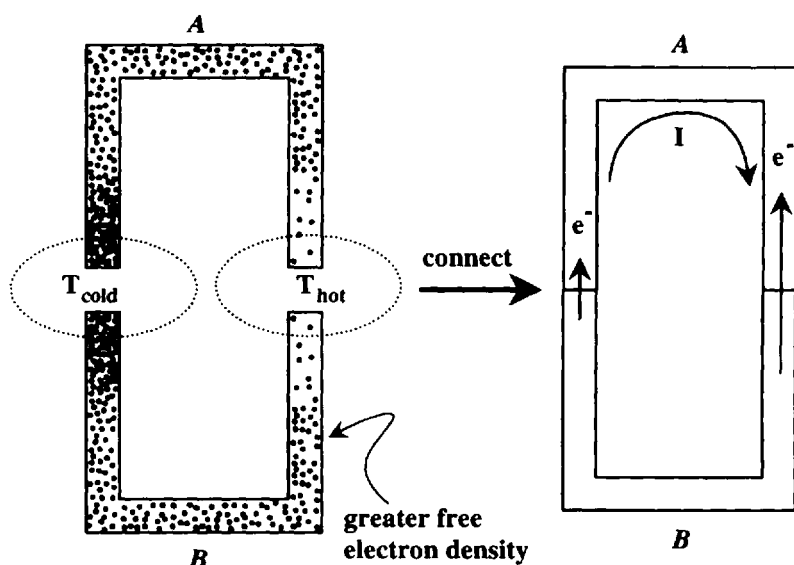


Figure 2.3: Free electron model of thermocouple behavior.

In comparing a ceramic material to a metal, it would not be difficult to distinguish which substance had more free (unbound) electrons. Similarly, different metals could be ranked as being more or less conductive. In the figure, material *B* is designated to have more free electrons than *A* (e.g. *B* is copper and *A* is aluminum). The left ends of these conductors are exposed to a cold temperature, while the right ends are exposed to a warm temperature. Visualizing the free electrons as a gas, the electrons would tend to condense closely together at the cold end while their fervent activity at the hot end would act to increase their mutual distances.

If the two materials were then electrically connected, electrons from the side with more free electrons would tend to diffuse toward the material with fewer free electrons.² This tendency would occur on both the hot and cold end, generating electron flows which oppose. However, the electrons on the high temperature side, propagating and impacting more forcefully, would overcome the opposing electron flow from the other side, and a net current would result. Note that if both materials were the same, one side would have the same free electron density as the other, producing no diffusion tendency and therefore no current. Further, if the temperatures were the same at both junctions of the dissimilar materials, then the diffusion currents would exactly cancel and there would also be

²A more precise description may be found by using the Fermi function which models the distribution of electrons (probability of occupancy) at various energy levels:

$$P(E) = \frac{1}{\exp \frac{E - E_F}{kT} + 1}$$

E_F is the "Fermi Energy", which indicates the average energy of electrons in a given material (the probability of a state at E_F being filled is 50%). When two dissimilar materials are joined at one point, the differences in Fermi energy between the materials acts as a driving force for electron motion. The Fermi energy takes a similar role as temperature or chemical potential; electron diffusion from the material of high E_F to that of low E_F will occur until the Fermi energies become equal. At that point, the buildup of negative charges in one conductor develops a field (Peltier voltage) which acts to resist further electron flow. This voltage is temperature dependent, thus a net Peltier voltage would result from connecting dissimilar materials at two junctions at different temperatures. The Seebeck voltage is the sum of the net Peltier voltage and a Thompson voltage. The latter voltage accounts for differences in electron energy distribution along the individual homogeneous wires because of temperature gradients.

no net current.

We can exploit some rules regarding thermocouple behavior so that these materials can be used for practical temperature measurement. The *law of intermediate elements* states that a third material can be added to a thermocouple pair without introducing error, provided the extremes of the material are at the same temperature. This is visually illustrated in Figure 2.4. As will be discussed later, some thermocouple mate-

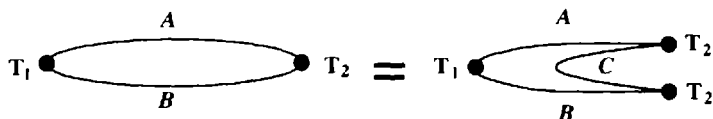


Figure 2.4: Law of intermediate elements.

rials are made of expensive precious metals. The introduction of inexpensive lead wire to extend the thermocouple signals to the data acquisition system permits appreciable cost savings.

Rather than measuring current, the complete circuit in a thermocouple pair is interrupted and the voltage (referred to as the Seebeck voltage) is measured. A configuration such as that in Figure 2.5 is used. Since both materials *A* and *B* connect to the lead-wire at the same temperature (0°C), no error is introduced. The EMF generated, V_{T_F} , is the result of the furnace temperature being different from the ice water bath temperature. For given thermocouple types, the corresponding temperatures for measured EMF's (generally in the 0-20 mV range) are tabulated, for example, in the *CRC Handbook of Chemistry and Physics* [4]. The National Institute of Standards and Technology (NIST) publishes [5] polynomials of the form:

$$T(V) = a + bV + cV^2 + \dots$$

where constants a , b , etc., are provided, and V is the measured voltage. With these polynomials, voltage/temperature

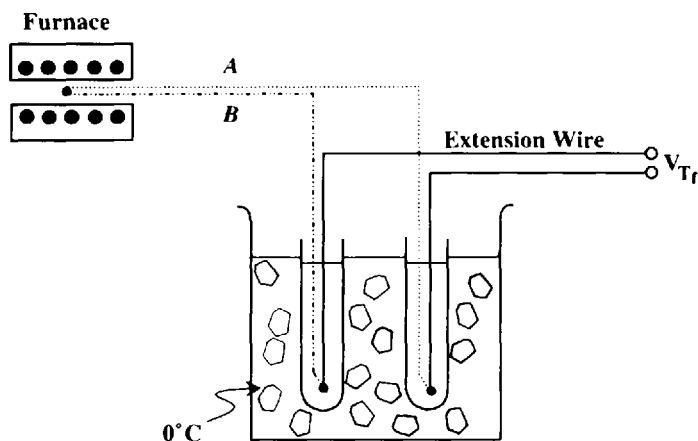


Figure 2.5: Application of the law of intermediate elements for thermocouple wire.

conversions may be easily generated, either by computer or calculator. Coefficients of the polynomials for several common thermocouples are listed in Table 2.1.

It is important to understand that the tables and polynomials are based on the assumption that the cold junction of the thermocouple pair is at zero degrees Celsius. In the laboratory, the cold junction is generally at room temperature or slightly above (the temperature at the screw terminals where the thermocouple wires and lead-wires join), hence a correction factor is needed. The *law of successive potentials* (Figure 2.6) may be stated as: The sum of the EMF's from the two thermocouples is equal to the EMF of a single thermocouple spanning the entire temperature range:

$$V_1 + V_2 = V_3$$

The successive potentials rule can be exploited to correct for the fact that the reference junction is not commonly at zero degrees Celsius. T_1 in the figure is assigned as 0°C , T_2 as room temperature, and T_3 as the furnace temperature. Knowing what room temperature is by using a thermometer, a ther-

Table 2.1: Thermocouple polynomial coefficients. All polynomials are from reference [6] with the exception of types *R* and *B*, which were determined by the author. Polynomials are of the form $T = a_0 + a_1V + a_2V^2 + \dots$, where T is temperature in $^{\circ}\text{C}$ and V is voltage in volts.

	Type E -100-1000 $^{\circ}\text{C}$ $\pm 0.5^{\circ}\text{C}$	Type J 0-760 $^{\circ}\text{C}$ $\pm 0.1^{\circ}\text{C}$	Type K 0-1370 $^{\circ}\text{C}$ $\pm 0.7^{\circ}\text{C}$	Type S 0-1750 $^{\circ}\text{C}$ $\pm 1^{\circ}\text{C}$
a_0	0.104967248	-0.048868252	0.226584602	0.927763167
a_1	17189.45282	19873.14503	24152.10900	169526.5150
a_2	-282639.0850	-218614.5353	67233.4248	-31568363.94
a_3	12695339.5	11569199.78	2210340.682	8990730663
a_4	-448703084.6	-264917531.4	-860963914.9	-1.63565E+12
a_5	1.10866E+10	2018441314	4.83506E+10	1.88027E+14
a_6	-1.76807E+11		-1.18452E+12	-1.37241E+16
a_7	1.71842E+12		1.38690E+13	6.17501E+17
a_8	-9.19278E+12		-6.33708E+13	-1.56105E+19
a_9	2.06132E+13			1.69535E+20
	Type R 0-1760 $^{\circ}\text{C}$ $\pm 0.8^{\circ}\text{C}$	Type T -160-400 $^{\circ}\text{C}$ $\pm 0.1^{\circ}\text{C}$	Type B 0-700 $^{\circ}\text{C}$ $\pm 8.1^{\circ}\text{C}$	Type B 700-1820 $^{\circ}\text{C}$ $\pm 0.9^{\circ}\text{C}$
a_0	2.04827	.100860910	36.9967	169.055
a_1	167954	25727.94369	1.65406E+6	366415
a_2	-3.22234E+7	-767345.8295	-5.82049E+9	-1.14871E+8
a_3	8.60144E+9	78025595.81	1.33216E+13	3.57672E+10
a_4	-1.48143E+12	-9247486589	-1.76704E+16	-7.7762E+12
a_5	1.60727E+14	6.97688E+11	1.41E+19	1.1317E+15
a_6	-1.09762E+16	-2.66192E+13	-6.87206E+21	-1.07335E+17
a_7	4.57554E+17	3.94078E+14	2.00084E+24	6.33792E+18
a_8	-1.0622E+19		-3.19443E+26	-2.10872E+20
a_9	1.05141E+20		2.15035E+28	3.01366E+21

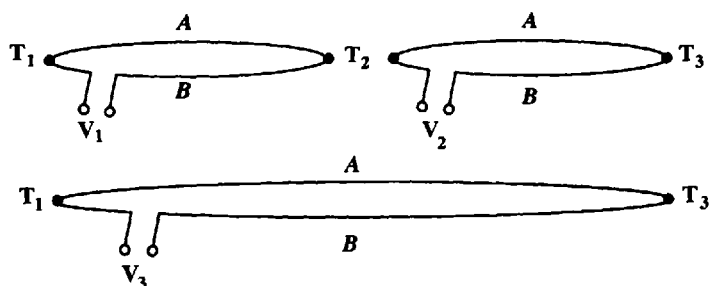


Figure 2.6: Law of successive potentials.

mocouple conversion table may be used to determine the corresponding EMF for the particular thermocouple type used. Adding this EMF to that measured from the thermocouple (from room temperature to the furnace temperature) provides a total EMF corresponding to 0°C to the furnace temperature, which can then be converted back to temperature (via the tables or polynomials) to establish the accurate furnace temperature. Circuits using thermistors or platinum resistance temperature detectors (RTD's) are often used,³ which automatically add the EMF corresponding to 0°C to the cold junction temperature for a particular thermocouple type.

It is important that the thermistor or RTD used for measuring the cold junction be physically located at the cold junction, as the temperature of the cold junction is often different from that of the room, generally because of heat leakage from the furnace. Special wire, referred to as compensating lead-wire,

³The simplest form of this measurement is to put the RTD or thermistor in series with a conventional resistor and apply a known voltage. By measuring the voltage drop across the thermistor, its resistance can be determined by $R_T = (R_B/(V/V_T - 1))$, where V_T is the voltage drop across the thermistor or RTD, V is the applied voltage, and R_B is the resistance of the conventional resistor. The manufacturer of the RTD or thermistor will provide data or polynomials to convert the measured resistance to temperature. If the current through the thermistor or RTD is excessive, the device will become self heating, giving false temperature readings. More sophisticated circuits can eliminate this problem. Care must also be taken with RTD's since their resistance is so low ($\sim 100\Omega$ as compared to $10\text{k}\Omega$ for thermistors) that the resistance of the connecting wire becomes significant and must be added to R_B .

Table 2.2: Common thermocouple types.

Type	Metal		Std. color code		Identification		Maximum useful range	
	+	-	+	-	Magnetic lead	Sliffer lead	Temperature (°C)	EMF (mV)
B	Pt-30% Rh	Pt-6% Rh	Grey	Red		+ve	0-1700	0-12.4
E	Chromel	Constantan	Violet	Red			-200-900	-8.8-68.8
J	Iron	Constantan	White	Red	+ve		0-750	0-42.3
K	Chromel	Alumel	Yellow	Red	-ve		-200-1250	-6.0-50.6
N	Nicrosil	Nisil	Orange	Red			-270-1300	-4.3-47.5
R	Pt-13% Rh	Pt	Black	Red		+ve	0-1450	0-16.7
S	Pt-10% Rh	Pt	Black	Red		+ve	0-1450	0-15.0
T	Cu	Constantan	Blue	Red			-200-350	-5.6-17.8
C	W-5% Re	W-26% Re	White	Red			0-2320	0-38.6

may be purchased which will have thermoelectric properties matched to a particular thermocouple type but is not nearly as costly. By connecting the compensating lead wire to the cold junction, the cold junction may be “moved” to the physical location of the thermistor or RTD. Care must be taken to ensure that the positive end of the compensating lead-wire is connected to the positive end of the thermocouple pair. Otherwise, the error of not using compensating leads will be doubled.

2.3 Commercial Components

2.3.1 Thermocouples

Table 2.2 shows various standardized thermocouple types commonly available. Each is optimal for a given set of conditions. For example, type *K* wire is used for lower temperature ($\sim 1100^\circ\text{C}$ max) furnaces and type *S* thermocouples for higher temperature furnaces ($\sim 1500^\circ\text{C}$ max). Type *K* is much less expensive than *S*, has a higher (voltage) output, but is less refractory. The two alloys in type *K* can be distinguished since alumel is magnetic and chromel is not. The rhodium content of

one of the type *S* conductors gives it a stiffer feel than the pure platinum side when bent with the fingers. Another clear way to determine polarity is to make a welded bead between the two wires at one end and connect the other ends to a multimeter, measuring in the millivolt range. By exposing the bead to the heat of a flame (or body heat via finger grasp), a positive or negative voltage on the meter will permit differentiation of the two materials.

Junction beads can be made for platinum-based thermocouples, such as types *R*, *S*, or *B*, by welding with a high-temperature flame (e.g. oxy-acetylene). Using a flame for junction formation in alloy-based (e.g. *K*- or *E*-type) thermocouples does not work well since the wires tend to oxidize rather than fuse. Beads are more effectively made by electric arc for these thermocouple types.

From the mV versus temperature plot in Figure 2.7, it might be interpreted that W-Re thermocouple wire would be a good choice (e.g. high output and high temperature), but it must be used in a reducing or inert atmosphere. For an oxidizing atmosphere, type *B* thermocouples are the most refractory, but they have a very low output at low temperatures, and show a temperature anomaly whereby a voltage reading could correspond to either of two temperatures (Figure 2.8). Thus, reading temperatures below $\sim 100^{\circ}\text{C}$ is not practical. One small advantage, however, is that room temperature compensation of this thermocouple type is practically negligible (e.g. the thermocouple output is -0.002 mV at 25°C).

2.3.2 Furnaces

Applying a potential difference across a conductive material causes current to flow. Depending on the electrical resistance of the materials, energy is given up in the form of heat as moving electrons scatter via collisions with the lattice and each other. The energy dissipated per unit time is related to the current

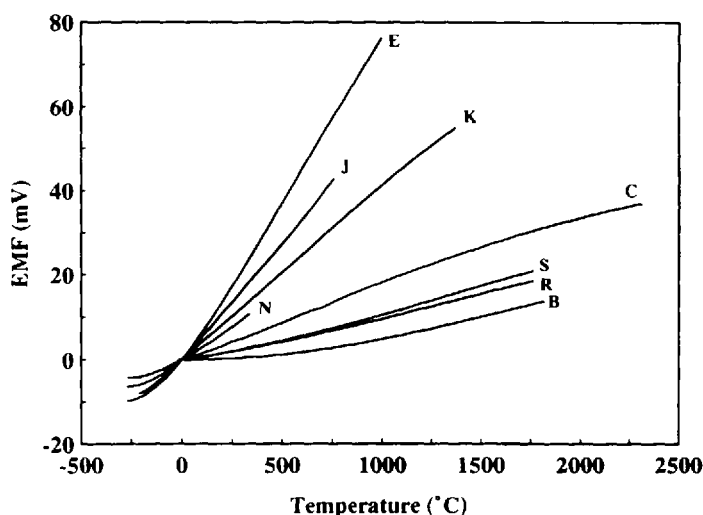


Figure 2.7: Thermocouple output as a function of temperature for various thermocouple types.

and material resistance by:

$$P = I^2 R$$

Alternating current works just as well as direct current for generating heat from resistance heating elements, since as long as the electrons are moving and impacting, they need not drift in a consistent direction.

Furnaces for thermal analysis instruments are nearly always electric resistance heated. Wound furnaces consist of a refractory metal wire wrapped around or within⁴ an alumina or other refractory tube. Nichrome (nickel/chromium alloy) or Kanthal (a trade name for an iron/chromium alloy: 72% Fe, 5% Al, 22% Cr, .5% Co) windings may be used inexpensively for heating to a maximum temperature of $\sim 1300^\circ\text{C}$. More expensive plat-

⁴In some designs, the windings are wound around a mold with a high-temperature ceramic casting mix added. After drying and removal of the mold, the elements spiral around the inner diameter of a cast tube, allowing line of sight between the elements and the specimen chamber. This generally eliminates the need for a separate control thermocouple, as discussed in section 3.1.

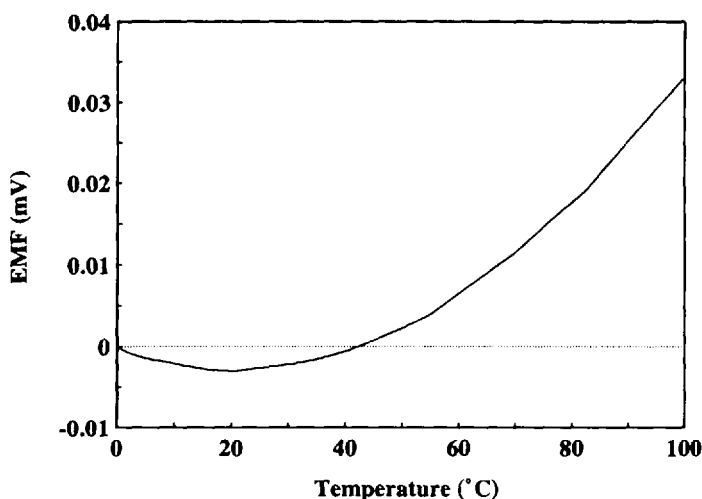


Figure 2.8: Temperature anomaly in type *B* thermocouple wire.

inum/rhodium wire has a maximum temperature on the order of 1500°C. The higher the rhodium percentage, the higher the maximum temperature. These windings are used on a myriad of professionally made instruments such as the Harrop (Cahn) TG and the TA Instruments DTA.⁵

Silicon carbide elements, usually in the form of tubes or bayonets, have a maximum temperature of about 1550°C and are cheaper than platinum windings. However, since the cross-sectional area of these elements is so large, their resistance is low. Thus a transformer (see section 2.4.2) and/or a current-limiting device may be needed to avoid blowing fuses. The electrical resistivity of silicon carbide elements decreases with increasing temperature (semiconductor) to about 650°C [7] and then increases again at higher temperatures. SiC elements are used in models of the Netzsch and Orton Dilatometers, as examples. One of the highest temperature oxidizing atmosphere heating elements (~1700°C) is molybdenum disilicide (trade

⁵See appendix A for names and addresses of contemporary thermal analysis instrumentation manufacturers.

name “Kanthal Super 33” [8]), which also requires a step down transformer (discussed in the next section). Stabilized zirconia [9] used after pre-heating to 1200°C with another heating element, can heat to 2100°C in air. Under reducing atmospheres, temperatures up to 2900°C can be obtained with graphite or tungsten heating elements. Considerable engineering is involved in the design of these furnaces.

For cryogenic temperature measurements, furnaces consist of thermally conductive jackets filled with liquid nitrogen (boiling point 77.35 K) or liquid helium (boiling point 4.215 K). The heat dissipation from resistance heating elements competes with the cooling effects of these fluids to permit stable temperature control down to near absolute zero [10].

Another style of furnace system, provided by Ulvac/Sinku-Rico Inc. [11], is an infrared heating furnace (Figure 2.9). This

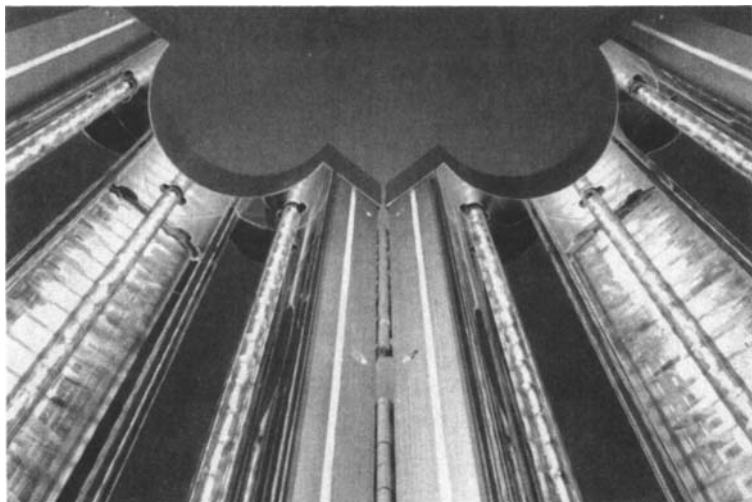


Figure 2.9: Ulvac/Sinku-Rico infrared gold image furnace [11]. Gold coated mirrors focus radiant energy to a 1 cm diameter zone along the central axis of the furnace. The gold coating is used for maximum reflectance in the infrared part of the spectrum.

furnace uses tungsten-halogen lamps and elliptical mirrors to heat specimens almost entirely by radiation. Controlled heating rates of $50^{\circ}\text{C}/\text{sec}$, are feasible because of the system's ability to rapidly heat and cool; only the specimen becomes appreciably hot, not the furnace structure. The rate of heating of a sample in such a furnace is dependent on its ability to absorb radiant heat (emittance). Thus opaque ceramics can generally heat faster than metals, with smooth polished surfaces, in such a furnace.

2.4 Furnace Control

A block diagram for a feedback control furnace system, used in thermal analysis instrumentation, is shown in Figure 2.10. The SCR receives a control instruction, and in turn permits a

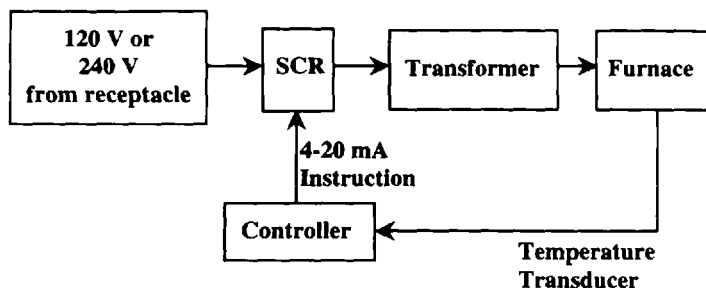


Figure 2.10: Block diagram of furnace instrumentation.

limited ac power output to the furnace elements. As discussed in section 2.3.2, low resistance elements require a transformer after the SCR. In the following, each component will be discussed in some detail.

2.4.1 Semiconductor-Controlled Rectifiers

The term SCR refers both to a $p - n - p - n$ semiconducting device,⁶ often referred to as a thyristor, and more generically, to a module containing the aforementioned device as a component, as well as other circuitry and convection cooling fins (Figure 2.11).

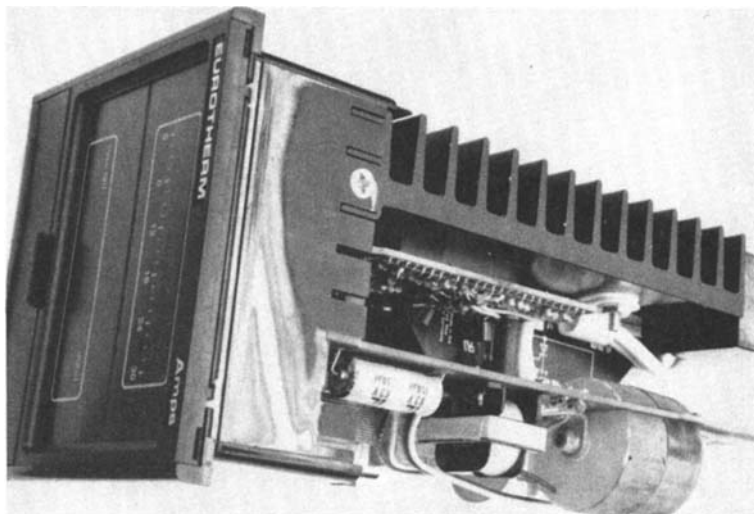


Figure 2.11: Eurotherm model 832 SCR [12].

A triac may be perceived as opposing SCR's (semiconductor controlled rectifier or silicon controlled rectifier) in parallel, each activated by a "gate" current (Figure 2.12). Current can flow in only one direction through the "diodes" in Figure 2.12. Electrical power from a wall socket, conventionally 110 or 220 ac volts is fed into the device. The SCR's act like diodes in the sense that current is allowed to flow in only one direction. During one half of the cycle, the current may flow through one

⁶This notation, where n -type refers to an electron conductor, and p -type refers to a hole (lack of electron) conductor, indicates how a semiconductor was processed. For example, a p -type semiconductor material layer grown on an n -type substrate forms a ($p - n$) diode, which can be used to rectify alternating current. A $p - n - p$ device may be used as a transistor, and is useful as a signal amplifier or for other applications.

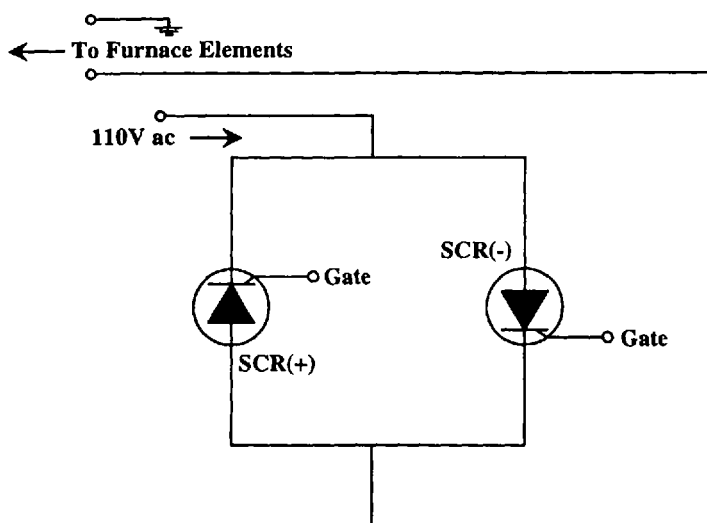


Figure 2.12: Schematic of a triac.

SCR, and during the other half of the cycle it is permitted to flow only through the other SCR—only if a (milliampere) current “turn-on pulse” (a few microseconds in duration) applied at the gate causes the devices to be conductive. One of the SCR’s continues to conduct until the current going through it goes to zero (e.g. “zero crossover” of the ac voltage). After a period of time, a pulse of current at the gate of the other SCR, configured for current flow in the opposite direction, permits limited current from the negative side of the voltage sine wave until the next zero crossover. This is illustrated in Figure 2.13. When the device receives an “instruction” for more power, the timing of the gate pulses changes so as to let more of the sine wave through, permitting more current to flow through the heating elements.

The external instruction to the SCR module is conventionally a 4 to 20 milliampere dc current from a control microprocessor, where 4 mA corresponds to zero power and 20 mA corresponds to full power. This signal is then translated by

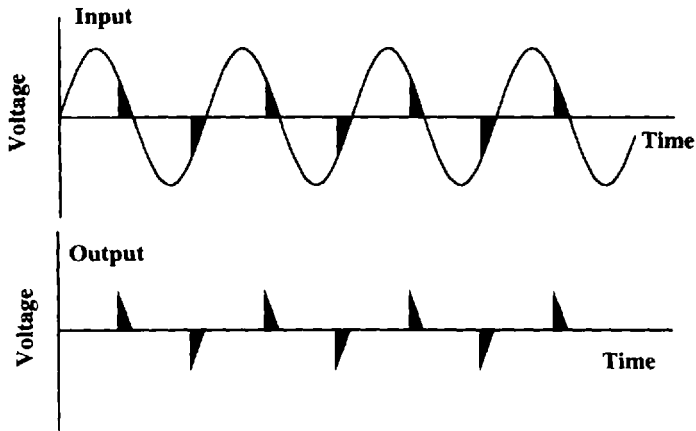


Figure 2.13: Operation of an SCR. The upper trace represents the ac voltage from the power supply as input into the SCR. The shaded regions, reproduced in the lower trace, indicate the voltage across the heating elements, as permitted by the SCR.

internal circuitry to the timed pulses sent to the gates of the (semiconductor) SCR's. The advantage of a (4-20 mA) current instruction over a voltage instruction is that, if a wire is inadvertently dislodged, the current loop is broken and the power instruction becomes zero. If the device was designed to act based on a voltage instruction, an open circuit would cause an arbitrarily varying power to be delivered to the furnace elements.

2.4.2 Power Transformers

Electrical power is equal to the product of current and voltage. A transformer (ideally) is a device which changes the current-voltage ratio, as compared to its input, while keeping their product (power) constant. In reality, transformers are not perfectly efficient ($\sim 90\%$), but for the sake of this discussion we will assume no power losses. Figure 2.14 shows schematic and practical transformers.

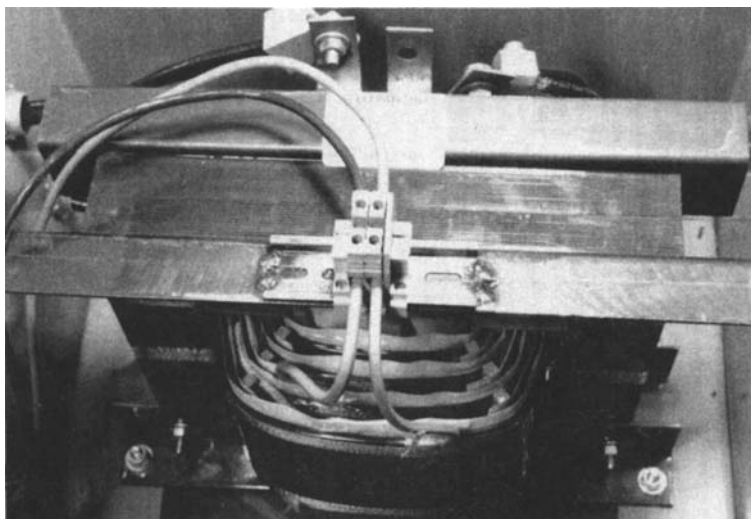
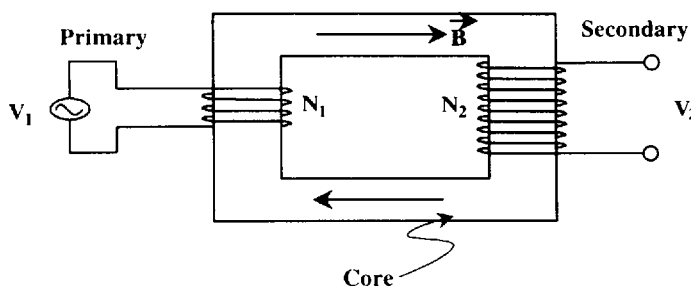


Figure 2.14: Conceptual schematic (top) and a photograph (bottom) of a (Neeltran [13]) power transformer.

Power from the SCR is input to the “primary”. The varying voltage in the primary induces varying magnetic flux in the core (usually made of laminated sheets⁷ of siliconized steel, which have a high magnetic permeability⁸). This sinusoidally varying flux in turn induces voltage in the other winding, the “secondary”. The same voltage is generated per turn (N) in both the primary and secondary, thus:

$$\frac{V_2}{N_2} = \frac{V_1}{N_1}$$

Therefore, if we wish to decrease 220 volts to 22 volts, we need ten times as many turns on the primary as on the secondary. This is an example of a “step down transformer”, which is the type generally needed for heating elements in furnaces and thermal analysis instruments. Conversely, a “step up transformer” is what might be used on a 200 kilovolt transmission electron microscope. Since “power in” must equal “power out” (neglecting losses) by conservation of energy, the current in the above step down transformer example must increase tenfold. Hence, low resistance heating elements can draw a large amount of current on the secondary without blowing fuses on the power lines feeding the primary. Transformers thus have the utility of “impedance matching” the power supply to the furnace heating elements.

2.4.3 Automatic Control Systems

In order for valid thermoanalytical measurements to be taken, strict control must be maintained over the thermal schedules to which the tested specimens are exposed. In this section,

⁷The advantage of laminated sheets as opposed to a solid core is that changing magnetic flux tends to produce circular currents (“eddy currents”) in the core material itself, which causes i^2R heating of the core, which translates to loss of efficiency of the transformer. The use of thin sheets decreases the induced voltage per sheet and the eddy current path is increased, increasing R , hence heat losses are minimized [14].

⁸Certain “ferromagnetic” materials, notably iron, steels, and some ceramics (ferrites), are far more receptive ($\sim 100\times$) to magnetic flux than is air. Permeability is a measure of the receptiveness of the material to having magnetic flux set up in it [15].

the proportional integral derivative (PID) control system will be discussed. This algorithm is commonly used for furnace temperature control as well as a wide variety of other industrial feedback control systems.

The simplest form of control, which is adequate for some applications, is on-off control, as depicted in Figure 2.15. The

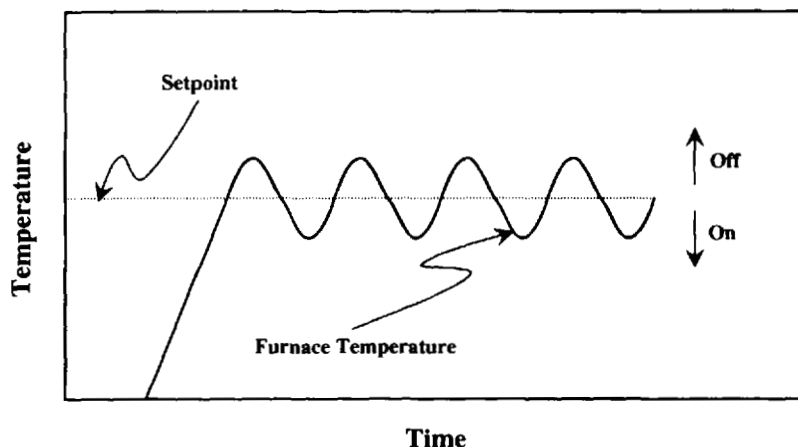


Figure 2.15: On-off furnace control.

setpoint temperature is specified as the desired temperature of the furnace at any given time. This is generally an isothermal value or a linear heating ramp. Under on-off control, if the furnace temperature is above the setpoint, the furnace shuts off. If the furnace temperature is below the setpoint, the furnace goes to full power. As a result, the furnace temperature tends to oscillate about the setpoint value. As on-off switching fatigues mechanical relays with time, a “dead band” is often introduced whereby the system does not shut off until the furnace temperature exceeds the setpoint by a few degrees, and does not turn on until the furnace temperature drops below the setpoint by a few degrees. The introduction of a dead band will increase the amplitude of the oscillation, but decrease its frequency, preserving the life of the relay.

An improvement over on-off control is *proportional* control, which generally eliminates furnace temperature oscillation by applying corrective action proportional to the deviation from the setpoint. As illustrated in Figure 2.16, a proportional band is assigned so that if the furnace temperature exceeds these outer limits, the system reverts back to on-off control. An arbitrary percentage of full furnace power is assigned when the furnace temperature is coincident with the setpoint, say 50%. Then, for example, if the furnace temperature is located halfway between the setpoint and the upper proportional band, the furnace power is instructed to drop to 25%.

The usual furnace temperature behavior under this form of control is shown in the middle trace in Figure 2.16. If the proportional band is adequately broad, the furnace temperature does not oscillate; rather, it runs parallel to the setpoint. As the proportional band is narrowed, this parallel ramping diminishes, but if the proportional band is too narrow, the furnace temperature will oscillate as if under on-off control.

Elimination of parallel ramping is accomplished by introducing an *integral* function (Figure 2.16 middle) which continuously sums the difference between furnace and setpoint temperatures as swept through time. This area, multiplied by a weighting factor, is added to the proportional portion of the control instruction. If the furnace temperature is persistently below the setpoint, this area continues to accumulate until the furnace temperature is forced up to the setpoint, at which time no additional area is accumulated.

When it is desired that a furnace adopt a particular heating rate from room temperature, the furnace often cannot immediately follow that rate (see bottom portion of Figure 2.16). A limited amount of time is required for heat to diffuse from the heating elements to the thermocouple junction. Thus, the furnace temperature initially lags behind that of the setpoint. The control system responds by instructing the SCR to permit more and more power through. Eventually the furnace temperature

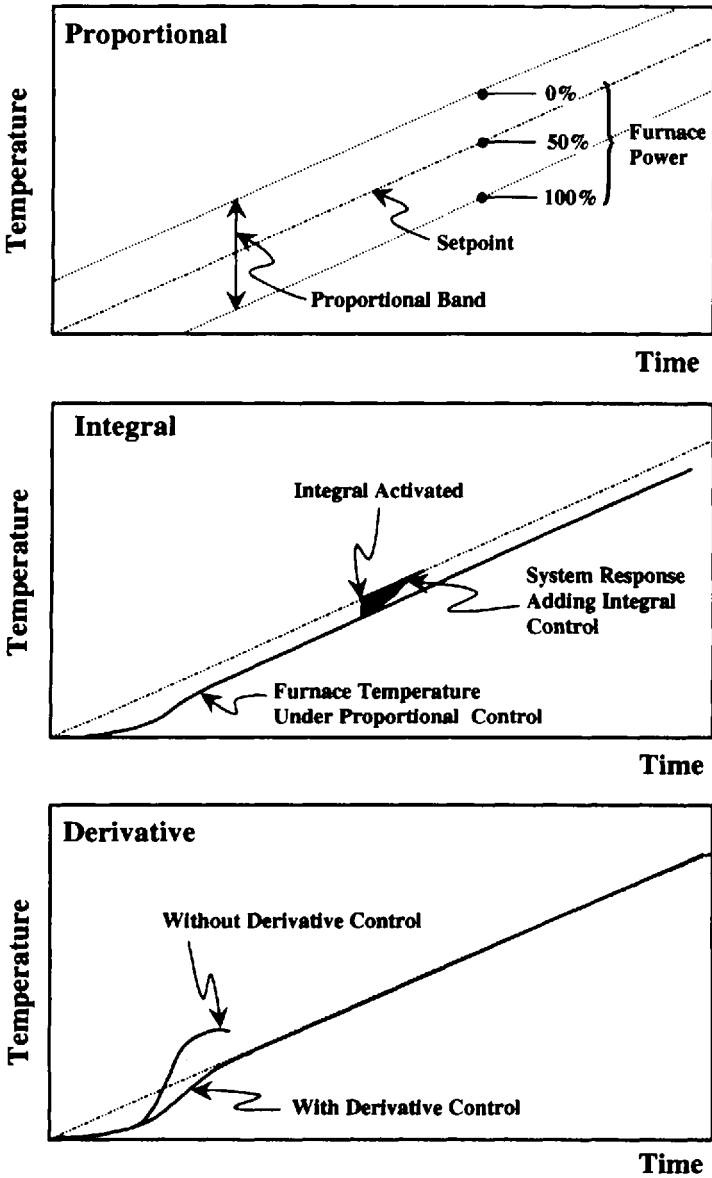


Figure 2.16: Proportional-integral-derivative furnace control logic.

does rise but with so much momentum that it overshoots the setpoint. To minimize overshooting and undershooting effects, *derivative* control may be introduced. This function strives to keep the slope of the furnace temperature with time the same as that of the setpoint with time. Derivative control acts as a predictive function, whereby if the furnace temperature is below that of the setpoint, but is rising rapidly, the derivative function (multiplied by a weighting constant) subtracts power from the control instruction. This acts to ease the furnace temperature into coincidence with the setpoint, minimizing overshoot.

The overall control function for a PID control system may be summarized as:

$$P = P_0 - U_P(T - T_S) - U_I \int_0^t (T - T_S) dt - U_D \left(\frac{dT}{dt} - \frac{dT_S}{dt} \right)$$

where P is power, P_0 is the arbitrarily assigned starting power, T is the furnace temperature, T_S is the setpoint temperature, and U_P , U_I , and U_D are the proportionality constants for the proportional, integral, and derivative control functions respectively.

Professionally made controller modules (Eurotherm, Leeds and Northrop, Barber Coleman, etc.) are often used to maintain a user specified thermal schedule for an experiment. These devices generally allow the control constants U_P , U_I , and U_D to be adjusted by the user.⁹ Adjustments are usually made by repeated trial and error using the following criterion:

Set the integral and derivative constants to a minimum so that the proportional band may be adjusted first. The proportional band should be set as tightly as possible so long as there is no indication of on-off oscillation. The derivative function should then be increased, which should act to minimize overshoot/undershoot during a sharp change in thermal schedule or on initial startup. Increasing the derivative constant too much

⁹Some of the newest controllers have self-adjusting PID parameters where the micro-processor evaluates the tracking behavior of a previous run, and makes appropriate adjustments to U_P , U_I , and U_D .

will cause a jagged oscillatory behavior. The derivative function, as a general rule, should not dominate the overall control instruction. Increasing the integral constant should eliminate parallel ramping more rapidly. Over-emphasizing this function will cause “integral windup”, where the accumulation of area has so much momentum that it causes the furnace temperature to adopt broad oscillations about the setpoint with continuously increasing amplitude.

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Chapter 3

DIFFERENTIAL THERMAL ANALYSIS

3.1 Instrument Design

Figure 3.1 is a schematic of the differential thermal analyzer (DTA) design. The device measures the difference in temperature between a sample and reference which are exposed to the same heating schedule via symmetric placement with respect to the furnace. The reference material is any substance, with about the same thermal mass as the sample, which undergoes no transformations in the temperature range of interest. The temperature difference between sample and reference is measured by a “differential” thermocouple in which one junction is in contact with the underside of the sample crucible, and the other is in contact with the underside of the reference crucible.¹ The sample temperature is measured via the voltage across the appropriate screw terminals (V_T) and similarly for the reference temperature (V_{T_r}); generally only one or the other is recorded (see section 3.5.1). Sample and reference

¹The type of thermocouple used for the differential measurement is critical since the measured temperature differences can be quite small. If measurements are to be made only to 1200°C, for example, a type *K* thermocouple could be used, which has approximately five times the output of platinum thermocouples such as types *S* or *R*. Type *K* thermocouples, however, tend to oxidize rapidly over repeated cycles, and hence need to be replaced more often than platinum-based thermocouples. The most critical component of a good DTA is the differential thermocouple signal amplifier, which must amplify minute voltages while eliminating random noise.

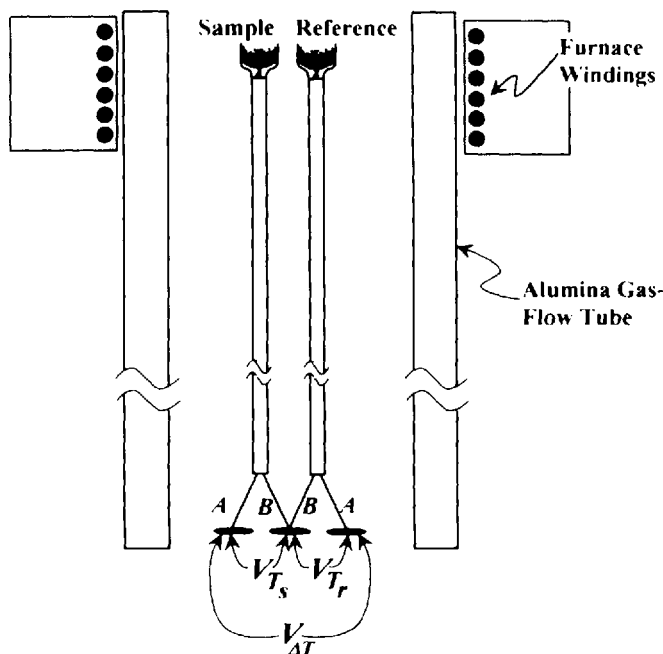


Figure 3.1: Schematic of a differential thermal analyzer.

temperature measurements require cold junction temperature correction.

When the sample undergoes a transformation, it will either absorb (endothermic) or release (exothermic) heat. For example, the melting of a solid material will absorb heat, where that thermal energy is used to promote the phase transformation. The instrument will detect that the sample is cooler than the reference, and will indicate the transformation as an “endotherm” on a plot of differential temperature (ΔT) versus time.² Figure 3.2 shows a typical DTA trace of the decomposition of dolomite. If the sample and reference are exposed to a constant heating rate, the x -axis is often denoted as tem-

²Generally the y -axis is left as an amplification of differential thermocouple voltage, showing exothermic and endothermic trends, where no effort is made to convert the abscissa values into temperatures.

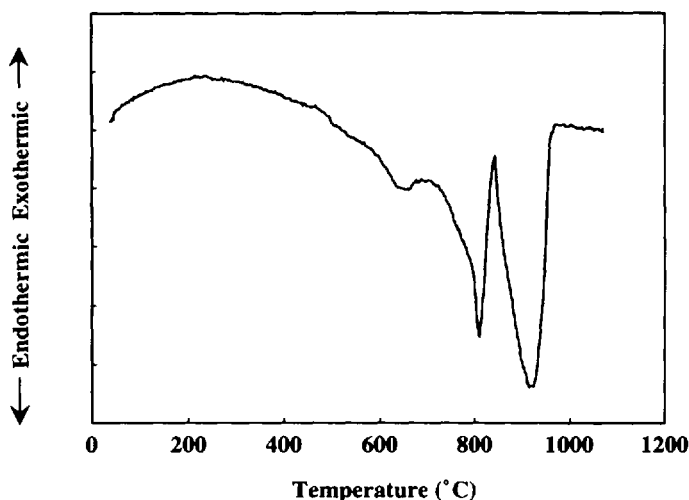


Figure 3.2: Typical DTA trace showing the decomposition of dolomite ($\text{CaMg}(\text{CO}_3)_2$). The endotherm peaked at $\sim 650^\circ\text{C}$ corresponds to the decomposition of free MgCO_3 in magnesitic [1] dolomite. The endotherm peaked at $\sim 805^\circ\text{C}$ coincides with the decomposition of dolomite: $\text{CaMg}(\text{CO}_3)_2(s) = \text{CaCO}_3(s) + \text{MgO}(s) + \text{CO}_2(g)$. The final endotherm peaked at $\sim 920^\circ\text{C}$ corresponds to the decomposition of calcite (freed from the previous dolomite decomposition): $\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g)$.

perature, since temperature is proportional to time. Plotting temperature on the x -axis thus implies an experiment in which a constant heating rate was used.

If there is good “communication” between the heating elements and the sample or reference thermocouple junctions, then the control system can make its power adjustments based on one of those temperatures. If there is substantial insulation between these locations, which may be necessary for heat flow uniformity to both sample and reference or to permit the introduction of special gases, then a separate “control” thermocouple is used which is placed near the furnace windings.

Although the output traces of a differential scanning calorimeter (DSC) are visually similar to a DTA, the operating principle of this device is entirely different. Figure 3.3 shows

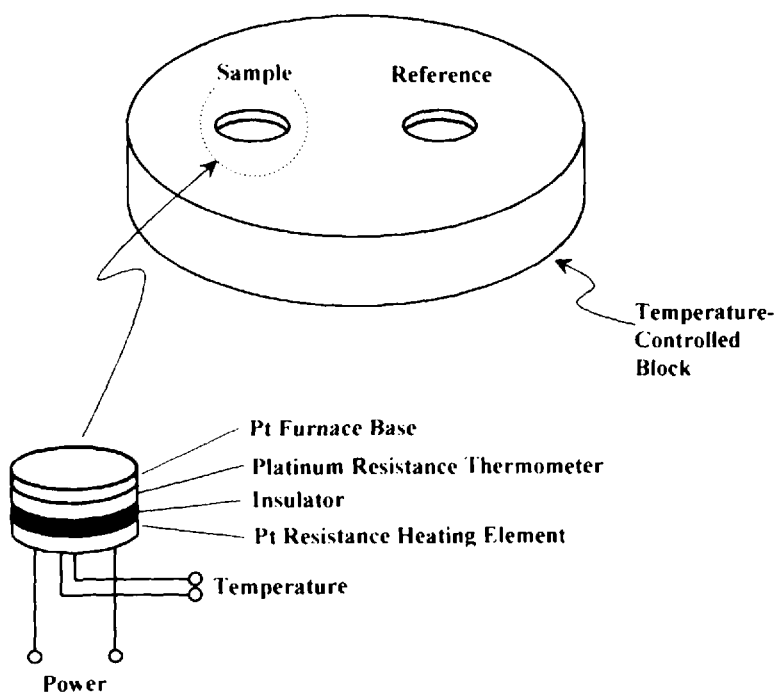


Figure 3.3: Schematic of a power-compensated differential scanning calorimeter.

a schematic of the DSC design. There are separate containers for both sample and reference, and associated with each are individual heating elements as well as temperature measuring devices.³ Both cells are surrounded by a refrigerated medium (usually via flowing water) which permits rapid cooling.

The sample and reference chambers are heated equally into a temperature regime in which a transformation takes place within the sample. As the sample temperature infinitesimally deviates from the reference temperature, the device detects it

³Both heating element and temperature measuring device are disks with imbedded platinum coils, which are in turn separated with thin electrically insulating wafers. Temperature is determined by the resistance of the platinum wire (RTD). The ensemble is designed for good thermal contact, yet with electrical insulation between the heating element and temperature measuring device. The small sample chamber is necessary in order to maintain good thermal contact for rapid system response to reactions in the sample.

and reduces the heat input to one cell while adding heat to the other, so as to maintain a zero temperature difference between the sample and reference, establishing a “null balance”. The quantity of electrical energy per unit time which must be supplied to the heating elements (over and above the normal thermal schedule), in order to maintain this null balance, is assumed to be proportional to the heat released per unit time by the sample. Hence, as shown in Figure 3.4, the y -axis is

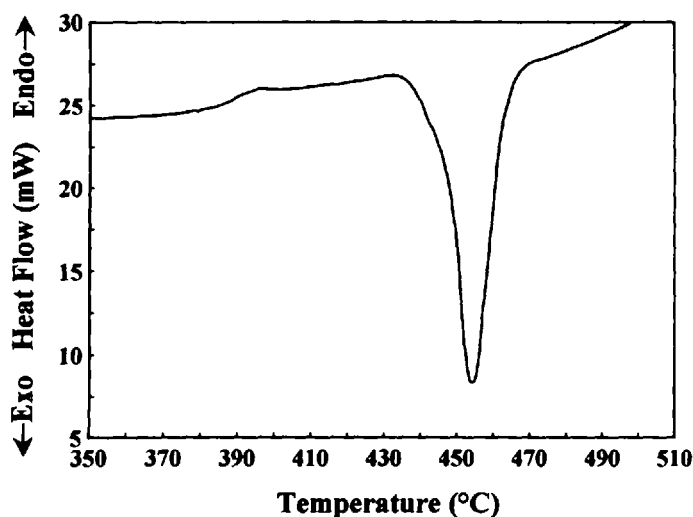


Figure 3.4: Typical power-compensated DSC trace; glass transformation and devitrification of amorphous CdGeAs_2 . 6.86 mg of sample was heated at $20^\circ\text{C}/\text{min}$. Indicated exothermic and endothermic directions are those used in power-compensated DSC, but are reversed as compared to the convention used in this book.

expressed in terms of energy per unit time (Watts).

This DSC has two control cycle portions. One portion strives to maintain the null balance between sample and reference, while the other strives to keep the average of the sample and reference temperature at the setpoint. These processes switch back and forth quickly so as to maintain both simultaneously.

Some confusion abounds with respect to instruments which

are called DSC's. Perkin-Elmer Corporation markets the only "power-compensated" DSC design, which corresponds to the above description of a DSC. Other devices referred to as a DSC's, such as those manufactured by TA Instruments (Figure 3.5) or Netzsch, actually operate based on a DTA principle, where a single heating chamber is used ("heat flux" DSC).⁴ A calibration constant within the computer software (determined using standard materials, discussed in section 3.3) converts the amplified differential thermocouple voltage to energy per unit time, which is plotted on the y -axis of the instrument output.

3.2 An Introduction to DTA/DSC Applications

Unlike structural or microscopic methods of materials characterization, DTA/DSC can provide information on how a substance "got from here to there" during thermal processing. The temperatures of transformations as well as the thermodynamics and kinetics of a process may be determined using DTA/DSC.

Figure 3.6 shows an example of a DTA trace of the heating of a glass. The material initially underwent a glass transition (section 7.6), then an exothermic transformation corresponding to crystallization from the glass, and finally an endothermic transformation representing the melting of the crystalline phase. The melting temperature, for example, is represented by the onset of the peak. The convention for determining the melting temperature is to extend the straight line portions of the baseline and the linear portion of the upward slope, marking their intersection. The convention is similar for locating T_g , the glass transition temperature. For melting point location, this procedure may not be quite correct. The point at which

⁴These devices have a disk (e.g. constantan alloy) on which the sample and reference pans rest on symmetrically placed platforms. Thermocouple wire (e.g. chromel alloy) is welded to the underside of each platform. The chromel-constantan junctions make up the differential thermocouple junctions with the constantan disk acting as one leg of the thermocouple pair.

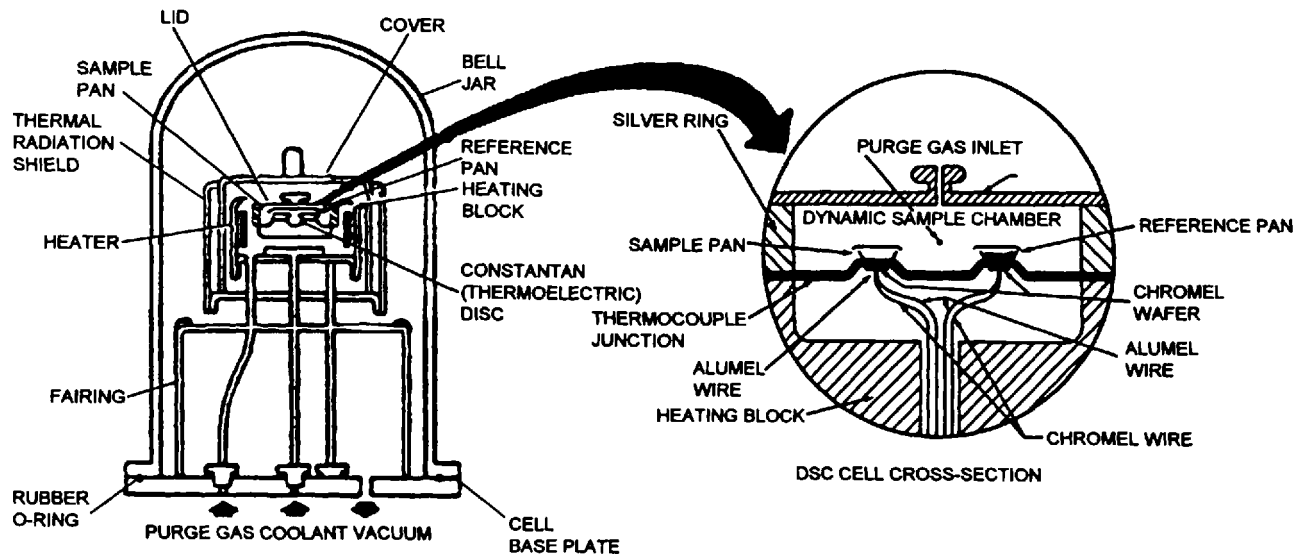


Figure 3.5: TA Instruments DSC cell [2].

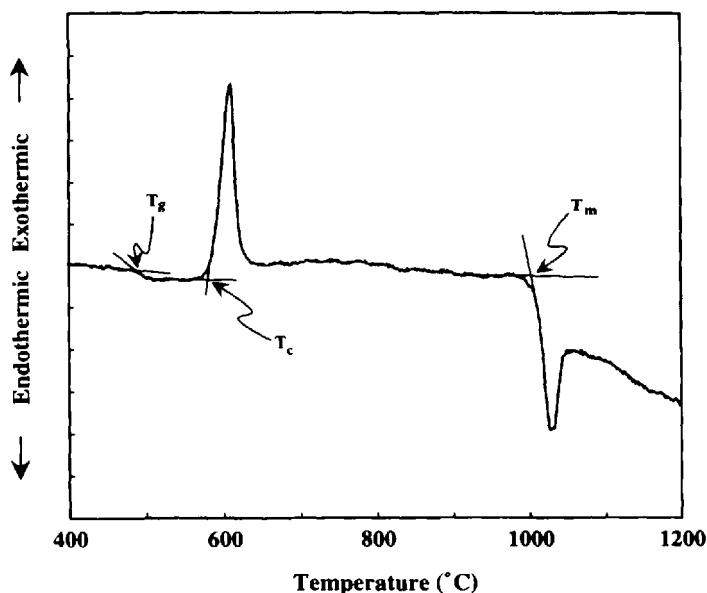


Figure 3.6: DTA trace showing glass transformation, devitrification, and melting of a $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ glass-ceramic composition.

the first indication of a deviation from the baseline is observed is actually more representative of the onset of the transformation, but it may be difficult to reach universal agreement as to where that location is. For slow heating ramps, the difference in temperature between onset temperatures located by the convention and that indicated by “first deviation” may be negligible.

Thermodynamic constants, such as the heat released or absorbed in a phase transformation (latent heat), may be determined by DSC and, as will be shown in section 3.3, by DTA as well. A DSC plot of dQ/dt versus temperature may be translated to a plot of dQ/dt versus time, using the heating rate. The heat released/absorbed in a reaction is simply the area under the peak:

$$Q = \int_{-\infty}^{\infty} \left(\frac{dQ}{dt} \right) dt$$

Ideally, there is no harm in integrating from such broad extremes, since there is no accumulated area except where the peak lies.⁵

How does this latent heat relate to other thermodynamic quantities? Whether Q is equal to the change in internal energy, or something else, is dependent on the conditions of the experiment. Recalling the first law of thermodynamics and further recalling that work is defined as force through a distance:

$$dU = dQ - dW$$

$$dW = Fdx = \frac{F}{A} dx A = pdV$$

where p is pressure and V is volume, thus:

$$dU = dQ - pdV$$

If a sample is sealed in a gas-tight container that does not deform and allows no mass exchange with the outside world, then the transformations that are measured in the instrument are under the conditions of constant volume. Hence, $dV = 0$ and $dU = dQ$ or $\Delta U = Q$.

If, on the other hand, the sample is placed in an open crucible (as is more commonly the case), the volume of the system is no longer constant. For example, if the sample decomposes during a transformation, releasing a gas, the gas spreads throughout the room and the volume of the system increases. However, the pressure to which the system (sample plus released gas) is exposed is constant, that is, whatever atmospheric pressure is—generally 1 atm. Another energy function, the “enthalpy”, has been constructed for these conditions, which is defined as:

$$H = U + pV$$

⁵ Assuming the baselines before and after the peak match up (discussed in section 3.7.2).

The total differential of this function has the form:

$$dH = dU + pdV + Vdp$$

Inserting the expression for dU :

$$dH = dQ - pdV + pdV + Vdp = dQ + Vdp$$

Thus under the conditions of constant pressure, $dH = dQ$ or $\Delta H = Q$. Since enthalpy is the sum of state functions (U and pV), it too is a state function.⁶

As a short aside, we can use the above equations to define "heat capacity", the ability of a substance to hold thermal energy (via atomic vibration, rotation, etc.). The constant volume heat capacity is defined:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{dQ_V}{dT}$$

The constant pressure heat capacity is defined:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = \frac{dQ_p}{dT}$$

The importance of heat capacity will become apparent throughout the discussion of these instruments. When heat capacity

⁶The path independence of enthalpy is an essential feature of "calorimetry". If two reactive substances are suddenly placed into a vessel in which no heat can escape (adiabatic), the temperature within the vessel will rise or fall depending on whether the reaction was exothermic or endothermic. Under conditions of constant pressure (e.g. if the chamber was a piston system with weight on it), the heat flow, which is zero, would be equal to the change in enthalpy of the system. An impossible process could be imagined wherein reactants transform to products isothermally (ΔH_1) and after completion of the process, the products change temperature from T_1 to T_2 (ΔH_2). Since enthalpy is a state function, any conceived path which begins with reactants at T_1 and ends with products at T_2 will still result in the same ΔH for the reaction. Hence, $\Delta H = \Delta H_1 + \Delta H_2$ or $\Delta H_1 = -\Delta H_2$. If the heat capacities of the products are known (plus the heat capacity of the heated portions of the calorimeter structure), $\Delta H_1 = -\Delta H_2 = -\int_{T_1}^{T_2} C_p dT$. Thus, exploiting the concept of path independence, the isothermal enthalpy of reaction can be determined by measuring initial and final temperature in an adiabatic calorimeter. Rather than a piston system, bomb calorimeters are generally used where the volume of the chamber is kept constant ($\Delta U = 0$), not pressure; the name suggests what happens when the pressure during reaction becomes too great. Modern systems maintain adiabatic conditions by monitoring the temperatures inside and outside the chamber, and via resistance heating elements or hot and cold flowing water, maintain the temperatures the same. Since there is no temperature gradient, no heat flows and adiabatic conditions are maintained.

is expressed on a per gram rather than per mole basis, it is referred to as the “specific heat”.

Information with respect to the kinetics of a reaction may be established from DTA and DSC output by determining the fraction of reactant transformed and then fitting these data to reaction kinetics models. Modeling will be dealt with in later sections; for now, we will only show how to determine the fraction of material transformed, based on a DSC/DTA trace. If we assume that the heat released per unit time is proportional to the rate of the reaction, then the partial area swept under the peak divided by the entire peak area is the fraction transformed:

$$F = \frac{\text{Partial Area}}{\text{Total Area}}$$

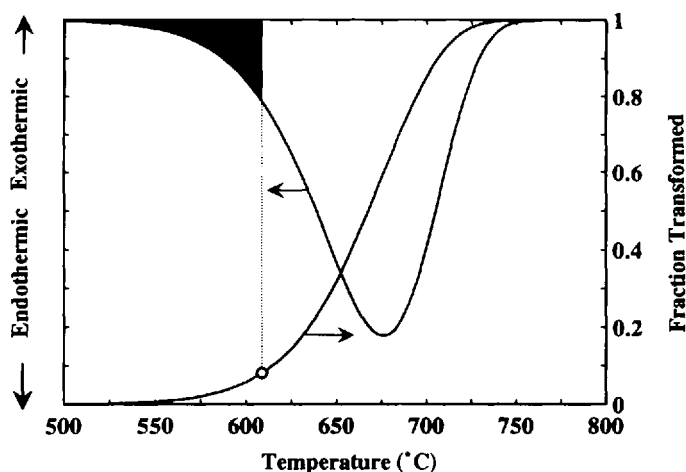


Figure 3.7: Fraction transformed via partial area integration of a DTA/DSC peak. A partial area, such as the shaded region, divided by the area under the entire endotherm contributes one datum to the fraction transformed versus temperature plot. Successive area calculations with increasing temperature will permit generation of the entire curve.

As shown in Figure 3.7, by determining the fraction transformed over successive times (or temperatures), the standard

“S”-shaped fraction transformed versus time curve can be generated.

3.3 Thermodynamic Data from DTA

Under limiting conditions, the area under a DTA peak, may be considered proportional to the change in enthalpy (constant pressure) or change in internal energy (constant volume) from the latent heat of a transformation. At first, this does not seem intuitive since the integration of ΔT over time or temperature does not yield units of energy. The original experimental configuration by Borchardt and Daniels [3] consisted of reactive and nonreactive fluids as sample and reference, respectively. These were stirred for temperature uniformity, as shown in Figure 3.8.

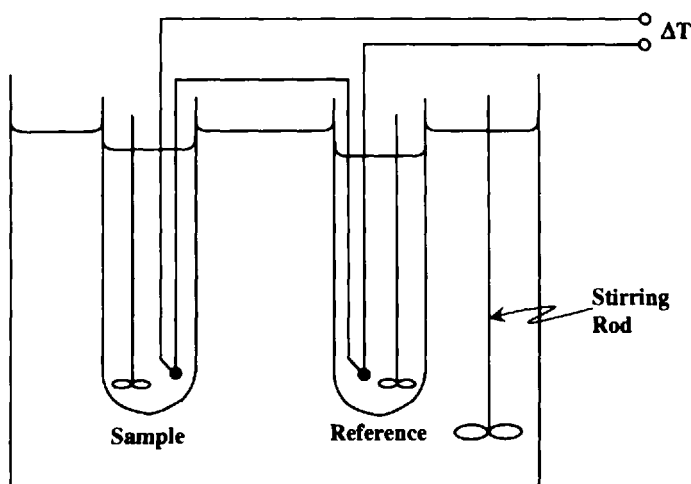


Figure 3.8: Borchardt and Daniels DTA [3]. Stirring rods maintain temperature uniformity within the sample and reference containers. The sample consisted of both reactive and reference fluid. Mixing in this way allowed the heat capacities and thermal conductivities of sample and reference to closely approach.

By rules of simple accounting, changes in the enthalpy of the sample at any point in time will either be manifested by a temperature change in the sample or heat flow in or out of it:

$$\frac{dH_s}{dt} = C_{p_s} \frac{dT_s}{dt} + \frac{dQ_s}{dt}$$

Similarly for the reference:

$$\frac{dH_r}{dt} = C_{p_r} \frac{dT_r}{dt} + \frac{dQ_r}{dt}$$

where the first term on the right-hand side represents enthalpy change from temperature rise, and the second term represents enthalpy change due to heat flow. Subscripts *s*, *r*, and *f* refer to sample, reference, and furnace, respectively. Heat only flows as a result of a temperature gradient; for steady state one-dimensional heat flow:

$$\frac{dQ_s}{dt} = \frac{kA(T_f - T_s)}{L}$$

$$\frac{dQ_r}{dt} = \frac{kA(T_f - T_r)}{L}$$

where *L* is the thickness of the test tube, *A* is the immersed test tube area, and *k* is the thermal conductivity of the test tubes.

If the test tubes are identical and we carefully match the total⁷ heat capacities of the sample and reference fluids, then it can be assumed that heat capacities as well as the thermal conductivities on both sides are equal. By subtracting the time rate of change in enthalpy of the reference from that of the sample, all enthalpy changes in the sample due merely to temperature change are eliminated. What is left must be enthalpy changes due strictly to transformations occurring within the sample:

⁷The "total" heat capacity refers to the heat capacity of the entire mass, that is the molar heat capacity multiplied by the mass, divided by the molecular weight. This is also referred to as the "thermal mass".

$$\frac{dH_{trans}}{dt} = \frac{dH_s}{dt} - \frac{dH_r}{dt} = C_p \left(\frac{dT_s}{dt} - \frac{dT_r}{dt} \right) + \frac{kA}{L}(T_r - T_s)$$

Let $\Delta T = T_s - T_r$ then:

$$\frac{dH_{trans}}{dt} = C_p \frac{d\Delta T}{dt} - \frac{kA}{L} \Delta T$$

If the thermal conductivity of the test tube is high, then the second term dominates:

$$\frac{dH_{trans}}{dt} \cong -\frac{kA}{L} \Delta T$$

or

$$\Delta H_{trans} \propto \int_{-\infty}^{\infty} \Delta T dt$$

Hence, the area under a DTA trace is proportional to the change in enthalpy of the sample (under conditions of constant pressure), as long as the following assumptions are valid:

1. The sample and reference heat capacities and container thermal conductivities are the same.
2. The thermal conductivity between the system and the medium is high.

Whether these assumptions are valid or not is dependent on a given DTA design. To determine the calorimetric capabilities of a particular instrument, one may simply test the melting endotherms of standard materials of known latent heats of fusion. The quantity:

$$M = \frac{\text{Area Under Peak}}{\text{Latent Heat of Fusion Per Gram} \cdot \text{Sample Mass}}$$

should be a constant for transformations in a series of different standard materials. For DTA designs where this holds true, the device may be considered capable of calorimetric measurements, and is coined a "heat-flux DSC".

Table 3.1: DTA/DSC calibration standards [4]

Standard	Transition Point ($^{\circ}\text{C}$)	Transition Energy (J/g)
Indium	156.60	28.45
Tin	231.88	60.46
Lead	327.47	23.01
Zinc	419.47	108.37
Potassium Sulfate	585.0 $\pm$ 0.5	33.26
Potassium Chromate	670.5 $\pm$ 0.5	35.56

3.4 Calibration

As alluded to in the introduction, thermal analysis instruments must be calibrated using well-characterized materials. The melting of pure metals is the most common calibrant for DTA's and DSC's. Table 3.1 provides the melting temperature and latent heats of transformation of standard materials. The software in more contemporary instruments permit input of peak area values and onset temperatures determined by a test run, as well as values from the literature, into a program. It then automatically applies abscissa and ordinate corrections to all future data collected by the instrument.

3.5 Transformation Categories

3.5.1 Reversible Transformations

Melting

For reversible transformations such as melting/solidification or the α to β quartz inversion in silica, heat flux DSC and power compensated DSC can each be equivalently precise in determining the latent heat of transformation. Transformations of

this sort obey LeChatelier's principle,⁸ which dictates, for example, that ice water will stay at 0°C until it fully transforms to ice or fully transforms to water. All added heat to the system contributes to the phase change rather than a change in temperature as long as both phases exist. For this reason, melting transformations (and similarly, solidification transformations upon cooling) have a distinct shape in DTA/DSC traces, as shown in Figure 3.9.

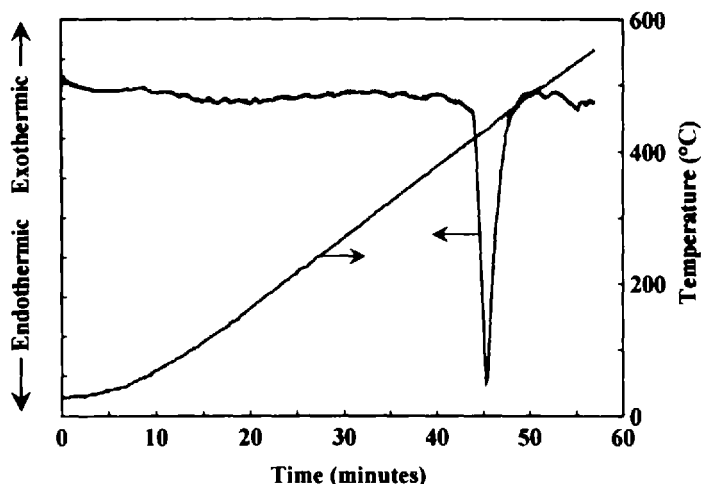


Figure 3.9: DTA trace showing the linear rise and exponential decay characteristic of a melting endotherm. The trace shown is for the melting of zinc in an argon atmosphere, heated at 10°C/min. DSC traces of fusion have a similar shape.

In a DTA scan at a constant heating rate where a solid sample fuses, the reference material increases in temperature at the designated heating rate, while the sample temperature remains at the melting temperature until the transformation is complete. Thus, when ΔT versus reference temperature is plotted, a linear deviation from the baseline value is seen on the leading

⁸Formally: If the external constraints under which an equilibrium is established are changed, the equilibrium will shift in such a way as to moderate the effect of that change.

edge of the endotherm. The peak of the endotherm represents the temperature at which melting terminates. When the transformation is complete, the sample is at a lower temperature than its surroundings; it thus heats at an initially accelerated rate, returning to the temperature of the surroundings. The corresponding DTA trace returns to the baseline. The return portion of the trace follows the shape of an exponential decay, where initially, the sample temperature rapidly catches up to that of the surroundings, and then more slowly as the sample and surrounding temperatures approach.

Note that the shape of the DTA trace would be different if the x -axis temperature was the sample temperature, as shown in Figure 3.10 (middle). Ideally, the melting portion of the trace would correspond to a vertical line since the sample temperature would not change until melting is complete. For thermocouple junctions immersed within the sample powder, this ideal case is approached; the heat flowing radially inward is absorbed by the exterior portion of the sample as latent heat. Heat does not flow to the region around the thermocouple junction and hence its temperature is thermostated until the reaction is complete [10]. Most contemporary DTA's, however, are designed so that the thermocouple junction is in contact with the underside of the sample container, and this container tends to increase in temperature to some extent under the influence of the surroundings, which are rising in temperature. For this configuration, the net result is that traces in which the x -axis temperature is the sample temperature tend to have a sharper rising slope and broader exponentially dropping slopes than traces in which the x -axis temperature is that of the reference. Whether the x -axis represents sample or reference temperature is dependent on which half (i.e. which two terminals in Figure 3.1) of the differential thermocouple the voltage is measured.

One technique for graphically representing data in which the x -axis represents sample temperature is to expand or contract

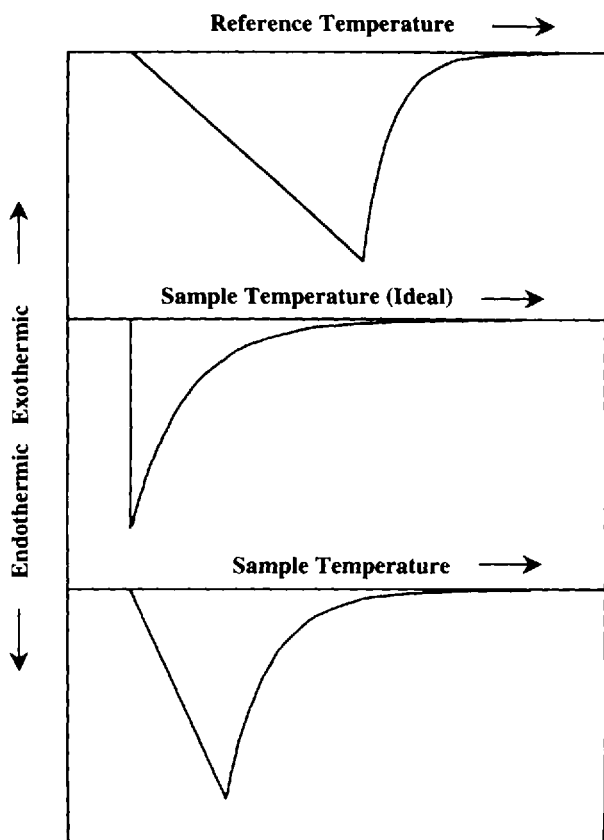


Figure 3.10: Effect of choice of x -axis temperature. Top: x -axis corresponding to reference temperature. Middle: idealized case for x -axis corresponding to sample temperature (immersed thermocouple junction). Bottom: x -axis corresponding to sample temperature (thermocouple junction in contact with underside of sample crucible).

the axis annotations during reactions (e.g. “DSC mode” in the Perkin-Elmer DTA, see Figure 3.11). In this case the x -

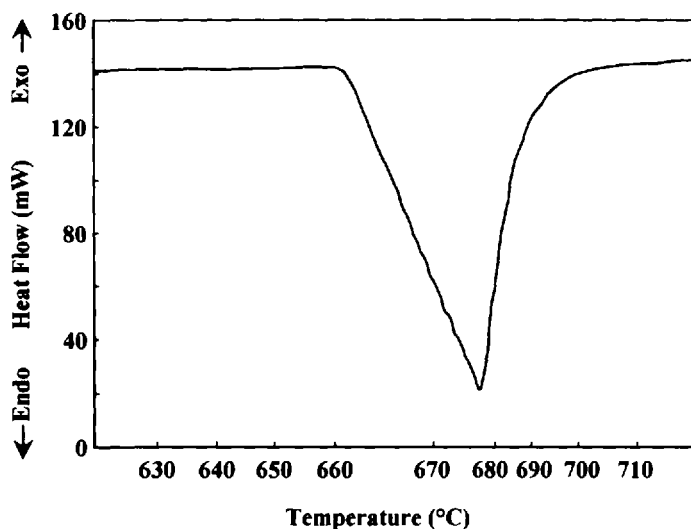


Figure 3.11: “DSC” mode in Perkin-Elmer DTA, where the x -axis annotations were stretched or compressed in temperature regions where transformations occurred. The endotherm represents the melting of 38.8 mg of aluminum, heated at $10^{\circ}\text{C}/\text{min}$ in a nitrogen atmosphere.

axis is linear with time, but the scale is non-linearly marked as sample temperature. During an endothermic reaction, for example, the sample temperature initially increases less rapidly than the furnace heating rate then increases more rapidly than the furnace after the peak. Thus, the temperature x -axis is expanded in regions between the onset and the peak, and it is compressed in regions between the peak and termination point of the exotherm. This method, however, is somewhat visually awkward.

It is important to note that even though the melting transformation is complete at the peak of the endotherm, it is still the entire area under the peak which represents the latent heat of fusion. Recall that the enthalpy of the reference increases during the time of the transformation since its temperature in-

creases ($\Delta H = \int_0^T C_p dT$), as dictated by the heating rate. In our derivation (Borchardt and Daniel's experiment), the time rate of change of reference enthalpy was subtracted from the time rate of change in sample enthalpy, leaving only the enthalpy change due to the latent heat of transformation in the sample. However, during sample melting (linear portion of the endotherm between onset and maximum of the endotherm), there is no enthalpy change due to temperature increase, simply because there is no temperature increase. Only after the completion of the transformation does the sample temperature catch up to that of the reference; this corresponds to the exponential decay portion of the endotherm. This portion of the peak thus needs to be included in the integral, so that both sample and reference have shown the same contribution to enthalpy change due to increased temperature.

The linear drop and exponential recovery shape of these transformations also appear in power-compensated DSC traces, but for different reasons. The temperature measuring device (RTD) measures its own temperature, which is influenced by all substances in the chamber, the housing, the sample crucible, as well as the melting sample. The device adds power to the sample side as needed to compensate for the cooling effect on the chamber due to sample melting. This energy requirement increases linearly since the setpoint sample temperature increases linearly. When melting is over, the need for extra heat flow to the sample chamber side drops exponentially as the chamber temperature quickly catches up to the setpoint.

Boiling

A heat-flux DSC trace of the boiling of water is shown in Figure 3.12. The shape of the peak differs from that of fusion in that there is a broad leading edge.

Condensed phases have characteristic vapor pressures, which increase with temperature. Given enough time, the water in a filled glass will completely evaporate. This is motivated by the

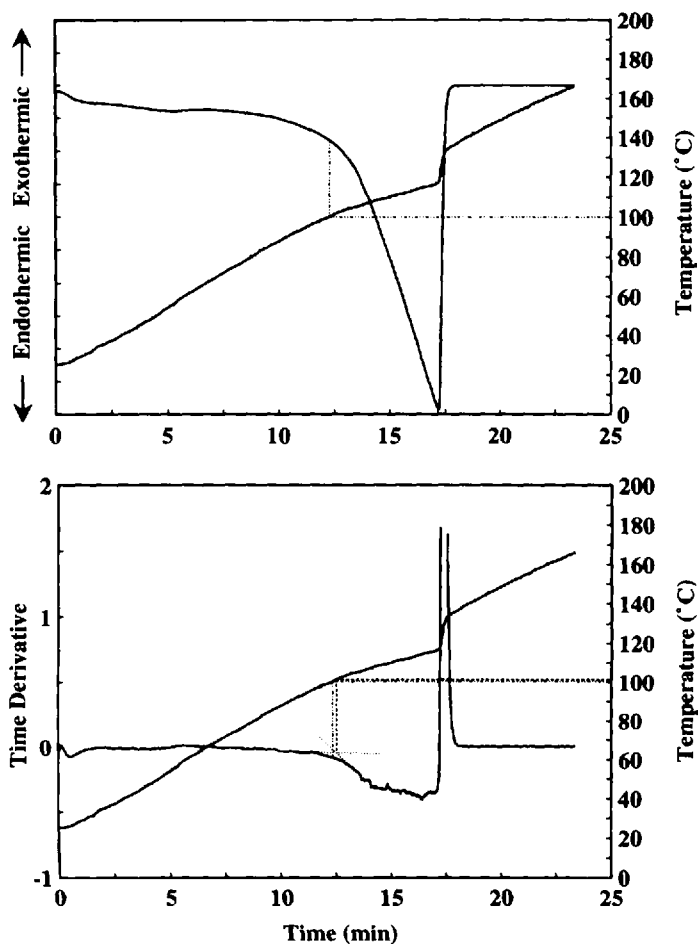


Figure 3.12: Boiling of water in a heat-flux DSC. A drop of water was hermetically sealed in an aluminum container and a pin-hole was pierced through the container top. This acted to discourage complete evaporation of the water during heat-up to the boiling temperature of water under 1 atm: 100°C. Distinguishing the boiling point from the DSC trace is hampered by the accelerating vaporization leading up to that temperature. The lower trace plots the time derivative of the DSC trace (slopes determined over 5 points in a data set of 1000 points, see section 4.2). The extrapolated inflection point at $\sim 102^\circ\text{C}$ comes very close to the correct boiling point. A shift of 2°C under a heating rate of $10^\circ\text{C}/\text{min}$ is a reasonable temperature lag (see section 3.8.3).

partial pressure of water in the atmosphere being less than the equilibrium vapor pressure of water, the extent of the driving force being dependent on the relative humidity. Some time is involved in the evaporation since random motion must diffuse away gaseous water released in the vicinity of the gas-liquid interface.

In the DSC, at a heating rate of $10^{\circ}\text{C}/\text{min}$, the equilibrium vapor pressure of water vapor increases with increasing temperature, so that the rate of evaporation increases. Diffusion of water vapor away from the gas-liquid interface requires more evaporation to re-establish equilibrium. This corresponds to an endothermic trend of increasingly vertical slope. When the water temperature reaches 100°C , its vapor pressure reaches 1 atmosphere (at an elevation where the air pressure is 1 atm). At that point, the vapor pressure of water vapor cannot increase (above 1 atm) since it would simply expand away. Thus, local equilibrium cannot be established and the water boils; any heat flow into the water would contribute to vaporization rather than a rise in temperature. The appearance of the DTA/DSC trace then follows closely that of a fusion endotherm, with a linear leading edge and an exponential-decay return. The return to the baseline is very rapid since all of the specimen has been removed from its container. It immediately follows that a much more significant change in sample chamber heat capacity results as compared to a fusion reaction. The corresponding baseline shift, however, is subtle in Figure 3.12, since the scale of trace is necessarily coarse due to the high intensity of the boiling endotherm: the latent heats from liquid to gas transformations are 9 to 12 times that of solid to liquid transformations [11].

Decomposition

A different DTA/DSC endotherm shape would be expected for calcination reactions such as $\text{CaCO}_{3(s)} = \text{CaO}_{(s)} + \text{CO}_{2(g)}$ (Figure 3.13). Given that the partial pressure of CO_2 in dry air is

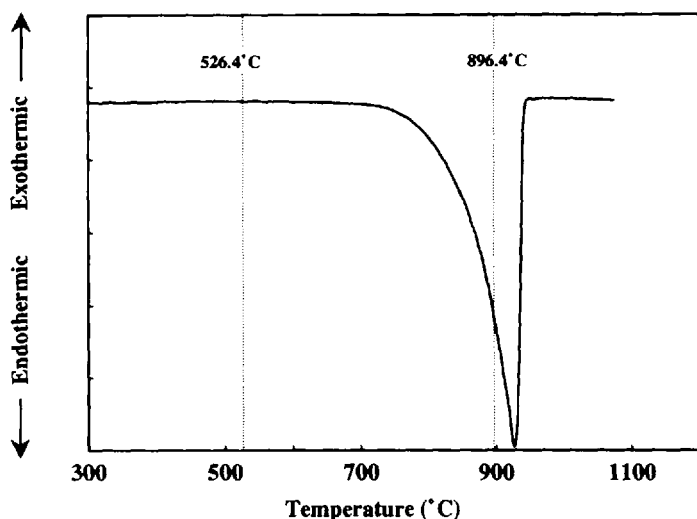


Figure 3.13: DTA trace of the decomposition of calcium carbonate.

0.033% [12], the thermodynamic⁹ decomposition temperature of CaCO_3 should be 526.4°C. This temperature, marked on the figure, does not correspond to any visible deviation from the baseline. Apparently, only a minute amount of CaCO_3 must decompose to locally meet the partial pressure requirements of CO_2 for this and somewhat higher temperatures, and such decomposition has an undetectable thermal effect. However, the equilibrium partial pressure of carbon dioxide increases exponentially with temperature, requiring a much more rapid decomposition; hence, the DTA trace begins to deviate from the baseline with increasing temperature. At 896.4°C, the temperature at which the equilibrium partial pressure of CO_2 reaches

⁹The thermodynamic criterion for the equilibria $\text{CaCO}_{3(s)} = \text{CaO}_{(s)} + \text{CO}_{2(g)}$ is $\Delta G^\circ = -RT \ln K_p$, where ΔG° is the change in Gibbs free energy of the reactants and products in their standard state, R is the gas constant, and K_p is the equilibrium constant. For this equilibria, $K_p = p_{\text{CO}_2}$ for pressure in units of atmospheres. Values for ΔG° are tabulated in the form $\Delta G^\circ = a + bT$; combining these expressions yields an exponential relationship between the partial pressure of CO_2 and temperature for the above equilibria. Complete derivations and discussion of these equations may be found in physical chemistry textbooks such as references [13] and [14].

1 atm, the reaction rate would be expected to significantly increase, using arguments similar to those used for the boiling of water. Other factors, such as the diffusivity of CO_2 gas out of the inwardly growing (into the CaCO_3 grain) porous oxide product layer and the rate of heat flow into the (endothermic) reaction zone [2], also may act to slow the decomposition process. Thermodynamically, decomposition reactions such as these are reversible; that is, given a CO_2 atmosphere and adequate time, CaCO_3 should form from CaO upon cooling.

Phase Equilibria

Phase diagrams can either be calculated [15] or determined experimentally. On the experimental side, cooling curves have often been used in which a molten mixture at sufficiently high temperature is slowly cooled and its temperature recorded as a function of time. At the transformation temperature, the sample temperature will remain invariant until the transformation is complete. By comparison, cooling traces using DTA/DSC provide greater phase equilibria sensitivity, since signals from only transformation events are detected and amplified.

In the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system, the DTA traces expected to be observed at various compositions are sketched in Figure 3.14.¹⁰ Upon cooling the eutectic composition at 4 mol% Al_2O_3 , a single sharp exotherm would be expected as silica and mullite form from the melt at 1595°C . A melt of 20 mol% alumina would show an exothermic trend, starting at 1754°C , which would endure until 1595°C since mullite would continue to precipitate out of solution. A sharp peak would be expected at the eutectic temperature as the remaining liquid phase solidified. A melt of 50 mol% alumina would follow a similar argument, but the peak shapes would be different. The slope of the liquidus line is significantly less steep at 50 mol% as compared to 20 mol% Al_2O_3 . Initial cooling below the liquidus for the 50 mol% alumina composition will cause rapid precipitation of mullite, as

¹⁰Reference [16] is recommended for background on phase diagrams.

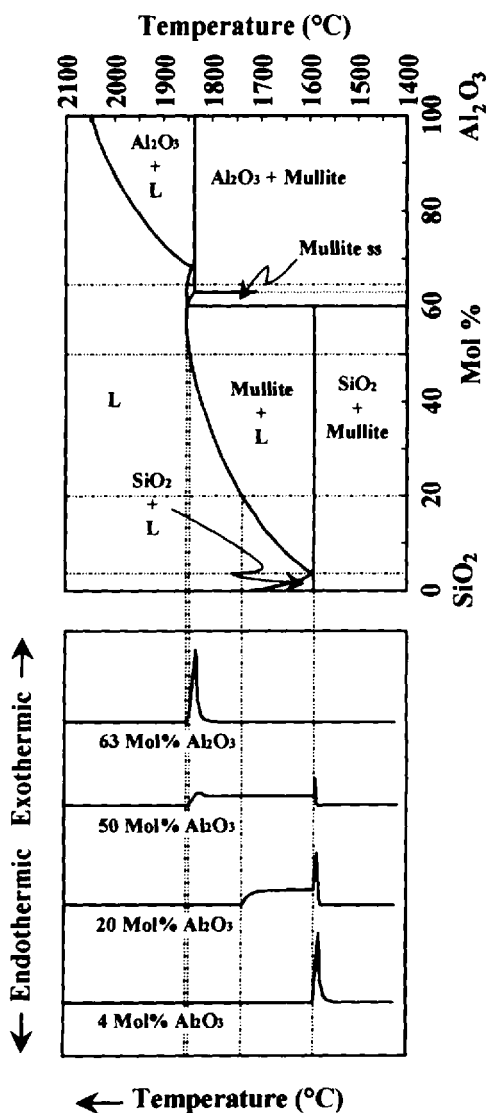


Figure 3.14: SiO₂-Al₂O₃ system with sketches of representative DTA traces from cooling the specified compositions.

implied by using the lever rule with decreasing temperature. This should result in an initially larger exothermic trend for the 50 mol% case. This exotherm should diminish to the level of the 20 mol% alumina trace at 1754°C since the composition of the melt phase at that point is identical to that of the 20 mol% alumina case.¹¹ The sharp exotherm at 1595°C should be smaller in the 50 mol% alumina case since there is less liquid phase remaining to solidify. The sharp peak observed for the 63 mol% Al_2O_3 composition is due to mullite formation over the narrow temperature range 1850-1840°C.

Experimental observation of the traces sketched in the figure may be compromised by the high viscosity of silicate containing melts. Often, compositions containing appreciable silica are rapidly quenched after slowly cooling to a specified temperature, where the phases formed are evaluated microscopically or with x-ray diffraction.¹² Further, transformations amongst more refractory ceramic materials may be above the operating range of most commercially available DTA's. Establishing a DTA signal from the output of infrared or optical pyrometers has been demonstrated, which extends the range of the technique to very high temperatures (3600°C) [18][19].

3.5.2 Irreversible Transformations

Irreversible transformations are those in which reactants do not reform from products upon cooling. Generally one of the reactants is in a metastable state, and only requires thermal agitation or the presence of a catalyst to initiate the transformation. Examples would be combustion of a fossil fuel or glass devitrification. Power-compensated DSC has a distinct advantage over heat-flux DSC in determining the kinetics of transformation from metastable phases. In these type of reactions,

¹¹Implied in this discussion is that the exothermic deviation of the trace (in the temperature region where liquid and solid are in equilibrium) should follow the slope of the liquidus line. Thus, it is conceivable that the shape of the liquidus line can be predicted from the shape of a single DTA cooling trace of a strategic (e.g. 59 mol% Al_2O_3) composition.

¹²See reference [17] for background on x-ray diffraction.

the sample temperature will not remain at a constant value during the transformation. As glass devitrification proceeds, for example, heat released at the glass-crystal interface raises the temperature of the sample. The rates of such transformations generally have an exponential temperature dependence, causing them to proceed more quickly, which in turn causes a more rapid temperature rise, and so on. As a result, these “self-feeding” reactions will show irregular temperature/time profiles when externally heated at a constant rate. A heat-flux DSC simply measures the temperature difference between sample and reference and makes no effort to maintain the sample temperature at the setpoint value (whether that is isothermal or a constant heating ramp). However, a precise value of sample temperature, or a linear sample heating rate, is necessary to fit these transformation data to kinetic equations in order to determine the activation energy of the transformation (section 3.6). Power-compensated DSC has the advantage that it measures the transformation by maintaining a null balance, while also maintaining the sample and reference temperatures at the setpoint.

Under slower heating rates in heat-flux DSC, the deviation of sample temperature from the setpoint during a self-feeding reaction may be maintained adequately small so as to be neglected. If the furnace feedback control is set to act based on the temperature of the sample (that is the sample temperature thermocouple is the control thermocouple), then the control system may be able to allow the transforming sample to heat itself at a constant rate, and the heat input from the furnace will retreat as needed.

To maintain the sample at the setpoint temperature during a self-feeding reaction in a power-compensated DSC, small sample mass (e.g. <10 mg) and excellent thermal contact between the sample and its container, as well as the container and the chamber, are required. Figure 3.15 shows the rather unusual effects of using excessive sample masses of glass in

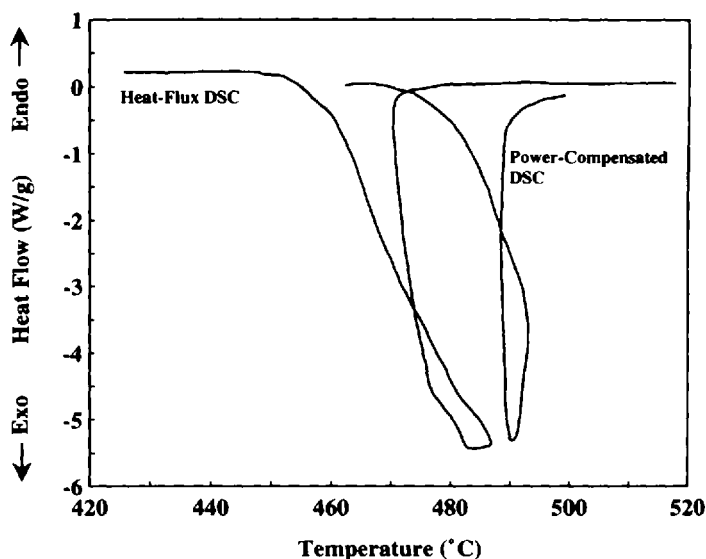


Figure 3.15: Devitrification of amorphous CdGeAs_2 in a heat flux and power-compensated DSC, heated at the same rate, as a function of sample temperature [6]. 61.4 mg and 41.4 mgs of glass were used in the heat-flux and power-compensated DSC's, respectively. Note that exothermic and endothermic directions are consistent with those used in power-compensated DSC, but reversed compared to the usual convention in this book.

heat-flux and power-compensated DSC's. In the case of the heat-flux DSC, the sample temperature rose by $\sim 35^\circ\text{C}$ before cooling to the temperature of its surroundings. The trace doubles back on itself, since when the transformation is complete, the sample temperature must cool to the temperature of the surroundings, even though the surroundings are being heated at a constant rate. The doubling back demonstrated for the power-compensated DSC indicates that the excessive sample mass did not allow the instrument to maintain the sample temperature at the setpoint (linear heating ramp). However, the comparatively diminished extent of self feeding in the case of the power-compensated DSC is apparent. The apparent reaction onset was $\sim 20^\circ\text{C}$ lower for the heat-flux DSC where there

was no attempt to control the "ignition" of the reaction.

3.5.3 First and Higher Order Transitions

Phase transitions in materials have been characterized as either first or "higher" order. Formally, if the Gibbs free energy function is discontinuous at the transformation temperature, it is a first order transformation; if not, it is of higher order. Examples of a first order phase transformation would be boiling, sublimation, and solidification. Most solid-state polymorphic transformations are also first order transitions. The quartz to trydimite (or cristobalite) reconstructive transformation requires the breaking of bonds to form a new crystal structure. Transformations such as this show an activated barrier associated with the breaking of bonds and the diffusion of atoms, and thus occur sluggishly at lower temperatures. The significant kinetic barrier to these transformations permits metastable presence of the high temperature phases at pressures and temperatures where they are not thermodynamically stable. For example, cristobalite may be permanently formed at room temperature by rapid quenching from elevated temperature. Displasive (martensitic¹³) transformations such as α - β quartz require only shifts in bond angle and occur quite rapidly. Quenching-in of the high temperature forms of these materials is more difficult, and sometimes cannot be accomplished without the introduction of impurity atoms into the high-temperature structure. The latent heats, and thus the DTA/DSC peak intensities of first order phase transitions, increase with increasing severity of structural change via the transformation. For example, the latent heat of the α to β quartz displasive transformation in silica is 0.63 kJ/mol. For the fusion of aluminum, the latent heat is 2.57 kJ/mol, and for the boiling of aluminum the latent

¹³Examples of important martensitic transformations are: 1) austenite (cubic) to martensite (tetragonal), important in the hardening of steels, 2) the ferroelectric (tetragonal) to paraelectric (cubic) transformation in BaTiO₃, used in capacitor dielectrics, and 3) the tetragonal to monoclinic transformation in ZrO₂, discussed in section 7.6.

heat is 67.9 kJ/mol [7].

Higher order transitions show little or no structural alteration. Second order and “lambda” transitions both fit in this category. An example of a second order transformation is the nonsuperconducting to superconducting transformation at cryogenic temperatures (e.g. lead at -265.96°C). An example of a lambda transformation is the Curie temperature in ferromagnetic materials. Below this temperature, the material can be made into a permanent magnet, while above this temperature it cannot (paramagnetic). In the ferromagnetic state, an applied magnetic field can bring the dipole moments of neighboring atoms into mutual parallelism, and they will remain that way even after the magnetic field is removed. As the Curie temperature is approached, the increasing disorder due to random thermal agitation of electrons diminishes the parallelism. The Curie temperature represents the point at which the last of the mutual parallelism disappears.

Figure 3.16 shows a comparison between the enthalpy and heat capacity (temperature derivative of enthalpy under constant pressure) as a function of temperature for the different types of transformations. Using the melting point of a solid as an example of a first order transformation, the large discontinuity in enthalpy at the melting point is due to the latent heat absorbed for the structural alterations of the transformation. During that period, the heat capacity is infinite, since all heat input contributes to the transformation and not temperature rise ($C_p = (\partial H / \partial T)_p$). With a second order transition, there is no latent heat associated with the transformation, hence the change in heat capacity at the critical temperature is finite. Since lambda transformations show minute structural change, they are placed in a different category (the “lambda” name is derived from the shape of the heat capacity versus temperature curve), since the associated latent heats result in infinite heat capacities at the critical temperatures under careful measurement [8]. These transformations are still often referred to

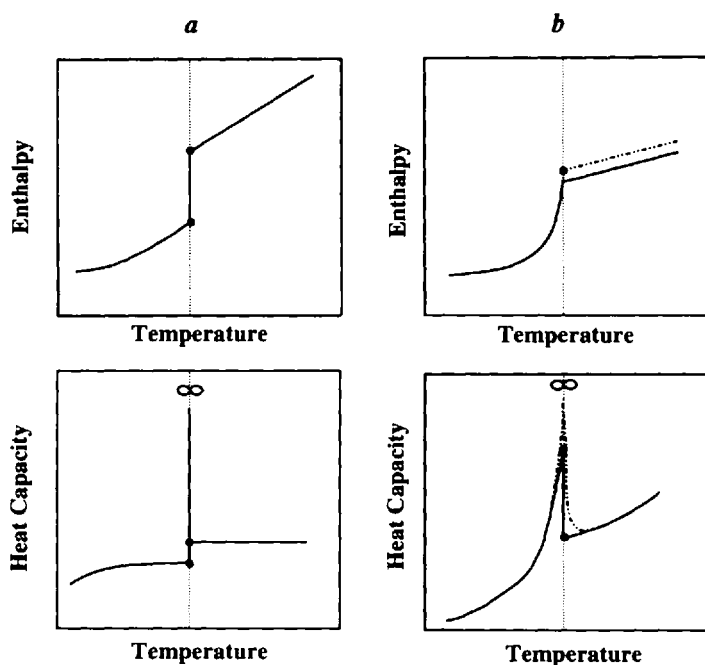


Figure 3.16: Enthalpy and heat capacity as a function of temperature for (a) first and (b) second order and lambda transformations [5][8]. Lambda transformation behavior is shown with dot-dot-dashed lines.

as second order. With both second order and lambda transformations, the materials show a premonition of the upcoming transition via an accelerating increase in heat capacity as the critical temperature is approached. Using the ferromagnetic to paramagnetic transformation as an example, as the critical temperature is approached, heat is increasingly absorbed by the material in order to annihilate the parallelism of neighboring dipole moments. At the critical temperature, this mechanism of energy absorption is terminated and the slope of the heat capacity curve sharply differs from that approaching the critical temperature. The heat capacity curve shows an infinite slope at the critical temperature, implying a latent heat of transformation. However, this latent heat is minute compared to that

of a first order transformation, where appreciable structural changes occur.

An example of a heat-flux DSC trace of a lambda transformation is shown in Figure 3.17. The endothermic trend ap-

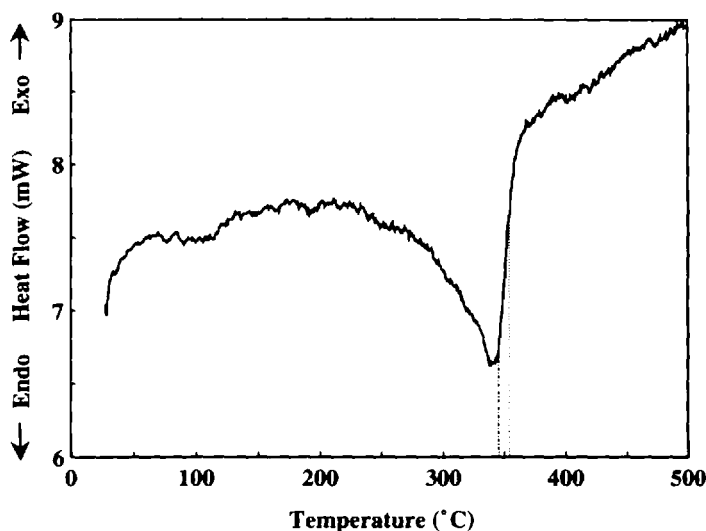


Figure 3.17: Heat-flux DSC trace at 10°C/min of the ferromagnetic to paramagnetic lambda transformation at 354°C in nickel (dotted line). The Curie temperature indicated by the DSC trace is 346°C (dot-dashed line).

proaching the Curie temperature is from randomization of the magnetic dipoles. Just after the Curie temperature, a sharp exothermic shift is apparent as heat is no longer absorbed by the sample for randomization.

3.6 An Example of Kinetic Modeling

Nucleation and growth processes such as glass crystallization generally follow the Johnson-Mehl-Avrami (JMA) model:

$$F = 1 - \exp(-kt^n)$$

where F is fraction transformed, k is a time independent but temperature dependent rate constant, and n is referred to as the mechanism constant. If in the derivation of this equation, it was assumed that nucleation occurs homogeneously (e.g. without impurity surfaces to catalyze the process) and the crystalline regions grew as spheres, an n value of 4 would be established. For different assumptions about the process, the mechanism constant will vary from unity to four. Therefore, if experimental data can be fit to this model, and if the model is appropriate to the phenomenon studied, then statements can be made about the mechanism of the experimentally measured transformation.

An isothermal experiment on the DTA/DSC can be run in which the sample temperature is quickly brought up into a temperature regime of interest and held during the crystallization transformation. Determining the fraction transformed as a function of time from partial areas under the DTA/DSC peak was described in section 3.2.

The above equation can be rearranged into the equation of a line:

$$\ln(1 - F) = -kt^n$$

$$\ln[-\ln(1 - F)] = \ln k + n \ln t$$

From fraction transformed versus time data, the values of F and t can be inserted into this function, to generate a plot which should take the form of a straight line. By crystallizing samples at various isothermal temperatures, a series of fraction transformed traces and corresponding JMA traces can be generated, as shown in Figure 3.18. The slopes of the lines in the JMA plot represent the mechanism constant; each slope should be the same, presuming that the mechanism of the reaction has not changed for crystallization at various isothermal temperatures.

The rate constant is generally taken to have an Arrhenius temperature dependence:

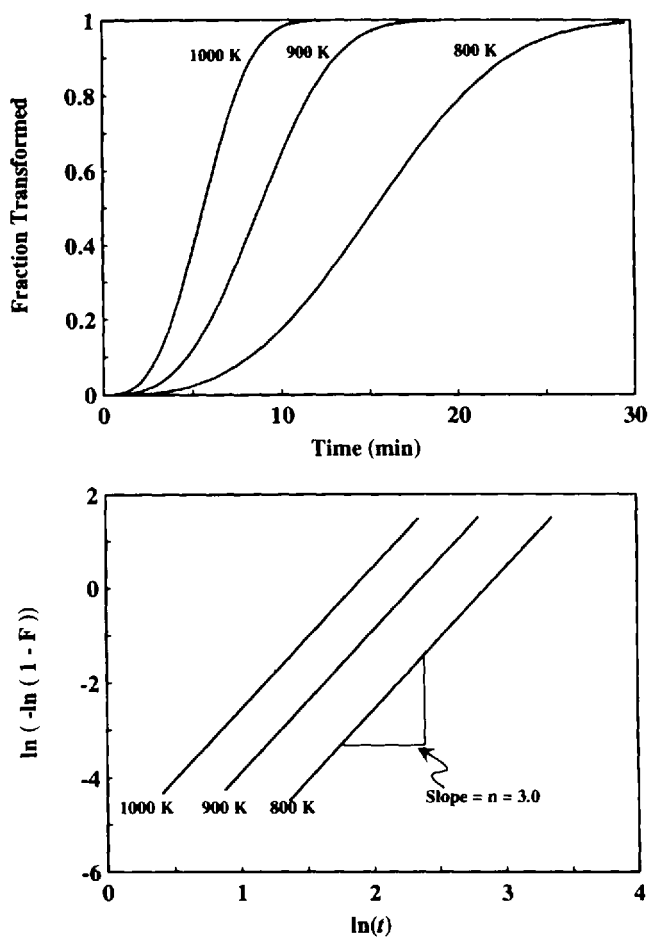


Figure 3.18: Illustration of a transformation of fraction transformed plot to a JMA plot.

$$k = k_0 \exp \left(\frac{-E_a}{RT} \right)$$

where k_0 is a pre-exponential constant and E_a is the activation energy of the transformation. The activation energy is an important descriptive factor of the extent of the exponential temperature dependence of a transformation and is the compared value for the kinetics of reactions. For each JMA trace in Figure 3.18, a value of $\ln k$ corresponding to each isothermal temperature can be determined from the y -intercept. These values can then be put into the logarithmic form of the Arrhenius equation ($\ln k = \ln k_0 - E_a/RT$). The best fit line to these points would establish the activation energy of the reaction as the slope (after multiplying by $-R$), as illustrated in Figure 3.19.

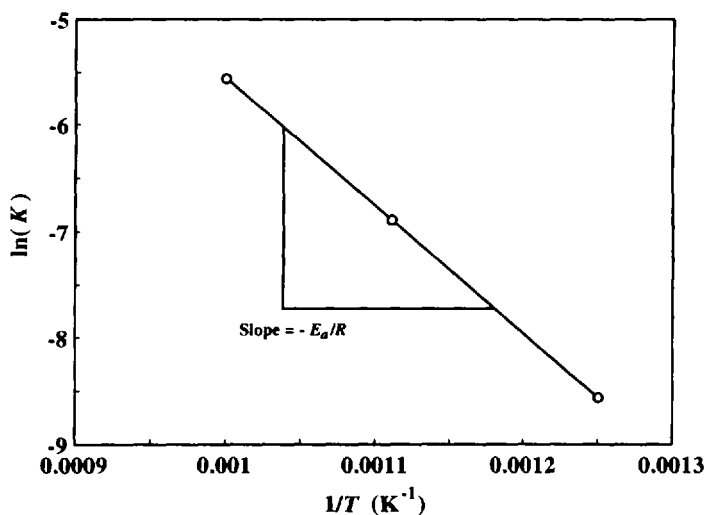


Figure 3.19: Arrhenius plot to determine the activation energy of crystallization. Based on the slope of the line in this example, $E_a=100$ kJ/mol.

Experimental methods involving rapid heating followed by isothermal crystallization become difficult to realize at higher

temperatures where the reaction proceeds rapidly. Methods of analysis have been developed in which samples are crystallized under a constant heating rate, but the theoretical basis for these methods have faced criticism [21].

3.7 Heat Capacity Effects

As the name implies, heat capacity refers to the ability of a substance to contain thermal energy. The mechanism by which solids sustain thermal energy is the vibration of atoms about a mean lattice position. Metallic solids have the additional energy storage mechanism of electron motion. Liquids have more mechanisms of energy storage than solids, e.g., atoms can translate and rotate amongst themselves, as well as vibrate. Thus, liquids generally have a higher heat capacity than their crystalline counterparts. The variation of heat capacity with temperature for a crystalline solid is depicted in Figure 3.20. As can be seen from the figure, the heat capacity of a solid increases steadily with temperature, starting from absolute zero (no atomic vibrations), then saturates at a value of $3R$ (24.95 J/mol·K), where R is the gas constant. The temperature at which heat capacity becomes nearly constant is the Debye temperature (Θ). For oxide ceramic materials this temperature is $\sim 1000^\circ\text{C}$, whereas for metals this value can be below room temperature.

The DSC/DTA trace sketched in Figure 3.21 shows the effect of a poor match between the total heat capacity of the sample and the reference. As can be seen, there is a distinct shift in the baseline at the beginning of the trace. The cause of this can be visualized by assuming an empty reference container and a sample container with a significant mass of sample granules. Starting at room temperature, the sample and reference temperatures would be the same, thus ΔT is zero. Since more thermal energy is required to raise the temperature of the large mass in the sample container as compared to the empty refer-

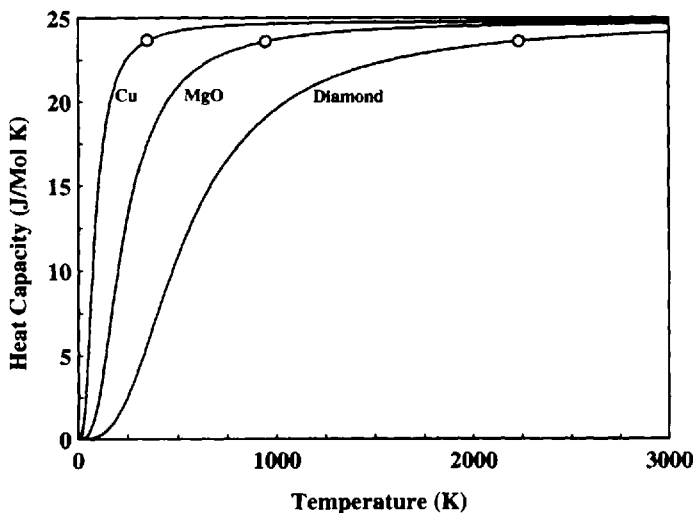


Figure 3.20: Heat capacity of copper ($\Theta = 343$ K [22]), magnesia ($\Theta = 946$ K [23]), and diamond ($\Theta = 2230$ K [23]) as a function of temperature, as predicted by Debye theory:

$$C_V = 3R \int_0^{\nu_m} \frac{(3\nu^2/\nu_m^3)(h\nu/kT)^2 \exp(h\nu/kT) d\nu}{(\exp(h\nu/kT)-1)^2}$$

where h is Planck's constant, k is Boltzmann's constant, ν is frequency, and $\nu_m = \Theta k/h$ [23]. Methods of numerical integration for functions such as this are discussed in section 4.1. Circles in the figure indicate the Debye temperatures for each substance.

ence container, the sample lags the reference in temperature. This lag initially increases until the difference in temperature reaches a steady-state value, at which point it may remain more or less constant as long as the heating rate does not change.

3.7.1 Minimization of Baseline Float

Random floating in the baseline is often observed, such as that illustrated in Figure 3.22. This occurs when the total heat capacities of the sample and reference are not matched, or if, for example, the reference container is positioned closer to the furnace windings than the sample container. This difference often

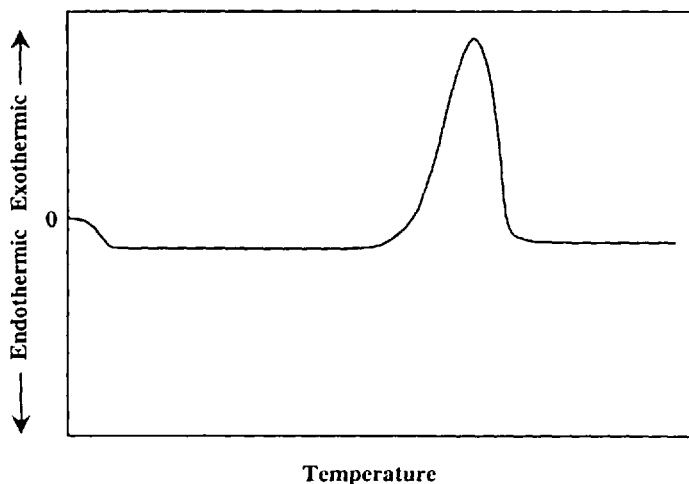


Figure 3.21: Effect of total heat capacity differences between sample and reference on baseline position in a DTA/DSC trace. See text for discussion. In addition, this sketch of glass crystallization shows the baseline shifted in the exothermic direction after crystallization: In the same region of temperature, the heat capacity of a crystal is less than the corresponding glass above T_g (see sections 3.7.2 and 7.6).

does not remain constant over temperature since, in temperature regions at or above $\sim 600^\circ\text{C}$, radiant heat transfer diminishes the lag in temperature between sample and reference.¹⁴

The DTA design most susceptible to this form of baseline float is the post-type (Figure 3.23a), where care must be taken to ensure that sample and reference are centered in the tube,¹⁵ and are of nearly identical total heat capacity. The older nickel (or other refractory metal) block design, shown in Figure 3.23b, where differential thermocouple beads reside directly within

¹⁴Stephan's law for blackbody (perfect absorber and perfect emitter of radiant energy) radiation, $R_T = \sigma T^4$, relates the radiancy R_T , which is the rate of heat flow from a unit surface area, to the fourth power of temperature, where σ is the Stephan-Boltzmann proportionality constant. This rapidly increasing heat transfer rate with temperature tends to even out temperature gradients, even with significant differences in total heat capacity between sample and reference.

¹⁵If the baseline float in a post-type DTA appears extreme, generally the first item to check is the centering of the sample and reference posts in the furnace tube.

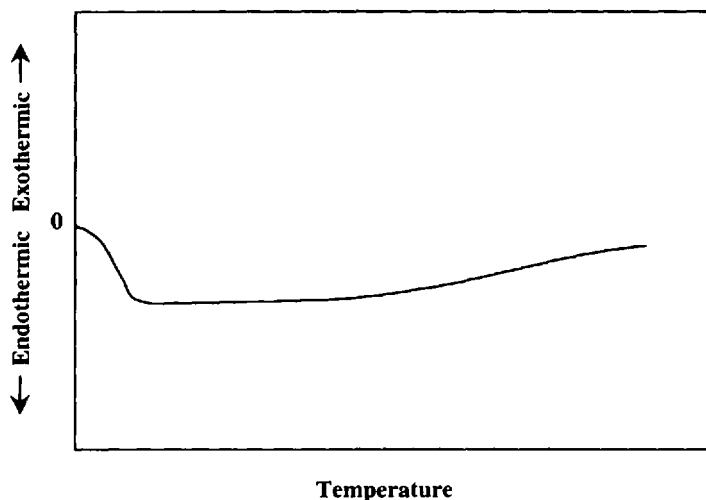


Figure 3.22: Random baseline float in a DTA trace.

the sample and reference powder, is very effective at minimizing baseline float. The high thermal conductivity of the metal block, along with its large heat capacity, tends to minimize any temperature non-uniformity in regions in thermal contact with sample and reference powders. Furthermore, peaks tend to be sharper with this design, since the block acts as a much more effective heat reservoir than air. Endothermic transformations are thus rapidly fed the thermal energy needed to go to completion, and heat is more easily ejected to the surroundings during exothermic transformations. However, the design cannot be used for fusion reactions, and even during solid state reactions, the design is sensitive to sample density changes, e.g. the sample powder may pull away from the thermocouple bead.

The TA Instruments heat-flux DSC design (Figure 3.23c and Figure 3.5), where the sample and reference rest on elevated platforms of a constantan disk, also has minimal baseline float since the high thermal conductivity of the disk has an effect similar to that of the nickel block. The latter device is generally more calorimetric than the nickel block design. By mea-

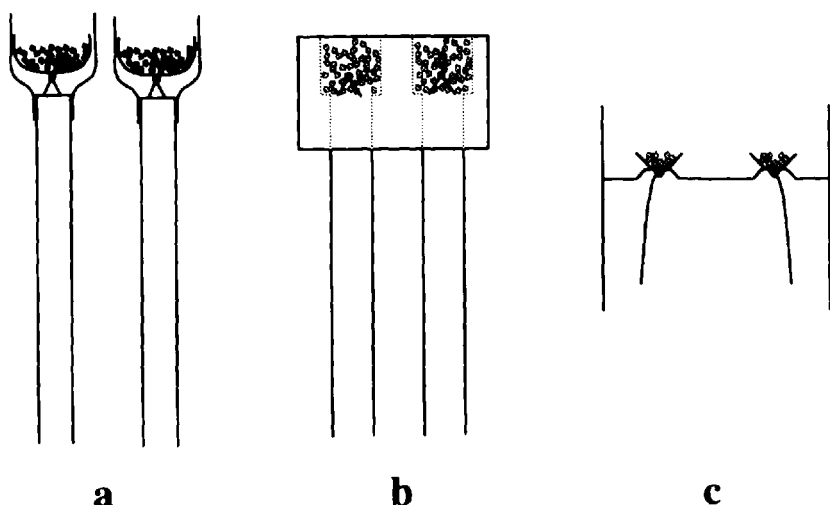


Figure 3.23: DTA design configurations: a) post type, b) nickel block, and c) constantan or platinum disk (heat-flux DSC).

asuring the temperature of the sample and reference container rather than the sample and reference powders directly, the effects of variable powder packing, particle size, and temperature distribution within the chamber are averaged out.

With irreversible transformations, it is often advantageous to expose the sample and reference to the same heating schedule twice. As long as the sample and reference are not moved, most of the thermal events that occurred during the first run will occur again, except for the irreversible transformation. Hence, by subtracting the second curve from the first (see section 4.4), a smooth baseline on either side of the transformation will result. The utility of this procedure depends on how similar the thermal properties (thermal conductivity and heat capacity) of the products are to those of the reactants, since it is the products that are being thermally processed on the second scan. Thus, solid state transformations (e.g. glass devitrification) may be a better candidate for this technique than chemical reactions in which the thermal mass of the product is appreciably different.

By diluting a reactive sample powder with an inert powder (e.g. Al_2O_3), the heat capacity of the sample can be made to match more closely that of the reference, hence baseline float can be dampened. This is a useful technique for reactions of significant thermal effect, e.g. combustion, since sample dilution diminishes the intensity of the differential temperature signal. Since the diluent adds a thermal resistance between the reaction zones and the temperature measuring device, the onset of reactions will shift to higher temperatures.

For reactions of minute thermal effect, e.g. second order transitions, it is advantageous to use as much sample mass as feasible in the heat-flux DSC sample pan. It is advisable to use an adequate thermal mass of reference powder to match that of the sample. This has the advantage of not only minimizing baseline float, but also smooths out what may appear to be signal noise: When the reference lacks thermal mass, its temperature will vary responsively to random thermal fluctuations in its surroundings. On a sensitive scale, the changing reference temperature will be manifested as noise on the amplified differential thermocouple signal.

3.7.2 Heat Capacity Changes During Transformations

To determine the area under an exotherm or endotherm, we generally integrate from the baseline which has shifted from zero ΔT (Figure 3.21). The lag between sample and reference temperature (baseline) will often remain constant as long as the total heat capacities of sample and reference do not increase divergently with increasing temperature. However, by the definition of a transformation, the products are different in nature than the reactants, and the heat capacity of each can, in some cases, be significantly different. The exotherm in Figure 3.21 represents not only the heat released due to a phase transformation in the sample, but also a gradual shift in sample total heat capacity from that of the reactants to that of the products. If it is desired to study the kinetics or thermo-

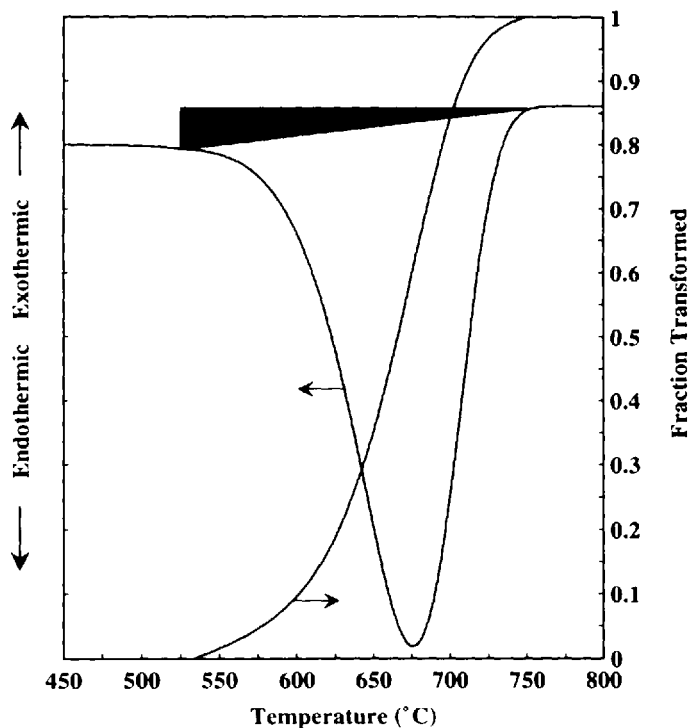


Figure 3.24: Estimation of fraction transformed for sample heat capacity change correction. A straight line is drawn between baselines at onset and termination of the endotherm, forming a triangle. After area determination based on the upper baseline, the triangle is subtracted (see section 4.1).

dynamics of this transformation, the exotherm (or endotherm) must be purged of this latter effect. A procedure for doing so is described below:

1. As illustrated in Figure 3.24, estimate the fraction transformed versus time by integrating the DSC/DTA peak. By drawing a diagonal line from one baseline to the other and integrating from that line, the best approximation will result.

2. In a mixture of two substances, the heat capacity of the composite will be somewhere between the heat capacities of the end members, the value of which can be approximated based on the mole percentage of each phase. Thus, the sample total heat capacity, and therefore the baseline position, will vary linearly with the fraction transformed, as illustrated in Figure 3.25.

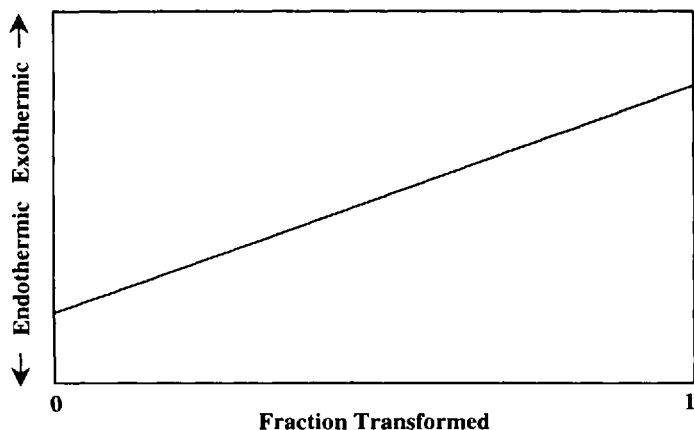


Figure 3.25: Baseline trend with composition during a transformation.

3. The fraction transformed of the overall reaction as a function of time (step 1) is known, as is the baseline shift as a function of fraction transformed (step 2). We can combine these two data sets to plot the baseline shift as a function of time, eliminating fraction transformed, as indicated by the line labeled $(dQ/dt)_{\Delta C_p}$ in Figure 3.26.

As shown in the Figure 3.26, subtracting the baseline shift from the peak containing both effects leaves a peak with aligned baselines representing the thermal effect of the reaction alone (e.g. latent heat of transformation only). In equation form:

$$\left(\frac{dQ}{dt}\right)_{\Delta C_p} + \left(\frac{dQ}{dt}\right)_{\text{reaction alone}} = \frac{dQ}{dt}$$

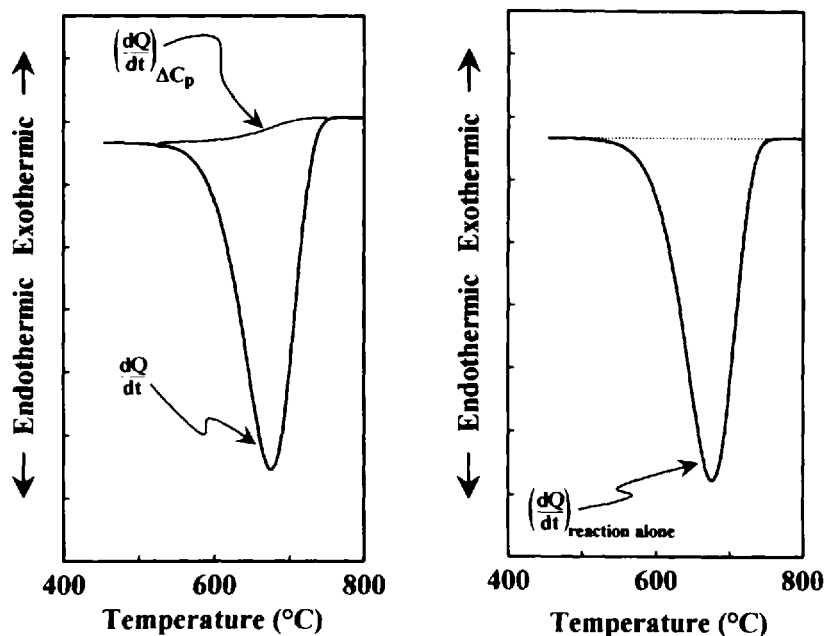


Figure 3.26: Subtraction technique for elimination of effect of sample heat capacity change. The endotherm from the DTA trace represents both the latent heat of transformation as well as a shift in heat capacity of the sample during the transformation. The baseline (which is the sample temperature lag relative to the reference) shifts most rapidly near the center of the endotherm, where the conversion of reactant to product is most fervent. The right-hand trace represents a DTA endotherm with the effects of sample heat capacity changes subtracted out. Note that in this case, where the total heat capacity of the product is less than the reactant, this subtraction has resulted in an endotherm of larger area.

The only unknown function is the heat flow due to the reaction alone.

3.7.3 Experimental Determination of Specific Heat

The sensitivity of the DTA/DSC baseline to sample total heat capacity can be exploited to determine the specific heat of unknowns. The procedure is outlined in Figure 3.27. First, an

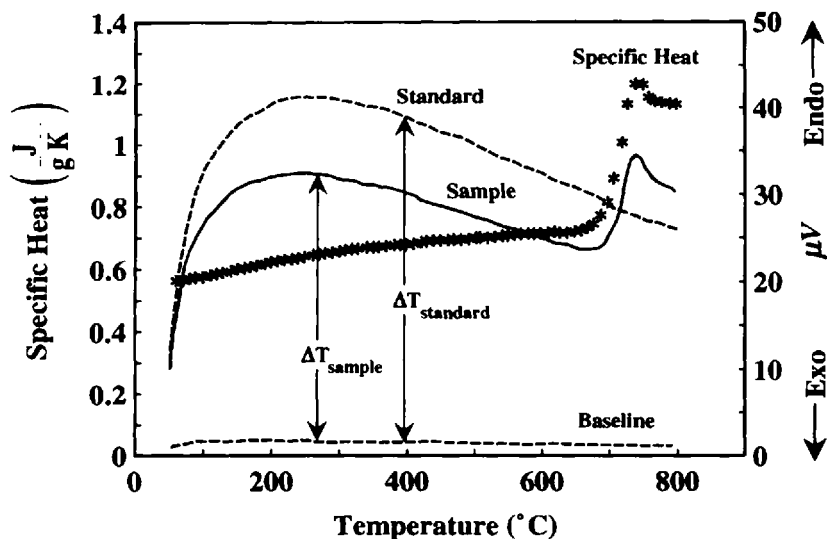


Figure 3.27: Calculation of heat capacity of an unknown using a Netzsch DSC200 heat-flux DSC [7]. The distinct shift in heat capacity at $\sim 690^\circ\text{C}$ corresponds to the glass transition temperature (see section 7.6). A 191 mg sapphire standard was used as calibrant for a 130 mg (laser special) glass sample. All heating ramps were at $20^\circ\text{C}/\text{min}$ (faster heating rates permit greater temperature lags). The right hand scale, in the original units of the differential thermocouple, is inverted in exothermic and endothermic directions as compared to the usual convention in this book.

empty sample container versus an empty reference container are run. A known mass of standard material with a known heat capacity behavior is then placed in the sample container and exposed to the identical heating rate. Finally, a known

mass of the material of unknown heat capacity is placed in the sample container and exposed to the same heating rate. All three traces are superimposed on the same plot, as shown in the figure.

If the total heat capacities of the empty sample and reference containers were perfectly matched, then the empty sample container versus empty reference container trace should appear as a flat baseline of zero value during the entire scan. This is rarely the case (due to asymmetries in instrument construction) and is actually not necessary for this calculation. The temperature deviation from this line for the other traces is a result of the extra thermal mass on the sample side, causing it to lag the reference in temperature during the heating ramp. Defining c_p as the specific heat (J/g·K), the sample specific heat is determined by the ratio:

$$\frac{\Delta T_{\text{unknown}}}{c_{p\text{unknown}} M_{\text{unknown}}} = \frac{\Delta T_{\text{standard}}}{c_{p\text{standard}} M_{\text{standard}}}$$

where M is mass as determined from an analytical balance, and ΔT 's are measured at the same temperature. For reproducibility, the standard and reference granules should be of the same size and the sample container should be placed in the same position in the DSC cell. Alternatively, a single-scan DSC design has also been recently described [25]. If the heat capacity of the unknown varies measurably with temperature, this variation is determined by taking sequential measurements of ΔT over the tested temperature range.

3.8 Experimental Concerns

3.8.1 Reactions With Gases

Special consideration must be taken when sample transformations involve reactions with gases. For example the decompo-

sition reaction¹⁶:



is affected by the partial pressure of carbon dioxide already in the vicinity of the sample. If the partial pressure of CO_2 is high in the region of the reaction zone, the reaction is suppressed to higher temperature. The reaction onset would be at lower temperatures under a pure inert gas or vacuum atmosphere.

Figure 3.28 shows the thermal decomposition and oxidation of siderite (FeCO_3) as a function of alumina dilution. Siderite decomposes ($\text{FeCO}_3 = \text{FeO} + \text{CO}_2$) endothermically and the resulting iron oxide oxidizes ($4\text{FeO} + \text{O}_2 = \text{Fe}_2\text{O}_3$) exothermically. Under conditions of 40 wt% siderite, both endotherm and subsequent exotherm are clearly separated; the appreciable CO_2 released delays diffusion of fresh air (containing O_2) to the particle surfaces. With higher percentages of diluent, the local partial pressure of CO_2 is diminished, and immediate oxidation is not suppressed. As a result, the exothermic and endothermic latent heats largely cancel [26].

Depending on the crucible dimensions and gas flow direction, lingering gases released by the reaction may remain in the proximity of the reaction zone, suppressing further transformation. If a flowing purge gas is used, heavy effluent gases (e.g. CO_2) may be swept away which would otherwise only sluggishly diffuse. Instruments have been designed [27] which allow purge gas flow directly through sample and reference granules, minimizing this effect.

3.8.2 Particle Packing, Mass, and Size Distribution

If powders are used for the sample material, the packing of the particles will have an effect on the rate of reactions involving gases. Tighter packing inhibits free diffusion of gaseous species in and out of the reaction zones. Hence, the decomposition

¹⁶The gas release from this reaction can occur quite rapidly and has the reputation for discharging sample powder from the container.

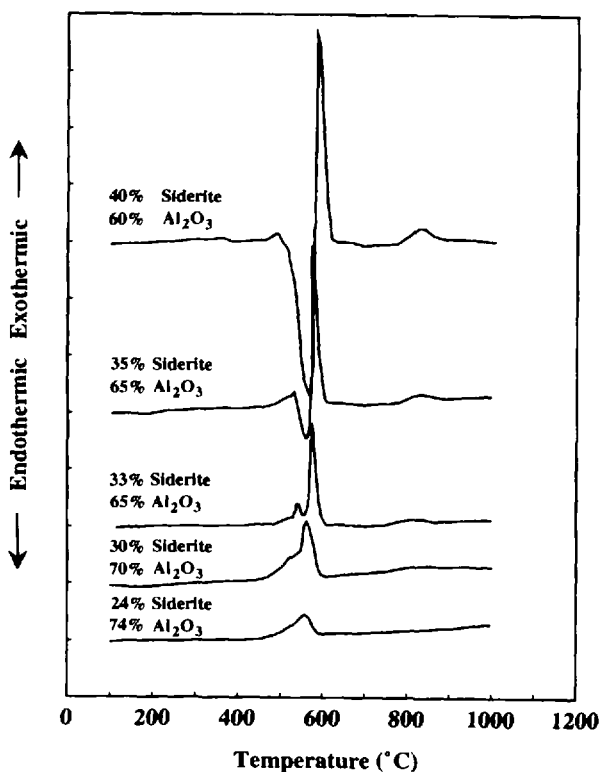


Figure 3.28: The DTA trace of the decomposition of siderite changes appreciably with increasing weight percent diluent (Al_2O_3) [26].

of calcium carbonate, for example, would shift or broaden toward higher temperatures with tighter particle packing, as the evolved CO_2 would more sluggishly diffuse away.

For post-type DTA's in which thermocouple junctions measure the temperature of the container of the sample (e.g. platinum or polycrystalline alumina crucibles), good mechanical contact between the sample and the bottom of the crucible will improve instrument sensitivity to transformations. Surface contact may be optimized by using samples shaped to match the crucible, or finely crushed granules, as opposed to more spherical or odd-shaped chunks. Optimum mechanical contact minimizes the lag time between when a reaction occurs and when heat propagates to/from the point of temperature measurement, and the reaction is recorded.

The properties of the sample must be known in advance, to some extent, in order to decide if granulating it will alter its behavior. For example, the added surface energy of crushing a glass may change the crystal nucleation and growth mechanism from a bulk to a surface effect. Dry grinding of α quartz damages (amorphizes) the quartz structure near the particle surface to the point where the α to β inversion at 573°C cannot be observed using DTA [28]. Grinding of metals will strain harden them, which will in turn cause a recrystallization¹⁷ exotherm when the specimen is heated. This exotherm will not appear when the sample is exposed to the same thermal schedule a second time.

For irreversible transformations (glass crystallization as example), the particle size in the sample container will effect the rate of reaction, more so in DTA than in power-compensated DSC (Figure 3.29). For spherical particles, the surface to volume ratio decreases by $3/r$ (where r is particle diameter) with

¹⁷The grinding process causes appreciable plastic deformation via dislocation formation and subsequent motion under load. Upon reheating, adequate thermal energy is provided to allow the microstructure to reform, motivated by the elimination of most of the high-energy dislocations. DTA/DSC is a useful technique for determining temperatures for annealing of metals which have been made brittle (strain hardened) during machining.

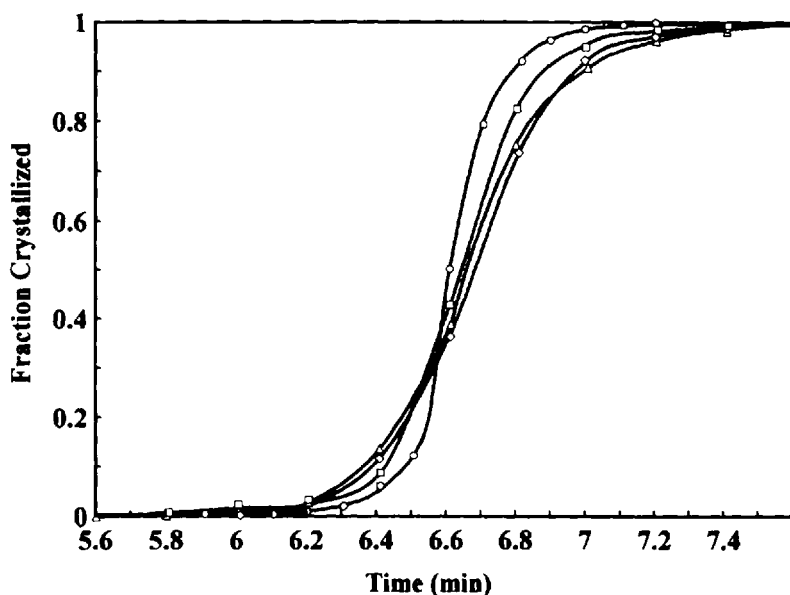


Figure 3.29: Effect of particle size on CdGeAs_2 glass crystallization using the DuPont (presently TA Instruments) model 1090. The overall sample mass was maintained constant. Circle: Granules of size greater than 16 mesh; Square: particles between 16 and 30 mesh; Triangle: particles between 30 and 40 mesh; Diamond: granules between 40 and 70 mesh [29].

increasing particle size. Heat flow from the surroundings to the interior of larger particles would be relatively suppressed¹⁸ because of diminished access. This, in turn, would cause a time delay in the onset of the transformation in larger particles. The heat released from transformations within more massive particles would also be more insulated from escape, further stalling detection of the transformation. The latent heat of transformation would then alternatively tend to increase large particle temperature more than in smaller particles. The greater temperature rise in larger particles accelerates the reaction rate,¹⁹

¹⁸This assumes that overall sample mass is low so that smaller particles do not act as a more effective thermal barrier to heat flow into the sample.

¹⁹Recall the Arrhenius temperature dependence for the reaction rate constant: $k = k_0 \exp(-E_a/RT)$.

causing the reaction to terminate earlier. Thus, for a fixed overall sample mass, samples composed of one large chunk (as opposed to many fine granules) will transform initially more sluggishly, but ultimately more quickly, for irreversible exothermic transformations of this form.

Excessive sample dimensions in either width or height, run the risk of appreciable temperature gradients within the material. A case could be envisioned, for example, where a sample powder is stacked in a tall DTA crucible which is located just below the hot zone of the furnace. The top portion of the powder will melt first, while at the same time the bottom of the crucible, where the thermocouple junction is, remains at a temperature below the melting point. The melting upper powder will act as a heat sink for heat propagating from the hot zone, motivating an endothermic deviation detected by the differential thermocouple. Thus, the onset of the melting endotherm would be indicated at the sample thermocouple junction at a temperature below the melting point of the sample. As a result, a falsely low melting point would be recorded.

3.8.3 Effect of Heating Rate

The effect of varying heating rate is significant and depends on whether the x -axis is denoted as time or temperature. Figure 3.30 shows the effect of varying heating rate for a melting endotherm, as a function of both time and reference temperature. This figure was generated using a heat-flux DSC. DTA and power-compensated DSC traces show analogous effects.

The onset times for the traces with time as the x -axis were artificially lined up. The onset of the melting endotherm for slower heating rates would normally be much later, since it would take a longer time for the furnace to reach the melting temperature. For the reference temperature as the ordinate, the higher temperature onset for faster heating rates is caused by the heat transfer lag from the sample interior to the thermocouple junction. During the limited amount of time needed for

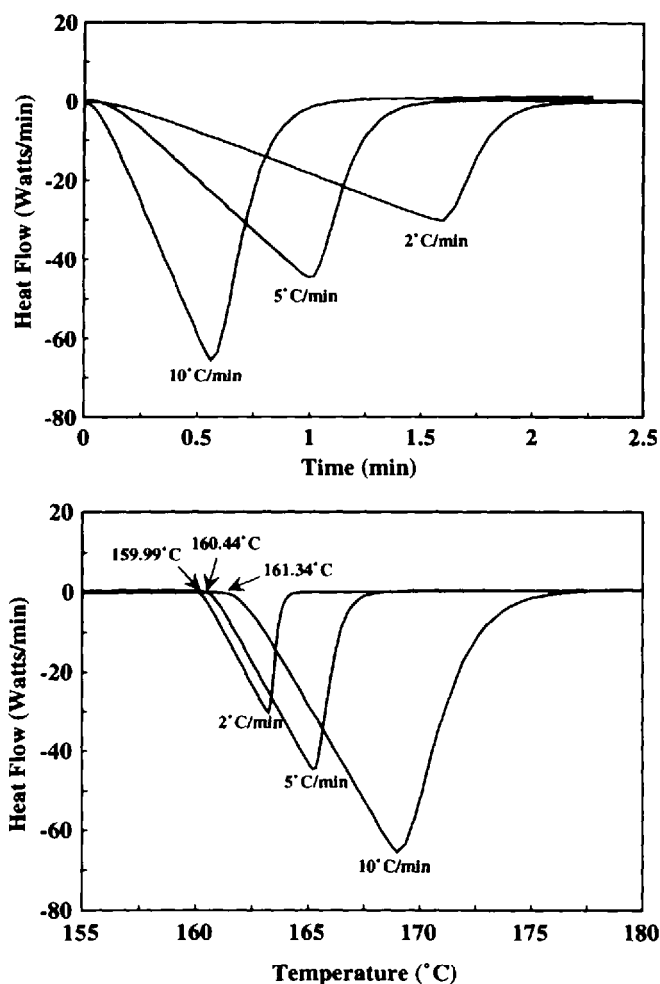


Figure 3.30: Effect of heating rate on shape of melting (indium) endotherm in a heat-flux DSC. The temperature scale on the lower figure represents reference temperature. If sample temperature were used, the peak shape would be deformed since temperature does not change linearly with time during the endotherm.

heat transfer, the sample under faster heating rates has covered a greater temperature interval, hence the shift in the onset temperature.

The intensity at peak maximum for the faster heating rates is greater than that for the slower heating rates, since for DTA the reference temperature increase is more rapid, while at the same time the sample strives to remain at the melting temperature. For faster heating rates in power-compensated DSC, the sample chamber temperature deviates more quickly from the rising setpoint, so the device compensates with more heat dissipation per unit time to the sample side.

The melting reaction terminates after a broader temperature interval for faster heating rates, since less time was permitted per degree of temperature increase for the reaction to proceed. On the same principle, the faster the heating rate, the more the peak maximum appears to shift toward higher temperature. However, the faster heating rate causes the rate of heat flow into the sample to be greater than under the slower heating rate, permitting a more rapid transformation rate. As a result, the time of transition under the fast heating rate is shorter. These considerations have an interesting effect: fast heating rate endotherms are narrower in traces with time as the x -axis and broader where temperature is the x -axis.

Heating rate is an important consideration in materials investigations. Slower heating rates will more accurately depict the onset temperature of a transformation. They will also diminish the accelerating effects of self-feeding reactions. Further, two transformations which are very close in temperature range may be more distinctly seen as separate peaks, whereas they may be mistaken for a single transformation under a rapid heating rate. On the other hand, as can be seen in Figure 3.30, slower heating rates make the peaks shorter and broader (in time). Thus, a transformation with a minute thermal effect may result in a peak height no more intense than the thickness of a line under slow heating rates, and therefore will not be

seen. In such a case, a faster heating rate will "pinch up" the peak intensity, making it visible.

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Chapter 4

MANIPULATION OF DATA

In order to translate DSC/DTA traces into answers to materials problems, data must be properly manipulated. Most contemporary instruments are computer interfaced for data acquisition so that a DSC/DTA trace actually exists as a series (often ~ 1000) of data pairs. Preferably, a data entry will consist of time, sample temperature, and heat flow or an exothermic-endothermic trend. Two of the three entries can be extracted and plotted using the instrument manufacturers software or with many of the commercially available spreadsheet programs. Data manipulation, such as numerical integration, differentiation, and trace subtraction, can be accomplished using standard programming languages (e.g. Basic, Fortran, Pascal, and C). Described below are some important fundamentals of numerical data manipulation, as well as a rather classical analog method of peak integration. A brief discussion of considerations for optimum data acquisition will follow at the end of the chapter.

4.1 Methods of Numerical Integration

While integrating a function such as $y = x^2$ seems straightforward, methods of integrating numerical data may not be as obvious. One simple method requires a good analytical balance and scissors. As indicated in Figure 4.1, by cutting out a

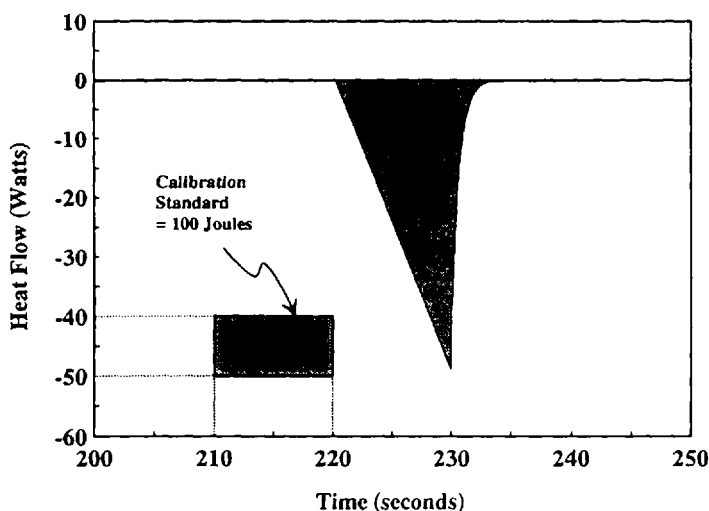


Figure 4.1: Illustration of the cut-and-weigh method for peak area integration.

rectangle of known value—that is, known seconds on the x -axis and known heat flow on the y -axis for a DSC trace—a calibration standard is obtained. After cutting and weighing the area under the peak, by the proportion:

$$\frac{\text{Mass of Standard}}{\text{Value of Standard}} = \frac{\text{Mass of Peak}}{\text{Value of Peak}}$$

all values are known short of the value of the peak, which thus can be determined. This technique is remarkably precise and only assumes that the thickness (density) of the paper is consistent throughout the sheet.

A second method is to numerically accumulate rectangles and triangles, as illustrated in Figure 4.2. As long as the rectangular and triangular areas are accurately measured, the only error introduced is the assumption that the curve between adjacent points can be approximated as a line. If the baselines before and after the transformation do not line up, a diagonal line can be drawn from one baseline to the other. After integrating from the lower baseline, the triangle (shaded area in

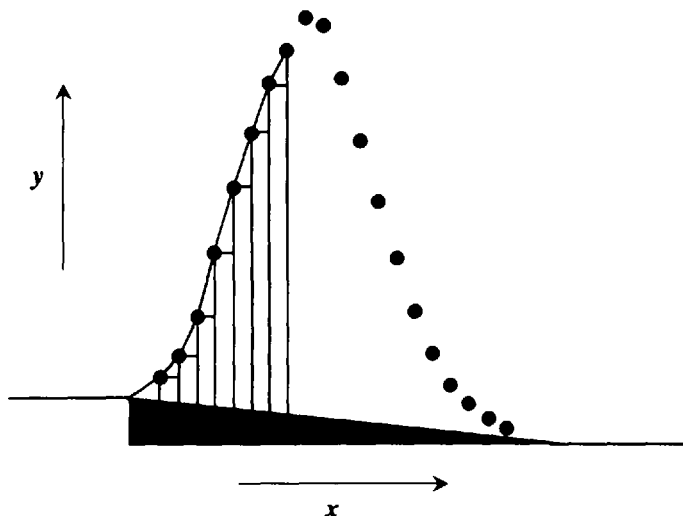


Figure 4.2: Trapezoidal method of numerical integration.

the figure) is subtracted. Listed below is a simple Basic program for peak area integration. The data for the program are assumed to reside in a data file:

```
'This is a Basic (Microsoft Quickbasic 4.5) program which integrates
'a peak made up of x-y data pairs. Allowance is made for unequal
'abscissa values at the chosen beginning and end of the peak by
'subtracting the triangle, corresponding to the mismatch, from
'the integrated area. A positive peak is assumed. Peaks extending
'in the negative y-direction should be inverted (multiply by -1).
```

```
'Arrays declared double precision.
```

```
DIM x$(1000), y$(1000)
```

```
'Open input file.
```

```
INPUT "Enter input filename: ", filein$
```

```
OPEN filein$ FOR INPUT AS #1
```

```
'Read into arrays x$ and y$ from data file.
```

```
i% = 1
```

```
DO UNTIL EOF(1)
```

```
    INPUT #1, x$(i%), y$(i%)
```

```
    i% = i% + 1
```

```
LOOP
i% = i% - 1

'Allow user to specify limits of integration.
PRINT "LIMITS OF INTEGRATION"
INPUT " Enter left x-axis limit: ", leftlim#
INPUT " Enter right x-axis limit: ", rightlim#

'Find y-values associated with limits of integration.
low# = 1E+30
high# = -1E+30
FOR j% = 1 TO i%
  IF x%(j%) >= leftlim# AND x%(j%) < low# THEN
    low# = x%(j%)
    ml% = j%
  END IF
  IF x%(j%) <= rightlim# AND x%(j%) > high# THEN
    high# = x%(j%)
    mr% = j%
  END IF
NEXT j%

'Determine which limit of integration is lower.
IF y%(ml%) >= y%(mr%) THEN
  ylow% = mr%
ELSE
  ylow% = ml%
END IF

'Integrate peak.
accum# = 0
FOR j% = 1 TO i% - 1
  IF x%(j%) >= x%(ml%) AND x%(j%) <= x%(mr%) THEN
    rect# = (x%(j% + 1) - x%(j%)) * (y%(j%) - y%(ylow%))
    tri# = .5 * (x%(j% + 1) - x%(j%)) * (y%(j% + 1) - y%(j%))
    accum# = accum# + rect# + tri#
  END IF
NEXT j%

'Subtract off bottom triangle.
xyz# = (ABS(x%(ml%) - x%(mr%)) * ABS(y%(ml%) - y%(mr%)) * .5)
area = accum# - xyz#

'Print peak area on screen.
PRINT ""
PRINT "Peak Area: "; area
```

CLOSE #1
END

4.2 Taking Derivatives of Experimental Data

Taking derivatives of experimental data (i.e. for determining the coefficient of linear thermal expansion) is not quite as straightforward as taking derivatives of algebraic functions, since data tend to have some scatter. If, for example, a data set has a visually upward trend but two adjacent points are stacked on top of each other, the slope between these points is infinite. An improvement would be to average the slopes from a cluster of points, but if infinity is one of the values, the average value is still infinity.

A more acceptable technique for taking derivatives of data is to determine the slope of a line which is the best fit to a series of points. As an example (Figure 4.3), the best fit line through five points are determined, and the slope of that line is assigned to the center (third) point. Moving over by one, where the left-hand point is discarded and a new right-hand point is included, a slope value is assigned to the next point, which is shifted one over from the previous slope assignment.

Determining the "best fit" line to a series of data involves minimizing the collective distances between the points and that line, as illustrated in Figure 4.4. To eliminate the canceling effects of some of these error distances e_i being positive, while others are negative, they are individually squared and the equation of a line is sought with the minimum sum of the squares of these error distances. It should be noted that while the y -value of a particular point as predicted by the line will miss the point by some error distance, the x -value is simply assigned to be the same as the actual datum and has no error. Thus, if y'_i represents the line's predicted value of the i th point in the

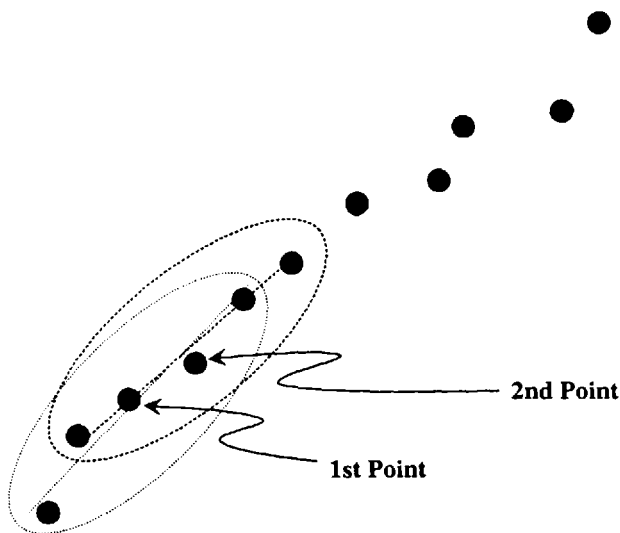


Figure 4.3: Five point slope calculation for taking derivatives of experimental data.

data set, we can express y'_i in terms of actual x_i position:

$$y'_i = mx_i + b$$

where m is the slope, and b is the y -intercept of the line. Thus, the sum of the squared error can be expressed:

$$\sum_{i=1}^N e_i^2 = \sum_{i=1}^N (y_i - y'_i)^2 = \sum_{i=1}^N (y_i - (mx_i + b))^2$$

where N is the total number of data pairs. The minimum of this function represents the condition of best fit, so derivatives of it are taken with respect to the coefficients m and b and each set equal to zero (since the optimum choice of these coefficients will define the best fit line):

$$\left(\frac{\partial \sum_{i=1}^N e_i^2}{\partial m} \right)_b = 2 \sum_{i=1}^N (y_i - (mx_i + b))(-x_i) = 0$$

$$\left(\frac{\partial \sum_{i=1}^N e_i^2}{\partial b} \right)_m = 2 \sum_{i=1}^N (y_i - (mx_i + b))(-1) = 0$$

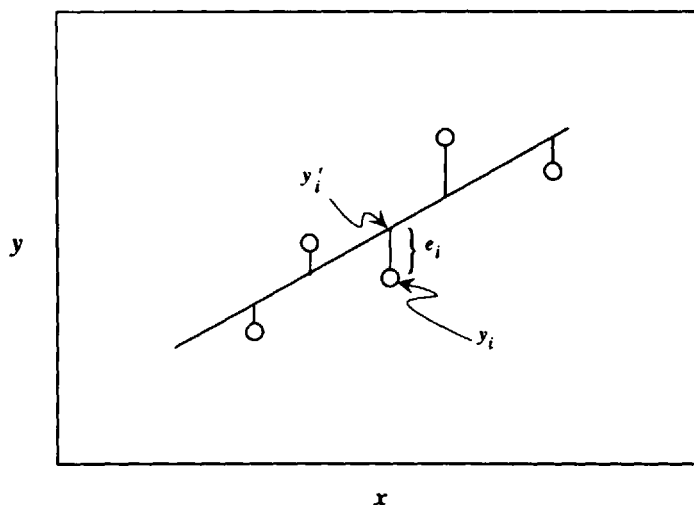


Figure 4.4: Method of least squares.

Rearranging:

$$-\sum_{i=1}^N y_i x_i + m \sum_{i=1}^N x_i^2 + b \sum_{i=1}^N x_i = 0$$

$$-\sum_{i=1}^N y_i + m \sum_{i=1}^N x_i + bN = 0$$

Hence:

$$m = \frac{\sum_{i=1}^N y_i x_i - \frac{\sum_{i=1}^N y_i \sum_{i=1}^N x_i}{N}}{\sum_{i=1}^N x_i^2 - \frac{(\sum_{i=1}^N x_i)^2}{N}}, \quad b = \frac{\sum_{i=1}^N y_i - m \sum_{i=1}^N x_i}{N}$$

In the previous example (Figure 4.4), the values of the sums would be tallied up for each set of five points, and the value of slope calculated from the above equation will be assigned to the center point. The choice of five points is arbitrary, but the number of points should be odd so that the number of points about the center point will be symmetrical. The following computer program determines the coefficient of expansion

(temperature derivative of expansion, see section 7) of a expansion/temperature data set using this technique, where the user selects the number of points for slope determination:

```
'This is a Basic (Microsoft Quickbasic 4.5) program for taking
'derivatives of experimental data.

'Declare arrays double precision.
DIM x$(1000), y$(1000)

CLS
'Open input (data) and output (numerical derivative of data).
INPUT "Enter input filename: ", filein$
INPUT "Enter output (derivative) filename: ", fileout$
OPEN filein$ FOR INPUT AS #1
OPEN fileout$ FOR OUTPUT AS #2

'Read in data.
i% = 1
DO UNTIL EOF(1)
    INPUT #1, x$(i%), y$(i%)
    i% = i% + 1
LOOP
i% = i% - 1

'Input the number of points to be averaged, insist that it is an
'odd number.
reenter:
PRINT ""
INPUT "Enter number of points to be averaged: ", pts%
IF pts% / 2 = INT(pts% / 2) THEN
    PRINT "Value needs to be an odd number"
    GOTO reenter
END IF
p = pts%

'Calculate slopes, note that slopes for the beginning few and the
'end few points are not calculated.
h% = (pts% - 1) / 2
FOR j% = h% + 1 TO i% - h%
    sumx# = 0: sumy# = 0: sumxy# = 0: sumx2# = 0
    FOR k% = j% - h% TO j% + h%
        sumx# = sumx# + x$(k%)
        sumy# = sumy# + y$(k%)
        sumxy# = sumxy# + x$(k%) * y$(k%)
    
```

```

    sumx2# = sumx2# + x#(k%) ^ 2
NEXT k%
slope = (sumxy# - sumx# * sumy# / p) / (sumx2# - sumx# ^ 2 / p)
WRITE #2, x#(j%), slope
NEXT j%

CLOSE #1
CLOSE #2
END

```

The criterion of least squares is quite powerful in dealing with experimental data. The technique for fitting data to a polynomial such as $y = ax^2 + bx + c$ is analogous to the above, where the minima of the sum of the squared error function is determined by taking derivatives with respect to a , b , and c , generating three equations and three unknowns. Higher order polynomial fits require solution of more simultaneous equations. Linear (matrix) algebra can be used, with the aid of computer, to determine the values of the coefficients. This technique can be used for developing polynomials to fit thermocouple voltage/temperature data, thermal expansion/temperature data, etc. Further, by taking least squares fits of sections of the data and fitting each to polynomials, the data set can be “smoothed”, that is, the random noise in the data can be removed without disturbing the trends in the data which represent material properties. Generally, these polynomials are fit to overlapping portions of the data set so that the smoothed data appears continuous.

4.3 Temperature Calibration

The program below corrects a data set for temperature:

'This is a Basic (Microsoft Quickbasic 4.5) program for shifting
'x-axis temperature values, based on melting point standards.

```
DIM temp(2000), yval(2000), newtemp(2000), meas(20), lit(20)
```

```
CLS
```

```
'Open input and output files
```

```
INPUT "Enter input data filename: ", filein$
```

```
INPUT "Enter corrected data output filename: ", fileout$
```

```
OPEN filein$ FOR INPUT AS #1
```

```
OPEN fileout$ FOR OUTPUT AS #2
```

```
'Read in temperature calibrations
```

```
again:
```

```
PRINT ""
```

```
PRINT "Enter measured followed by literature calibration"
```

```
PRINT "temperatures, separated by a comma. At least two"
```

```
PRINT "data pairs must be entered. Terminate entries by"
```

```
PRINT "pressing ENTER:"
```

```
PRINT ""
```

```
i% = 1
```

```
DO
```

```
  LINE INPUT "*", h$
```

```
  IF h$ = "" THEN
```

```
    i% = i% - 1
```

```
    GOTO doneentry
```

```
  END IF
```

```
  a% = INSTR(h$, ",")
```

```
  meas(i%) = VAL(LEFT$(h$, a% - 1))
```

```
  lit(i%) = VAL(MID$(h$, a% + 1, 50))
```

```
  i% = i% + 1
```

```
LOOP
```

```
doneentry:
```

```
IF i% < 2 THEN
```

```
  CLS
```

```
  PRINT "Must be at least two pairs, try again."
```

```
  GOTO again
```

```
END IF
```

```
'Sort calibration pairs, lowest to highest (bubble sort).
```

```
FOR j% = i% - 1 TO 1 STEP -1
```

```
  FOR k% = 1 TO j%
```

```
    IF meas(k%) > meas(k% + 1) THEN
```

```
      a = meas(k%)
```

```
      meas(k%) = meas(k% + 1)
```

```
      meas(k% + 1) = a
```

```
      a = lit(k%)
```

```
      lit(k%) = lit(k% + 1)
```

```
      lit(k% + 1) = a
```

```

        END IF
    NEXT k%
NEXT j%

'Read in data.
y% = 1
DO UNTIL EOF(1)
    INPUT #1, temp(y%), yval(y%)
    y% = y% + 1
LOOP
y% = y% - 1

'Determine between which two calibration points a particular
'datum falls and shift to calibrated value.
FOR j% = 1 TO y%
    low = -1E+30
    high = 1E+30
    FOR k% = 1 TO i%
        IF meas(k%) >= temp(j%) AND meas(k%) < high THEN
            high = meas(k%)
            lowk% = k%
        END IF
        IF meas(k%) < temp(j%) AND meas(k%) > low THEN
            low = meas(k%)
            highk% = k%
        END IF
    NEXT k%
    'If the data point falls outside the calibration values,
    'then extrapolate.
    IF high = 1E+30 THEN
        lowk% = i% - 1
        highk% = i%
    END IF
    IF low = -1E+30 THEN
        lowk% = 1
        highk% = 2
    END IF
    slope = (lit(highk%) - lit(lowk%))
    slope = slope / (meas(highk%) - meas(lowk%))
    intercept = lit(lowk%) - slope * meas(lowk%)
    newtemp(j%) = slope * temp(j%) + intercept
NEXT j%

'Write corrected data to a file.
FOR j% = 1 TO y%
    WRITE #2, newtemp(j%), yval(j%)

```

NEXT j%

END

After a series of melting standards (see Table 3.1) have established a correlation between indicated temperature and correct temperature, this table may be entered into the program. The routine determines between which two calibration points a particular temperature in the experimental data set fall, and then it shifts the temperature to a corrected temperature in accordance with a calibration line between the points. For experimental data whose temperature values fall before the lowest calibration temperature or above the highest calibration temperature, extrapolation of the line defined by the two nearest calibration points is used.

4.4 Data Subtraction

As was discussed in section 3.7, a floating baseline can often be purged out of a DTA/DSC trace by subtracting a second run. The process of subtraction is complicated by the fact that the x -axis values of the two data sets may not line up. Extrapolation from nearby points is necessary so that abscissa values from the two data sets may be properly subtracted. The following is a Basic program which reads two data sets into memory, subtracts the second from the first using extrapolation, and then stores the subtracted data set:

'This is a Basic (Microsoft Quickbasic 4.5) program which subtracts
'the abscissa values of two data sets.

'Declare arrays.

DIM x1(1000), y1(1000), x2(1000), y2(1000), subx(1000), suby(1000)
CLS

'Open two input files and output (subtracted) file.

PRINT "For [file #1 - file #2],"

INPUT " Enter file #1: ", file1\$

```

INPUT " Enter file #2, ", file2$
PRINT ""
INPUT "Enter output filename: ", outfile$
OPEN file1$ FOR INPUT AS #1
OPEN file2$ FOR INPUT AS #2
OPEN outfile$ FOR OUTPUT AS #3

'Read input files.
i1% = 1
DO UNTIL EOF(1)
  INPUT #1, x1(i1%), y1(i1%)
  i1% = i1% + 1
LOOP
i1% = i1% - 1
i2% = 1
DO UNTIL EOF(2)
  INPUT #2, x2(i2%), y2(i2%)
  i2% = i2% + 1
LOOP
i2% = i2% - 1

'Find points in second data set which straddle that of the
'selected point in the first data set. Extrapolate between
'points in the second data set to a value which matches
'the ordinate in the first data set, and subtract. If a point
'in the the first data set is out of range of the second,
'throw the point out and continue.
FOR j% = 1 TO i1%
  IF x1(j%) >= x2(1) AND x1(j%) <= x2(i2%) THEN
    low = -1E+30
    high = 1E+30
    FOR k% = 1 TO i2%
      IF x2(k%) < x1(j%) AND x2(k%) > low THEN
        low = x2(k%)
        klow% = k%
      END IF
      IF x2(k%) > x1(j%) AND x2(k%) < high THEN
        high = x2(k%)
        khigh% = k%
      END IF
      IF x2(k%) = x1(j%) THEN
        yval = y2(k%)
        GOTO subtr
      END IF
    NEXT k%
    slope = (y2(khigh%) - y2(klow%)) / (x2(khigh%) - x2(klow%))
  
```

```

    intercept = y2(khigh%) - slope * x2(khigh%)
    yval = slope * x1(j%) + intercept
subtr:
    suby(j%) = y1(j%) - yval
    END IF
NEXT j%

'Store subtracted array.
FOR j% = 1 TO i1%
    IF x1(j%) >= x2(1) AND x1(j%) <= x2(i2%) THEN
        WRITE #3, x1(j%), suby(j%)
    END IF
NEXT j%

END

```

As illustrated in Figure 4.5, the program searches for the two

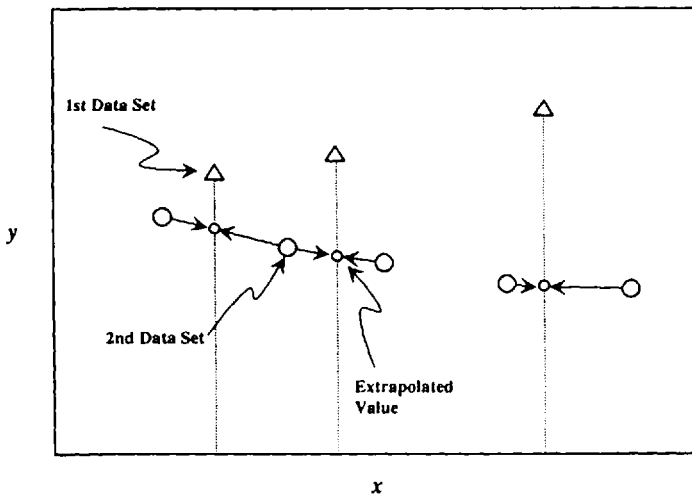


Figure 4.5: Linear extrapolation of points in a second data set to match the x -axis value in the first data set, which allows subtraction of the two data sets.

points in the second data set which fall immediately before and after a point on the first data set. By linear extrapolation, a new point is located for the second data set which has the same

ordinate value as the first. This algorithm is bypassed if there is a point in the second data set which exactly corresponds to the point in the first. The second point can then be subtracted from the first. The program then moves on to the next data point in the first data set and repeats the process of search and extrapolation in the second data set.

4.5 Data Acquisition

Conventionally, most signals from transducers in scientific instrumentation of this sort are of the low voltage dc variety. These are fed to chart recorders in older apparatus and analog to digital converters in contemporary instruments. To exploit the full measurement precision of A/D converters, their input signals should be amplified so the measurable extremes of their amplified output match that of the converter. For example, consider feeding a type "S" thermocouple with a maximum output of 16 mV directly into a 12 bit (explained shortly) A/D converter with a full scale range of ± 1 V. Assuming linearity between temperature and thermocouple voltage (not a good assumption), the temperature measurement precision will be $\sim 50^\circ\text{C}$. This is, of course, unacceptable. Amplifying so that the full scale of the A/D converter is exploited, the temperature precision would be $\sim 0.4^\circ\text{C}$.

Amplification is accomplished using integrated circuit chips, which can be remarkably inexpensive (e.g. ~ 25 cents for a "741" operational amplifier). The amplification of a chip is set by connecting precision resistors between specific pins, where the ratio of resistances defines the gain (amplification). The use of capacitors in conjunction with resistors and operational amplifiers in a circuit can serve to filter noise from the signal as well as amplify it [1]. Time constants can be designated which do not allow a signal to change faster than a specified time period. Thermal analysis instrumentation has a distinct advantage over other scientific instrumentation in that thermal

Table 4.1: Correlation between base ten and binary counting systems. The left-hand column is base-ten numbers and the right hand column is binary numbers.

0	0	8	1000	16	10000	24	11000	32	100000
1	1	9	1001	17	10001	25	11001	33	100001
2	10	10	1010	18	10010	26	11010	34	100010
3	11	11	1011	19	10011	27	11011	35	100011
4	100	12	1100	20	10100	28	11100	36	100100
5	101	13	1101	21	10101	29	11101	37	100101
6	110	14	1110	22	10110	30	11110	38	100110
7	111	15	1111	23	10111	31	11111	39	100111

events generally occur slowly. Thus, a time constant as slow as 0.5 sec should do no harm to signals representing materials properties; however, it will wipe out noise generated from 60 Hz interference such as heating element coils and light fixtures.

Analog to digital converters convert voltage levels into a binary code. The correlation between base-ten decimal numbers and binary numbers is illustrated in Table 4.1. Note that the binary numbers with ones followed by zeros are 2^n in base ten numbers. For example, $2^2 = 4$, $2^3 = 8$, $2^4 = 16$, and so on. A twelve bit converter has twelve registers which can send out a "high" or "low" pulse that corresponds to "0" or "1". Thus a twelve bit converter can indicate an analog input signal using $2^{12} = 4096$ unique numbers. This is often adequate precision for thermoanalytical instrumentation; consider that on a "VGA" computer monitor there are only 480 vertical dots to display data, so more precision is stored in twelve bits than can be seen. For some applications, a sixteen bit converter having 65536 unique numbers is needed and is commercially available. Twelve bit converters are generally available in the form of plug-in boards to personal computers, while sixteen bit converters are often available as independent microprocessors which link to a computer through a communications port (e.g.

RS232 “serial” port or IEEE488 interface bus). The plug-in cards use the computer power supply which tends to contain noise generated by all of the digital pulses generated in the computer. Higher bit conversion would not introduce improved measurement accuracy because of this noise.

A “digital” filter can be introduced in software where a series of values are rapidly taken from the A/D converter and averaged. Figure 4.6 shows a schematic of a “noisy” signal.

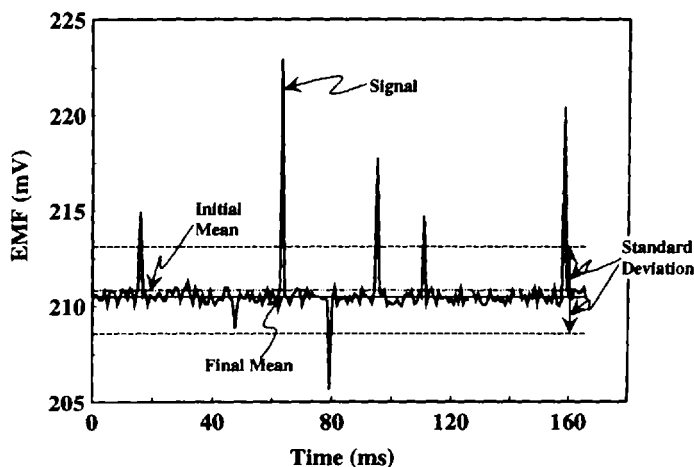


Figure 4.6: Simulated thermocouple output illustrating technique for determining a mean value for the signal.

The trace represents the rapid collection of 200 thermocouple readings. The spikes in the signal originate from 60 cycle noise. Taking the mean of all of the values would result in a temperature reading influenced by the predominant direction of the noise spikes. Rather, the mean is calculated along with the standard deviation. All points one standard deviation away from the mean are thrown out and a final mean is calculated from the remaining values. A Basic program which performs this function follows:

'This is a Basic (Microsoft Quickbasic 4.5) program which eliminates
'the influence of noise spikes on the calculation of a mean value
'from a collection of 200 thermocouple readings. For simplicity,
'the 200 values are read in from a data file. In the more common
'case, they would be read in from the data bus or an axillary
'port. Programming instructions for accessing data from various
'A/D converters are generally provided from the manufacturer.

```
OPEN "filein.dat" FOR INPUT AS #1
```

```
DIM x(200), y(200)
```

```
tot = 0
```

```
FOR m% = 1 TO 200
```

```
    INPUT #1, x(m%), y(m%)
```

```
    tot = tot + y(m%)
```

```
NEXT m%
```

```
'Calculate mean.
```

```
mean = tot / 200
```

```
'Calculate standard deviation.
```

```
tot = 0
```

```
FOR m% = 1 TO 200
```

```
    tot = tot + (y(m%) - mean) ^ 2
```

```
NEXT m%
```

```
standdev = (tot / 199) ^ .5
```

```
'Excluding values outside one standard deviation, recalculate mean.
```

```
tot = 0
```

```
numb = 200
```

```
FOR m% = 1 TO 200
```

```
    IF y(m%) > mean + standdev OR y(m%) < mean - standdev THEN
```

```
        numb = numb - 1
```

```
        GOTO marker
```

```
    END IF
```

```
    tot = tot + y(m%)
```

```
marker:
```

```
NEXT m%
```

```
tot = tot / numb
```

```
pointval = tot
```

```
PRINT pointval
```

```
CLOSE #1
```

```
END
```

Reference

- [1] P. Horowitz and W. Hill, *The Art of Electronics*, Cambridge University Press, NY (1987).

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Chapter 5

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TG) is the study of weight changes of a specimen as a function of temperature. The technique is useful strictly for transformations involving the absorption or evolution of gases from a specimen consisting of a condensed phase. Most TG devices are configured for vacuum and/or variable atmospheres. The balances associated with TG's are highly sensitive, with resolutions down to $1\mu\text{g}$. These instruments may be used for a wide variety of investigations, from the decomposition of clays to high temperature oxygen uptake in the processing of superconducting materials.

5.1 TG Design and Experimental Concerns

A typical TG design is shown in Figure 5.1. Specimen powder is placed on a refractory pan (often porcelain or platinum). The pan, in the hot zone of the furnace, is suspended from a high precision balance. A thermocouple is in close proximity to the specimen but not in contact, so as not to interfere with the free float of the balance. The balances are electronically compensated so that the specimen pan does not move when the specimen gains or loses weight.

The Cahn balance design is shown in Figure 5.2. The balance arm is connected at the fulcrum to a platinum taut band

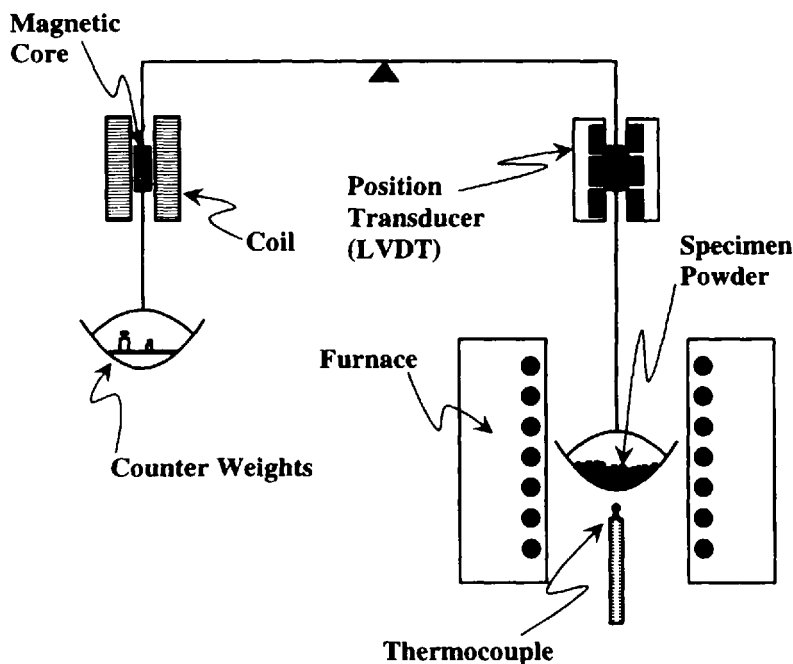


Figure 5.1: Example TG design. As the specimen changes weight, its tendency to rise or fall is detected by the LVDT (see section 7.3). A current through the coil on the counterbalance side exerts a force on the magnetic core which acts to return the balance pan to a null position. The current required to maintain this position is considered proportional to the mass change of the specimen.

which is held in place by roller pins extending orthogonally from the balance arm. This design permits the motion of the balance arm to be essentially frictionless. In a galvanometer-type action, the taut band is deflected (twisted) by the current through the coil surrounding it. A flag beneath the balance arm interferes with infrared light propagating from a source to a photo-cell detector. A servo mechanism feedback control loop adjusts the current in the coil, and hence the position of the flag, in order to maintain a constant illumination level at the detector. The current sent to the coil in order to maintain the flag position is proportional to the weight lost or gained

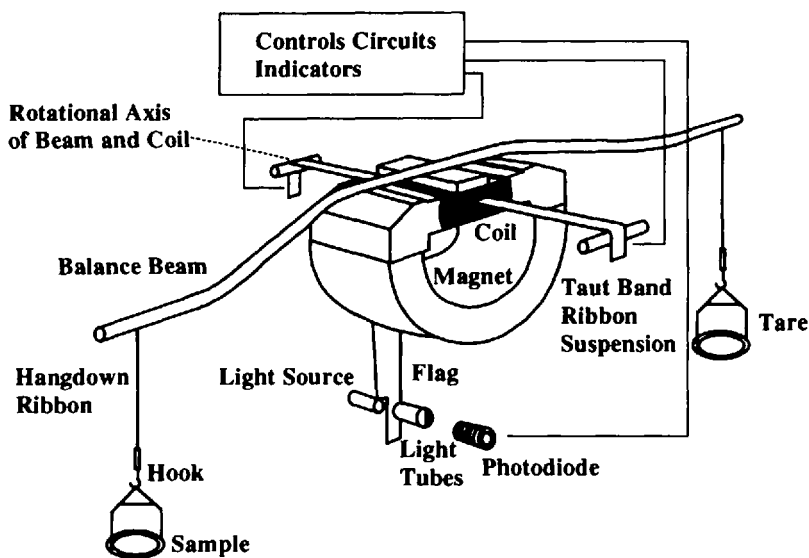


Figure 5.2: Cahn microbalance design [1].

by the specimen. A dc voltage proportional to this current is provided for external data acquisition. These balances have a manufacturer's reported precision of $0.1 \mu\text{g}$.

If reactive (potentially corrosive) gases are passed through the specimen chamber or gases are released by the specimen, the chamber containing the balance is often maintained at a slightly more positive pressure via compressed air or inert gas; this is in order to protect the balance chamber and its associated electronic components from exposure to corrosive gases. The balance chamber is not completely protected since gases released from the specimen can still diffuse into the balance chamber. Further, maintaining the specimen in a pure inert gas or other special gases is limited by back-diffusion of air through the exit port. To protect against this, the exit gas should be bubbled through a fluid. The fluid will permit exiting gas to bubble out, but will not permit back diffusion of

gases (with exception of the equilibrium vapor of the fluid).¹

A typical instrument output of mass versus increasing temperature is shown in Figure 5.3. This figure shows three distinct

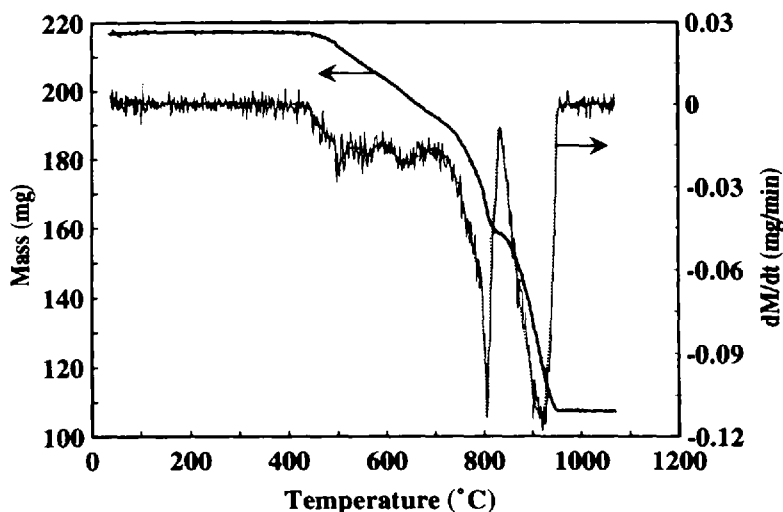


Figure 5.3: The solid line represents a typical TG trace of dolomite. The grey data set is the time derivative (calculated over 5 points in a 1000 point data set) of mass, DTG trace. The dotted line is the visually smoothed DTG trace.

transformation regions, all indicating mass loss. Also shown in the figure is the numerical derivative TG trace (DTG), which is a smoothed (section 4.2) plot of the instantaneous slope of the specimen mass with respect to time. DTG does not contain any new information, however it clearly identifies the temperatures at which mass loss is at a maximum—the DTG “peak”. Superimposed transformations, which are seen only as subtle slope changes in a TG trace appear more clearly shown as DTG peaks. Comparison of DTG data with DTA data of the same material shows striking similarity for those

¹Bubbling the exit gas through a fluid has the added benefit of a continuous check for specimen chamber gas leaks. If a gas leak exists, the fluid will not bubble, even though a positive pressure is applied at the inlet.

transformations with an associated weight change (see DTA trace for dolomite in Figure 3.2). Thus, combining DTA and DTG traces is useful for differentiating the types of transformations depicted by the DTA trace.

Most of the rules for optimum data resolution discussed for DTA/DSC apply for TG as well: Under increasingly rapid heating rates the transformation will appear to shift toward higher temperatures, occurring over shorter times but over broader temperature ranges. Under rapid heating rates, two reactions may appear as one. One important difference between TG behavior and that of DTA/DSC is that once mass is lost or gained, it stays lost or gained. Thus, the discussion regarding faster heating rates "pinching up" minute transformations in DTA/DSC does not apply to TG. There is, therefore, no disadvantage in sensitivity by the use of slow heating rates in TG.

In order to avoid temperature gradients and gaseous compositional gradients within a granulated specimen, highly sensitive balances which permit the use of small (~ 20 mg) specimens are preferable. For a Cahn-type system, increasing noise in the mass signal is observed with increasing gas flow tube diameter (above 20 mm dia.) [2], apparently due to increased radial gaseous convective flow currents (turbulent rather than laminar flow).

The effects of particle packing and atmosphere discussed in conjunction with DTA/DSC apply to TG as well. Additional concerns are *thermocouple shielding* and *pan floating*. Figure 5.4 illustrates the effect of thermocouple shielding. Purge gas flows vertically downward, cooling the specimen powder. To some extent, the pan shields the thermocouple bead from convection cooling via the flowing gas; as a result, the temperature of the thermocouple bead is higher than that of the specimen, and incorrect temperature measurements are taken. A better configuration would be to place the thermocouple bead just over the specimen powder, but no part of the thermocouple

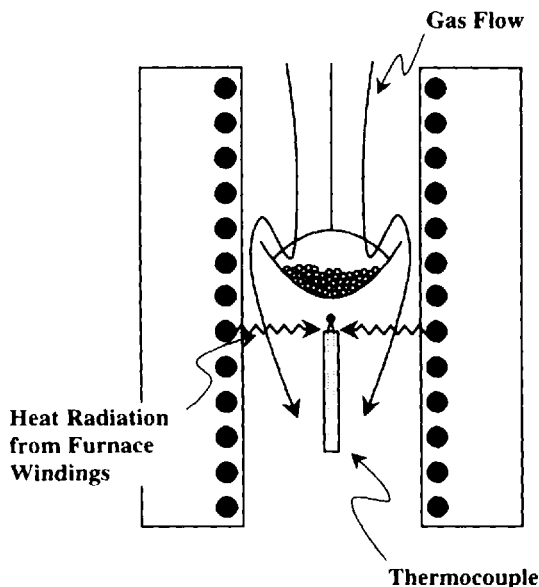


Figure 5.4: Illustration of thermocouple shielding.

should touch the specimen or the basket so as not to interfere with the free float of the balance.

Archimedes' principle can be stated: When a body is immersed in a fluid, the fluid exerts an upward force on the body equal to the weight of the fluid which is displaced by the body. Using this principle, the change in buoyancy force (where the "fluid" in this case is air) can be calculated for a typical TG specimen pan with powder in it. Using a standard Cahn balance as example, assume the specimen and pan occupy 1 cm^3 . Assuming the ideal gas law is valid, the difference in moles of gas occupied in that volume at 1000°C as opposed to 20°C at 1 atm is 2.87×10^{-5} moles. Assuming air is 20% O_2 and 80% N_2 , the mass displaced in that volume over the temperature range is 0.505 mg. For many experiments, this weight gain is significant and must be corrected for in calculations based on experimental results. The buoyancy of the specimen will change if

the specimen changes volume via a transformation. However, if the transformation results in appreciable weight change, the change in buoyancy force may be negligible by comparison.

Figure 5.5 shows a vertical gas flow applying an upward

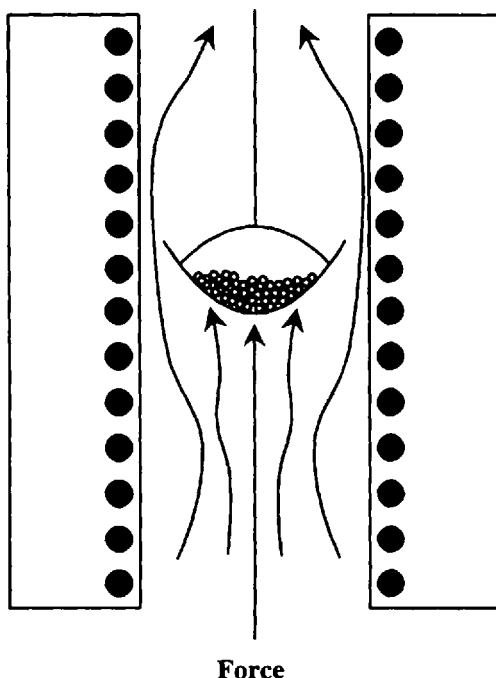


Figure 5.5: TG pan floating.

force to the specimen pan. If this effect were constant with temperature, calibration could remove its effect. However, the force on the pan has a temperature dependence as well as a dependence on how much mass is in the specimen container, which changes during the experiment. Even without purge gas flow, convective gas flow will result from temperature gradients in the furnace, and this flow behavior will be dependent on the temperature of the hot zone of the furnace and the position of the specimen pan within the hot zone.

One instrument manufacturer (TA Instruments) markets a

TG with a horizontal gas flow to minimize these problems by having the specimen basket show minimal profile with respect to the gas flow direction. Still another interesting design to minimize gas flow and buoyancy effects is described in section 5.2.

Significant temperature gradients in the furnace chamber will cause gaseous flow from hot to cold, which may apply a spurious force to the specimen pan. This is a more severe effect for chambers under moderate vacuum ('thermomolecular flow' [3]). Purge gas flow direction may be an important consideration, in order to avoid condensation of gaseous products on the hangdown wire, or along the balance beam, as the gas flows out of the hot zone of the furnace.

Temperature calibration of a thermogravimetric analyzer is more complicated than with other thermoanalytical devices, since in most designs, the thermocouple junction cannot be in contact with the specimen or its container. Beyond gas flow shielding problems, temperature differences between the specimen and thermocouple junction can be exacerbated by a vacuum atmosphere in which there is no conductive medium for heat transfer and thus temperature equilibration. Even if both the specimen and thermocouple junction are exposed to the same heat flow at a given time, the specimen has a much higher total heat capacity; hence, the specimen will lag the thermocouple junction in temperature.

Calibration techniques may be used to correlate specimen temperature to that measured by the thermocouple. A series of high purity wires may be suspended in the region where the specimen crucible would normally be located. If the furnace temperature is slowly raised through the melting point of a particular wire, a significant weight loss will be recorded when the wire melts. Care must be taken that the wires do not extend into a zone of the furnace at a higher temperature than that seen by the specimen. A series of fuseable wires, such as: Indium (156.63), lead (327.50), zinc (419.58), aluminum

(660.37), silver (961.93), and gold (1064.42°C) should give a reasonable calibration curve. A second technique is to place a series of ferromagnetic materials in the specimen basket and a magnet below or above it, external to the furnace. When each material goes through its Curie temperature (ferromagnetic to paramagnetic), it will cease being attracted by the magnet and a sharp weight change will be indicated (Figure 5.6). A corre-

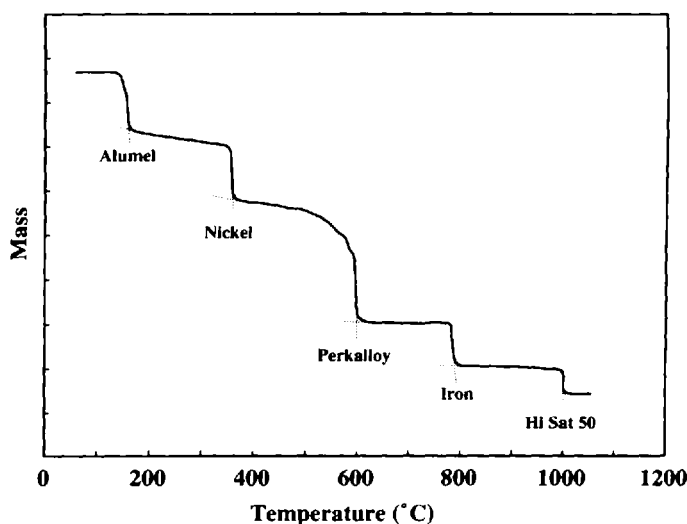


Figure 5.6: Calibration of TG thermocouple using the Curie temperatures of ferromagnetic materials [8]. Curie temperatures: alumel 163°C, nickel 354°C, perkalloy 596°C, iron 780°C, hi sat 50 1000°C. Since Curie temperatures are temperatures at which all ferromagnetism ends (lambda transformation), the extrapolated end-points of weight loss are measured from the trace.

lation curve can be established (see section 4.3) between temperatures indicated by the thermocouple and actual specimen temperature. It should be noted that even after calibration of this sort, specimen temperature still cannot always be known with confidence since the thermal effect of reactions (exothermic or endothermic) will cause the specimen temperature to vary, largely undetected by the thermocouple.

5.2 Simultaneous Thermal Analysis

A popular and useful device is a combined DTA/TG (simultaneous thermal analysis: STA) system in which both thermal and mass change effects are measured concurrently on the same sample. An example STA study comprising DTA, TG, and DTG for the decomposition of calcium oxalate is shown in Figure 5.7.

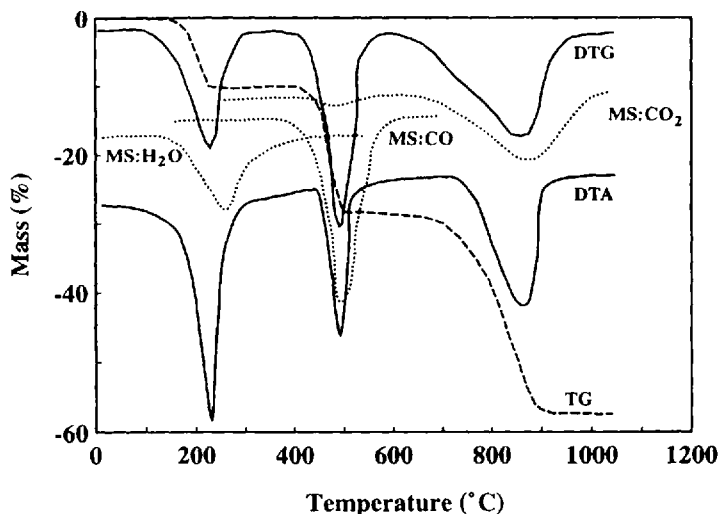


Figure 5.7: Decomposition of calcium oxalate hydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) in a Setaram TG-DTA [4]. A heating rate of $10^\circ\text{C}/\text{min}$ and an argon atmosphere were used. Mass spectroscopy (see subsequent discussion) was also used. Three successive steps in the decomposition are shown: (1) $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} = \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$, (2) $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}$, and (3) $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$. Note that there is a low concentration of CO_2 measured with mass spectroscopy (MS) associated with the release of CO . The exotherm associated with the oxidation of CaC_2O_4 is not present because of the inert atmosphere.

The design of these systems are generally comprised of a post with sample and reference cups at the top, while the base fits into a sensitive analytical balance (e.g. Harrop, Mettler, and Netzsch); or, the sample and reference cups at the bottom, with the post suspended from a balance arm from above

(e.g. Polymer Laboratories and Setaram). The main concern in the design of these instruments is extracting the thermocouple signals without interfering with the free float of the balance. A hanging cable technique using tiny gold ribbons of the consistency of Christmas tree tinsel is employed by the Netzsch STA, for example, to transmit thermocouple signals. The advantageous feature of these designs is that the sample thermocouple junction is in mechanical contact with the sample through the sample container. Thus, more accurate temperature correlations to mass change data can result.

A schematic of the Seiko STA is shown in Figure 5.8. This

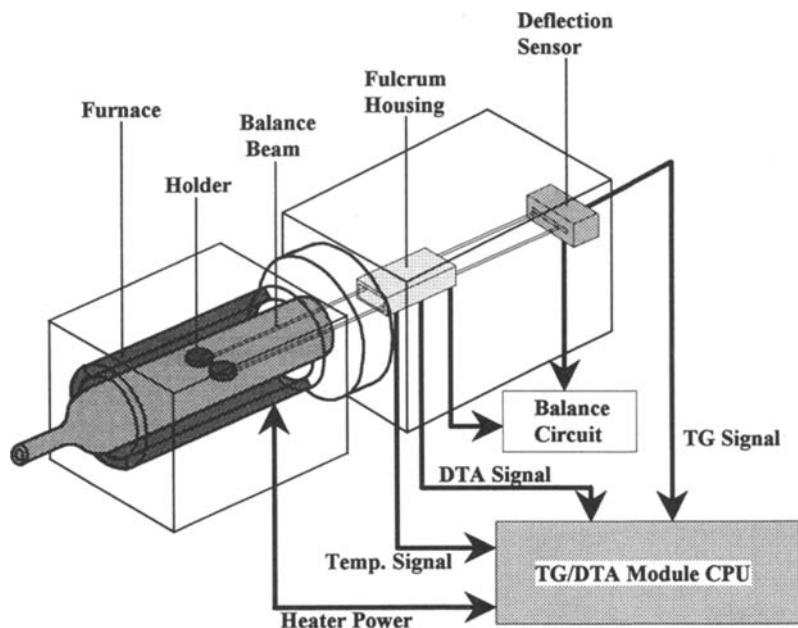


Figure 5.8: Schematic of the Seiko (SSC5000) TG/DTA model 200 [5].

system has the advantage of horizontal gas flow, as in the TA Instruments TG, but has both a sample and reference as part of the balance arm, which are immersed into the hot zone of the furnace. The Setaram model TAG24S STA has a unique feature

for minimization of buoyancy effects. A hangdown STA stage is suspended into one furnace, while an identical dummy stage is suspended into another furnace. Furnaces are heated equally so buoyancy effects cancel. Manufacturers such as Polymer Laboratories, Netzsch, and others provide simultaneous TG and heat-flux DSC. The sample and reference chamber of the Polymer Laboratories TG-heat-flux DSC is shown in Figure 5.9.

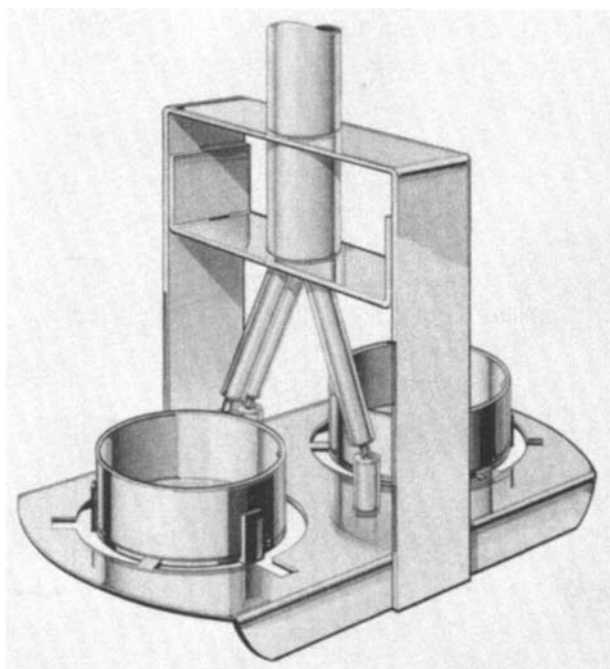


Figure 5.9: DSC stage in a Polymer Laboratories DSC/TG [6].

In combination with DTA and TG measurements, mass spectrometry attachments are provided by manufacturers such as Netzsch (Figure 5.10). Such a device is useful in the determination of the nature of evolved gaseous reaction products (Figure 5.7). A simplified schematic of a mass spectrometer system is shown in Figure 5.11. Gaseous atoms are collected

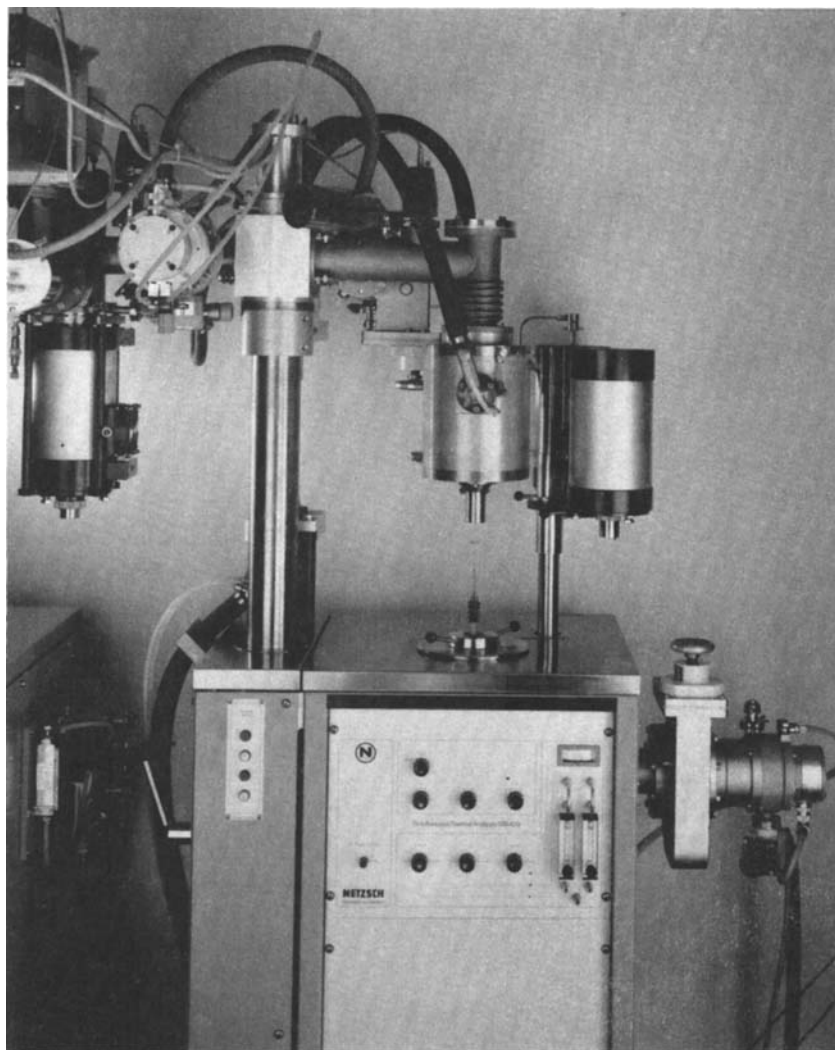


Figure 5.10: Netzsch STA with mass spectrometer attachment [7].

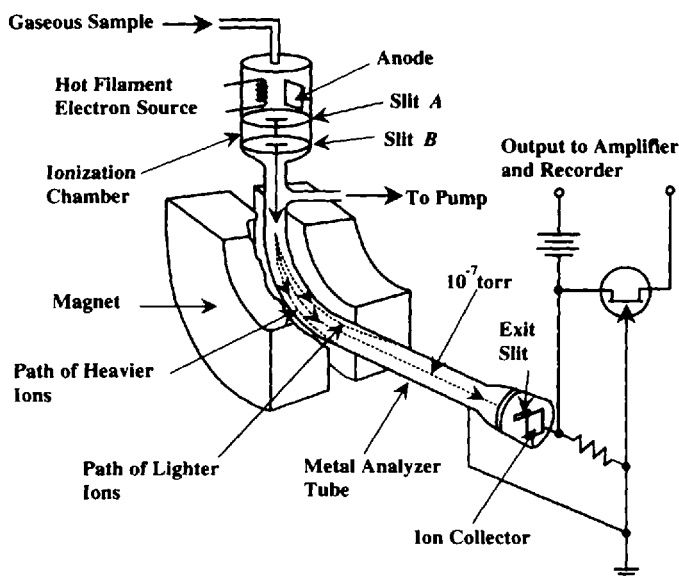


Figure 5.11: Schematic of a mass spectrometer [9].

and ionized by electron bombardment in an ionization chamber. Between slits in plates *A* and *B* an electric field accelerates the ions. The trajectories of particles which pass through slit *B* are bent by a magnetic field: A magnetic field exerts a constant force, always perpendicular to the velocity of the particle. The orbit of a charged particle in a uniform magnetic field is a circle when the initial velocity is perpendicular to the field [16]. The centripetal acceleration of the particle is v^2/r , where v is the velocity of the particle and r is the radius of the orbit. Recognizing that the force on a particle exerted by a magnetic field H is qvH , where q is the charge of the particle and force is mass m times acceleration:

$$qvH = m \frac{v^2}{r}$$

Since the kinetic energy of a particle set in motion by cath-

ode/anode accelerating voltage V is:

$$E = qV = \frac{1}{2}mv^2$$

combining:

$$\frac{m}{q} = \frac{H^2 r^2}{2V}$$

By holding V and r constant and varying the magnetic field (via altering the current through the magnet coils), particles of different mass can be focused through the exit slit. The ions impacting the ion collector result in a current which can be amplified and recorded. The mass (per unit charge) for the focused ion can be calculated and compared against the known masses of ions, resulting in identification of the gaseous species from which it originated.

Computer interfacing permits scanning for the presence of various gases periodically through the STA thermal processing. Mass spectroscopy systems work at vacuum levels of $\sim 10^{-7}$ torr. Hence, there is some engineering design skill involved in sampling the gas through a heated capillary tube in the STA chamber without disturbing the gas stream and avoiding condensation of the sampled gas.

5.3 A Case Study: Glass Batch Fusion

Thus far, only the effects of simple categories of transformations on DTA/DSC and TG signals have been discussed. The practical utility of these techniques, however, is in the investigation of unknown “messy” systems, demonstrating multiple transformations upon heating. The following case study on the reactions amongst glass batch particles provides some intuition into the interpretation of complex thermal analysis “spectra”. Also demonstrated is the use of thermal analysis in conjunction with other techniques, in this case x-ray diffraction, in a materials investigation.

5.3.1 Background

Industrial melting of glass is performed by floating batch powder onto the surface of a melt and exposing it to predominantly radiant energy via combustion gas from above and thermal conduction from molten glass below. The three main constituents in container glass or window glass are sand (silica: SiO_2), lime (calcite: CaCO_3), and soda ash (Na_2CO_3). Silica alone forms a clear, low expansion glass, but requires such high temperatures to melt that its fabrication for household applications would be prohibitively expensive. Adding soda ash to a silica batch allows the two to react at less elevated temperatures, but the resulting sodium-silicate glass is water soluble. The addition of lime stabilizes the glass against moist environments. Various other additions, such as dolomite ($\text{CaMg}(\text{CO}_3)_2$) and feldspar (albite: $\text{NaAlSi}_3\text{O}_8$), act as inexpensive secondary sources of fluxes and stabilizers.

Small particle sizes of raw batch materials accelerate melting and homogenization via an increase in the reaction area between raw materials. However, the use of very fine raw materials has an associated dusting problem along with the added cost of particle size reduction. In the following, simultaneous thermal analysis in conjunction with x-ray diffraction were used to determine the fusion path in a typical glass composition as a function of particle size.

5.3.2 Experimental Procedure

Glass batches of varying average particle size were prepared consisting of 58.1 wt% sand,² 17.8 wt% soda ash³ (Na_2CO_3), 7.6 wt% calcite⁴ (CaCO_3), 9.7 wt% dolomite⁵ ($\text{CaMg}(\text{CO}_3)_2$), and 6.8 wt% feldspar⁶ (albite: $\text{NaAlSi}_3\text{O}_8$). The resultant fi-

²Keyston No. 1 dry glass sand, U.S. Silica, Mapleton, PA.

³Green River, WY, courtesy of FMC Corporation, Philadelphia, PA.

⁴Code R1 calcitic limestone, Mississippi Lime, St. Gemavive, MO.

⁵Dolomitic limestone, Steetly Ohio Lime Company, Woodville, OH.

⁶Grade 340, Indusmin Ltd., Nephthton, Ontario.

nal composition was calculated as 73.40 wt% SiO₂, 13.05 wt% Na₂O, 8.03 wt% CaO, 2.97 wt% MgO, and 2.07 wt% Al₂O₃ (0.48 wt% residual).

Before mixing, raw materials were ground and separated by size via dry sieving into five different mesh ranges: 60 to 120 (125-250 μm), 120 to 170 (90-125 μm), 170 to 230 (63-90 μm), 230 to 325 (45-63 μm), and smaller than 325 mesh (45 μm). From these, five 500 g batches were prepared, each of matched particle size ranges. They were then mixed by vigorous shaking in a container with 12 alumina grinding media for five minutes.

Samples were exposed to a 10°C/min heating rate for thermal analysis studies. A Netzsch⁷ STA was used with an Innovative Thermal Systems⁸ control and data acquisition system. This system entails both sample and reference being supported by an alumina post which rests on an analytical balance. This balance has a manufacturer's reported precision of 20 μg . Samples weighing ~300 mg were loaded into platinum crucibles with powdered alumina in a platinum crucible acting as a reference. "S"-type thermocouples were used for furnace control (SiC heating element) as well as for temperature and differential temperature signals. Derivative TG data (DTG) were determined by visual smoothing of continuous slopes of least squares fit tangent lines to mass versus time data.

In preparation for XRD, 0.50 g samples were placed in platinum pans and heated at 10°C/min in a furnace where the control thermocouple was in contact with the specimen container. Specimens were quenched by immediate exposure to room temperature then ground with a mortar and pestle to pass through a 325 mesh screen. X-ray diffraction was performed using a Philips⁹ x-ray diffractometer. Diffraction patterns were obtained with 2θ values ranging from 20° to 60° 2θ . The diffracted x-rays were counted over 0.02° intervals for 2

⁷Model STA 409C, Netzsch Inc., Exton, PA.

⁸Innovative Thermal Systems, Atlanta, GA.

⁹Model 12045 x-ray diffraction unit, Philips Electronic Instruments Co., Mount Vernon, NY.

seconds at each interval. Data were analyzed using a Siemens Diffrac 500¹⁰ computer system using a JCPDS data base.

5.3.3 Results

Figure 5.12 shows the DTA trace of the base glass composition of the most coarse particle size (125-250 μm) as well as the DTA traces of several binary pairs, a soda ash-calcite-silica mixture, and soda ash alone, all of particle size 90-125 μm . The soda ash, binary, and ternary mixtures were used in order to determine (by comparison) the constituents in the base glass batch which were the significant contributors to various endothermic features along the DTA trace. The carrots along the trace correspond to the points of quench for x-ray diffraction analysis.

The effect of particle size on reactions in the base glass composition are shown in the superimposed DTA and DTG traces in Figure 5.13. The DTG traces follow closely the shape of the DTA traces for transformations involving decompositions and other reactions involving gas release, but do not correspond to transformations involving solely fusion or crystallographic inversions. Hence, superposition of the two traces facilitates separation of types of transformations recorded in the DTA traces. Figure 5.14 shows the superposition of XRD traces taken after quenching (125-250 μm) glass batches following heat treatment to various temperatures. Similar data were obtained for the -45 μm glass batches (henceforth 125-250 μm is referred to as "coarse" and -45 μm as "fine") but is not shown. Figure 5.15 is a plot of XRD peak heights of various identified phases superimposed on DTA and DTG traces for the coarse and fine particle sizes. Since no internal standards were used during XRD analysis, the values of relative peak heights are considered only semi-quantitative. The vertical bars distributed along the trace refer to temperatures at features of interest along the trace, used in the discussion of results.

¹⁰Model VAX-11/730, Digital Equipment Co., Northboro, MA.

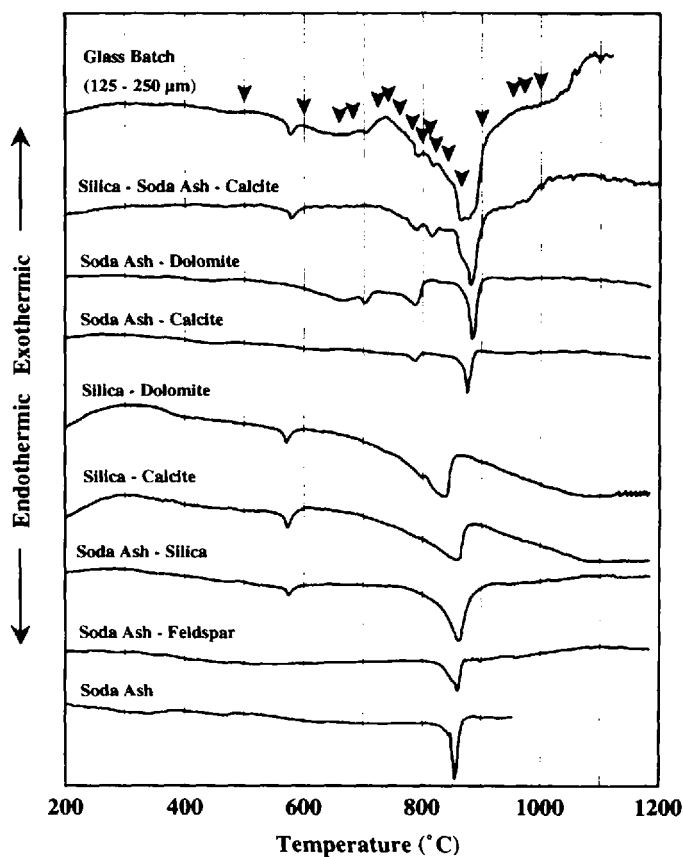


Figure 5.12: DTA traces of the base glass composition of particle size 125-250 μm , the ternary mixture soda ash-calcite-silica with a particle size of 90-125 μm , as well as various binary mixtures and soda ash alone from previous work [12]. All mixtures maintained the same relative percentages of constituents as those in the base glass batch.

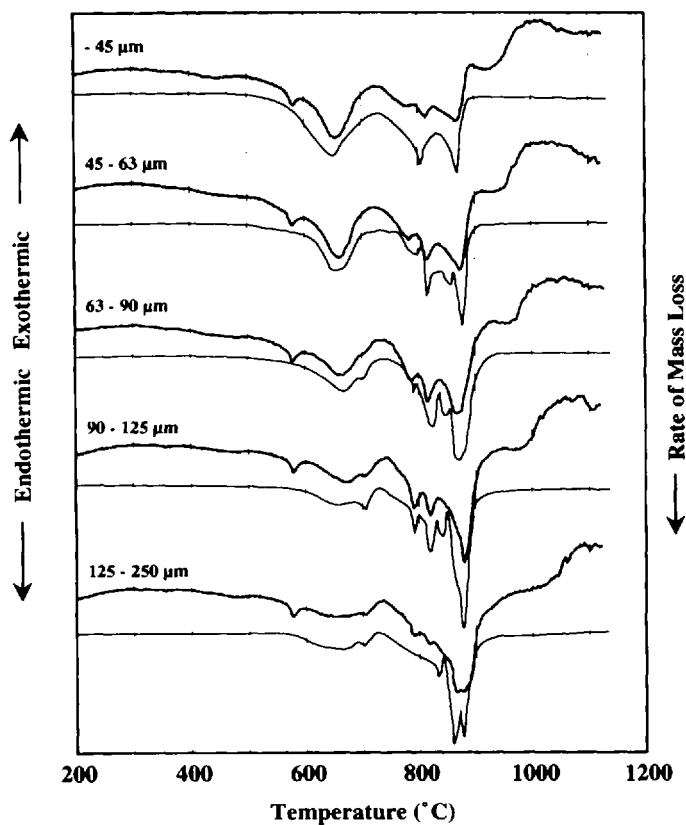


Figure 5.13: DTA and DTG traces, simultaneously measured, of the base glass batch composition of various particle sizes.

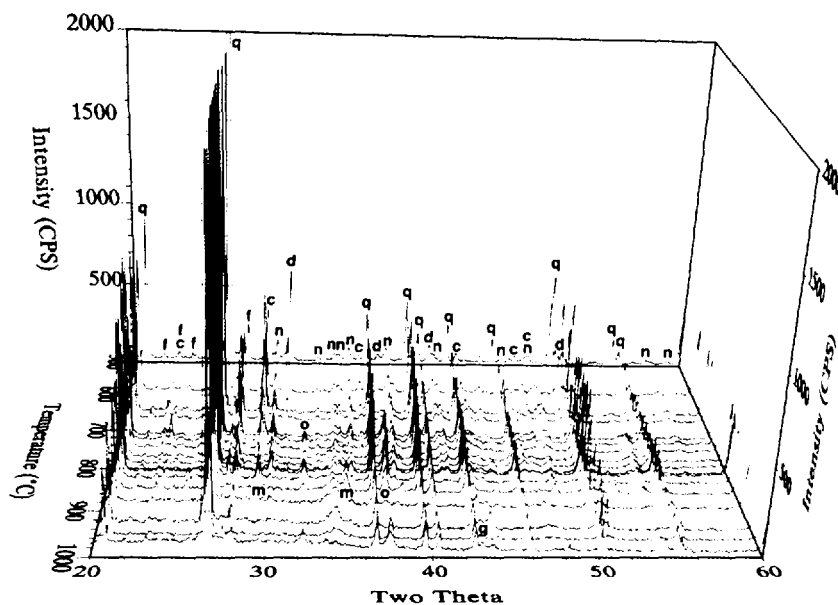


Figure 5.14: Superimposed x-ray diffraction traces for the base glass composition after heat treating to specified temperatures. Front to back: 502°C, 600°C, 660°C, 680°C, 725°C, 740°C, 760°C, 785°C, 800°C, 815°C, 820°C, 840°C, 850°C, 865°C, 925°C, 940°C, 980°C, 1000°C. Phases: q=quartz, f=feldspar, c=calcite, n=soda ash, d=dolomite, o=calcium oxide, m=sodium metasilicate, g=magnesium oxide.

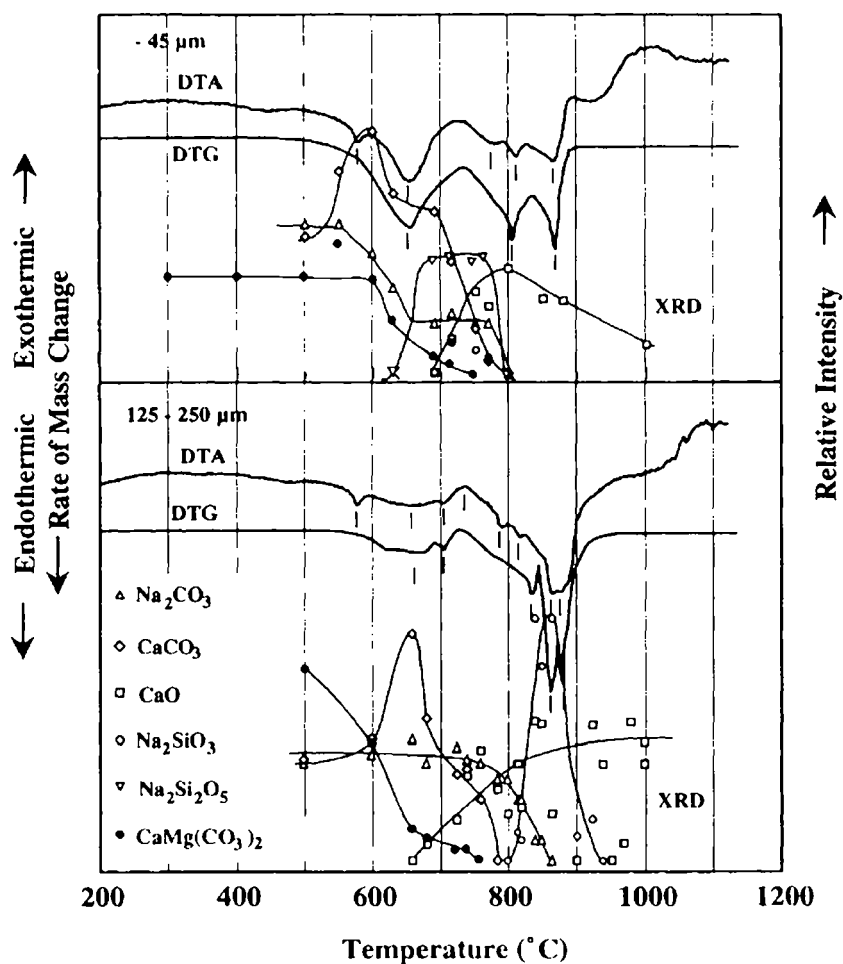


Figure 5.15: DTA and DTG traces, as well as relative XRD peak heights of various phases for the base glass composition. Upper: $-45\ \mu\text{m}$ particle size. Lower: $125-250\ \mu\text{m}$ particle size.

5.3.4 Discussion

Coarse Particle Size

In Figure 5.15, the endotherm peaked at 576°C (onset at 572°C) resulted from the α - β quartz transformation in silica. The broad, low intensity endotherm which peaked at 651°C correlates to the broad endotherm in the soda ash-dolomite system (Figure 5.12) and coincides with continuous reductions in dolomite content indicated in the XRD traces at 600, 660, and 680°C.

Dolomite does not decompose ($\text{CaMg}(\text{CO}_3)_2(s) = \text{CaCO}_3(s) + \text{MgO}(s) + \text{CO}_2(g)$) until $\sim 777^\circ\text{C}$ [12], implying reaction between dolomite and other batch constituents occurred in the base glass batch, resulting in first-formed liquid phase (further justification will be given subsequently). The endotherm peaked at 706°C (onset at 700°C) corresponds to that observed in the soda ash dolomite mixture, but there is no corresponding endotherm in the soda ash-calcite mixture (Figure 5.12). The endotherm at 706°C is thus interpreted to correspond to eutectic liquid formation between CaCO_3 , MgO , and Na_2CO_3 . If MgO did not play a role in the liquid phase formation, this melting endotherm would have appeared in the soda ash-calcite system.¹¹ DTG data (Figure 5.13) indicates a weight drop in that temperature region. This may have been caused by CO_2 release from calcite decomposition when it went into solution. Conversely, it may have resulted from CO_2 release from liquid phase attack on silica grains forming sodium disilicate: $\text{Na}_2\text{CO}_3(l) + 2\text{SiO}_2(s) = \text{Na}_2\text{O} \cdot 2\text{SiO}_2(s) + \text{CO}_2(g)$. Since the XRD peaks for sodium disilicate are superimposed on those of feldspar, it was not feasible to confirm its presence for the coarse particle size in this temperature range.

¹¹ A second interpretation is that the liquid phase previously formed between dolomite and soda ash was required for the reaction endotherm peak at 706°C, implying a fusion reaction rather than eutectic melting amongst solids. This is refuted by evidence discussed subsequently where the disappearance of this endotherm with decreasing particle size (increasing volume of liquid phase) implies that interparticle contact was required for this reaction.

A broad endothermic trend begins at 733°C and continues until 879°C. This was accompanied by an accelerating weight loss, as indicated by the DTG peak starting at the same temperature. This trend corresponds in part to the solid state decomposition of $\text{CaCO}_{3(s)}$ to $\text{CaO}_{(s)}$ and $\text{CO}_{2(g)}$ as indicated by the decreasing CaCO_3 and increasing CaO relative XRD peak intensities in Figure 5.15.

The final four endotherms (peaked at 789, 816, 862, and 879°C) superimposed on the broad endothermic trend, imply fusion reactions rather than decomposition reactions.¹² The sharp endotherm peaked at 789°C has corresponding endotherms in the soda ash-dolomite and the soda ash-calcite system. This endotherm also corresponds well to the Na_2CO_3 - CaCO_3 eutectic at 785°C [13]. The fact that this endotherm appears in the soda ash-calcite system implies that the pre-existing liquid phase in the base glass composition was not a factor in the liquid phase formed at 785°C, nor was the presence of MgO . The Na_2CO_3 - CaCO_3 mixture lacked the sharp DTG peak (not shown) as compared to the DTG peak corresponding to the endotherm for the glass batch at 785°C. It is thus interpreted that the soda ash content of the newly formed eutectic liquid attacked the quartz grains, forming (additional) sodium disilicate and releasing CO_2 .

The endotherm which peaked at 816°C has no corresponding endotherm in any of the chosen binary systems. However, this endotherm was clearly apparent in the ternary mixture, silica-soda ash-calcite, implying liquid formation amongst these three constituents. This fusion process was not eutectic, since an active participant in this reaction is expected to have been the

¹²DTA traces of melting appear as linear deviations from the baseline due to the sample temperature remaining isothermal (LeChatelier's principle) while the reference increases in temperature at the scheduled linear rate. The peak represents the termination of melting, which is followed by an exponential decay-type of relaxation of the trace to the baseline, as the sample temperature catches up to the temperature of its surroundings. In contrast, the rates of decomposition reactions are hampered by the diffusion of ejected gaseous species, which tends to cause an initially sluggish reaction rate which accelerates with increasing temperature, resulting in a comparatively broad endotherm.

liquid formed from the previous Na_2CO_3 - CaCO_3 eutectic melting (DTA peak at 785°C). After fusion amongst these components, adequate liquid phase was available for the formation of sodium metasilicate from excessive liquid phase attack on the sodium disilicate coated silica grains via: $\text{Na}_2\text{CO}_3(l) + \text{Na}_2\text{O} \cdot 2\text{SiO}_2(s) = 2\text{Na}_2\text{O} \cdot \text{SiO}_2(s) + \text{CO}_2(g)$. This is evidenced by the appearance of this phase in the XRD pattern at 815°C as well as the DTG peak at 835°C . The fact that the DTG trace reaches a maximum at 835°C followed by a slowing of CO_2 release, implies that the reactive constituents of the existing liquid phase were consumed by this process.¹³

The sharp increase in the endothermic trend, starting at 850°C corresponds to the onset of melting of pure soda ash (melting point 851°C , see Figure 5.12). The endotherm peaked at 862°C corresponds to the termination point of Na_2CO_3 fusion; the elimination of the XRD peaks for soda ash (Figure 5.15) coincides with this. Associated with the sharp increase in liquid phase from soda ash fusion was a lack of clear XRD evidence of a significant additional quantity of sodium metasilicate having formed via liquid phase attack on the coated silica relic. However, the carbon dioxide evolution, implying such a reaction, is clearly apparent from the DTG peak at 862°C .

The DTA peak at 879°C coincides with a sharp drop in sodium metasilicate content as indicated by XRD. The sodium metasilicate outer coating in contact with the liquid phase disguised the sodium disilicate in contact with quartz from detection by XRD (along with masking of the sodium disilicate peak from the presence of feldspar). At the congruent melting temperature of sodium disilicate (873°C [14]), the innermost coating layer liquified, causing the sodium metasilicate outer shell to also go into solution; any sodium metasilicate in

¹³The diffusion distance of reactive species into and products out of coated quartz grains could have hampered the reaction as well. However, this interpretation is refuted by significant enhancement of sodium metasilicate content after the fusion of soda ash, indicating soda ash availability controlled the rate of sodium metasilicate formation.

contact with silica relics or silica-rich liquid phase would have been converted to sodium disilicate (since the reaction zone is silica rich) which was a liquid phase at those temperatures. As a result, no sodium metasilicate would be observed in XRD patterns above the congruent melting temperature of sodium disilicate.

Feldspar and CaO remained in XRD traces at and above 1000°C (Figure 5.14). The relative peak heights for both compounds had more scatter than the other batch constituents and phases which formed during heating. There appeared to be no discernible reaction between these phases and the liquid phase; their elimination was hence interpreted strictly as a dissolution process, based on the available evidence.

Fine Particle Size

There is 5.5 times more exposed particle surface area in the fine batch as compared to the coarse (assuming spherical 250 μm coarse and 45 μm fine particles). This permitted a significant enhancement in the intimacy of particle contact, as evidenced by the shift in DTA, TG, and XRD data. After the α - β quartz transformation (peak temperature 578°C) in the DTA trace for the fine particle size in Figure 5.15, the broad endotherm peaked at 651°C coincides with the temperature range at which liquid phase was first formed. The reduction in Na_2CO_3 content in the XRD pattern at 630°C indicates liquid phase formation prior to that temperature. The sodium carbonate content continued to drop (e.g. XRD pattern at 690°C) throughout the temperature range associated with the broad endotherm. TG data (not shown) indicated a 43.2% mass loss for the fine batch as compared to 21.5% for the coarse at 700°C. The XRD pattern at 690°C shows the formation of appreciable sodium disilicate ($\text{Na}_2\text{CO}_{3(l)} + 2\text{SiO}_{2(s)} = \text{Na}_2\text{O} \cdot 2\text{SiO}_{2(s)} + \text{CO}_{2(g)}$, $\Delta H_{700^\circ\text{C}} = +60.5 \text{ kJ/mol}$ [15]). This DTG peak corresponds, to a large extent, to $\text{Na}_2\text{CO}_{3(l)}$ attack on silica grains. The presence of sodium metasilicate was not indicated

by XRD. Contact between silica grains and molten soda ash would be adequately intimate so that the vast majority of the (reactive constituents of) contacting liquid phase at this temperature range would be consumed via the formation of sodium disilicate. Sodium metasilicate would then not be expected to form to any significant extent, since there would be no sodium disilicate/reactive liquid phase interface to mediate.

The broad endothermic trend leading into the peak at 782°C and the corresponding accelerating weight loss indicated in the DTG trace correlates in part to the decomposition of the remaining CaCO_3 to CaO . The DTA peak at 782°C corresponds to the Na_2CO_3 - CaCO_3 eutectic as well as to the sodium disilicate-quartz melting eutectic at 787°C. The Na_2CO_3 - CaCO_3 eutectic caused the elimination of solid soda ash, as indicated by the XRD trace at 800°C. The sharp DTG peak at 804°C and the endotherm peaked at 814°C correspond to direct soda ash-rich liquid phase attack on quartz, once the fusing sodium disilicate shells became perforated¹⁴ and quartz grains were exposed. This reaction released CO_2 and formed additional silica-rich liquid phase. It is also possible that CO_2 became highly insoluble after the silicious and carbonaceous liquid phases mixed [16].

The endotherm that peaked at 868°C with a corresponding DTG peak at 870°C coincides with a significant dissolution of CaO as indicated by XRD relative peak heights. It is speculated that the reaction peaked at 816°C for the coarse batch (seen in the soda ash-silica-calcite mixture) was suppressed in the fine particle sizes because of the silicious nature of the liquid phase. The endotherm that peaked at 868°C would then represent a shift to higher temperature for this reaction, with corresponding reduction in solid CaO . The weight loss associated with this endotherm would correspond to decreased CO_2 solubility in a liquid phase enriched in calcia.

¹⁴Liquid phase formed at the sodium disilicate-quartz interface above the eutectic melting temperature and worked its way outward. Perforation refers to when the outer sodium disilicate shells were no longer continuous.

Effect of Particle Size on Reaction Path

The endotherm that peaked at 651°C intensifies steadily with decreasing particle size, as is the case for the associated DTG peak. This endotherm represents increased formation of liquid phase with decreasing particle size. The enhanced weight loss, indicated by the DTG traces with decreasing particle size, does not coincide with the formation of detectable new crystalline phases in the coarse particle sizes, but does correspond to XRD detection of the formation of sodium disilicate in the fine particle size. Thus, decreasing particle size results in a significantly enhanced low temperature liquid phase attack on silica grains.

The endotherm that peaked at 706°C was correlated to eutectic melting between CaCO_3 , Na_2CO_3 , and MgO . It could also be interpreted as a fusion reaction involving these phases and pre-existing liquid phase. This endotherm appears in the 90-125 μm and 63-90 μm particle size mixtures as well, albeit more diffusely, but does not appear in DTA traces for the two finest particle size mixtures. It is interpreted that for the 45-63 μm particle size and smaller, an adequate quantity of liquid phase was formed (associated with the peak at 651°C) to have prevented the solid particle contact necessary for CaCO_3 - Na_2CO_3 - MgO eutectic melting. This further implies that pre-existing liquid phase was not a participant in this reaction.

The DTA peak at 789°C for the coarse batch becomes more pronounced, then less pronounced, with decreasing particle size. The DTG peak at 791°C for the 90-125 μm and 63-90 μm particles shifts to $\sim 801^\circ\text{C}$ for the 45-65 μm and -45 μm particles. More intimate particle contact with decreasing particle size would be expected to enhance eutectic melting between CaCO_3 and Na_2CO_3 , until a continuous liquid phase had formed which isolated particles from mutual contact (45-63 μm and -45 μm mixtures). For these finer particles, this endotherm is expected to correspond more to eutectic melting between sodium disilicate coatings and quartz. This reaction would have no corresponding weight loss. Weight loss would

only be expected when the sodium disilicate shells became perforated wherein soda ash-bearing liquid phase could directly attack quartz, or mix with silicacious liquid, releasing CO_2 . Hence, the observed delayed DTG peak for finer particles.

A similar scenario is not observed for the DTA peak at 816°C , which remains endothermic with about the same intensity for particle sizes $90\text{--}125\text{ }\mu\text{m}$ and smaller. This endotherm is a result of liquid phase formation amongst CaO , silica, and liquid phase. Hence, intimacy of particle contact is not so much an issue for this transformation.

The soda ash melting endotherm that peaked at 862°C and the sodium metasilicate (interpreted as sodium disilicate with a sodium metasilicate outer shell) dissolution endotherm at 870°C merge into one endotherm at 868°C for particle sizes of $45\text{--}63\text{ }\mu\text{m}$ and smaller. For the coarse particle size, the sodium metasilicate formed en masse only after a liquid phase was provided by the melting of soda ash. This phase completely fused only at its congruent melting temperature (873°C). Along with the elimination of the Na_2CO_3 melting endotherm, decreasing particle size resulted in a significant increase in the quartz-sodium disilicate interfacial contact area. Thus, eutectic melting would go to completion at temperatures lower than the aforementioned congruent melting temperature.

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Chapter 6

ADVANCED APPLICATIONS OF DTA AND TG

6.1 Deconvolution of Superimposed Endotherms [1]

6.1.1 Background

With slower heating rates, transformation peaks in DTA and DSC often show features implying the superposition of multiple peaks. If these individual peaks could be isolated, much information about the onset temperatures, rates, and mutual interdependence of individual reactions governing an overall transformation could be discerned.

The superposition principle for heat flow as measured by power-compensated DSC should apply—just as it would be expected that the water flow into one tank from two pipes would be additive. Assuming Fourier’s law holds (steady state heat flow proportional to temperature gradient), the temperature differences measured in DTA (and heat-flux DSC) are additive via contributions from multiple transformation sources within the sample material.

The process of “deconvolution” of superimposed endotherms and exotherms requires modeling individual reactions to heat flow functions, which when added together, emulate the exper-

imental data. The models derived herein—melting and first order decomposition are used as examples—they certainly do not exhaust the possibilities of transformation phenomenon studied by thermal analysis. Rather than deconvolute experimental data, DSC/DTA data was “fabricated” by generating equations. In that way, the solution coefficients were known in advance, so that the capabilities of the deconvolution technique could be properly evaluated.

In addition to deconvolution, the computer fitting of model equations to single transformation peaks has the utility of establishing important parameters of the reaction, such as reaction order and activation energy. This sort of modeling has previously been undertaken by sometimes cumbersome and questionable [2, 3] mathematical manipulation of experimental data.

Before actual data can be fit to a model, extraneous effects manifested in the trace must be removed, such as the shift in baseline as a result of the change in heat capacity of the sample during the transformation (see section 3.7.2). It may, for some device designs (e.g. post-type DTA), be difficult to purify the instrument output to represent only the latent heat from the transformation because of random baseline float. Hence, the data set fitting a particular model is a necessary but insufficient criterion for guaranteeing that the model describes the measured phenomenon.

6.1.2 Computer Algorithm

The computer least squares optimization algorithm used is termed “Simplex” [4] which was programmed using Microsoft QuickBasic 4.5. A version of the program is provided at the end of this section.

A model equation for the transformation phenomenon (see following sections), as well as seed coefficients for the equation, are entered into the program code. These seed coefficients are estimates which, after plotting the equation, create a data set

within reasonable proximity of the actual data set. By an iterative process, the program will determine the coefficients to the equation which best fit the experimental data by the criterion of least squared error.

For simplified visualization, the optimization process is described for an equation with three coefficients (e.g. $y = ax^2 + bx + c$, where a , b , and c are coefficients). The three coefficients may be visualized as cartesian coordinates in space. Another coordinate set (or "point") is created by multiplying the first coefficient by 1.1. Still another point is made by maintaining the first coefficient at its original value, and multiplying the second coefficient by 1.1. Continuing this process creates four points, the original plus the three others created by slightly increasing the value of any one of the coefficients (Figure 6.1).

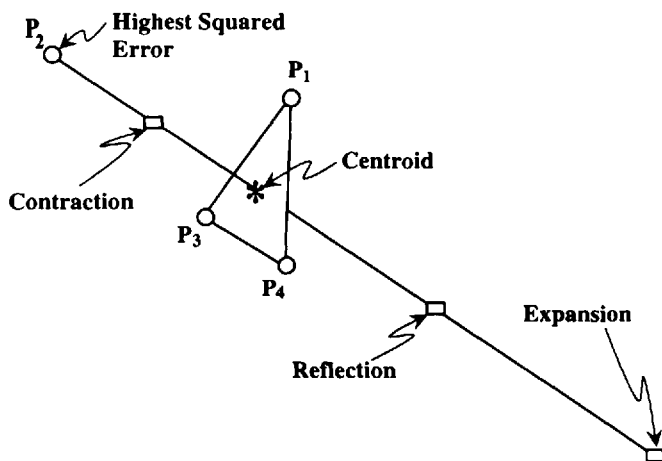


Figure 6.1: Simplex numerical optimization algorithm shown for three dimensions. The point with the highest squared error is relocated to one of the three new positions, whichever one assumes the lowest squared error.

The program calculates the sum of the squared error between the predicted (from the equation) and actual (from the data set) abscissa values for each point, and in turn determines

which of the four points has the largest squared error. The “centroid” is then calculated from all points other than that of highest squared error by averaging the values in each dimension. The point with the highest squared error is moved toward or past the centroid either by “reflection”, “expansion”, or “contraction” (as indicated schematically in the figure) depending on which new point results in minimum squared error. The high squared error point is moved to one of these points, and the process begins again with the point of next highest squared error. The four points, referred to as the “simplex”, “tumble and roll” toward minimum squared error. The simplex as a whole can move in a direction which decreases squared error by repeated reflections about the centroids. The simplex can accelerate its propagation in a “good direction” by expansions about the centroids. An expansion is made when the expanded point is of lower squared error than the lowest squared error point of the simplex. When the simplex surrounds a region of minimum squared area, it will successively contract, closing all points in on the solution.

If none of the three relocations of the mobile point with respect to the centroid act to lower its squared error, then the program uses “scaling” to move all of the points away from the one with the least squared error. Scaling is useful to “shake loose” the simplex from a local minima, and allow it to propagate toward the absolute minima of squared error. Repeated scaling without any change in the point of lowest squared error indicates either that the solution has been found, or that the program could not break out of a local minima.

6.1.3 Models and Results

Superimposed Melting Endotherms

A melting endotherm is characterized by a linear deviation from the baseline as the sample temperature remains at the melting temperature, while the reference increases in temperature

at the programmed rate (for DTA). After the point at which the sample has fully melted (peak), its temperature must then catch up to that of its surroundings. This recovery is initially rapid when the temperature gradient is large and then slower as the temperatures of sample and surroundings approach each other. Hence, melting endotherms take the shape of a line on the low temperature side and a decaying exponential on the high temperature side (similarly for power-compensated DSC but by different arguments [5]):

$$\frac{dQ}{dt} = C(T - T_o)_{T \geq T_o \text{ and } T \leq T_m} + C(T_m - T_o) \exp(-D(T - T_m))_{T > T_m} \quad (6.1)$$

where T is temperature, T_o is the sample temperature at the onset of the transformation, T_m is the sample temperature at the peak, and C and D are constants, defining the slope of the rise and the shape of the decay, respectively. The constant C is equal to or proportional to the heating rate, depending on the units of the abscissa. The constant D is dependent on the thermal resistance to heat flow between the sample container and its surroundings [5].

For melting transformations which are partially superimposed, we assume that the heat absorption detected by the instrument may be taken as the sum of the heat flow from each transformation. Thus:

$$\frac{dQ}{dt} = \frac{dQ_1}{dt} + \frac{dQ_2}{dt} \quad (6.2)$$

Hence:

$$\begin{aligned} \frac{dQ}{dt} = & \sum_{i=1}^2 [C_i(T - T_{oi})]_{T \geq T_{oi} \text{ and } T \leq T_{mi}} \\ & + [C_i(T_{mi} - T_{oi}) \exp(-D_i(T - T_{mi}))]_{T > T_{mi}} \end{aligned} \quad (6.3)$$

Coefficient values of $T_{o1} = 220^\circ\text{C}$, $T_{m1} = 230^\circ\text{C}$, $C_1 = 5 \text{ W/K}$, $D_1 = 1.5 \text{ }^\circ\text{C}^{-1}$, $T_{o2} = 228^\circ\text{C}$, $T_{m1} = 237^\circ\text{C}$, $C_2 = 3 \text{ W/K}$, $D_2 = 2 \text{ }^\circ\text{C}^{-1}$ were chosen to put into equation 6.3 to generate a "data set" of 500 x-y pairs, shown by the thick-lined trace in

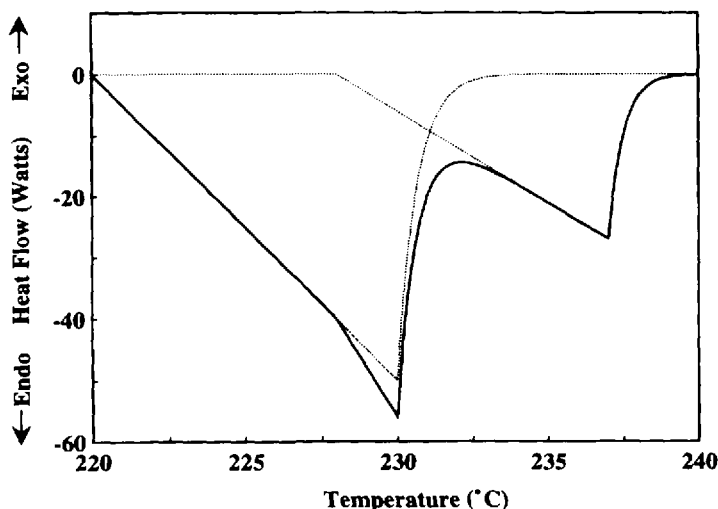


Figure 6.2: Simulated superimposed melting endotherms (dark line). Final simplex-program coefficients match those used for the simulation. Dotted lines are plots of each term in the sum in eq. 6.3, representing the deconvoluted melting endotherms.

Figure 6.2. Since the peak values T_{m_i} for this model as well as the first onset temperature T_{o1} are clear from the data, they were pinned at their correct values. Estimates of $C_1 = 2 \text{ W/K}$, $D_1 = 1 \text{ }^\circ\text{C}^{-1}$, $T_{o2} = 225^\circ\text{C}$, $C_2 = 8 \text{ W/K}$, and $D_2 = 1 \text{ }^\circ\text{C}^{-1}$ were used as seed values for the program. Within about 10 minutes, the program settled on values for the coefficients which matched the coefficients used to create the simulated data, within single precision roundoff error. Each term in the sum, representing the deconvoluted endotherms, is plotted in the figure as dotted lines.

Superimposed First Order Decomposition Endotherms

The partial area divided by the total area under a DSC/DTA peak is taken [6] as equal to the fraction F of the transformation

completed at a given time:

$$F = \frac{\int_0^t \frac{dQ}{dt} dt}{A} \quad (6.4)$$

or in differential form:

$$\frac{dQ}{dt} = A \frac{dF}{dt} \quad (6.5)$$

Hence, dividing the purified DSC/DTA output by the area under the peak results in a plot of dF/dt , which is a convenient function to fit to model equations. Combining equations 6.5 and 6.2:

$$\frac{dQ}{dt} = A_1 \frac{dF_1}{dt} + (A - A_1) \frac{dF_2}{dt} \quad (6.6)$$

where $(A - A_1)$ was substituted for the area A_2 under the second endotherm, since the total area A can be determined by numerical integration.

If we assign time zero to be at a temperature where the reaction rate is infinitely small (assigned arbitrarily to be room temperature $T_r = 293\text{K}$) the relationship between temperature and time is simply

$$T = \phi t + T_r \quad (6.7)$$

where ϕ is the heating rate (assigned to be 10 K/min). This requires the sample temperature to not deviate from the programmed schedule, which is more acceptably the case in power-compensated DSC than in DTA or heat-flux DSC.

A first order transformation is simply one in which the rate of reaction is proportional to how much reactant is left:

$$\frac{dX}{dt} = -kX \quad (6.8)$$

where X is the mole fraction of reactant, and k is "rate constant" which is invariant for isothermal transformations. The rate constant is taken to follow an Arrhenius temperature dependence:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (6.9)$$

where E_a is the activation energy, and R is the gas constant (8.314 J/mol·K). Substituting eqs. 6.7 and 6.9 into eq. 6.8 and integrating:

$$\int_1^X \frac{dX}{X} = \ln X = \int_0^t -k_0 \exp\left(\frac{-E_a}{R(\phi t + T_r)}\right) dt \quad (6.10)$$

or:

$$X = \exp\left(\int_0^t -k_0 \exp\left(\frac{-E_a}{R(\phi t + T_r)}\right) dt\right) \quad (6.11)$$

Differentiating:

$$\frac{dX}{dt} = -k_0 \exp\left(\frac{-E_a}{R(\phi t + T_r)}\right) \exp\left(\int_0^t -k_0 \exp\left(\frac{-E_a}{R(\phi t + T_r)}\right) dt\right) \quad (6.12)$$

The fraction transformed F is simply $F = 1 - X$, thus $\frac{dF}{dt} = -\frac{dX}{dt}$, hence:

$$\frac{dF}{dt} = k_0 \exp\left(\frac{-E_a}{R(\phi t + T_r)}\right) \exp\left(\int_0^t -k_0 \exp\left(\frac{-E_a}{R(\phi t + T_r)}\right) dt\right) \quad (6.13)$$

The integral in eq. 6.13 is evaluated numerically by the trapezoidal rule in the computer program (see section 6.1.5). As a check, the numerical integration of the peak represented by equation 6.13 was unity (within single-precision roundoff error), which is as expected when integrating a unitless fraction. The choice of T_r does not effect the location or shape of the peak, with exception if T_r is chosen too high (such that the function to be integrated in eq. 6.13 deviates appreciably from zero), then the assumption in eq. 6.10 that $X = 1$ when $t = 0$ is not valid, hence eq. 6.13 would not be valid. This equation adopts an asymmetrical shape as shown (after multiplying by A_1 or A_2) by either one of the dotted lines in Figure 6.3. By inserting eq. 6.13 into eq. 6.6, and by designating coefficient values $A_1 = -1 \text{ W}\cdot\text{min}$ (-60 J), $k_{01} = 9 \times 10^7 \text{ min}^{-1}$, $E_{a1} = 105000 \text{ J/mol}$, $A_2 = -0.7 \text{ W}\cdot\text{min}$ (-42 J), $k_{02} = 1 \times 10^8 \text{ min}^{-1}$, and $E_{a2} = 120000 \text{ J/mol}$ ($\phi = 10^\circ\text{C/min}$ assigned), the plot shown by the thick-lined trace in Figure 6.3 was obtained.

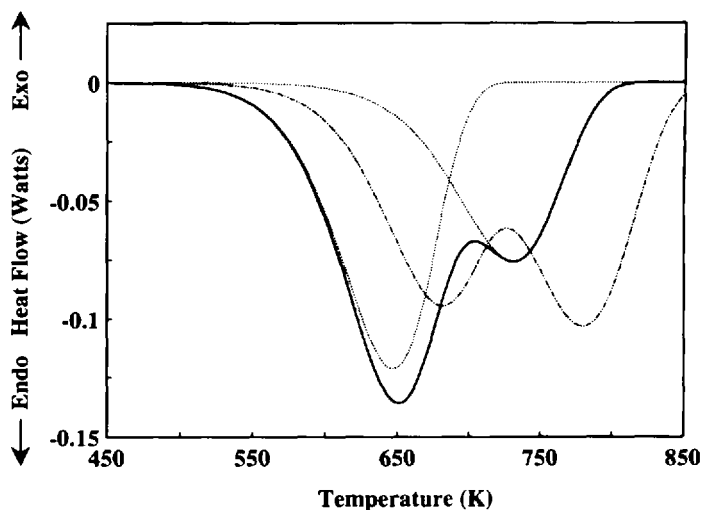


Figure 6.3: Simulated superimposed decomposition endotherms (dark line). Dot-dot-dash line represents plot of equation with seed coefficients inserted. Final simplex-program coefficients match those used for the simulation. Dotted lines are plots of each term in the sum in eq. 6.6, representing the deconvoluted first order reaction endotherms.

The data trace was then numerically integrated to determine a value of total area of $A = -1.7 \text{ W} \cdot \text{min}$ (-102 J). Seed values of $A_1 = -.7 \text{ W} \cdot \text{min}$ (-42 J), $k_{01} = 1.1 \times 10^8 \text{ min}^{-1}$, $E_{a1} = 111000 \text{ J/mol}$, $k_{02} = 1.3 \times 10^8 \text{ min}^{-1}$, and $E_{a2} = 130000 \text{ J/mol}$ were used. The trace shown by the dot-dash curve in Figure 6.3 is a plot of eq. 6.6 with these seed coefficients.

The program successfully converged on the solution in about 15 minutes. The text of the program in section 6.1.5 corresponds to this model. Portions of the code which must be changed for more superimposed peaks or different models are indicated in the imbedded comments.

6.1.4 Remarks

For the models derived herein, the program was able to converge on the absolute minima—the correct coefficients. For

more superimposed peaks or models with more coefficients, the algorithm may become trapped at local minima. The problem which will be faced when attempting to fit experimental data to such models with this algorithm is that since the solution will not be known, local and absolute minima cannot be differentiated, and one can never be certain if the "correct" solution coefficients were generated.

The utility of the algorithm remains, however, even if confidence in the values of simplex-determined individual coefficients is not high. The routine never fails to find a visually correct fit of the model to the data, which allows good estimates of hidden onset temperatures and individual peak areas (which correspond to the latent heats of transformation).

6.1.5 Sample Program

```
'This is a Basic (Microsoft Quickbasic 4.5) version of the simplex
'algorithm by Richard W. Daniels, An Introduction to Numerical
'Methods and Optimization Techniques, North Holland Press,
'New York, 1978.
```

R.F. SPEYER

```
DECLARE SUB refl (p!(), cent!(), pr!(), ih%, i%)
DECLARE SUB expan (p!(), pr!(), pex!(), cent!(), i%)
DECLARE SUB contr (p!(), pc!(), cent!(), ih%, i%)
DECLARE SUB scale (p!(), il%, i%)
DECLARE SUB phigh (p!(), xerror!(), ih%, il%, i%)
DECLARE SUB centroid (p!(), cent!(), ih%, i%)
DECLARE SUB onerr (pr!(), t!(), hdot!(), erref!, n%)
DECLARE SUB sqerror (p!(), hdot!(), t!(), xerror!(), i%, n%)
```

```
't() is time, hdot() is heat flow read in from the data file.
'p(i%+1,i%) is the array of i%+1 'points' corresponding to
'i% coefficients. pc() pr() and pex() represent contracted,
'reflected and expanded points, respectively. phi is the
'heating rate, r is the gas constant, artot# is the area under
'the superimposed peaks, and tr# is the starting temperature.
```

```
DIM t(4000), hdot(4000)
DIM cent(12), pc(12), pr(12), pex(12), p(12, 12), xerror(12)
DIM SHARED phi, r, artot#, tr#
```

```

phi = 10
r = 8.314
tr# = 293
'Seed coefficients are in the order k01, ea1,k02,ea2,ar1
'where K01 and k02 are arrhenius pre-exponential constants,
'ea1 and ea2 are activation energies, and ar1 is the area
'under peak 1. For insertion of a different model, p(1,?)
'will have to be added and the assignment of i%, the total
'number of coefficients, will have to be revised.
i% = 5
p(1, 1) = 1.1E+08
p(1, 2) = 111000
p(1, 3) = 1.3E+08
p(1, 4) = 130000
p(1, 5) = -.7

CLS
'Read in data, temperature data converted to time.
filename$ = "dout.dat"
OPEN filename$ FOR INPUT AS #11
n% = 1
DO UNTIL EOF(11)
    INPUT #11, t(n%), hdot(n%)
    t(n%) = (t(n%) - tr#) / phi
    n% = n% + 1
LOOP
n% = n% - 1
'Determine total area under superimposed peaks.
gral# = 0
FOR g% = 2 TO n%
    rec# = (hdot(g% - 1) - 0) * (t(g%) - t(g% - 1))
    tri# = .5 * (hdot(g%) - hdot(g% - 1)) * (t(g%) - t(g% - 1))
    gral# = gral# + rec# + tri#
NEXT g%
artot# = gral#
'Generate P(2,-) through P(i%+1,-)
FOR k% = 1 TO i% + 1
    IF k% > 1 THEN
        FOR j% = 1 TO i%
            p(k%, j%) = p(1, j%)
        NEXT j%
        p(k%, k% - 1) = 1.1 * p(k%, k% - 1)
    END IF
NEXT k%

```

```

'Generate error functions for all P's
711 :
CALL sqerror(p(), hdot(), t(), xerror(), i%, n%)

'      ****CENTRAL PROGRAM****

'Sort and find phigh and plow: ih% and il% are point numbers of
'highest and lowest squared error points.
645 :
CALL phigh(p(), xerror(), ih%, il%, i%)

'Periodically print current status to screen, expansion and scaling
'events also printed. This will need to be amended for changes in
'models or coefficients.
IF lis% > 10 THEN
    a$="CUR SOL: "; p(il%, 1); ", "; p(il%, 2); ", "; p(il%, 3); ", "
    b$=p(il%, 4); ", "; p(il%, 5); ", "; p(il%, 6); ", "; p(il%, 7)
    PRINT a$;b$
    PRINT , "XERROR(low): "; xerror(il%)
    lis% = 0
END IF
lis% = lis% + 1

'Calculate centroid.
CALL centroid(p(), cent(), ih%, i%)

'Reflect point with highest squared error.
CALL refl(p(), cent(), pr(), ih%, i%)

'Calculate error for reflected point.
CALL onerr(pr(), t(), hdot(), erref, n%)

'Determine what to do with reflected point.
IF erref <= xerror(ih%) THEN
    test% = 1
END IF
IF erref < xerror(il%) THEN
    PRINT , "EXPANSION"
    test% = 2
END IF
IF erref > xerror(ih%) THEN
    test% = 3
END IF

'Branch off into expansion, contraction and scaling.
IF test% = 1 THEN

```

```

FOR k% = 1 TO i%
  p(ih%, k%) = pr(k%)
NEXT k%
xerror(ih%) = erref
'Stay with reflection.
GOTO 645
END IF

IF test% = 2 THEN
  CALL expan(p(), pr(), pex(), cent(), i%)
  CALL onerr(pex(), t(), hdot(), erexp, n%)
  IF erexp < erref THEN
    FOR k% = 1 TO i%
      p(ih%, k%) = pex(k%)
    NEXT k%
    xerror(ih%) = erexp
  'Expansion.
  GOTO 645
  END IF
  IF erexp >= erref THEN
    FOR k% = 1 TO i%
      p(ih%, k%) = pr(k%)
    NEXT k%
    xerror(ih%) = erref
  'Reflection.
  GOTO 645
  END IF
END IF

IF test% = 3 THEN
  CALL contr(p(), pc(), cent(), ih%, i%)
  CALL onerr(pc(), t(), hdot(), ercon, n%)
  IF ercon < xerror(ih%) THEN
    FOR k% = 1 TO i%
      p(ih%, k%) = pc(k%)
    NEXT k%
    xerror(ih%) = ercon
  'Contraction.
  GOTO 645
  END IF
  IF ercon >= xerror(ih%) THEN
    CALL scale(p(), il%, i%)
  'Scaling.
  GOTO 711
  END IF
END IF

```

```

'      *****END OF CENTRAL PROGRAM*****

SUB centroid (p(), cent(), ih%, i%)
' Subroutine calculate centroid.
  sum = 0
  i = i%
  FOR k% = 1 TO i%
    sum = 0
    FOR j% = 1 TO i% + 1
      sum = sum + p(j%, k%)
    NEXT j%
    cent(k%) = (1 / i) * (sum - p(ih%, k%))
  NEXT k%
END SUB

SUB contr (p(), pc(), cent(), ih%, i%)
' Subroutine contraction.
  gamma = .4985
  FOR j% = 1 TO i%
    pc(j%) = (1! - gamma) * cent(j%) + gamma * p(ih%, j%)
  NEXT j%
END SUB

SUB expan (p(), pr(), pex(), cent(), i%)
' Subroutine expansion.
  beta = 1.95
  FOR j% = 1 TO i%
    pex(j%) = beta * pr(j%) + (1 - beta) * cent(j%)
  NEXT j%
END SUB

SUB onerr (pr(), t(), hdot(), erref, n%)
' Subroutine find error for one new value of P.
' Equations and assignments of pr() would have to be
' changed for different models and/or number of coefficients.
' Currently, two superimposed 1st order reactions are used
' for models.

DIM tt$(2000), a$(2000)
DIM hhdot$(2000), b$(2000)

k01# = pr(1)
ea1# = pr(2)
k02# = pr(3)
ea2# = pr(4)

```

```

ari# = pr(5)
FOR b% = 1 TO n%
    tt#(b%) = t(b%)
    hhdot#(b%) = hdot(b%)
NEXT b%
phi# = phi
r# = r
tot# = 0
FOR b% = 1 TO n%
    a#(b%) = -k01# * EXP(-ea1# / (r# * (phi# * tt#(b%) + tr#)))
    rec# = (a#(b% - 1) - 0) * (tt#(b%) - tt#(b% - 1))
    tri# = .5 * (a#(b%) - a#(b% - 1)) * (tt#(b%) - tt#(b% - 1))
    grala1# = grala1# + rec# + tri#
    hval1# = -ari# * a#(b%) * EXP(grala1#)

    b#(b%) = -k02# * EXP(-ea2# / (r# * (phi# * tt#(b%) + tr#)))
    rec# = (b#(b% - 1) - 0) * (tt#(b%) - tt#(b% - 1))
    tri# = .5 * (b#(b%) - b#(b% - 1)) * (tt#(b%) - tt#(b% - 1))
    grala2# = grala2# + rec# + tri#
    hval2# = -(artot# - ari#) * b#(b%) * EXP(grala2#)

    hval# = hval1# + hval2#
    valsq# = (hhdot#(b%) - hval#) ^ 2
    tot# = tot# + valsq#
NEXT b%
erref = tot#
END SUB

SUB phigh (p(), xerror(), ih%, il%, i%)
'Subroutine find phigh and plow.
'ih% is the number of the point with highest error.
'il% is the number of the point with the lowest error.

low = 1E+29
high = 0
ih% = 0
il% = 0
FOR j% = 1 TO i% + 1
    IF xerror(j%) > high THEN
        high = xerror(j%)
        ih% = j%
    END IF
    IF xerror(j%) < low THEN
        low = xerror(j%)
        il% = j%
    END IF

```

```

NEXT j%
END SUB

SUB refl (p(), cent(), pr(), ih%, i%)
'Subroutine reflection.
  alpha = .9985
  FOR j% = 1 TO i%
    pr(j%) = (1 + alpha) * cent(j%) - alpha * p(ih%, j%)
  NEXT j%
END SUB

SUB scale (p(), il%, i%)
'Subroutine scaling.
  PRINT "scaling"
  KAPPA = -1
  FOR j% = 1 TO i% + 1
    FOR k% = 1 TO i%
      p(j%, k%) = p(j%, k%) + KAPPA * (p(il%, k%) - p(j%, k%))
    NEXT k%
  NEXT j%
END SUB

SUB sqerror (p(), hdot(), t(), xerror(), i%, n%)
'Subroutine that calculates the squared error.
'Equations and assignments of p(?,?) would have to be
'changed for different models and/or number of coefficients
'currently, two superimposed 1st order reactions are used
'for models.

  DIM tt$(2000), b$(2000)
  DIM hhdot$(2000), a$(2000)

  FOR l% = 1 TO i% + 1
    k01# = p(l%, 1)
    ea1# = p(l%, 2)
    k02# = p(l%, 3)
    ea2# = p(l%, 4)
    ar1# = p(l%, 5)
    r# = r
    phi# = phi
    tot# = 0
    FOR b% = 1 TO n%
      tt$(b%) = t(b%)
      hhdot$(b%) = hdot(b%)
    NEXT b%
    tot# = 0

```

```

grala1# = 0
grala2# = 0
FOR b% = 1 TO n%
  a#(b%) = -k01# * EXP(-ea1# / (r# * (phi# * tt#(b%) + tr#)))
  rec# = (a#(b% - 1) - 0) * (tt#(b%) - tt#(b% - 1))
  tri# = .5 * (a#(b%) - a#(b% - 1)) * (tt#(b%) - tt#(b% - 1))
  grala1# = grala1# + rec# + tri#
  hval1# = -ari# * a#(b%) * EXP(grala1#)

  b#(b%) = -k02# * EXP(-ea2# / (r# * (phi# * tt#(b%) + tr#)))
  rec# = (b#(b% - 1) - 0) * (tt#(b%) - tt#(b% - 1))
  tri# = .5 * (b#(b%) - b#(b% - 1)) * (tt#(b%) - tt#(b% - 1))
  grala2# = grala2# + rec# + tri#
  val2# = -(artot# - ari#) * b#(b%) * EXP(grala2#)

  hval# = hval1# + hval2#
  valsq# = (hhdot#(b%) - hval#) ^ 2
  tot# = tot# + valsq#
NEXT b%
xerror(1%) = tot#
NEXT 1%
END SUB

```

6.2 Decomposition Kinetics Using TG [7]

Previously shown was how the activation energy of crystallization may be determined using DTA/DSC (section 3.6). A technique for determining the activation energy of a decomposition reaction using TG will now be developed.

Decomposition (e.g. decomposition of CaCO_3 to CaO and CO_2) differs from nucleation and growth in that the transformation of one site is not dependent on whether the neighboring sites have transformed. This can be illustrated by visualizing popcorn kernels in hot oil. From experience, we know that once the popcorn kernels transform, they do so fervently. With time, the rate of popping dies down since there are less and less kernels left to pop. Thus, it is expected that the rate of this reaction is proportional to how many kernels are left unpopped. The same argument would hold true for a first order reaction:

$$\frac{dX}{dt} = -kX$$

where X is the mass of the reactant, and k is a rate constant. Decomposition reactions may be more complicated since there may be restrictions to the transformation, such as diffusion of a gaseous species out of the bulk of a solid or heat flow into the reaction zone. Hence, an exponent on the mass of the reactant is often used:

$$\frac{dX}{dt} = -kX^n$$

where n is the "order" of the reaction. This expression can be related to information which may be extracted from a TG trace using:

$$X = m_0 - m_0 \frac{w}{w_\infty}$$

where m_0 is the initial mass of the specimen, w_∞ is the maximum mass lost, and w is the mass lost, which varies with time through the reaction (see Figure 6.4). Prior to the onset of the reaction, $w = 0$, hence $X = m_0$. After the reaction is complete, $w = w_\infty$, hence $X = 0$. The derivative of this expression yields:

$$\frac{dX}{dt} = -\frac{m_0}{w_\infty} \frac{dw}{dt}$$

Substituting the previous expression for dX/dt as well as the expression for X :

$$\frac{-m_0}{w_\infty} \frac{dw}{dt} = -km_0^n \left(1 - \frac{w}{w_\infty}\right)^n$$

or:

$$\frac{d(w/w_\infty)}{dt} = km_0^{n-1} \left(1 - \frac{w}{w_\infty}\right)^n$$

The weight fraction product is defined as $f = w/w_\infty$, which shortens the previous expression to:

$$\frac{df}{dt} = km_0^{n-1} (1 - f)^n$$

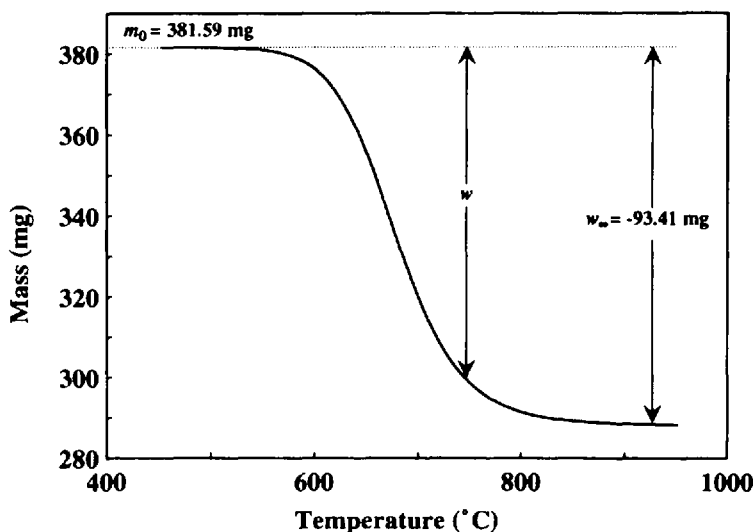


Figure 6.4: Defined variables in TG decomposition kinetics analysis.

Assuming that decomposition is an activated process, the rate constant is taken to follow an Arrhenius temperature dependence:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right)$$

Hence:

$$\frac{df}{dt} = k_0 m_0^{n-1} (1-f)^n \exp\left(\frac{-E_a}{RT}\right)$$

All that remains is to manipulate this equation into the form of a line. Taking logarithms:

$$\ln \frac{df}{dt} = \ln [k_0 m_0^{n-1}] + n \ln(1-f) - \frac{E_a}{RT}$$

Then taking a time derivative:

$$\frac{d}{dt} \left(\ln \frac{df}{dt} \right) = \frac{d^2 f / dt^2}{df/dt} = \frac{-n(df/dt)}{1-f} + \frac{E_a}{RT^2} \frac{dT}{dt}$$

Adding the relationship between temperature and time (see section 6.1.3) for a constant heating rate experiment and rear-

ranging:

$$(\phi t + T_r)^2 \frac{d^2 f / dt^2}{df / dt} = -n \left[\frac{(\phi t + T_r)^2 (df / dt)}{1 - f} \right] + \frac{E_a \phi}{R}$$

The terms f , df/dt , and $d^2 f / dt^2$ may be obtained directly from the TG output and its derivatives, as shown in Figure 6.5.

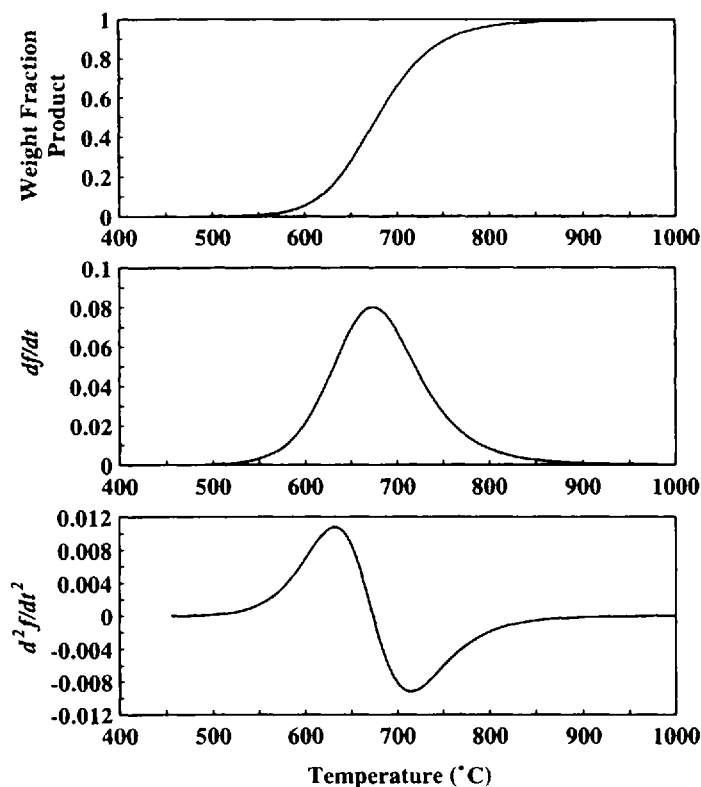


Figure 6.5: Method for determining f and its derivatives. Slopes were calculated using linear regression over 5 points in a data set of 500 points. Double precision was required in the computer program in order to avoid noise in the second derivative. The fraction transformed versus temperature trace was numerically generated assuming a second order reaction.

Techniques for taking derivatives of experimental data were discussed in section 4.2. Since the above expression is in the

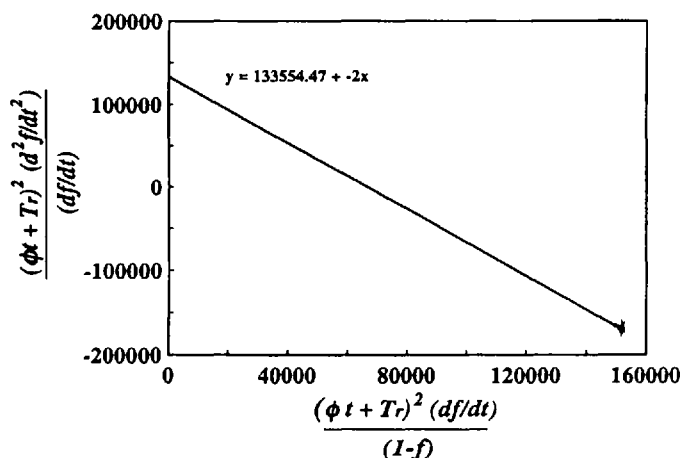


Figure 6.6: Plot to determine the activation energy and reaction order of a decomposition reaction. The slope indicates a second order reaction and the intercept, being $E_a\phi/R$ ($\phi = 10^\circ\text{C/min}$), indicates that the activation energy is 111 kJ/mol. The noise at the end of the trace is a result of double precision round-off error.

form of a line, a plot such as that in Figure 6.6 will yield the reaction order from the slope and the activation energy from the y -intercept.

References

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- [5] A. P. Gray, *Analytical Calorimetry* (R. F. Porter and J. M. Johnson, eds.), Plenum Press, NY p. 209 (1968).
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- [7] J. Vachuska and M. Voboril, "Kinetic Data Computation from Non-Isothermal Thermogravimetric Curves of Non-Uniform Heating Rate", *Thermochim. Acta* **2**: 379 (1971).

Chapter 7

DILATOMETRY AND INTERFEROMETRY

Dilatometry and interferometry are techniques used for measuring the change in length of a specimen as a function of temperature. They are useful for studying a myriad of materials' behavior, such as martensitic transformations in the quenching of steels, the shrinkage from a green ceramic body during binder burnout and sintering, glass transformation temperature, devitrification in glasses, and solid-state transformations such as the α to β quartz inversion. In this chapter, dilatometry, the more common and commercially available technique, will first be treated. Discussion of the more precise, but experimentally more cumbersome interferometry technique will be left to the end of the chapter.

Since different instruments are designed to accept a variety of sample lengths, the change in length per unit starting length is conventionally recorded as a function of temperature, as shown in Figure 7.1. The slope of the trace is the coefficient of linear thermal expansion, defined by:

$$\alpha_l = \frac{1}{l_0} \left(\frac{\partial l}{\partial T} \right)_F$$

where the subscript F stands for constant force. The temperature which is generally assigned as a reference point (for NIST standard expansion reference materials), that is, zero expansion, is 20°C.

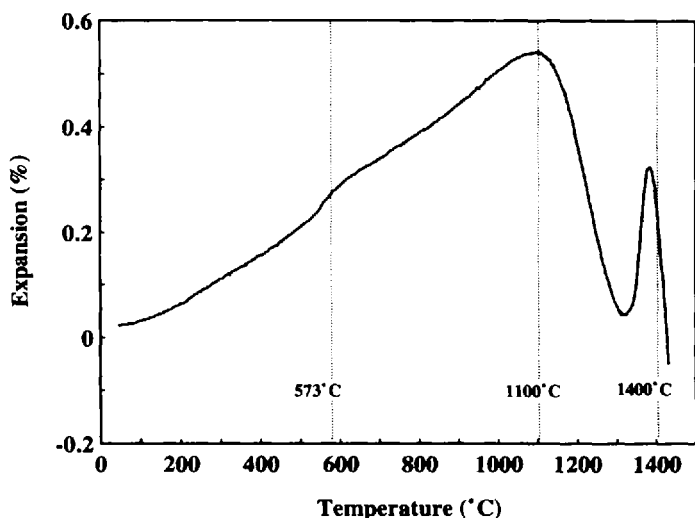


Figure 7.1: Typical thermal expansion trace; kyanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) + quartz (SiO_2) at $5^\circ\text{C}/\text{min}$. The α - β quartz inversion is apparent at 573°C . Kyanite converts to mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and residual glass starting at 1100°C , reaching a maximum rate at 1400°C [1]. The sharp contraction starting at $\sim 1100^\circ\text{C}$ is interpreted to correspond to sintering. At $\sim 1320^\circ\text{C}$, the rapid formation of the less dense decomposition products of kyanite cause a temporary expansion [2].

7.1 Linear vs. Volume Expansion Coefficient

At first glance, we may interpret the coefficient of volume thermal expansion,

$$\alpha_V = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_p$$

(where p is pressure), as the cube of the linear coefficient. As will now be shown, the volume coefficient is actually three times the linear coefficient (under restricted conditions).

Consider a cubic element within a material of volume $V = l_x l_y l_z$. Substituting into the definition of coefficient of volume expansion and using the product rule:

$$\alpha_V = \frac{1}{l_{x0}l_{y0}l_{z0}} \left(\frac{\partial(l_x l_y l_z)}{\partial T} \right)_p$$

$$\alpha_V = \frac{1}{l_{x0}l_{y0}l_{z0}} \left(l_y l_z \left(\frac{\partial l_x}{\partial T} \right)_p + l_x l_z \left(\frac{\partial l_y}{\partial T} \right)_p + l_x l_y \left(\frac{\partial l_z}{\partial T} \right)_p \right)$$

The sample lengths can be written in terms of initial length plus change in length:

$$l_x l_z = (l_{x0} + \Delta l_x)(l_{z0} + \Delta l_z)$$

$$l_x l_z = l_{x0} l_{z0} + l_{x0} \Delta l_z + l_{z0} \Delta l_x + \Delta l_x \Delta l_z$$

If the change in length is small compared to the overall sample length, the last three terms may be considered insignificant:

$$l_x l_z \cong l_{x0} l_{z0}$$

Thus:

$$\alpha_V = \frac{1}{l_{x0}} \left(\frac{\partial l_x}{\partial T} \right)_p + \frac{1}{l_{y0}} \left(\frac{\partial l_y}{\partial T} \right)_p + \frac{1}{l_{z0}} \left(\frac{\partial l_z}{\partial T} \right)_p$$

or:

$$\alpha_V = \alpha_{l_x} + \alpha_{l_y} + \alpha_{l_z} = 3\alpha_l$$

Two assumptions have been made which will certainly not be true for all specimens:

1. The change in length is insignificant as compared to the original specimen length.
2. Expansion in each dimension is the same. This would only be true for isotropic materials, that is, those with a cubic crystal structure, or glass. Polycrystalline materials with non-isotropic crystalline grains would also generally demonstrate a direction independent expansion behavior, due to the averaging effect of the random orientation of their grains.

7.2 Theoretical Origins of Thermal Expansion

The atomistic cause of thermal expansion is often explained by the attractive and repulsive forces between atoms in a solid. The potential energy functions (force applied through a distance) for interatomic attraction, repulsion, and their sum are plotted in Figure 7.2. The base of the trough in the com-

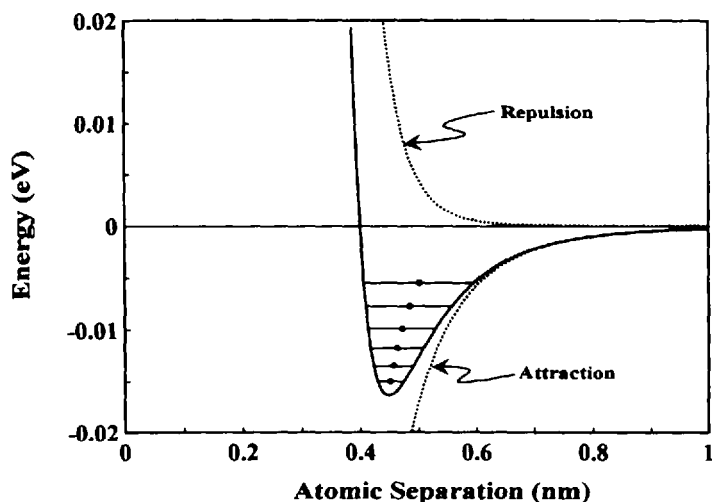


Figure 7.2: Theoretical origins of thermal expansion. Plot of the “12-6” [3] equation: $V = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$. The twelfth power term represents repulsive energy while the sixth power term represents the attractive energy. Values of $\epsilon = .01738$ eV and $\sigma = .4$ nm were used in the figure, representing solid CO_2 (dry ice). The points marked in the curve, shifting to the right with increasing energy, represent the mean atomic spacing between neighboring atoms.

bined energy function represents the minimum energy contained within the atom, and its ordinate position indicates the equilibrium atomic separation from other atoms when the atoms are static, e.g. at zero Kelvin. As temperature rises, the energy of the solid increases, and atoms vibrate to greater and

shorter distances about a mean position. The two values of the combined energy curve at a given energy represent the distances of farthest extension and closest approach of the vibrating atoms.¹ Since the repulsion term between atoms changes more rapidly than the attractive term, the potential well is not symmetrical. Thus, for a given energy (i.e. temperature), the atoms can move farther apart more readily than they can be pushed together. Their mean atomic distance increases, as shown by the dots in the figure; and hence, materials expand with increasing temperature. There are rare exceptions, notably the net negative expansion coefficient of β -quartz, discussed in section 7.6.

Strongly bonded solids have deep, symmetrical potential wells and expand at lower rates with temperature than weakly bonded solids with shallow, asymmetrical potential wells. It follows that materials with low melting points (weakly bonded solids) have high coefficients of expansion.

The increased volume of a material with increasing temperature is a result of the same atomic vibration phenomenon which stores thermal energy. Consequently, changes in coefficient of thermal expansion generally parallel changes in heat capacity. Both increase rapidly at low temperature and approach nearly constant values above the Debye temperature (section 3.7).

7.3 Dilatometry: Instrument Design

The design of a dilatometer is depicted in Figure 7.3. One end of the specimen is placed in contact with a spring-loaded pushrod, and the other end of the specimen is butted against

¹Vibrating atoms can be envisioned as analogous to a swinging pendulum. The lowest point in the pendulum path is where it moves the fastest and its energy is entirely kinetic. At the highest points of the arc, on either side of the lowest point, all of the energy is potential; the velocity is momentarily zero since the pendulum is turning around. The energy everywhere else is a combination of both kinetic and potential, but the total energy remains the same. Hence the curve making up the "potential well" in the figure represents points in which the vibrating atoms have only potential energy, which is where they are at distances of maximum extension or approach.

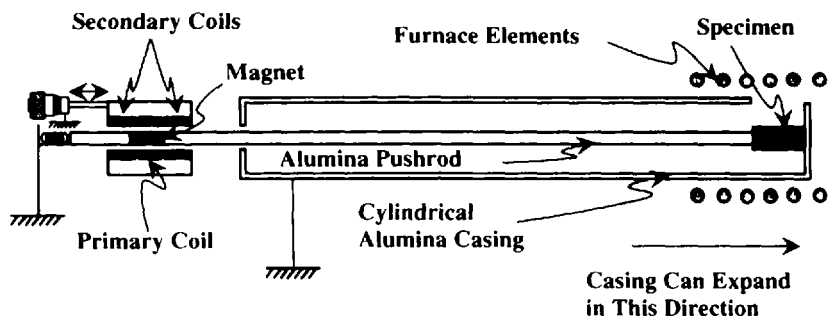


Figure 7.3: Schematic of a single push rod dilatometer.

the back wall of the casing. The casing and the pushrod are made of the same material (often fused silica up to $\sim 1100^\circ\text{C}$, or polycrystalline alumina for higher temperatures). When the furnace heats, the casing material as well as the specimen and pushrod expand. The casing is unrestricted from expanding at its free end (to the right in Figure 7.3). When the casing expands, the specimen in contact with it is drawn in the “contraction” direction. Hence, the expansion of the specimen, *relative to the casing*, is measured at the room-temperature end of the casing. The expansion/contraction occurring along the distance from the hot zone to room temperature in which the casing and pushrod are adjacent will exactly cancel, since the materials are identical. Dilatometry furnaces are designed so that the zone in proximity to the sample is at a uniform temperature.

If an alumina specimen were placed against the pushrod in an alumina (pushrod and casing) dilatometer, then no deflection would be measured at the cold end, since the pushrod/specimen and the casing are made of the same material, and their expansions would cancel. If an unknown material is placed in contact with the pushrod and the back of the casing, the deflection of the pushrod at the cold end may be inward or outward, depending on whether the specimen expands more

or less than the equivalent length of alumina. To determine the true expansion of the material, the expansion of an equivalent length of casing material must be added to the deflection measured at the cold end.

An alternate design using two pushrods (such as that used by Theta Industries) is shown in Figure 7.4. In this configuration,

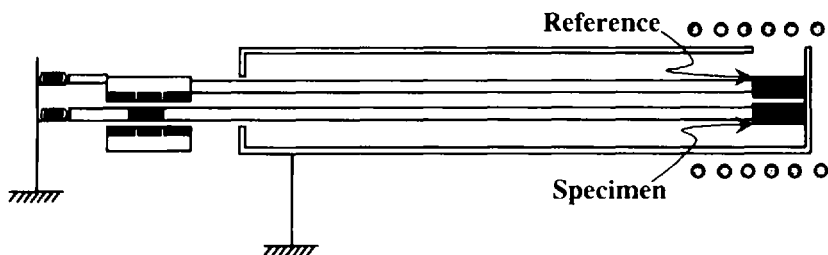


Figure 7.4: Schematic of a dual pushrod dilatometer.

the expansion or contraction of the sample is measured relative to the expansion or contraction of a NIST reference material, since the expansion/contraction of the reference shifts the location of the position-transducer housing. The advantage of this design is that the expansion behavior of the reference material is known precisely. With a single pushrod device, the expansion behavior of the casing material may not be as accurately documented.

The transducer used to determine this deflection is referred to as a linear variable differential transformer (LVDT). The operating principle carries some similarities to the power transformer described in section 2.4.2. When an alternating current is passed through the center coil, the acceleration and deceleration of electrons in this coil induce a magnetic flux in the core (Figure 7.5). The core is a material of high magnetic permeability (nickel-iron alloy) which is connected to the end of the pushrod. If a portion of the core is aligned with either of the outer coils, an ac voltage is induced in them, the amplitude of which is dependent on the number of windings in line with the

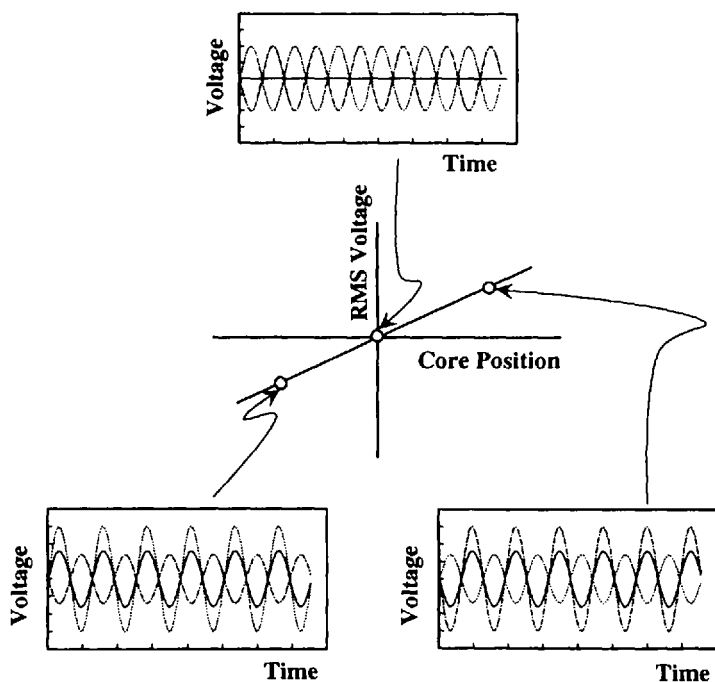


Figure 7.5: Operating principle of an LVDT. The dotted line represents the output of the left secondary, the dot-dashed line is the output of the right secondary. The solid line is their sum. The root mean squared amplitude of the solid line represents the core position.

core. One of the outer (secondary) coils is offset 180 degrees out of phase with respect to the primary coil. The secondary coils are connected so that if the core is exactly centered, the sine waves cancel and the output is zero. If the core is skewed away from one secondary and deeper within the other, the amplitude of one sine wave is greater than the other and a net RMS (root mean squared) voltage is measured. If the output sine wave is in phase with the input, then a “positive” displacement about the centerpoint is measured. If the output sine wave is 180 degrees out of phase, then a “negative” displacement is measured. As shown in the figure, the net RMS voltage measured is linearly related to the position of the core.

Another transducer used in place of an LVDT is the digital displacement transducer. Equally spaced markings ($1\text{ }\mu\text{m}$ apart) are photo engraved onto a low expansion glass scale. As the scale in contact with an expanding specimen moves past a photo cell, the dark/light transitions are recorded. This digital information can then be retrieved and translated into a displacement [4]. Assuming that the graduations are precisely positioned, this transducer has the advantage that it is not vulnerable to slow drift of analog signals which may affect LVDT calibrations.

7.4 Dilatometry: Calibration

The voltage output of the LVDT must be converted to units of length via a calibration constant. Most dilatometers are constructed with a rotary micrometer which can move the LVDT housing back and forth. Graduations on commercially supplied micrometers are usually 0.01 mm apart, but high precision micrometers with non-rotating spindles may be purchased with graduations of 0.001 mm [5]. By comparing the electrical output of the LVDT to the micrometer displacement readings,² a least squares fit to a series of data pairs will permit an optimum calibration. Plotting these data will allow a check of the LVDT for any non-linearity. A standard gauge block may also be used as a check against the accuracy of the micrometer. The user must ensure that all contact points are square and that the magnet moves along the cylindrical axis of the LVDT housing. However, LVDT's are reasonably insensitive to radial shifts in core position [5].

To determine the correct value of the change in length per unit (20°C) length for a specimen in a single pushrod dilatometer, the expansion of an equal length of casing material must be added to that of the specimen,

²A magnifying glass will permit better alignment of the micrometer graduations and ultimately a better displacement calibration.

$$\left(\frac{\Delta l}{l_0}\right)_{\text{sample}} = \frac{V-V_0}{C} + \left(\frac{\Delta l}{l_0}\right)_{\text{casing}}$$

where V is the LVDT output, V_0 is the LVDT output for the starting (20°C) specimen length, and C is the calibration constant. The casing expansion may be represented by a polynomial of the form:

$$\left(\frac{\Delta l}{l_0}\right)_{\text{casing}} = a + bT + cT^2 + \dots$$

To determine the correct values for the coefficients $a, b, c, \dots$, an NIST standard material may be tested, whereby a polynomial may be fit³ to the experimental pushrod deflection data set, converted from the LVDT voltage output. By subtracting (like terms) this polynomial from that of the NIST data for the standard material:

$$\left(\frac{\Delta l}{l_0}\right)_{\text{casing}} = \left(\frac{\Delta l}{l_0}\right)_{\text{NIST data}} - \left(\frac{V-V_0}{C}\right)$$

a polynomial representing the expansion of the casing material may be calculated. This polynomial can then be used in software to correct for casing expansion in all future specimen expansion measurements.

If a double pushrod configuration is used, not only the expansion of the reference material must be added, but differences in length between sample and reference must be accounted for.⁴ If, for example, a one-inch sample and a 1/2-inch reference are used, then the expansion of 1/2-inch of reference and 1/2-inch of pushrod material must be added to the displacement indicated by the position transducer. When the sample and reference lengths are closely matched, the expansion of the pushrod

³Software may be purchased that will fit an x - y data set to a polynomial, often up to 9th order [6].

⁴Preferably, the two pushrods should originate from the same manufactured rod, cut in half with the cut surfaces acting as interfaces to the sample and reference; thus, the expansion effects of locations where only pushrods exist exactly cancel.

material corresponding to the difference in sample and reference length will approach negligible importance. The conversion between position transducer output and length change is thus:

$$\frac{\Delta l}{l_{0s}} = \frac{\frac{V-V_0}{C} + \left(\frac{\Delta l}{l_0}\right)_r l_{0r} + \left(\frac{\Delta l}{l_0}\right)_p (l_{0s} - l_{0r})}{l_{0s}}$$

where the subscripts s , r , p stand for sample, NIST reference, and pushrod material, respectively.

7.5 Dilatometry: Experimental Concerns

When samples of unknown behavior are tested, investigators will often line the bottom of the casing (under the specimen) with alumina pellets or platinum foil. This will protect the casing against accidental specimen melting. Platinum foil can be used as an interface between pushrod/specimen and specimen/casing back in order to protect against inadvertent reaction. The expansion of the known thickness of platinum used must then be corrected for in the specimen expansion data.

Fused silica casing/pushrod dilatometers can more easily generate more accurate results than alumina dilatometers, since the expansion of fused silica is about one order of magnitude lower than alumina. A slightly imperfect correction polynomial for casing expansion of fused silica will introduce much less error than for an alumina casing. Polycrystalline alumina casings are generally restricted to $\sim 1600^\circ\text{C}$. Graphite casing/pushrod systems used in an argon atmosphere have been used for the temperature range $25\text{--}2000^\circ\text{C}$ [7].

While the common heating rate for DTA and TG investigations is $10^\circ\text{C}/\text{min}$, a more appropriate heating rate for dilatometry is 3 to $5^\circ\text{C}/\text{min}$. The specimen dimensions used in dilatometry are generally much larger than those used in DTA or TG; time must be allowed for heat to propagate from the specimen surface to its interior. Temperature gradients within

the specimen will be more severe with increasing heating rate and specimen diameter.

Longer specimens permit higher accuracy in expansion measurement. However, longer specimens run the risk of non-uniformity of temperature along the specimen axis. LVDT's with shorter "strokes" (full scale displacement range) are more accurate than longer ones. However the ultimate accuracy of the device is generally more dependent on the precision use of the micrometer or gauge block during calibration.

Depending on instrument design, a specimen contraction may be indicated during initial heating, followed by expansion. This is generally caused by the heat propagating from the heating elements, raising the temperature of the casing material in advance of the specimen. The result is that the casing expands initially more rapidly than the specimen and a false contraction is recorded. Slower heating rates will minimize this effect. The casing material calibration routine described in section 7.4, using an NIST standard will eliminate this effect; a polynomial for casing expansion is determined which *forces* the calibrated output to fit the NIST data for the tested standard—compensating for any radial temperature gradients. Since the temperature gradient will vary with heating rate, the heating rate used in the determination of the casing expansion polynomial should be used for all subsequent experimentation.

On older analog dilatometers, analog circuitry is often provided which corrects LVDT output for casing expansion. These devices are designed for samples of specific (20°C) lengths, e.g. 50 mm. Thus for accurate results, initial sample sizes must be maintained at strict tolerances. Computer/microprocessor-based instruments generally require only accurate measurement of sample length (via caliper or micrometer) which is subsequently entered via a software prompt. In the strictest sense, initial sample lengths should be maintained at 20°C and not an arbitrary room temperature, although the difference with conventional length measuring devices would be difficult to ob-

serve. Spraying the sample with acetone, exploiting the cooling (endothermic) effects of the latent heat of vaporization, is a simple way to facilitate a 20°C measurement. Care must be taken to ensure that the front and rear faces are flat and parallel, and the specimen is positioned in the sample chamber without being at a skewed angle. Friction in the spring-loaded pushrod assembly will cause noise in the output signal of the device. Instruments usually have set screws which allow for minor alignment adjustments to eliminate friction.

Often it is not practical to prepare, for example, a one-inch long sample (as required by the design of the sample chamber). A spacer made out of identical material as the pushrod may be used without introducing error. Care must be taken to ensure that the spacer material has the exact expansion behavior as the pushrod material. For example, some manufacturers may use sintering aid additives in the fabrication of polycrystalline alumina which introduces a glassy phase into the grain boundaries. This continuous glassy phase will result in a different expansion behavior of this material as compared to alumina fabricated (sintered) with no additives.

For most dilatometer designs, a spring maintains the pushrod, sample, and casing back in firm contact. Springs follow, more or less, Hooke's law; the force applied by the spring is proportional to its displacement (from its unstretched or uncompressed state). For many investigations, such as simple coefficient of expansion measurements variable force on the specimen will not effect the measurement. Other experiments, such as the softening point of a glass or polymer, will largely depend on the load applied to the glass. One dilatometer design using a hanging weight and pulley system, maintains a constant force on the sample, regardless of the specimen displacement due to contraction/expansion (Figure 7.6). Dilatometers are professionally manufactured in both horizontal and vertical versions, the latter having the advantage of taking up less table space. Vertical systems may be configured without springs,

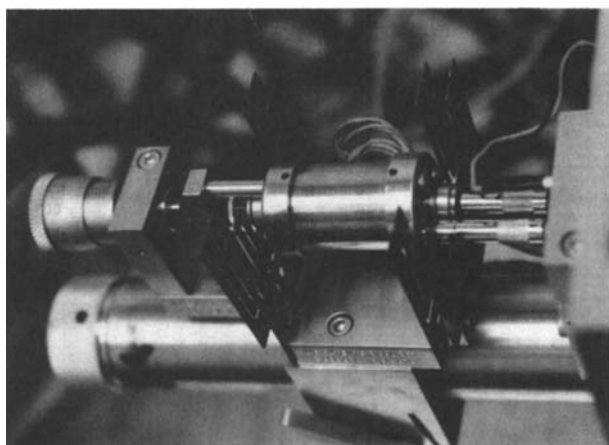
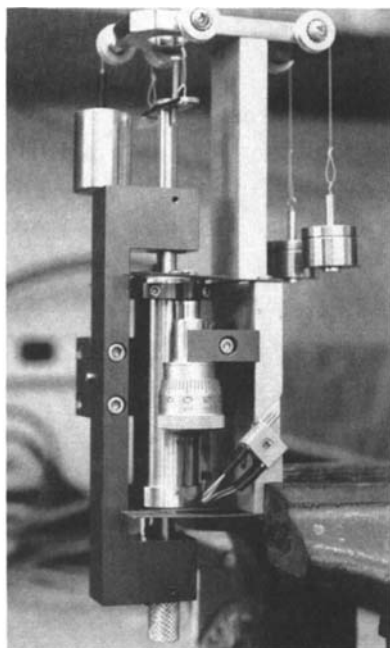


Figure 7.6: Two example LVDT stages offered by Theta Industries. Top: constant force system, used for vertically mounted dilatometers and parallel plate viscometers. Bottom: horizontally mounted dual pushrod system with leaf springs.

using gravity to maintain pushrod, specimen and casing back contact. A stage may be set up in contact with the cold end of the pushrod so that known masses may be placed on it. Studies such as high temperature creep of metals and ceramic refractories or the viscosity of glasses⁵ are investigated with such a configuration. When a purposeful load is applied to the sample, the term “thermomechanical analysis” (TMA) is applied, whereas for expansion where load is not a consideration in the measurement, the term “thermodilatometric analysis” (TDA) is sometimes applied.

7.6 Model Solid State Transformations

Figure 7.7 displays the thermal expansion behavior of two commercially important ceramic oxides. The β quartz phase in the figure has the unusual property of having a slightly negative net coefficient of thermal expansion. In the manufacture of consumer glass-ceramic products (e.g. Corning’s [10] Visions Cookware), the thermal processing steps in devitrification of the glass are designed to preferentially form a stuffed (with other cations) β -quartz structured solid solution, which shows this slightly negative net⁶ coefficient of expansion behavior. That phase, combined with residual glass demonstrating a positive coefficient, results in a body with near zero expansion in temperature ranges in which the product is commonly used. Since the thermal expansion is negligible, the product will not fracture via thermal shock under rapid temperature changes such as when it is removed from a freezer and placed in a conventional oven.

Zirconia refractories are used for extreme temperature ap-

⁵Such a device is referred to as a “parallel plate viscometer”, where the rate of compression of a glass pellet between two (alumina) parallel plates is proportional to its viscosity. See section 10.4.1.

⁶In general, all crystal structures alter with increasing temperature toward greater symmetry. In β -quartz, some crystallographic directions contract while others expand with increasing temperature toward this end. The net, or average, coefficient of expansion of this crystal structure is slightly negative.

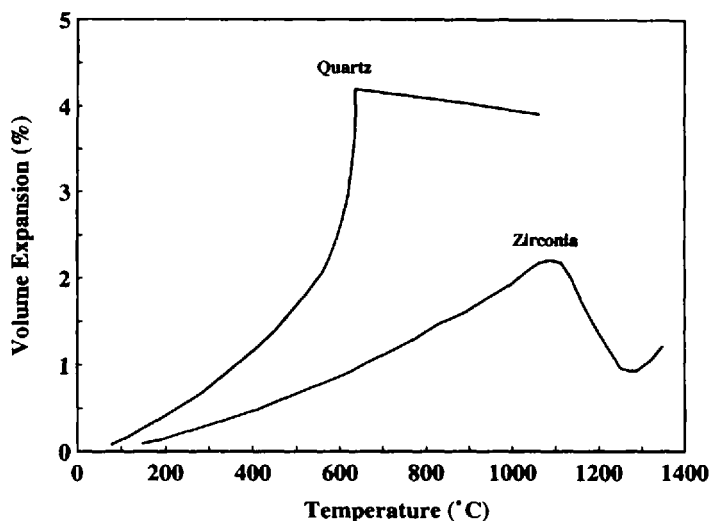


Figure 7.7: Examples of volume changes during solid state transformations [9]. For fine grained polycrystalline forms of these materials, the volume expansion would be the third power of the linear expansion.

plications (up to $\sim 1925^{\circ}\text{C}$) and are not easily attacked by solutions (e.g. molten glass). Zirconia, however, transforms from a monoclinic to tetragonal structure with increasing temperature as shown in Figure 7.7. This transformation is very disruptive and would cause severe damage to refractory structures made from it. The common corrective technique is to “stuff” the structure (so called “stabilized” zirconia) with CaO , MgO , or Y_2O_3 so that the material forms a cubic structure which does not transform throughout its entire usable temperature range (see the phase diagram in Figure 7.8.) The useful properties of this transformation can also be exploited: A crack of post-critical size, extending through a brittle material (e.g. Al_2O_3) containing particles of metastable tetragonal zirconia, can initiate a local transformation to monoclinic zirconia ahead of the crack tip. This acts to relieve the stresses at the crack tip and arrest further crack propagation until a greater load is applied

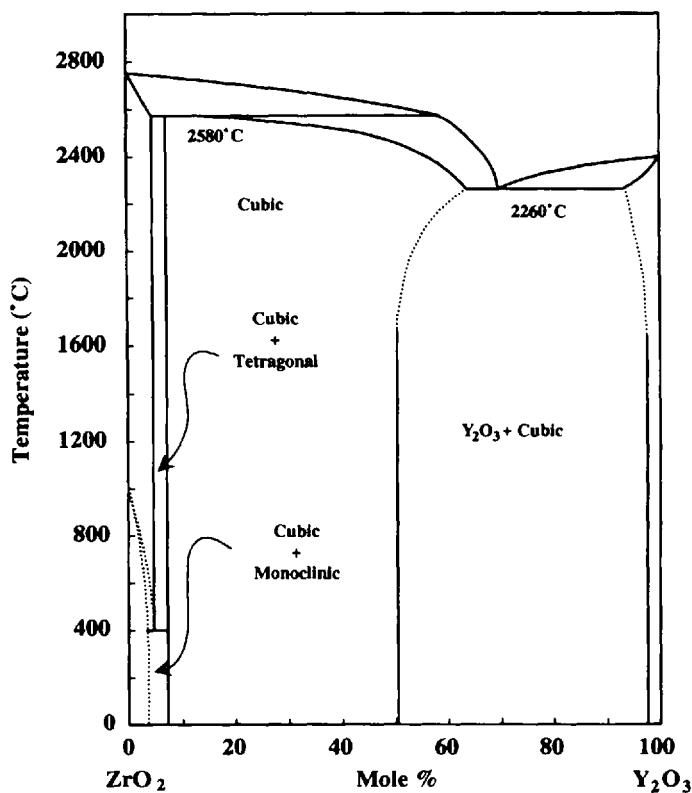


Figure 7.8: Zirconia-yttria binary system. The introduction of yttria into zirconia (~ 15 - 51% Y_2O_3) stabilizes the structure into the cubic form throughout the usable temperature range of the refractory material [11].

to the composite. These are referred to as dispersion-toughened ceramics [12].

Glasses and amorphous polymers have a characteristic thermal expansion behavior, an example of which is shown in Figure 7.9. These materials pass through a glass transition tem-

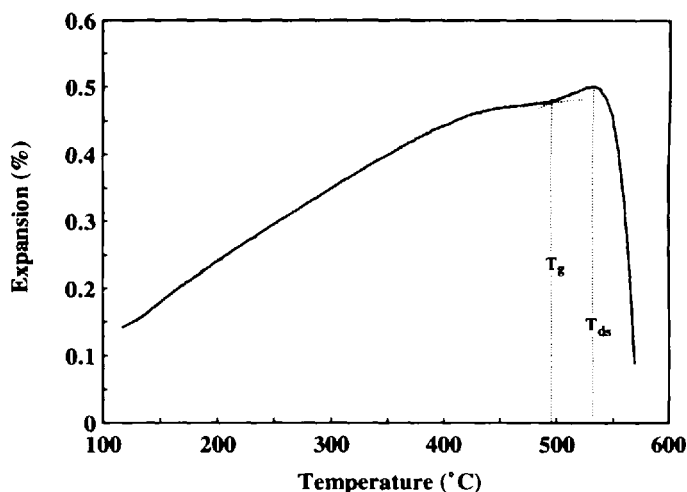


Figure 7.9: Thermal expansion behavior of reheated soda-lime-silica glass. The decrease in slope just before T_g implies the thermally induced relaxation of a rapidly quenched glass.

perature, T_g , followed by a dilatometric softening point, T_{ds} , with increasing temperature. The phrase “dilatometric softening point” is used since this maximum expansion point, representing the temperature at which the glass softens to the point of collapsing on itself,⁷ depends on the cross-sectional area of the specimen, and the force the pushrod spring applies to the specimen, which will vary from instrument to instrument.

The glass transition temperature is the point at which the glass stops behaving like a liquid and begins to behave like a solid on cooling, and vice versa on heating, as illustrated in

⁷Because of the tendency for glasses to collapse and flow, ultimately adhering to and damaging the dilatometer casing, many dilatometers have a contraction limit switch which shuts the furnace off when the sample contracts past a specified level.

Figure 7.10. This figure shows the molar volume as a function of temperature for a glass forming melt being cooled. If the

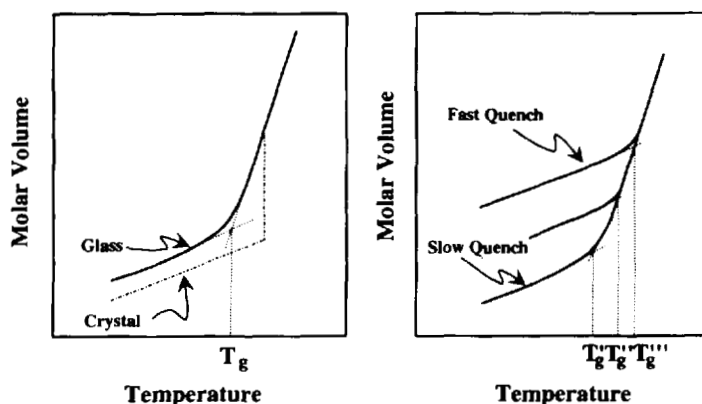


Figure 7.10: Origins of the glass transition. The left-hand schematic shows the molar volume of the glass relative to the equilibrium (crystalline) state. T_g is located as an extrapolation of the straight line portions of the curve. The right-hand schematic shows the effect of quenching rate on the glass transition. The more rapid the quench rate, the higher the value of T_g .

melt is cooled infinitely slowly, it will crystallize at the equilibrium melting point, and its expansion behavior will follow that indicated by the dashed line. Faster cooling will act to form a glass; a “frozen in” liquid whose expansion behavior will depend on how rapidly it was cooled. The more slowly the melt is cooled, the more the molar volume behavior with temperature closely resembles that of the crystalline form. The point at which the expansion behavior changes slope (becoming solid-like in its expansion behavior as opposed to liquid-like) is the glass transition temperature, which depends on the thermal history (quench rate) of the glass, as shown in the figure.

Since T_g is determined by a change in expansion behavior, there will be an associated shift in heat capacity behavior; the expansion of a material is a result of an increase in the mean atomic vibration amplitude between atoms, and this vibration

is the mechanism of thermal energy storage. For this reason, T_g can be measured using DTA/DSC and will appear as an endothermic trend with increasing temperature, as shown in Figure 7.11. This trend represents an increase in heat capac-

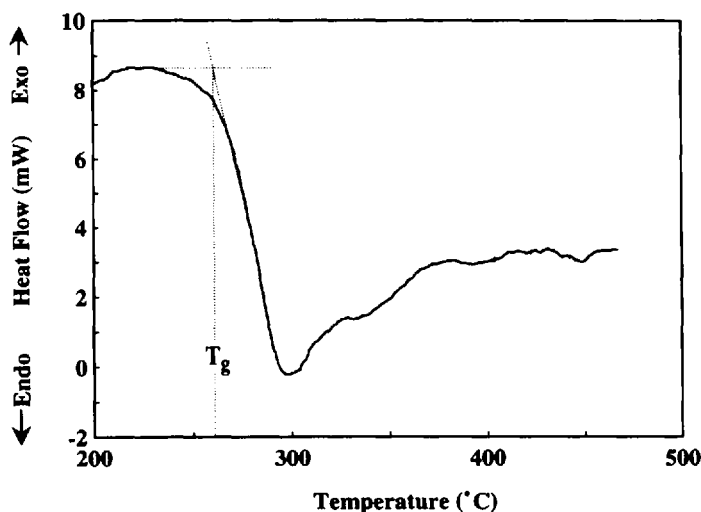


Figure 7.11: Glass transition of B₂O₃ glass as determined by heat-flux DSC. Silicate glasses, because of their three dimensional network tend to have smaller volume changes at T_g and hence DTA/DSC traces of this transformation in those glasses are less distinct [13].

ity of the glass when it becomes “liquid-like”, where its energy storage mechanisms begin to include atomic rotation and translation, in addition to vibration.

The matching of expansion behavior is of the utmost importance to manufacturers of, for example, multi-layer capacitors, porcelain enameled cast iron sinks, fiber reinforced composites, light bulbs, etc. In all cases, various materials in rigid contact must have their expansion characteristics carefully matched. Inattention to this runs the risk of cracking and shattering of a light bulb at its seal to aluminum, delamination of metallic conductive leads from the ceramic substrate in a hybrid circuit, etc. By changing the composition of a constituent material, its

expansion behavior can be altered without significantly altering other required properties (e.g. strength, electrical resistivity, etc.). For example, decreasing the sodium oxide content of a porcelain enamel composition will result in a glassy coating with a decreased coefficient of thermal expansion. Porcelain enamel coatings are generally designed to have a slightly lower coefficient of expansion than their metallic (e.g. cast iron) substrate, so that upon cooling the metal will contract more, putting the glassy coating in a compressive state at room temperature. Glasses are significantly stronger in compression than in tension.

Dilatometry is a useful method of studying the sintering of ceramics. Sintering involves shrinkage of a body as particles pull closer together and porosity is eliminated. This can occur in the solid state by atomic diffusion, by the formation of a liquid (glassy) phase between the particles, or by reactions at the grain boundaries. The mechanism of sintering defines the ultimate mechanical (including high temperature creep) properties of the ceramic as well as its dielectric properties.

The sintering behavior of ZnO , a PTCR⁸ material, is shown in Figure 7.12. The figure shows two means of studying sintering using dilatometry: temperature control and shrinkage rate control. Under temperature control, the specimen was heated at $15^\circ\text{C}/\text{min}$, where its contraction was initially rapid and then more sluggish as it approached near-full density. By contrast, in rate controlled sintering, a PID feedback control on furnace power was based on specimen shrinkage. In the figure, a linear rate of shrinkage of $0.005/\text{min}$ was maintained; the temperature schedule accelerated in heating rate in the later stages of sintering in order to maintain linear shrinkage.

For shrinkage rate control [15], the specimen is generally heated at a constant rate into a temperature region where shrinkage begins, and then the system switches over to shrinkage rate control. If the setpoint temperature required to main-

⁸PTCR: positive temperature coefficient resistor.

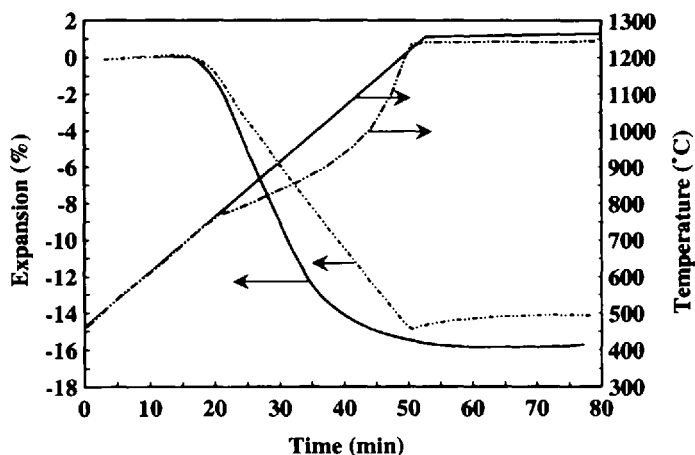


Figure 7.12: Shrinkage curves (dropping from left to right) and temperature schedules (rising from left to right) for sintering under a linear temperature control of $15^{\circ}\text{C}/\text{min}$ (solid line) and under a linear shrinkage rate control of $0.005\text{ in}/\text{min}$ (dotted line). [14]

tain linear shrinkage exceeds a specified value (e.g. the body is fully sintered and increased temperature will not maintain linear shrinkage), the system switches back to temperature control. A computer algorithm for such a system is shown in Figure 7.13.

7.7 Interferometry

An interferometer can be used to very accurately measure the thermal expansion of solids. Although not utilized commercially to the level of dilatometry, NIST standard materials, which are in turn used to calibrate dilatometers, have had their expansion characteristics determined using interferometry. In fact, the formal definition of the meter is based on interferometric measurements. The operation of the device is based on the principle of interference of monochromatic light. The fundamental relations between wavelength and distance will first

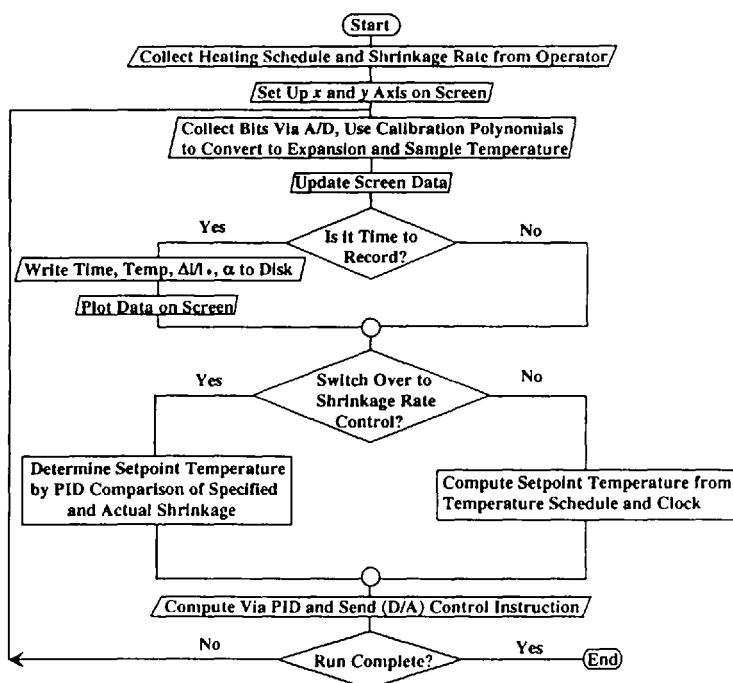


Figure 7.13: Flowchart of computer algorithm for shrinkage rate controlled sintering [14].

be developed, followed by a correlation of these principles to devices used in the measurement of thermal expansion of solids.

7.7.1 Principles

If two waves such as those depicted in Figure 7.14 are added together, their sum will result in complete annihilation since the two waves are $\lambda/2$ out of phase, where λ is wavelength. If the waves are exactly matched, or offset by some integral number of λ , e.g. $m\lambda$, where $m = 0, 1, 2, \dots$, complete reinforcement will be observed.

The interference of light waves can be easily demonstrated using a two-slit experiment (Figure 7.15). Monochromatic (sin-

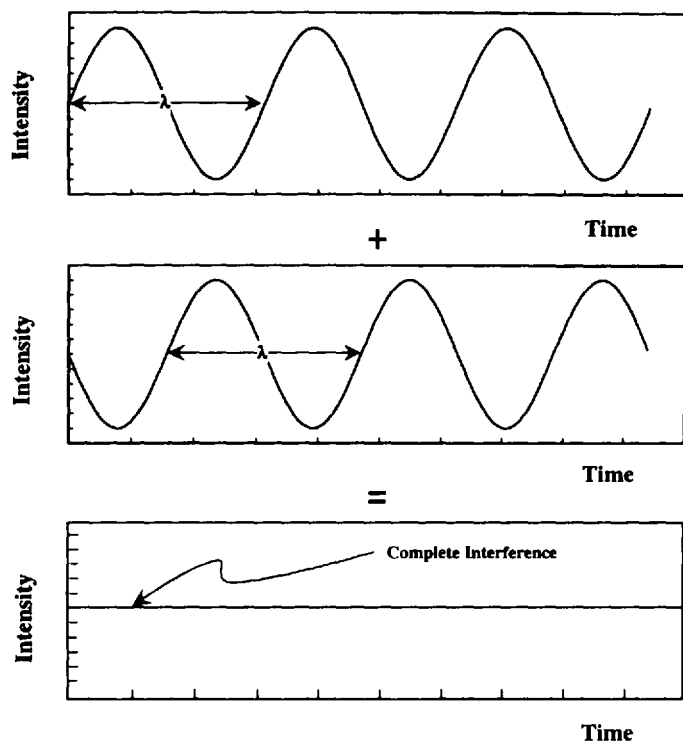


Figure 7.14: Complete interference of one-dimensional electromagnetic waves $\lambda/2$ out of phase. This phenomenon occurs for three-dimensional (spherical) light waves as well.

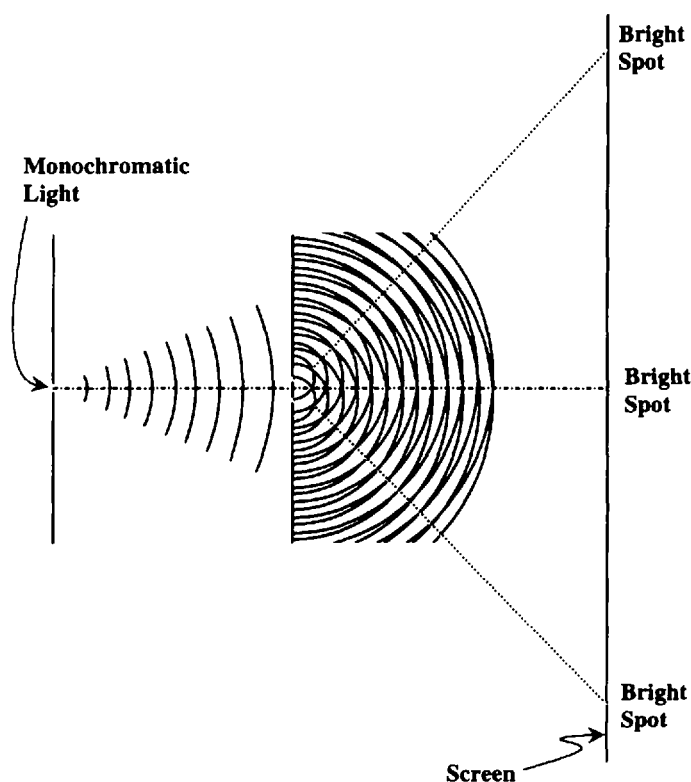


Figure 7.15: Two slit experiment demonstrating the interference of monochromatic light. Concentric curves (cylinders) represent locations of maximum intensity of light waves propagating from the slit sources. Dimensions have been accentuated for clarity; generally the slits are ~ 0.1 mm wide and ~ 1 mm apart, the distance from the source slit to the double slit screen is ~ 0.6 m and from the double slit to the screen, ~ 3 m [16]. As the double slits are brought closer together, more interference fringes will appear on the screen.

gle wavelength) light propagates from a single source S_0 to two slits, separated by a distance d (Figure 7.16). The two slits

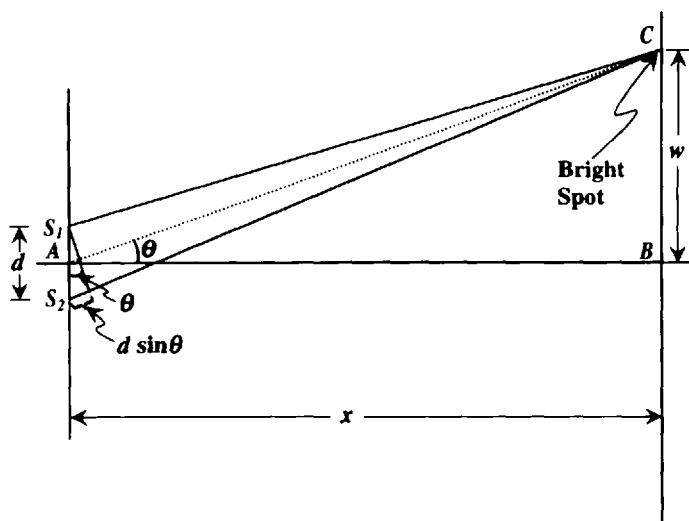


Figure 7.16: Geometric construction for the determination of the relationship between distances and wavelength.

then act as individual point sources of light, which can be visualized as releasing spherical waves of light exactly in phase. The light wave from each source would be expected to propagate to the center of the screen (centered between the two slits) in phase, since the waves had to travel the exact same distance. Hence, complete reinforcement would be expected at that position (bright spot). Moving along the screen, away from the centerline, light from one source would have to travel a different distance than the other, and annihilation (dark spot) or reinforcement events would depend on how close the path difference was to $m\lambda/2$ or $m\lambda$ respectively. The point C in Figure 7.16 represents an arbitrary location of complete reinforcement on the screen. An arc may be struck from point S_1 to where it intersects line S_2 - C . The distance from S_1 to this intersection point represents the path difference of the two light beams

(propagating spherical waves) from the two slits to point C . If the distance between the slit plane and screen x is large and d is small, the arc can be approximated as a line, which makes 90° angle intersections with both light beams (lines $S2-P$ and $S1-P$). For complete reinforcement, this path difference, $d \sin \theta$, represents the difference of an integral number of wavelengths:

$$m\lambda = d \sin \theta$$

From the geometry indicated in the figure, $w = x \tan \theta$. For small θ , $\sin \theta \cong \tan \theta$. Combining and eliminating $\sin \theta$:

$$\lambda = \frac{wd}{mx}$$

This is the fundamental equation of interferometry. By measuring d , w , and x and counting the number of fringes from the center to determine m , the wavelength of the monochromatic light used can be determined. Our interest, however, is the use of monochromatic light of known wavelength to determine distance changes.

An example of commonly observed light interference is that from films such as soap bubbles. As illustrated in Figure 7.17, incident light may be reflected from the top surface or may transmit through this surface only to be reflected from the bottom surface of the film. The resulting path difference, as the light beams propagate to the eye of the observer, contribute to the visual resolution of an interference pattern on the film. If the two surfaces are exactly parallel, then the interference pattern will appear as concentric circles (Haidinger fringes), whereas if the surfaces are skewed, the interference pattern will be hyperbolas which appear more as adjacent lines (Fizeau fringes) [17].

7.7.2 Instrument Design

One type of interferometer which measures changes in position using monochromatic light of a known wavelength is a Michelson interferometer (Figure 7.18). In this device, monochro-

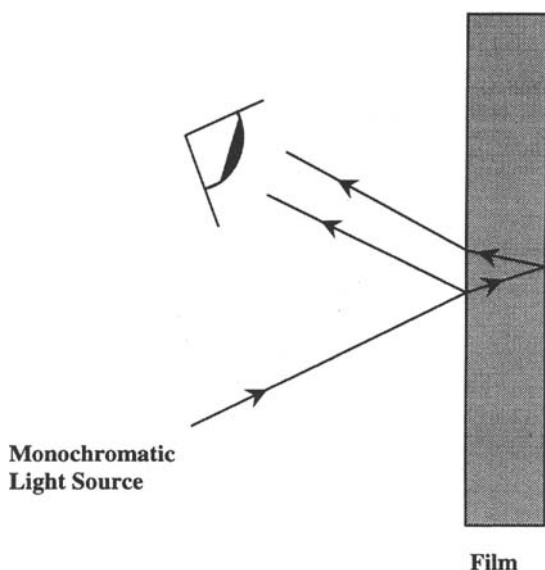


Figure 7.17: Interference of light from a thin film.

matic light⁹ either reflects from or propagates through a glass plate which is partially mirrored on one side. This plate is referred to as a “beam splitter”. The transmitted portion of the light beam reflects from a fixed mirror, then reflects off of the mirrored surface of the beam splitter to the detector, while the reflected portion of the light beam in turn reflects off of the moveable mirror and transmits through the beam splitter to the detector. A “compensator plate” is inserted in the path toward the fixed mirror to cause both beams to propagate though the same distance of glass.

If the two mirrors are perfectly orthogonal and $L_1 = L_2$, then the distance of either path to the detector is identical and there would be no observed interference. If, however, $L_1 \neq L_2$, the situation would be the same as interference from a thin film. If the mirrors are slightly offset (not orthogonal), the interference pattern will form a near-straight line image. If the movable mir-

⁹Generally a laser beam is used, wherein the light is coherent as well as monochromatic.

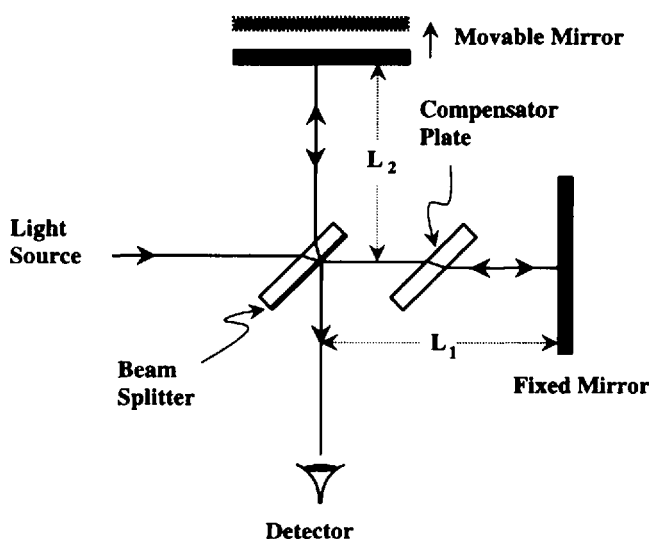


Figure 7.18: Michelson interferometer.

ror was moved backwards by distance x , the path differences to various points along the detector surface would change, causing a shift in the fringe pattern (Figure 7.19). When the fringes shift from one bright spot to the next, the mirror has shifted a corresponding distance of $\lambda/2$ (that is, the path difference has changed by $\lambda/2$). Note that this path difference is $\lambda/2$ rather than λ since by moving the mirror by a distance $\lambda/2$, the light beam must propagate to and reflect back from it, travelling a total distance of λ , which would correspond to one fringe shift. A suitable optical detector can be used to count the number of passing fringes m , so that the distance x that the mirror was moved would be $m\lambda/2$.

The moving mirror could be replaced by a solid with a mirrored surface (Figure 7.20). If the solid (specimen) is a metal, the top surface could be ground and polished to optical quality; if the solid is ceramic or polymeric, a thin metallic film could

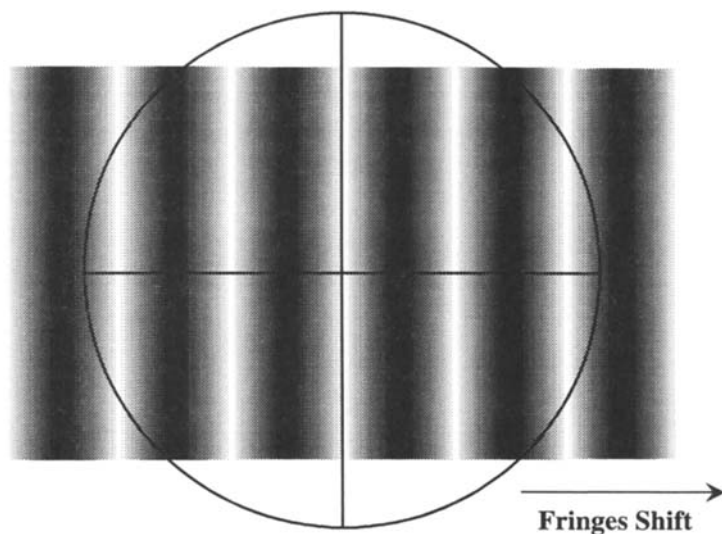


Figure 7.19: Fringe pattern and fringe shift resulting from moving one of the mirrors in a Michelson interferometer.

be vapor deposited on it.¹⁰ If the specimen is heated, the top surface will move due to thermal expansion, and a fringe shift will occur. It is not feasible to heat the specimen uniformly without heating the stage on which it rests. Therefore, this stage is generally mirrored as well. The difference in fringe shifts corresponding to the sample and the stage (using dual beams) represents the specimen expansion.

The average wavelength of visible light is ~ 400 nm, so each fringe shift would represent an expansion or contraction of 200 nm. A manufacturer's claimed [18] resolution of 20 nm is $1/32$ of the wavelength of the gas laser used: A photograph of the Ulvac/Sinku-Rico laser interferometer is shown in Figure 7.21.

¹⁰The expansion of this coating must be accounted for, or it would have to be assumed that the deposited film would have negligible thickness, hence make a negligible contribution to the measured expansion.

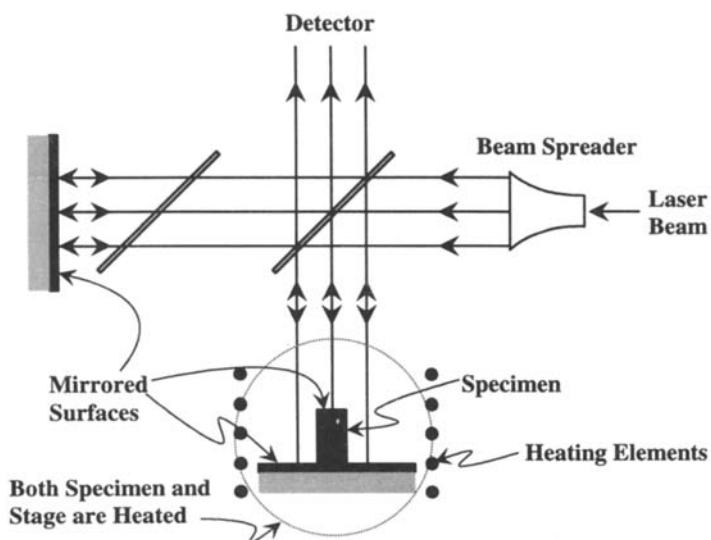


Figure 7.20: Schematic of a dilatometric interferometer.

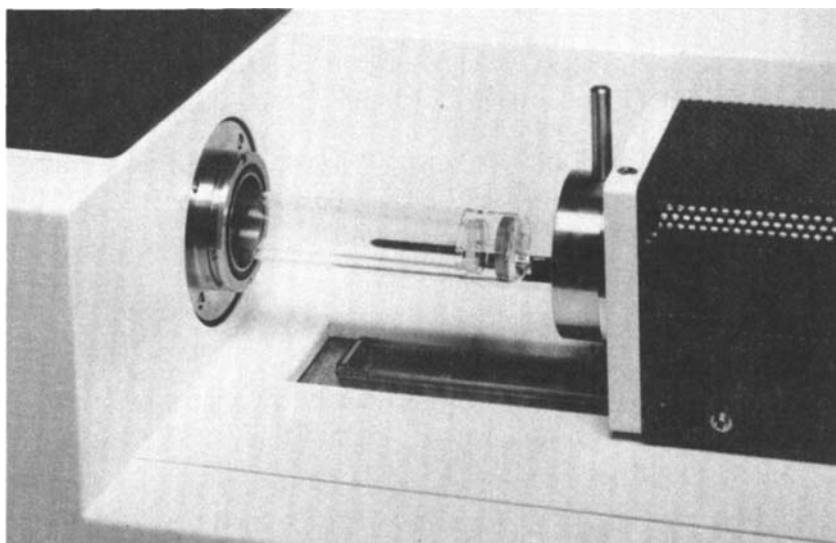


Figure 7.21: Sample chamber of the Ulvac/Sinku-Riko model LIX-1 laser interferometer [18].

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Chapter 8

HEAT TRANSFER AND PYROMETRY

8.1 Introduction to Heat Transfer

8.1.1 Background

The transport of thermal energy can be broken down into one or more of three mechanisms: *conduction*—heat transfer via atomic vibrations in solids or kinetic interaction amongst atoms in gases¹; *convection*—heat rapidly removed from a surface by a mobile fluid or gas; and *radiation*—heat transferred through a vacuum by electromagnetic waves. The discussion will begin with brief explanations of each. These concepts are important background in the optical measurement of temperature (optical pyrometry) and in experimental measurement of the thermally conductive behavior of materials.

8.1.2 Conduction

Heat transfer by conduction can be most simply stated as “heat flows as a result of a temperature difference”:

$$q = -kA \frac{dT}{dx}$$

where q is the heat flow rate (dQ/dt), A is the cross-sectional area, dT/dx is the temperature gradient, and k is the constant

¹Liquids show both mechanisms.

of proportionality referred to as the *thermal conductivity*, with MKS units of $\text{W}/(\text{m}\cdot\text{K})$. Example values of thermal conductivity (in $\text{W}/(\text{m}\cdot\text{K})$) are: 406 for silver, 385 for copper, 109 for brass, 0.8 for glass, 0.15 for insulating brick, and 0.024 for air [1]. The above expression is Fourier's law, which is often referred to as a "thermal ohm's law", as has been used throughout this book. The latter refers to the analogy between voltage and temperature gradient, current and rate of heat flow, and resistance and the inverse of thermal conductivity. This expression is valid for the simplest case of steady state one-dimensional heat transfer.

Steady state heat transfer refers to the condition where the rate of heat flowing into one face of an object is equal to that flowing out of the other. If, for example, a slab of metal were placed on a hot-plate, the heat flowing into the metal would initially contribute to a temperature rise in the material, until ultimately a linear temperature gradient formed between the hot and cold faces, wherein heat flowing in would equal heat flowing out and steady state heat transfer would be established. The time involved before steady state conditions are encountered is dependent on the thermal requirements, that is, the total heat capacity of the material. A useful constant, therefore, in depicting transient, or non-steady state heat transfer is the thermal diffusivity:

$$\alpha = \frac{k}{\rho c_p}$$

where c_p is the specific heat (heat capacity per gram of material) and ρ is the density. The units of thermal diffusivity are thus m^2/sec . From the expression, it is clear that a high thermal diffusivity material has a high thermal conductivity, with minimum thermal storage requirements.

Thermal conductivity does not remain constant with temperature. For gases, the thermal conductivity increases with (the square root of) temperature. The atoms in a higher tem-

perature gas move move fervently, hence, they translate thermal energy more rapidly.

Thermal conduction through electrically insulating solids depends on the vibration of atoms in their lattice sites, which, as discussed in section 3.7, is the mechanism of thermal energy storage. These vibrations act as the conduit for heat transfer by the propagation of waves (“phonons”) superimposed on these vibrations (schematically depicted in Figure 8.1). An analogy

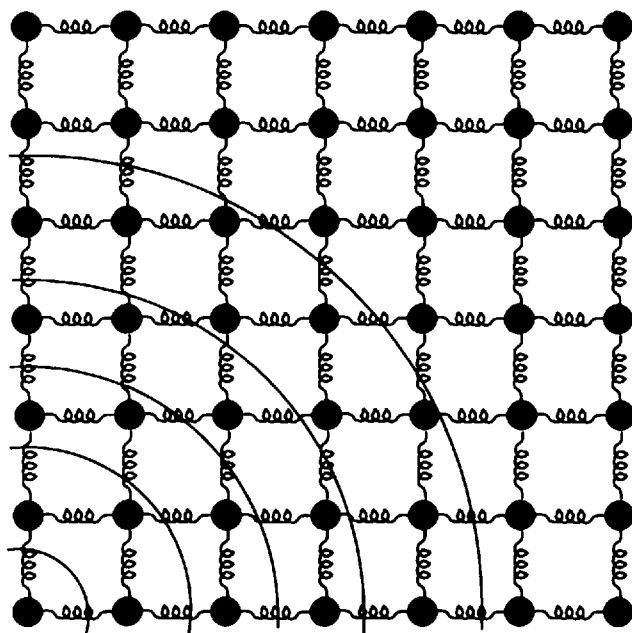


Figure 8.1: Schematic of phonon motion superimposed on atomic vibrations in a solid.

would be the ease of motion of a puck on an air-hockey table; the bed of air corresponding to the local atomic vibrations in the lattice.

The behavior of thermal conductivity with increasing temperature is highly material dependent—some examples are depicted in Figure 8.2. The thermal conductivity of a solid at the

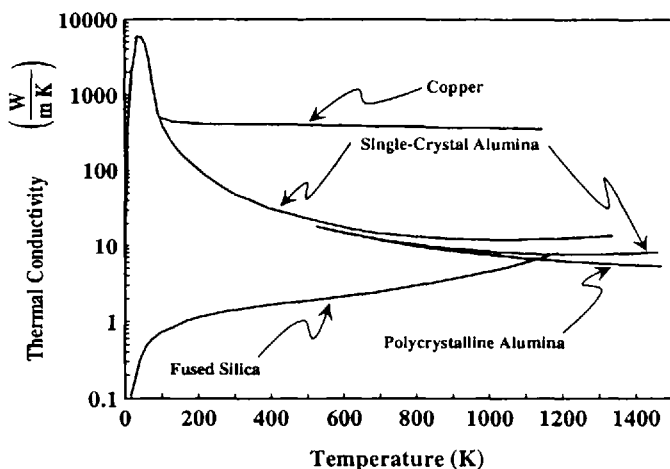


Figure 8.2: Thermal conductivity as a function of temperature for various solids [2][3]. The two traces of single-crystal alumina were from separate investigations.

absolute zero of temperature is zero since there is no mechanism for heat transfer; atoms are not vibrating. As temperature is increased, the thermal conductivity initially rapidly increases. For single-crystal Al_2O_3 (sapphire), the thermal conductivity reaches a maximum well below room temperature (~ 35 K), and then decreases. This decrease results from increased scattering of phonons by other phonons with increasing temperature. Phonon scattering can be described, by analogy, by dropping two stones into still water, and observing the interference and partial annihilation of the waves moving toward each other from the initial points of impact. The higher the temperature of the material, the more phonon activity, wherein the probability of phonons interfering with each other increases.

Discontinuities in the lattice such as vacancies, impurities, or grain boundaries also act to scatter phonon propagation, hence a lower thermal conductivity is expected in solids containing these defects at cryogenic temperatures. Whichever mecha-

nism of phonon scattering occurs over the shortest distances (shortest “mean free path”) is the dominant mechanism. For crystalline materials at room temperature, the phonon mean free path has decreased to less than 10 nm [2]. Hence, for room temperature and above, the presence of grain boundaries has no bearing on phonon conduction. As a result, the thermal conductivity of alumina resembles that of sapphire in the temperature interval 245°C to 400°C in Figure 8.2. At higher temperatures, the (effective²) thermal conductivity of sapphire becomes higher because of photon conductivity (radiation). Second phases at grain boundaries and minute porosity in polycrystalline alumina restrict radiation heat transfer (photon scattering).

Amorphous materials have no long-range structural order, so there is no continuous lattice in which atoms can vibrate in concert in order for phonons to propagate. As a result, phonon mean free paths are restricted to distances corresponding to interatomic spacing, and the (effective) thermal conductivity of (oxide) glasses remains low and increases only with photon conduction (Figure 8.2).

Metals, on the other hand, have an additional mechanism of conductive heat transfer—electron motion—which can be envisioned to transfer heat in an analogous fashion to that of the kinetic behavior a gas. Good electrical conductors tend to be good thermal conductors. However, the thermal conductivity of metals decreases with increasing temperature because of increased electron-electron scattering.

8.1.3 Convection

Convection is a mechanism of heat transfer wherein a flowing fluid, liquid or gas, acts as a heat sink or source to a solid object. An example of *forced* convection is where water, under pressure, moves through copper cooling coils to act as a heat

²The term “effective” implies attributing both conductive and radiative heat transfer to the value of thermal conductivity, which linearly relates heat flow to temperature difference.

sink to the outer metal casing of a hot furnace. By contrast, *free* convection is observed when, for example, air adjacent to a hot object expands, becoming less dense, in turn causing air flow patterns to develop as surrounding air moves in to relieve the density gradient. In both types of convection, heat transfer is enhanced over that of conduction by the the continuous removal of thermal energy by a mobile fluid (liquid or gaseous).

Using water flowing through a pipe as an example; as long as the water is not moving too rapidly, it should act as a “Newtonian fluid” whereby the water at the center of the pipe moves most rapidly, and the velocity of the water decreases parabolically as the inner walls are approached. The water directly adjacent to the inner surface of the pipe is motionless due to the frictional drag of the solid surface. In elementary heat transfer calculations, an effective *film conductance*, h , is used to describe the (inverse) thermal resistance of an effective immobile layer of fluid between a hot pipe and a mobile fluid. The mobile fluid is taken as a reservoir; its temperature does not change regardless of the heat flowing into it. This is generally expressed in a Fourier’s law form, but is referred to as Newton’s law of cooling:

$$q = hA(T_w - T_\infty)$$

where T_w is the temperature at the inner wall of the tube, and T_∞ is the temperature of the moving fluid.

Film conductances are also often defined for the impedance to thermal conduction when two solid conductors are placed in mechanical contact. A significant “contact resistance” is often observed when, on a microscopic scale, heat transfer involves an air-gap between the materials. Under such conditions, phonon propagation must be replaced by the kinetic interaction amongst gaseous atoms and then back to phonon heat transfer in the next solid. Fibrous and foam insulation are effective thermal insulators because of the numerous contact resistances involved in the transfer of heat.

Although experimental methods of studying convective heat transfer are not discussed in this book, convective cooling of components is ubiquitous in thermal analysis instrumentation. The power-compensated DSC uses water cooling of a metallic alloy block surrounding sample and reference chambers to allow rapid cooling, in order for the system to maintain a null balance. Most dilatometers are constructed with a water cooling system in thermal contact with the LVDT housing to protect against anomalous measurements taken due to inadvertent heating and consequent expansion of the components of the LVDT assembly.

8.1.4 Radiation

Radiation, which involves the transfer of heat by electromagnetic waves (light), requires no medium for its propagation, e.g. it can travel in vacuum. Radiant energy is transmitted through a spectrum of frequencies as depicted in Figure 8.3. Although radiative heat transfer is apparent when a hot body becomes self-luminous (e.g. “glowing red-hot”), most of the radiant energy is emitted in the infrared region of the spectrum. As temperature increases, the area under the radiant energy distribution (representing the heat released from the body) increases rapidly, and the location of the peak maximum shifts linearly in frequency with increasing temperature (Wein’s displacement law).

This energy distribution is the same for all materials behaving as “blackbodies”. A blackbody is a radiating body which is a perfect absorber and perfect emitter of radiant energy (no transmission, no reflection). These conditions can be emulated using a “blackbody cavity” (Figure 8.4) where light admitted through a small orifice will be internally reflected until it is ultimately absorbed. Radiant energy escaping through the orifice would have originated (emitted) from within the cavity walls. Hence, the radiation viewed from the orifice would emulate that coming from a perfectly absorbing/emitting surface. Planck’s

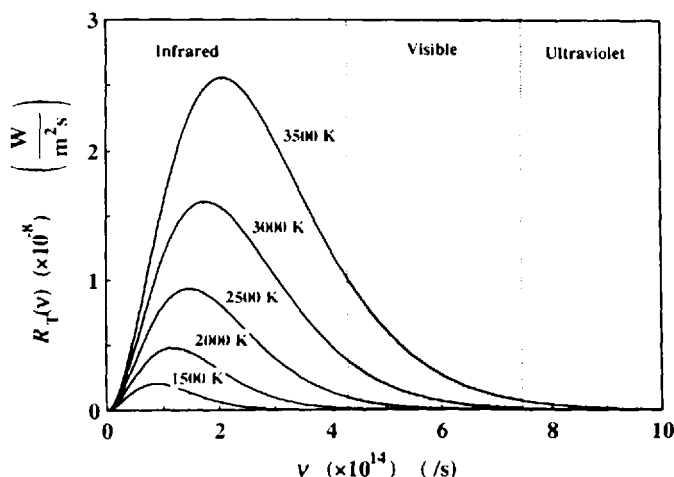


Figure 8.3: Spectral radiant power (per unit time per unit area) distribution of a blackbody at various temperatures. Note that the maximum intensity, even at 3500 K, is still in the infrared region of the spectrum. The displacement of the maximum of the radiant energy shifts linearly with absolute temperature (dotted lines) in accordance with Wein's displacement law.

equation depicts the spectral behavior of blackbodies:

$$\rho_T(\nu)d\nu = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{\exp\left(\frac{h\nu}{kT} - 1\right)} d\nu$$

where $\rho_T(\nu)$ is the radiant energy contained in a unit volume in a given frequency interval ($d\nu$), referred to as the spectral radiant energy density, ν is frequency, c is the velocity of light, h is Planck's constant, and k is Boltzmann's constant. This equation is derived in full in reference [4]. The energy contained in a unit volume of a blackbody and the rate of heat emitted per unit surface area, $R_T(\nu)$, from that body are linearly related by $R_T(\nu) = (c/4)\rho_T(\nu)$. With this relation and integrating Planck's equation (by multiple integration by parts and combining constants) over the entire spectrum, the total heat flow radiating from the blackbody results:

$$q = \sigma T^4$$

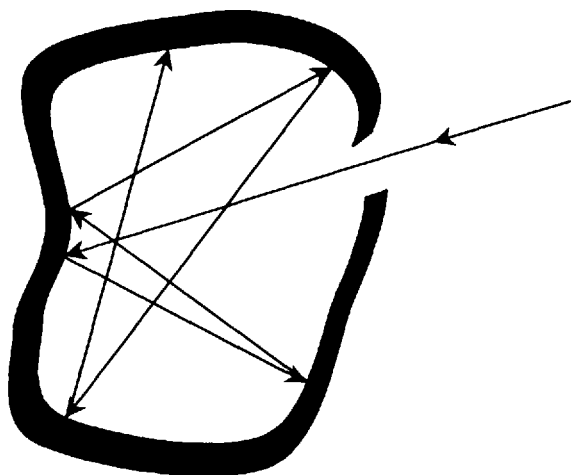


Figure 8.4: Blackbody cavity. All incoming radiation is internally reflected until it is ultimately absorbed. All exiting radiation was emitted from within the cavity.

where the constant of proportionality, σ , which contains all of the constants in Planck's law, is the Stefan-Boltzmann constant. This expression is highly significant, showing that the heat transfer from a radiating body increases much more rapidly with increasing temperature (T^4 dependence) than conductive heat transfer ($q \propto \Delta T$). The linear shift in frequency of the maximum of the radiant energy distribution with temperature (Wein's displacement law: $\nu_{max}T = \text{const}$, see Figure 8.3) may be derived by determining the maximum of Planck's function via taking the first derivative and setting it equal to zero.

The radiative behavior of real materials generally falls short of blackbody behavior, depending on the material. Figure 8.5 shows the spectral radiance of a real body is always less than that of a blackbody, and the deviation is inconsistent with wavelength.³ The *spectral emissivity* is defined as the ratio

³In this figure, wavelength, which is more common in pyrometry literature, is plotted on the ordinate rather than frequency ($\nu = c/\lambda$). The units of the abscissa values necessarily change so that in either case, the integrated areas under each curve yields the total energy per unit time per unit surface area emitted from the body.

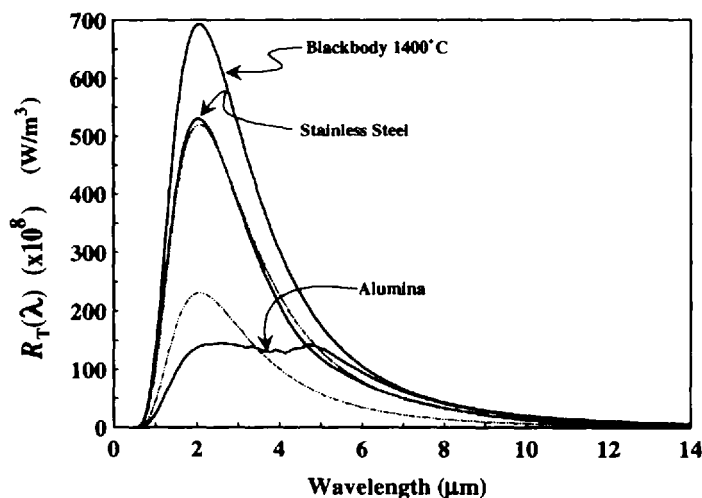


Figure 8.5: Spectral radiancy of a blackbody, real bodies stainless steel (1400°C) and alumina (1200°C), and greybody approximations. Real body spectra were calculated based on emittance values from reference [5]. Greybody approximations (dot-dot-dashed lines) were based on emittances of 0.33 for alumina and 0.75 for stainless steel. The high emittance of stainless steel is a result of oxidation to form a rough iron oxide surface. The greybody approximation appears good for stainless steel and poor for alumina. This may not be the case for different temperatures where the most intense portion of the blackbody spectra shifts in wavelength; the constancy of emittance differs in different regions of the spectrum.

of the spectral radiancy of a non-blackbody to that of a blackbody:

$$\epsilon_T(\lambda) = \frac{R_T(\lambda)_{\text{NBB}}}{R_T(\lambda)_{\text{BB}}}$$

As implied from the expression, the spectral emissivity of a blackbody is unity. As a first approximation, a “greybody” is a non-blackbody in which the spectral emissivity is taken as invariant with wavelength. Under such conditions, the spectral emissivity is simply the emissivity.

Emissivity is a material’s property which indicates the ten-

dency to absorb an incoming quanta of light. However, the absorptive nature of a body is also dependent on its surface condition, as depicted in Figure 8.6. The probability of an in-

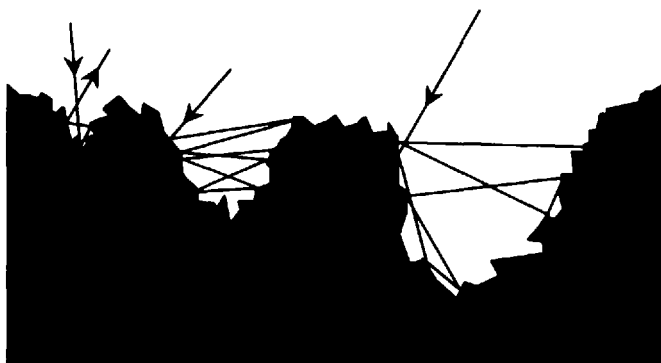


Figure 8.6: Effect of surface roughness on absorption of radiant energy. The rougher the surface, the greater the probability of internal reflection and ultimate absorption.

coming quanta of radiant energy being internally reflected is greater with increasing surface roughness. This internal reflection in turn leads to a greater probability that the quanta of light will be absorbed rather than reflected away. The spectral “emittance” of a body is defined as the ratio of spectral radiance from a *real surface* to that of a blackbody.⁴ The emittance is equal to the emissivity only for perfectly smooth, defect-free surfaces. With increasing surface roughness, the emittance approaches unity (blackbody behavior).

Radiative heat transfer through optically transmitting condensed matter such as molten glass can be appreciable (see higher temperature behavior of fused silica in Figure 8.2). In contrast, radiative heat transfer is not a viable mechanism in opaque condensed matter until high temperatures. Impurities and porosity act as scattering centers for radiative heat

⁴As with emissivity, the spectral emittance and the emittance are the same when there is no frequency dependence.

transfer (*photon* scattering). The effective thermal conductivity measured for a body in which radiation heat transfer is active (transparent and translucent media) shows a sharp temperature dependence (T^3 to T^5). The sharpness not only has to do with Stephan's law, but also with the fact that with increasing temperature the maximum of the spectral distribution (Figure 8.3) shifts to shorter wavelengths, where materials tend to have a higher percent transmission of radiant energy [6].

Radiant energy incident on a body is either reflected, transmitted through the body, or absorbed by it:

$$a + t + r = 1.0$$

where a is the absorbance, t is the transmittance, and r is the reflectance, the fractions of incident energy absorbed, transmitted, and reflected, respectively. For the body to remain at the same temperature, it must emit radiant energy at the same rate at which it absorbs, i.e. $\text{emittance} = \text{absorbance}$. Hence:

$$\epsilon = 1 - r - t$$

8.2 Pyrometry

Thermal processing at very high temperatures (e.g. 1700°C and above) makes the use of thermocouples for temperature monitoring difficult. Plant workers and supervisors with years of experience take pride in their ability to interpret the temperature of a radiating body by the way it looks—its brightness and its color. Instrumentation has been developed, much of it automated, which uses optical means to determine the temperature of a self-luminous body. Optical and infrared pyrometry are also important in applications where induction heating is used. A thermocouple inserted inside the coils would suscept and become self-heating; thus an optical method is the only method of determining temperature for feedback induction furnace control.

8.2.1 Disappearing Filament Pyrometry

Instrumental Design

A disappearing filament (Figure 8.7) pyrometer is a form of a spectral radiancy pyrometer, which is a device that evaluates

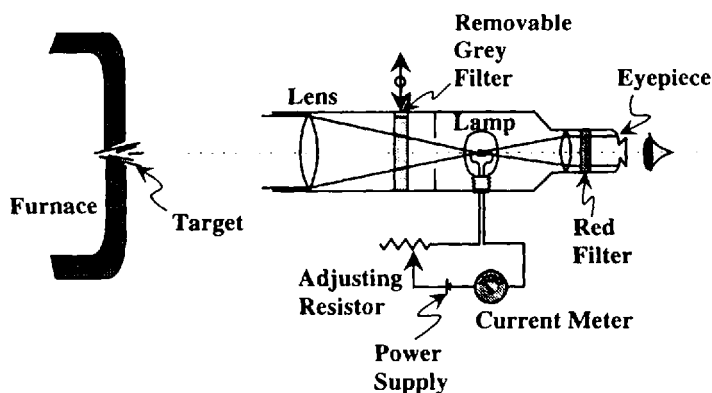


Figure 8.7: Schematic of a disappearing filament pyrometer.

temperature from radiation at a single wavelength. A lens system permits telescopic viewing of a distant luminescent body through a red filter. The filter permits only a narrow band of wavelengths to pass (see subsequent discussion). Along the optical path, a thin tungsten filament is viewed. By adjusting the current through the filament, its brightness can be made to match that of the luminescent body, at which point the filament will disappear from view. If the filament current has been previously calibrated against blackbody temperatures, the temperature of the body will be divulged, assuming it is a blackbody.

Calibration

The filament calibration curve can be obtained by comparison against previously calibrated pyrometers or from the output of high-temperature thermocouples in thermal contact with

the radiating body that is focused upon. External tungsten lamps may be purchased, the current from which was calibrated against blackbody temperature at NIST. These lamps may then be used to calibrate other disappearing filament pyrometers. Calibrated lamps are generally the preferred method of disappearing filament pyrometer calibration.

On a more absolute level, a blackbody cavity surrounded by gold at its melting point (1064.43°C) can be focused upon for one calibration datum. Such a cavity is depicted in Figure 8.8. By placing a rotating sectored disk, or varying thicknesses of

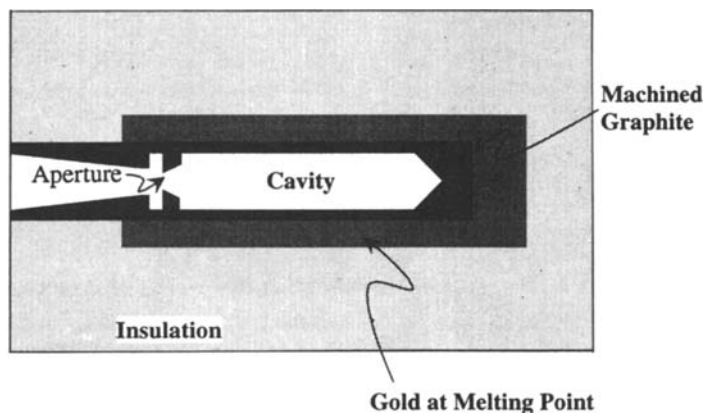


Figure 8.8: Schematic of a blackbody source for temperature calibration. The graphite surface has a high emittance. The molten liquid (e.g. gold) surroundings guarantees temperature uniformity, and as it solidifies or fuses, its temperature is single-valued.

an absorptive glass (grey filter), in the optical path to the gold-point blackbody source, lower calibration temperatures can be “synthesized”. Using the absorptive glass filter as example, the mathematical justification follows:

A partially transmitting glass of known absorption coefficient at a specific wavelength, k_λ , absorbs increasing levels of radiant energy with increasing thickness. The decay of radiation at any given cross-sectional area within the glass would be

proportional to how much radiation was left:

$$\frac{dW_T(\lambda)}{dx} = -k_\lambda W_T(\lambda)$$

where $W_T(\lambda) = \phi R_T(\lambda)$, the geometric constant ϕ converting the spectral power released per unit area (in all directions) from the body to the power incident on the glass plate. Integrating from the front surface ($x = 0$) where the intensity is the incident intensity $W_T(\lambda)_0$ to some position x within the glass:

$$\int_{W_T(\lambda)_0}^{W_T(\lambda)_x} \frac{dW_T(\lambda)}{W_T(\lambda)} = \int_0^x -k_\lambda dx$$

which integrates to:

$$\ln \left(\frac{W_T(\lambda)_x}{W_T(\lambda)_0} \right) = -k_\lambda x$$

or:

$$\exp(-k_\lambda x) = \frac{W_T(\lambda)_x}{W_T(\lambda)_0}$$

Since $\nu = c/\lambda$ (hence $d\nu = -(c/\lambda^2)d\lambda$), Planck's law can be rewritten in terms of wavelength:

$$W_T(\lambda)d\lambda = \phi \frac{2\pi hc^2}{\lambda^5} \frac{d\lambda}{\exp\left(\frac{hc}{\lambda kT}\right) - 1}$$

Planck's law becomes Wein's law if the “-1” term is considered insignificant; combining constants yields:

$$W_T(\lambda) = \lambda^{-5} C_1 \exp\left(\frac{-C_2}{\lambda T}\right)$$

Combining with the expression for the absorptive glass:

$$\exp(-k_\lambda x) = \frac{\lambda^{-5} C_1 \exp\left(\frac{-C_2}{\lambda T_x}\right)}{\lambda^{-5} C_1 \exp\left(\frac{-C_2}{\lambda T_0}\right)}$$

Taking logarithms and rearranging:

$$k_\lambda x = \frac{-C_2}{\lambda} \left(\frac{1}{T_0} - \frac{1}{T_x} \right)$$

By varying filter thickness or using filters of different known absorption coefficients, the synthesized blackbody temperature after the filter can be calculated (note C_2 is simply hc/k). By correlating these temperatures against the disappearing filament current, a calibration curve for the pyrometer can be established for the temperature range of the melting point of gold and below.

By using absorbing filters, the radiation from blackbody sources at higher temperatures can be down-rated to temperatures within the calibration range of the pyrometer. As a result, the range of the pyrometer can be extended well above the melting temperature of gold.

The Assumption of a Single Wavelength

The red filter used in a disappearing filament optical pyrometer transmits a range of wavelengths, but a combination of human and spectral factors result in the imaging of only a narrow range of wavelengths in a disappearing filament pyrometer (Figure 8.9). As shown in the figure, the red filter becomes transmittive to wavelengths of $\sim 0.63 \mu\text{m}$ and longer. The human eye is more sensitive to green than red, and ultimately it is human visual acuity which acts as a long wavelength cutoff. Further, the Planck's law distribution results in rapidly diminishing intensity of incident radiation with shorter wavelength.

Determination of Spectral Emissivity

One advantage of a spectral radiation pyrometer is that the emissivity or emittance at only a specific wavelength (e.g. $0.653 \mu\text{m}$) is of importance. A non-blackbody source will be less luminescent than a blackbody source at the same temperature. Thus, a falsely low temperature will be determined by sighting a calibrated disappearing filament pyrometer on the non-blackbody. This temperature has been referred to as the "brightness temperature".

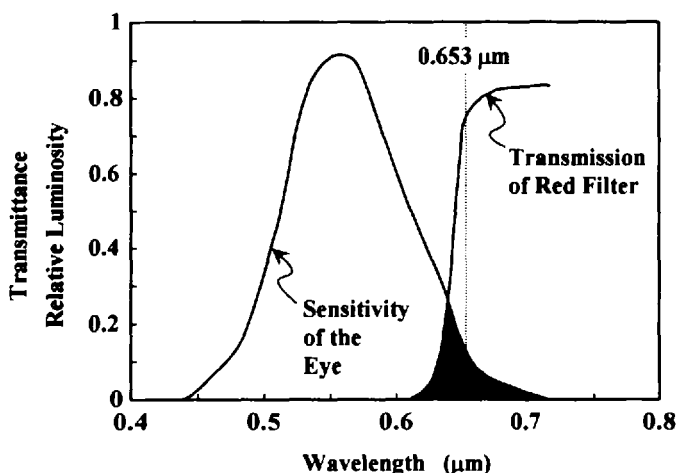


Figure 8.9: The combination of the visual acuity of the human eye and the transmittance of a red glass filter acts to restrict the detected wavelength to a narrow band [7]. The effective wavelength for optical pyrometers of this form is $0.653 \mu\text{m}$ [8].

Beginning with the definition of spectral emissivity:

$$\epsilon_T(\lambda) = \frac{R_T(\lambda)_{\text{NBB}}}{R_T(\lambda)_{\text{BB}}}$$

where the notation BB refers to blackbody and NBB refers to non-blackbody. Inserting Planck's law:

$$\epsilon_T(\lambda) = \frac{\frac{1}{\lambda^5} (2\pi hc^2) \left(\exp\left(\frac{hc}{\lambda k T_{\text{NBB}}}\right) - 1 \right)^{-1} d\lambda}{\frac{1}{\lambda^5} (2\pi hc^2) \left(\exp\left(\frac{hc}{\lambda k T_{\text{BB}}}\right) - 1 \right)^{-1} d\lambda} = \frac{\exp\left(\frac{hc}{\lambda k T_{\text{BB}}}\right) - 1}{\exp\left(\frac{hc}{\lambda k T_{\text{NBB}}}\right) - 1}$$

Again assuming Wein's law can be substituted for Planck's law ("−1" term is negligible) and taking logarithms:

$$\ln \epsilon_T(\lambda) = \frac{hc}{\lambda k T_{\text{BB}}} - \frac{hc}{\lambda k T_{\text{NBB}}}$$

or:

$$\ln \epsilon_T(\lambda) = \frac{hc}{\lambda k} \left(\frac{1}{T_{\text{BB}}} - \frac{1}{T_{\text{NBB}}} \right)$$

At temperatures below 200°C, a strip of masking tape across the target will act as a near blackbody radiator ($\epsilon = 0.95$) because of its rough textured surface [9]. For high temperature measurements, the emittance can be determined by calibrating against another temperature transducer such as a thermocouple. If a blackbody cavity and a non-blackbody of interest are situated in a furnace so that they are at the same temperature, the emittance may be determined using a pyrometer sighting on each object. A hole can be drilled in the body itself (the depth at least six times the diameter) which will act as a blackbody cavity. The important consideration when using a cavity as calibrant is whether the target surface and the blackbody cavity are truly at the same temperature when they are displaced from one another. The emittance of most common materials has been tabulated in references [10]-[13] as cited in reference [14].

A calorimetric method may be used where an electric heater is imbedded in the object of interest, and the power dissipated by the element is accurately calculated from voltage and current. Once steady state is established and the object is at constant temperature, the body must emit radiation at the same rate at which it is supplied. As long as conduction and convection are eliminated as mechanisms of heat transfer (e.g. vacuum conditions), the blackbody temperature is known by $R_T = \sigma T^4$. The emittance can then be determined after pyrometric measurements of the brightness temperature of the object.

8.2.2 Two Color Pyrometry

A “two color” pyrometer requires evaluation of the temperature of a body using two wavelengths, historically via red and green filters, having effective wavelengths of 0.65 μm and 0.55 μm respectively. The concept can be applied to older user-interactive optical pyrometers or with greater precision using solid state detectors with wavelengths in the infrared spectrum. Under

greybody conditions, the emissivity of a target is the same at the two wavelengths:

$$\epsilon_T(\lambda_1) = \epsilon_T(\lambda_2)$$

Thus:

$$\frac{hc}{\lambda_1 k} \left[\frac{1}{T_{BB}(\lambda_1)} - \frac{1}{T_{NBB}(\lambda_1)} \right] = \frac{hc}{\lambda_2 k} \left[\frac{1}{T_{BB}(\lambda_2)} - \frac{1}{T_{NBB}(\lambda_2)} \right]$$

where $T_{NBB}(\lambda_1)$ and $T_{NBB}(\lambda_2)$ are the brightness temperatures determined at the two wavelengths. The blackbody temperature T_{BB} is the true temperature of the body and is independent of wavelength ($T_{BB}(\lambda_1) = T_{BB}(\lambda_2)$). Rearranging:

$$T = \frac{\frac{1}{\lambda_1} - \frac{1}{\lambda_2}}{\frac{1}{\lambda_1 T_{NBB}(\lambda_1)} - \frac{1}{\lambda_2 T_{NBB}(\lambda_2)}}$$

By measuring the brightness temperature using a disappearing filament pyrometer at two wavelengths, the blackbody (actual) temperature can be calculated.

One design of two color pyrometer uses a rotating disk containing two filters which alternately exposes a solid state detector to one of two wavelengths. The device works on a similar principle of null balance as the Cahn microbalance (section 5.1): A filter, partially blocking the incoming radiation, is moved via a servo mechanism until it attenuates the intensity of one of the wavelengths⁵ (the other unaffected) until the two wavelengths are equal. The position of the filter is then graduated in units of temperature. A more contemporary device is depicted in Figure 8.10. In this device, an indium phosphide filter acts to transmit radiation over 1 μm and reflects radiation of narrower wavelength. Superposition of the band gap of the silicon detectors with the InP filter results in effective wavelengths of 0.888 μm and 1.034 μm at the reflected and transmitted detectors, respectively. The current required to equate the output of the

⁵Presumably, the higher intensity, longer wavelength.

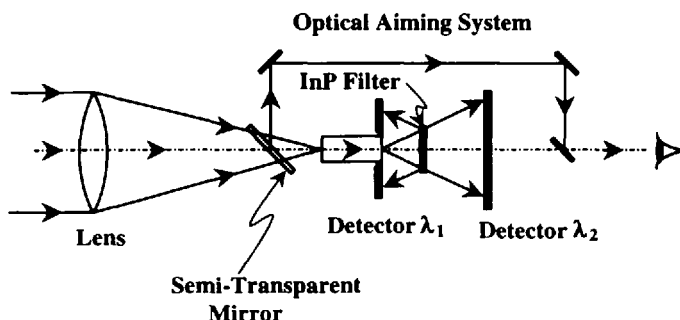


Figure 8.10: Schematic of Ardocol two color pyrometer. The optical aiming system allows an operator to site the device so that only the target is in view [15].

two detectors mimics the equalization of intensities, and the temperature is exponentially related to the intensity ratio:

$$\frac{W_{\lambda_1}}{W_{\lambda_2}} = \frac{\phi C_1 \epsilon_{\lambda_1} \lambda_1^{-5} \exp\left(\frac{-C_2}{\lambda_1 T}\right)}{\phi C_2 \epsilon_{\lambda_2} \lambda_2^{-5} \exp\left(\frac{-C_2}{\lambda_2 T}\right)} = \left(\frac{\lambda_2}{\lambda_1}\right)^5 \exp\left[\frac{C_2}{T} \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)\right]$$

An advantage of a two color pyrometer is in circumventing the need to know the emissivity of the body in order to determine its temperature. Greybody conditions, however, are often an unwarranted assumption. Use of this device without prior confirmation of greybody conditions for the two wavelengths may result in appreciable temperature measurement error. The real advantage of a two color pyrometer over other pyrometers is that it can be used under conditions of sighting through dust and smoke, where the interference of particles would attenuate radiation from both wavelengths equally, and hence cancel out.

8.2.3 Total Radiation Pyrometry

While disappearing filament pyrometers are convenient and accurate, they require human interaction and hence are not well suited for use in feedback control systems. In a total radiation pyrometer, a lens system focuses incoming radiation onto

a blackened surface (detector) of low total heat capacity. A sensitive series of thermocouples (thermopile) or a solid state detector (e.g. thermistor) in contact with the surface, monitors its temperature. The thermopile is generally set up to measure the temperature difference between the detector and the pyrometer housing. Heat is conducted from the detector to the water-cooled pyrometer housing, establishing a steady state heat transfer and a constant temperature detector. As long as the detector is of low mass, the response time in which it reaches a constant temperature will be adequately rapid.

The heat flow focused onto the detector originates from the radiant energy emitted from the luminescent source; $q_T = \phi' \sigma T_{BB}^4$, where ϕ' is a constant accounting for the fact that only a fraction of the emitted radiant power from the body is incident on the lens system and focused onto the detector. The heat flow conducted from the detector to the pyrometer housing originates from the temperature difference; $q_T = k'(T_d - T_h)$, where $T_d - T_h$ is the difference in detector and housing temperature and k' is proportional to the thermal conductivity. Equating heat flows:

$$T_d \propto T_{BB}^4$$

In practicality, this relationship does not hold exactly, with the exponent of T_{BB} varying from 3.8 to 4.2. Reflections from the pyrometer case may act to increase detector heating, while absorption of some frequencies by the lens system acts to decrease detector heating. The inevitable lens absorption indicates that the term "total" radiation pyrometer is not quite correct but is still in common usage. Calibration of the device can be made via calibrated pyrometer, thermocouples, tungsten lamps, or gold-point measurements, correlating the output of the detector temperature transducer with the black-body temperature of the source. Replacing the fourth power in the above expression with the variable n (which accounts for deviations from ideality) and taking logarithms:

$$\ln T_D = \ln C + n \ln T_{BB}$$

Fitting blackbody and detector temperature data to this function should yield a straight-line fit, allowing determination of n and $\ln C$ as slope and intercept, respectively.

Usage of this device for non-blackbody sources is not practical. Greybody conditions would have to be valid over the entire spectrum incident on the detector in order to legitimately apply an emittance correction.

Focusing mirrors can be used without lenses to focus radiation onto the detector. Lens-free devices are capable of measuring temperatures as low as 100°C [16]. Miniature total radiation pyrometers may be obtained with a sapphire light guide which may be sealed into the housings of furnaces which must remain gas-tight. Target tubes are closed-ended tubes where the closed end is located in the zone of interest in the furnace and its temperature is measured. Given the geometry, the emittance of the end of the tube is nearly unity. Target tubes with light guides are often used in conjunction with total radiation pyrometers so that changes in the ambient atmosphere (temperature, dust, etc.) do not effect the measurement and so that holes in the furnace, leaking radiation, are not needed. Target tube materials range from inconel to silicon carbide depending on application temperature.

8.2.4 Infrared Pyrometry

Spectral radiancy pyrometers can also be automated using photoelectric semiconductor-based devices rather than disappearing filaments. Historically, these instruments were designed around the 650 nm wavelength range, since a significant database of emittance had already been developed. However, the principal advantage of solid state detectors is their capability of operating in the infrared range, where radiation from objects of moderate temperature is much more intense. Broad-band sensors are also available for use as near total radiation pyrometers (some of the spectrum still goes undetected). These devices are rendering disappearing filament and total radiation

pyrometers obsolete.

While the operating principle of solid state detectors requires some background in semiconductor physics, the basic principle is analogous to that described for the thermistor in section 2.1. In this case, photons of light excite electrons from the valence to the conduction band, changing the electrical properties of the irradiated material. Since the excitation can only occur if the incident photon has energy equal to or in excess of the band gap energy, the device has an inherent spectral cutoff. For example, Si, PbS, and InSb have band gaps of 1.11, 0.37, and 0.18 eV [9], respectively; these would correspond ($E = hc/\lambda$) to wavelength cutoffs of 1.11, 3.35, and 6.69 μm . Optical filters are used to further define the band of wavelengths “detected” by the device. To increase the sensitivity of the detectors, they may be cooled to liquid nitrogen temperatures so that minimal ambient thermal excitation of electrons occurs. Many systems have internal standards where a rotating sector disk exposes a detector alternately to the object of interest and to a light-emitting diode or a temperature-controlled blackbody source. The more expensive variety of these detectors can determine temperatures from the ice point to higher temperatures. Depending on cost, precision levels of 0.05°C near room temperature have been claimed [18].

The problem of spectral emittance discussed for the disappearing filament pyrometer is present for infrared pyrometers as well. The great advantage of infrared pyrometers is the ability to custom select the wavelength in which to make the temperature measurement. In some regions of the spectrum, materials are highly absorbing of radiant energy while at others the emittance is rather low. Figure 8.11 shows the spectral transmittance of soda-lime-silica glass. Using an infrared pyrometer sensitive the 8- μm range will permit temperature evaluation of the material as if it were a blackbody.⁶ However,

⁶This is based on the assumption that the spectral emittance follows the spectral absorbance.

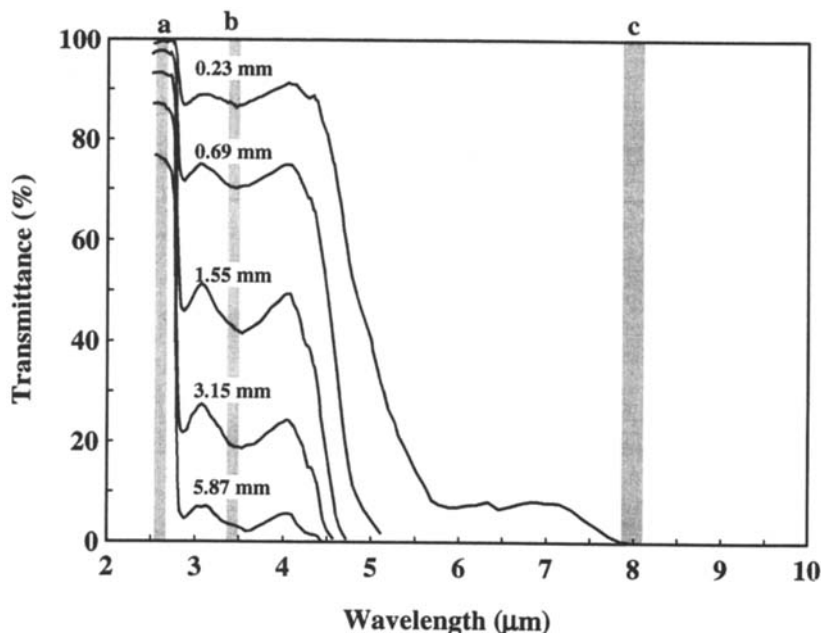


Figure 8.11: Spectral percent transmittance for soda-lime-silica glass [19] as a function of thickness. Using an infrared pyrometer to determine temperature in region *a* would require prior knowledge of the glass emittance. Temperature evaluation in region *b* would divulge the temperature of the glass interior. Using a pyrometer sensitive to spectrum range *c* would indicate the blackbody surface temperature of the glass.

if a hot object is to be viewed through the glass (acting as a window), a detector sensitive to wavelengths shorter than $2.7 \mu\text{m}$ is necessary.

A significant concern in the use of total radiation pyrometry is that it must be calibrated at the distance it will be from the source because of the influence of the atmosphere. Normal atmosphere contains a small fraction of carbon dioxide and water vapor (the latter dependent on the relative humidity, which varies with the day). When combustion is used for furnace heating (e.g. $\text{CH}_4 + 2\text{O}_2 = 2\text{H}_2\text{O} + \text{CO}_2$), water vapor and carbon dioxide are the predominant atmospheric constituents. As

shown in Figure 8.12 these polyatomic gases can absorb radiant energy strongly in certain bands of wavelength. Selection of an

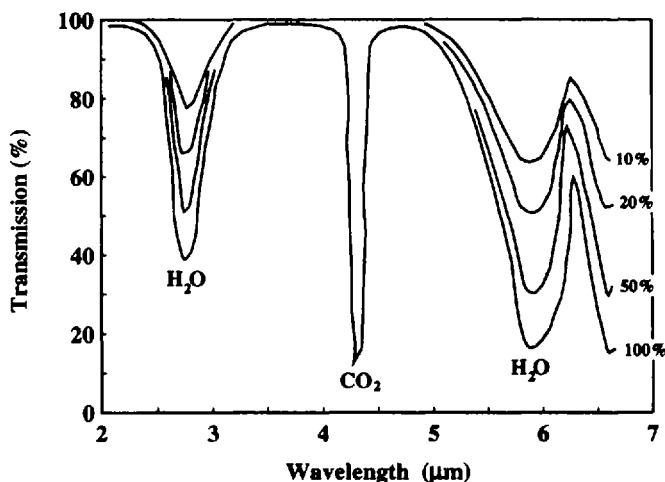


Figure 8.12: Spectral percent transmission of an atmosphere at several relative humidities. Measurements were taken over a path length of 1.83 m at a temperature of 26.67°C [19].

infrared pyrometer sensitive to a wavelength region in which the atmosphere is highly transmitting is desirable.

For maximum sensitivity, the wavelength of the infrared pyrometer should also be selected based on where the spectral radiance changes most rapidly. For example, in the temperature range depicted in Figure 8.3, a frequency of 1.5×10^{14} Hz ($2 \mu\text{m}$) will permit more precise temperature measurement than a frequency of 0.4×10^{14} Hz ($7.5 \mu\text{m}$).

Microprocessor-based infrared pyrometers can be quite elaborate. Figure 8.13 shows a schematic of a scanning device which can determine the temperature of, and temperature gradients within, a large part during manufacture.

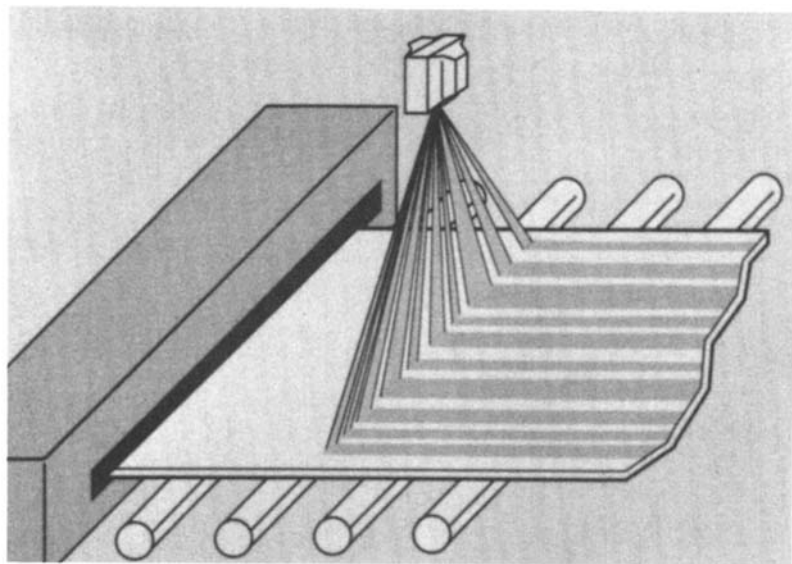


Figure 8.13: Ircon scanning infrared pyrometer [19].

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Chapter 9

THERMAL CONDUCTIVITY

In this chapter, five methods of determining the thermal conductivity of solids are described. The final technique, laser flash, is a method of measuring the thermal diffusivity, from which the thermal conductivity may be obtained if the specific heat and density are known. In the following sections, the operating principles of each technique are described. Novel techniques for measurements of this form appear every year—reference [1] is suggested for a start on contemporary literature.

9.1 Radial Heat Flow Method

Fourier's law for steady state heat transfer can be translated to the cylindrical geometry sketched in Figure 9.1. Recognizing that the surface area of a cylinder is $2\pi rL$:

$$q_r = -kA_r \frac{dT}{dx} = -k2\pi rL \frac{dT}{dr}$$

Heat flows from inner (r_i) to outer (r_o) radii at temperatures T_i and T_o respectively:

$$\int_{r_i}^{r_o} \frac{dr}{r} = -\frac{k2\pi L}{q_r} \int_{T_i}^{T_o} dT$$

or:

$$\ln \left(\frac{r_o}{r_i} \right) = -\frac{k2\pi L}{q_r} (T_o - T_i)$$

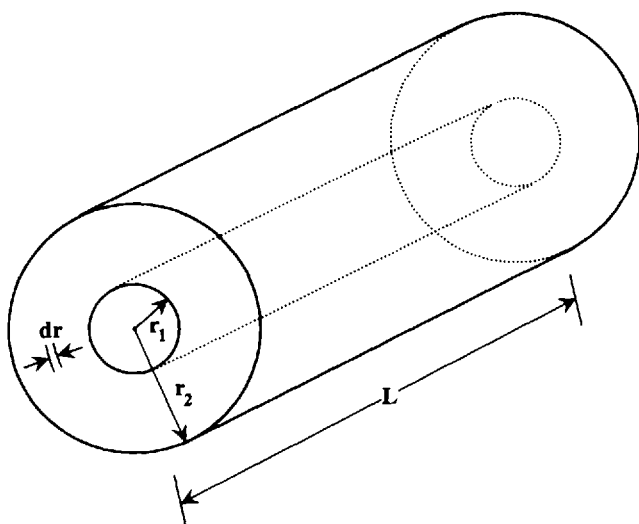


Figure 9.1: Cylindrical geometry for calculation of thermal conductivity from radial heat flow.

Rearranging:

$$k = \frac{q \ln(r_o/r_i)}{2\pi L (T_i - T_o)}$$

A schematic of an Anter radial thermal conductivity measuring instrument using this principle is shown in Figure 9.2. A specimen in the form of an annular cylinder is placed to surround a central heater. Often the cylinder is made up of a series of stacked rings. Alternatively, a granulated or fibrous form of the specimen may be poured or placed between the central heater (~ 1.2 cm OD) and a mullite outer casing (~ 10.5 cm ID).

Thermocouples are placed at the same height along the axis, one radially extended from the other. When particulate specimens are poured in, a perforated template is used to maintain the correct positions of the thermocouples. The template is removed after the specimen material is in place. Averaging

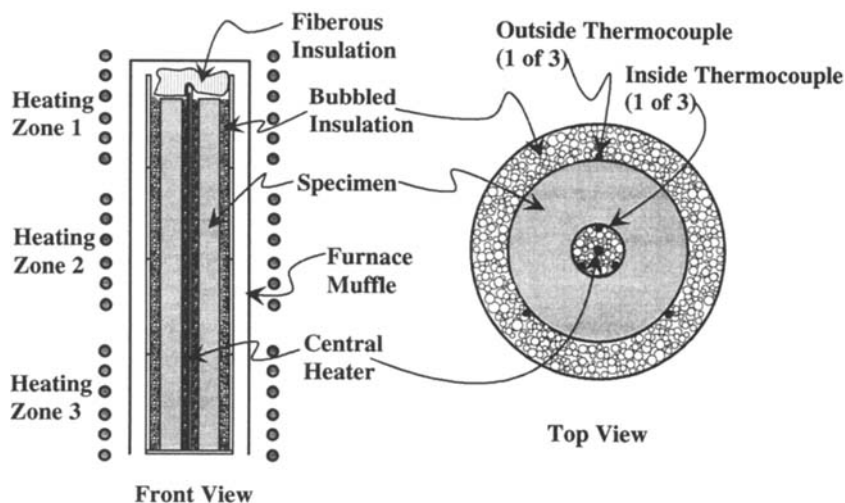


Figure 9.2: Schematic of radial thermal conductivity apparatus. Specimen dimensions are ~ 2.75 cm in radial thickness and 56 cm in length. Not shown are thermocouples placed axially along the central heater and voltage taps ~ 5 cm apart. Inner and outer thermocouple junctions extend out radially, centered axially between the voltage taps.

the output from three thermocouples, 120° apart, acts to minimize the effects of slightly asymmetrical specimen geometries. Solid specimens are positioned between inner and outer thermocouples. The thermocouple wires are then bent so that their junctions are in mechanical contact with the specimen. Bubbled alumina insulation is then poured to fill the inside and outside gap. Alternatively, holes can be drilled within larger specimen rings to accommodate the thermocouples in the specimen interior.

The central heater is made up of a platinum heater assembly within an alumina or mullite sheath.¹ Voltage taps symmetrically placed about the center allow determination of power per unit length dissipated radially past the inner and outer ther-

¹Mullite has the advantage that its lower thermal conductivity diminishes axial heat flow along the central heater more effectively.

mocouples, which are centered axially with respect to the taps. Thermocouple junctions are strategically placed at points along the heater assembly to allow monitoring of any axial temperature gradients along the central heater.

A tube furnace drawn over the mullite outer casing is used to heat the contents to a specified temperature, based on a furnace control thermocouple. At the same time, a constant ac voltage² is applied across the central heater. The microprocessor waits until temperature fluctuations (within $\sim 0.1^\circ\text{C}$, over one minute) at any of the inside or outside thermocouples are eliminated.³ At that point, steady state conditions are assumed to exist.

The heat flow dissipated by the central heater is then calculated by measurement of current and voltage (see section 9.3). The thermal conductivity is then computed based on the heat flow, temperature gradient, and known radial distances. The outer furnace then heats the contents to a higher (e.g. 100°C) temperature and the process repeats. The thermal conductivity of the specimen as a function of temperature is thus determined by a series of isothermal steps.

The primary concern for accurate thermal conductivity measurements using this technique is to eliminate axial heat flow. As long as the central heater is long, its temperature near the central portion is uniform. Devoid of an axial temperature gradient, heat will strictly flow radially outward from the central

²The full sine wave is used, rather than using an SCR, so that the heat dissipated by the central heater can be accurately determined. The RMS voltage across the central heater can be manually adjusted using a variable transformer (variac) or a signal amplifier/deamplifier. This adjustment would be made based on the heat required for a given specimen in order to establish a reasonable temperature gradient between inner and outer thermocouples.

³The power dissipated by the outside furnace heating elements is adjusted via a PID algorithm based on temperature measured by the control thermocouple. At the same time, the central heater dissipates a more constant supply of heat from the constant voltage applied to it. Eventually, the PID algorithm backs off the furnace power instruction, since some of the heat acting to raise the control thermocouple temperature is supplied by the central heater. As a result, the furnace temperature adjusts to be at a lower temperature than regions closer to the central heater. Thus, a temperature gradient forms from inside to outside.

heater. The outer furnace is designed with one central and two outer furnace windings, all controlled independently. The purpose of this three-zone configuration is to guard against axial temperature gradients along the specimen. Further minimization of axial heat flow can be accomplished via the use of guard heaters above and below the specimen (see section 9.4).

9.2 Calorimeter Method

The calorimeter method is an older technique which is a direct measurement of Fourier's law. It is one of the ASTM [2] standard tests for thermal conductivity, designation C201. The experimental configuration is shown in Figure 9.3. A SiC slab

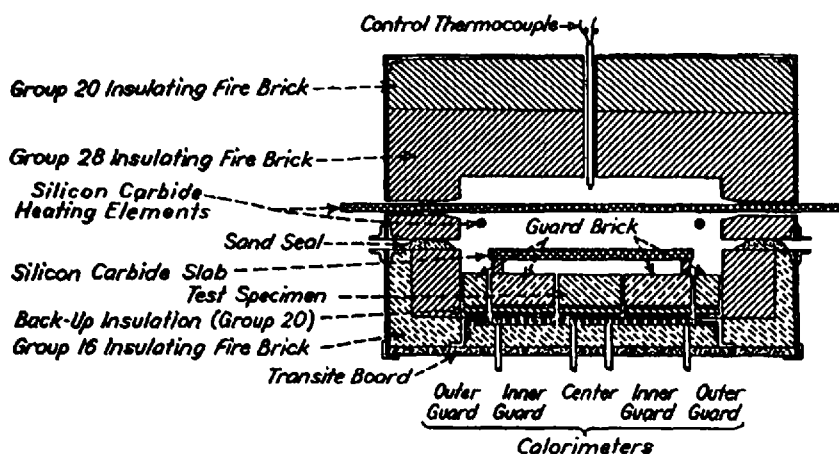


Figure 9.3: Schematic of the calorimeter method of measuring thermal conductivity [2]. Specimen sizes are approximately three bricks of dimensions $23 \times 11.4 \times 6.4 \text{ cm}^3$.

acts to distribute temperature gradients from the heat source (usually SiC or MoSi₂ heating elements). The test specimen is bordered by two insulating guard bricks, and these guard bricks as well as the specimen are in thermal contact with a water-cooled copper base. The copper base is made up of separate

water cooling systems, as shown in Figure 9.4. The center series of coils is the “calorimeter”, which is surrounded by the inner and outer “guards”. The calorimeter has a smaller area than the test brick. The configuration of calorimeter and guards is designed so that there are no temperature gradients in the horizontal planes along the heat flow path to the calorimeter. Thus, the heat flow into the calorimeter is one dimensional.

Two thermocouples separated by distance L are imbedded in the test specimen, one directly above the other, whereby the temperature drop $T_2 - T_1$ between them is measured. A differential thermocouple measures the temperature rise ΔT_w of the exit water of the calorimeter as compared to its entrance temperature. The mass flow rate of water F into the calorimeter is monitored, so that over a specific time interval Δt , the total heat absorbed by the calorimeter may be calculated, knowing the specific heat c_p of water. Dividing by the time interval will give the rate of heat flow into the calorimeter under steady state conditions:

$$\frac{dQ}{dt} = \frac{c_p \Delta T_w F \Delta t}{\Delta t} = c_p \Delta T_w F$$

Hence, the thermal conductivity may be determined by a rearrangement of Fourier’s equation (section 8.1.2):

$$k = \frac{\frac{dQ}{dt} L}{A (T_2 - T_1)}$$

where A is the cross sectional area of the calorimeter, and L is the distance between the two imbedded thermocouple junctions. Note that since heat flow is constant throughout a vertical section of the specimen (steady state conditions), thermocouple junctions measuring T_1 and T_2 can have vertical positions anywhere along the specimen.

The back-up insulation between the base of the test specimen and the calorimeter is optional. Under conditions of steady state heat flow, introduction of back-up insulation diminishes the heat flow to the calorimeter as well as the temperature drop across the specimen; the thermal conductivity, as

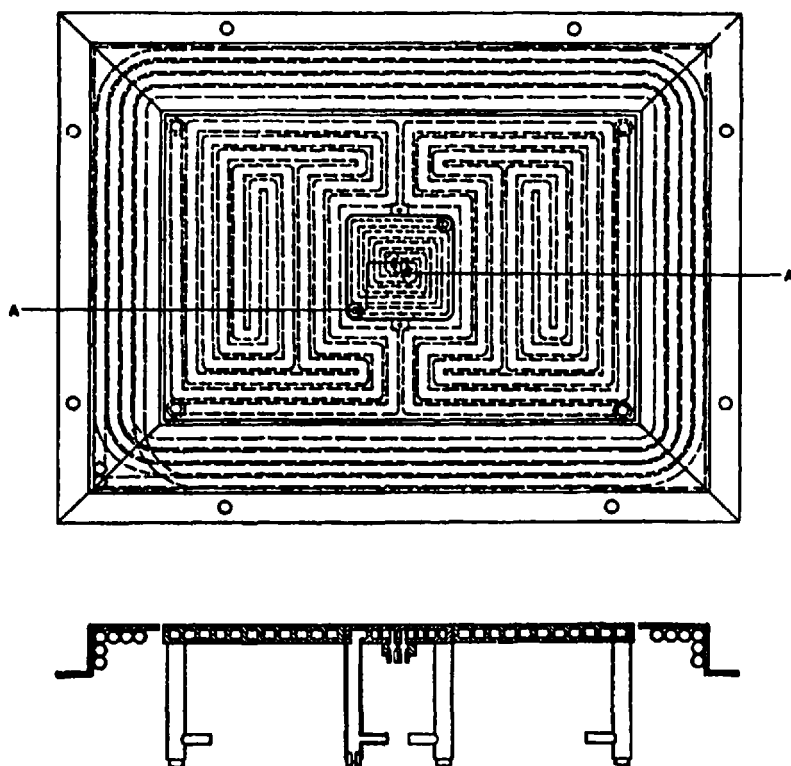


Figure 9.4: Water cooling system specified in ASTM thermal conductivity standard C201. The center-most series of cooling coils makes up the “calorimeter”. Outside of the calorimeter are the “inside guard” cooling coils, which in turn are surrounded by the “outside guard” coils [2].

established by the ratio of these quantities, is not effected. Its presence would be needed to curtail the rate of heat flow into the calorimeter when using moderately (thermally) conductive specimens. Additionally, for investigations at high temperatures, the back-up insulation permits evaluation of specimen thermal conductivity without very large temperature gradients across it, since most of the temperature drop can be across the back-up insulation. Such large specimen temperature gradients make it difficult to attribute measured thermal conductivity to a specific temperature.

The calorimeter method is considered highly accurate. However, many hours (days) are required at a specific furnace temperature in order to establish steady state conditions, hence, establishing a k versus T relationship may take weeks to complete.

9.3 Hot-Wire Method

The hot-wire thermal conductivity method involves the placement of a thin refractory wire (e.g. platinum or nichrome) between two identical refractory plates under investigation. Historically, this is an adaptation of a hot-wire method used in the determination of thermal conductivities of liquids and gases. A constant electrical power is dissipated by the wire as heat into the surrounding refractory, and the temperature of the wire is monitored. If the refractory is highly thermally conducting, the wire temperature will be lower than if the refractory is highly insulating. A schematic of the experimental design is shown in Figure 9.5.

The theoretical model assumes a line heat source dissipating heat radially into an infinite solid, initially at uniform temperature. The fundamental heat conduction equation in cylindrical coordinates, assuming uniform radial heat transfer, is [3]:

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right]$$

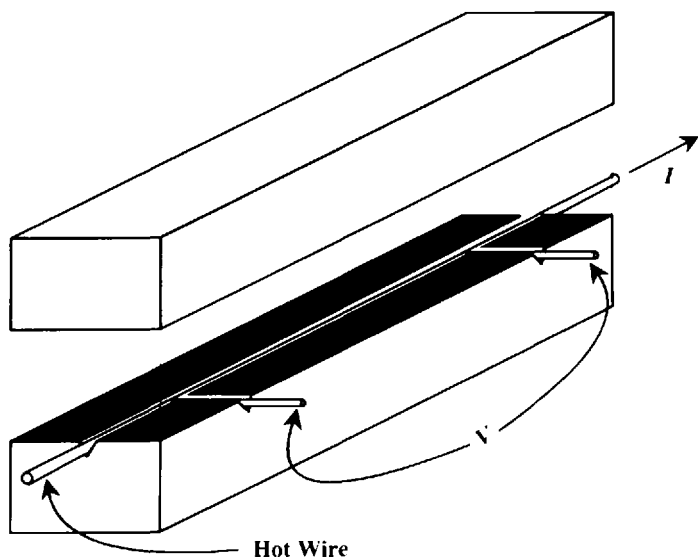


Figure 9.5: Schematic of the hot-wire thermal conductivity test. Refractory bricks would be of the same size as in Figure 9.3.

where r is the radial distance from the center axis of the wire. With an initial condition that the temperature of the wire at zero time is T_0 , and after some time t , boundary conditions: (1) at infinite radial distance from the wire, the temperature is still T_0 , (2) at a radial position within the refractory, approaching the radius of the wire, steady state radial heat transfer occurs. Formally:

$$\begin{aligned} \text{I.C.} \quad & T(r, 0) = T_0 \\ \text{B.C. (1)} \quad & \lim_{r \rightarrow \infty} T(r, t) = T_0 \\ & (2) \quad \left[-2\pi k \frac{\partial T}{\partial r} \right]_{r=r_w} = q_l(t) \end{aligned}$$

The solution [4][5][6] is obtained using Laplace transforms and the convolution theorem [7]:

$$T(r, t) - T_0 = \Delta T(r, t) = \frac{q_l}{4\pi k} E_1 \left(\frac{r^2}{4\alpha t} \right)$$

where q_l is the rate of heat flow per unit length of wire, and k is the thermal conductivity of the surrounding refractory. The function $E_1(r^2/4\alpha t)$ is the first exponential integral which may be expanded:

$$\begin{aligned} E_1 \left(\frac{r^2}{4\alpha t} \right) &= \int_{\frac{r^2}{4\alpha t}}^{\infty} \frac{\exp(-u)}{u} du \\ &= -\gamma - \ln \left(\frac{r^2}{4\alpha t} \right) + \frac{\left(\frac{r^2}{4\alpha t} \right)}{1 \cdot 1!} - \frac{\left(\frac{r^2}{4\alpha t} \right)^2}{2 \cdot 2!} + \dots \end{aligned}$$

where γ is Euler's constant (0.5772). For long times and small values of r , all but the first two terms of the series can be neglected, hence:

$$\Delta T(r, t) = \frac{q_l}{4\pi k} \ln \left(\frac{4\alpha t}{r^2 C} \right)$$

where $C = \ln \gamma$. The radial position r is taken to be at the wire surface r_w , and the temperature of the wire is assumed to be constant throughout its volume. Based on this expression, a plot of $\Delta T(r, t)$ versus log-time should be a linearly increasing function, where the thermal conductivity of the refractory can be directly calculated from the slope, if q_l is known.

The implication of this logarithmic relation is that the temperature of wire initially raises rapidly and then more slowly as the heat flow acts to raise the temperature of greater differential volumes with subsequent differential radial distances. In practice, only a portion of the log-time/temperature plot is linear, as shown in Figure 9.6. The non-linear portion at the start of the curve is a result of steady state conditions not immediately being met at r_w . Similarly, the long-time condition used truncate higher order terms in the expansion of the first exponential integral is not immediately valid. The curvature

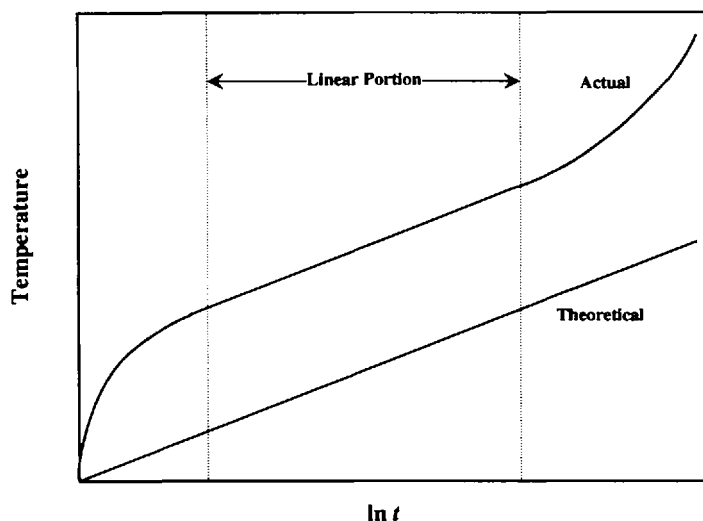


Figure 9.6: Actual and theoretical hot wire curves [8].

after longer times results from the refractory block not actually being of infinite dimensions. Heat cannot conduct/convect from the specimen surface nearly as efficiently as it can conduct through the specimen interior. The additional thermal resistance at the specimen extremes results in an accelerated rate of temperature rise at the hot wire. The linearly increasing portion represents the time period where the heat flow behavior fits the model.

Thermal conductivity measurements are taken at a series of isothermal temperatures, created by an external furnace. The furnace must provide enough stability so that there are negligible temperature gradients within the refractory blocks. The furnace is maintained at a particular temperature for a matter of hours before power is applied to the wire in order to assure temperature uniformity.

The power through the wire can be ac or dc. In order to accurately determine voltage, SCR regulation of ac power is not recommended since the ac waveform is disturbed, mak-

ing RMS voltage measurements difficult. Variacs or integrated circuit amplifiers (used for de-amplification) may be used to vary the ac voltage. Variacs require mechanical (manual or motor-driven) adjustment. Power transistors may be used to vary dc voltage. Voltage is measured via connections at symmetrical points along the hot-wire within the refractory (Figure 8.13). The voltage drop across an interior portion of the wire is measured so that non-uniform heat dissipation through the sidewalls does not effect the measurement. The length of the hot-wire which enters the calculation of q_i is then the length between these two connections. The current in the circuit may be measured using a low ballast resistance (e.g. $0.1\ \Omega$) in series with the hot-wire. The current through the circuit is simply the voltage drop across the resistor divided by the resistance.⁴ The dc current can also be established without interruption of the circuit using a Hall [9] effect device; ac current can be determined using a galvanometer in conjunction with a full-wave rectifier.

Inherent in the derivation of the mathematical model for the technique was a constant power dissipation by the line source (wire). However, as the temperature of the wire increases so does its resistivity, therefore, under a constant voltage supply, the current going through the wire drops. As a result, the power dissipated by the wire decreases with time. A feedback control mechanism on the power dissipated from the wire, based on measuring voltage and current, can alter the voltage across the wire in order to maintain constant power. If the maximum temperature rise of the wire is maintained small (e.g. 20°C), the power variation will be minimized. For minute variations, an average dissipated power over the period of the test might then be used in the calculation.

Various configurations [8, 10] of the test have been demon-

⁴The resistor will need to be about two orders of magnitude lower resistance than the platinum wire so that minimal power is dissipated in the resistor. Further, the resistor would need to be adequately large so that heating from power dissipation within it would not change its resistance.

strated. The predominant difference is in how the temperature of the wire is determined. In one configuration, a thermocouple junction is welded to the center of the hot-wire. The legs of the thermocouple extend perpendicularly in either direction to the hot-wire, and grooves must be cut in the refractory for these wires. A pitfall of this technique is that the thermocouple wires may act as heat sinks for the hot-wire. By using thermocouple wire of minimal diameter and a junction bead as small as possible, the heat extracted by the thermocouple wire will be minimized. As long as the thermocouple junction makes contact with the hot-wire at a single point, the EMF generated by the thermocouple should not be altered by the voltage drop along the hot-wire.

Another configuration for determination of hot-wire temperature is measurement of the resistance of the hot-wire. This exploits the fact that the resistivity versus temperature relationship for platinum has been well characterized. Since the voltage drop across and the current through the hot wire are measured, the resistance of the hot-wire is known ($R = V/I$). The voltage and current measurement must be of high precision in order to determine the temperature of the hot-wire.

A typical test at a particular temperature will last on the order of 10 minutes after power is applied to the hot-wire. Time must be allowed prior to that for thermal equilibrium to be established in the test bricks. Tests are conventionally performed every 200°C. Since temperature gradients are not as great as those in the calorimeter method, the determined thermal conductivities are for a narrower temperature spectrum. Heat leakage through the thermocouple or voltage measurement leads will result in falsely high thermal conductivities being determined; such values are generally not welcomed by the refractories industry. The generally accepted upper limit of thermal conductivity measurement is on the order of 2 W/(m·K), which rules out most high alumina firebricks and basic refractories [12]. With higher thermal conductivity

materials, heat propagates to the ends of the bricks before a linear portion on the temperature-log time plot can be realized.

Revisions to the technique continue to be reported. A “parallel wire” technique has been described wherein the thermocouple wire runs parallel, about 15 mm away from the hot wire [10]. A transient “hot strip” technique for thermal conductivity measurement has also been recently described [13].

9.4 Guarded Hot-Plate Method

The guarded hot-plate method is a steady state axial heat flow measurement of thermal conductivity for disk-shaped specimens. It differs from the calorimeter method in that the heat flow is measured in a similar way as the radial heat flow and hot-wire method; thermal dissipation due to I^2R heating of a central heater. The technique is generally regarded [14] to be the most accurate of the methods listed in this chapter and is covered by the ASTM standard C177 [15]. The experimental configuration for the technique is shown in Figure 9.7. The test specimens are symmetrically placed above and below the main heater. The temperature drop across the specimens ΔT is measured by two thermocouples immersed in each specimen, spaced distance L apart. Assuming perfect symmetry in dimensions, thermocouple junction placement, and heat flow through the upper and lower specimens:

$$\frac{dQ}{dt} = \frac{kA\Delta T}{L} + \frac{kA\Delta T}{L}$$

or:

$$k = \frac{\frac{dQ}{dt} L}{2A\Delta T}$$

In order to guarantee that the heat flow from the metered area is one dimensional, that is, it flows strictly through the specimens and not out of the side walls of the main heater, guard heaters are used (primary guard). Air gaps between the metered area and the guard heaters form a significant thermal

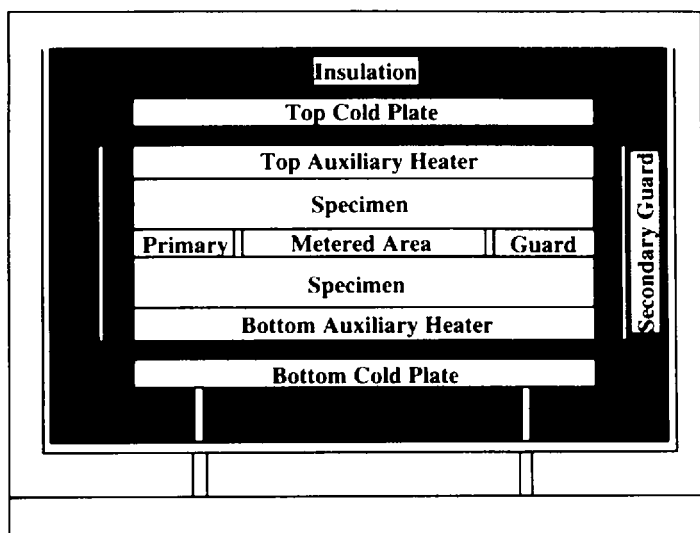


Figure 9.7: Guarded hot-plate method for the measurement of thermal conductivity [15]. Typical specimen dimensions are disks of ~ 25 cm diameter and 5 cm thick [14].

barrier to lateral heat flow. Based on the output of a differential thermocouple, a (PID) feedback control system monitors the temperature of the main heater block (metered area) and maintains the guard heater temperature at the same temperature. Since there is no temperature gradient in the radial direction, no heat will flow in that direction. A secondary heater ring placed outside a gap filled with insulation is used to maintain a high resistance to lateral heat flow out of the specimen slabs. This is an imperfect thermal barrier; but as long as the specimen slabs are thin in the axial direction and long in the lateral direction, no horizontal temperature gradients should be measured near the center of the specimens. Hence, heat flow near the center should be purely axial.

The bottom and top auxiliary heaters can be used to decrease the temperature gradient across the specimens. Since temperature measurements are taken under steady state heat

flow conditions, heat input from the auxiliary heaters does not alter the measurement. The heat input from the individual auxiliary heaters can be adjusted to maintain the temperature drops across the top and bottom specimens the same, if there is some asymmetry.

The bottom and top cold plates are either water or liquid nitrogen cooled, depending on the temperature range of interest for the thermal conductivity measurement. These act as isothermal heat sinks. Thermocouples are positioned in the axial direction for specimen temperature gradient measurements, to reveal any uneven temperature distributions, and to establish an average temperature. The metered area as well as the auxiliary heaters are usually made of refractory metallic housings of significantly higher thermal conductivity than the specimens, in order to minimize temperature variations along the heater-specimen interfaces.

The technique has also been demonstrated with a single specimen. In that case, one of the cold plates is removed and the auxiliary heater on that side is heated to match the temperature of the metered area. Since no temperature gradient exists in that direction, heat generated from the metered area flows uniaxially through the single specimen.

9.5 Flash Method

The flash method entails a short pulse of high intensity energy, absorbed by the front surface of a small specimen shaped in the form of a disk. The radiant energy source can be a (xenon) flash lamp, laser, or electron beam. The energy absorbed on the front surface propagates (conduction, and at higher temperatures, radiation) toward the back surface, as depicted in Figure 9.8.

A number of simplifying assumptions allow for a mathematical model for this method: The radiation pulse is uniformly distributed across the front face of the specimen and is ab-

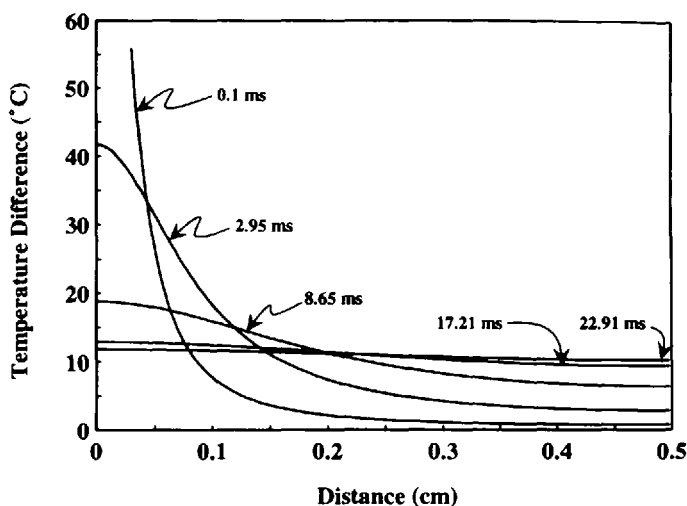


Figure 9.8: Temperature distribution calculated for a 0.5 cm thick alumina specimen, based on $\alpha = 0.007078 \text{ cm}^2/\text{s}$, $c_p = 0.0496 \text{ J/g}\cdot\text{K}$, $\rho = 3.965 \text{ g/cm}^3$, and $Q = 101.521 \text{ J/cm}^2$. Note the increase in temperature, ΔT , of the rear face from 0 to 11°C .

sorbed within a thin layer of specimen relative to its overall thickness. Heat then propagates one-dimensionally toward the back face of a homogeneous specimen. The duration of the pulse is negligible as compared to the time required for heat to propagate through the specimen. Adiabatic conditions are maintained, i.e. no heat losses from the specimen occur during the time frame of the measurement ($\sim 30 \text{ ms}$). With this foundation, Carslaw and Jeager [18]⁵ have developed the diffusion equation for the temperature of the specimen after absorption of the energy burst as a function of time and position:

$$T(x, t) = \frac{1}{l} \int_0^l T(x, 0) dx + \frac{2}{l} \sum_{n=1}^{\infty} \exp\left(\frac{-n^2 \pi^2 \alpha t}{l^2}\right) \cdot \cos\left(\frac{n \pi x}{l}\right) \int_0^l T(x, 0) \cos \frac{n \pi x}{l} dx$$

where ρ is the density (g/m^3), l is the length in meters from

⁵As referenced by [19].

front to back face of the specimen, c_p is the specific heat (J/g·K), and α is the thermal diffusivity (m^2/s). Under initial conditions that a finite thickness g has absorbed the radiant heat Q , and assuming the specific heat is constant with temperature:

$$T(x, 0) = \frac{Q}{\rho c_p g} \quad 0 < x < g,$$

Further assuming that at $t = 0$, no heat has propagated into the remainder of the specimen:

$$T(x, 0) = 0 \quad g < x < l$$

Integrating:

$$\begin{aligned} T(x, t) = & \frac{1}{l} \frac{Qg}{\rho c_p g} \\ & + \frac{2}{l} \sum_{n=1}^{\infty} \exp\left(-\frac{n^2 \pi^2 \alpha t}{l^2}\right) \cos\left(\frac{n\pi x}{l}\right) \left(\frac{Q}{\rho c_p g}\right) \frac{\sin\left(\frac{n\pi g}{l}\right)}{\left(\frac{n\pi g}{l}\right)} \end{aligned}$$

For small g relative to l , $\sin(n\pi g/l) = n\pi g/l$. Thus:

$$T(x, t) = \frac{Q}{l\rho c_p} \left[1 + 2 \sum_{n=1}^{\infty} \cos\left(\frac{n\pi x}{l}\right) \exp\left(-\frac{n^2 \pi^2 \alpha t}{l^2}\right) \right]$$

At the back wall $x = l$, the cosine function simply exchanges between 1 and -1, with successive values of n . This term can be rewritten as $\cos(n\pi) = (-1)^n$. Substituting:

$$T(l, t) = \frac{Q}{l\rho c_p} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2 \pi^2 \alpha t}{l^2}\right) \right]$$

The function within the brackets goes from zero to unity with time, hence the maximum temperature of the back face is:

$$T_{max} = \frac{Q}{\rho c_p l}$$

Defining the unitless quantity t' as:

$$t' = \frac{\pi^2 \alpha t}{l^2}$$

Thus [19]:

$$T' = \frac{T(l, t)}{T_{max}} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 t')$$

The above dimensionless function showing the rise in temperature of the rear face is plotted in Figure 9.9. The time cor-

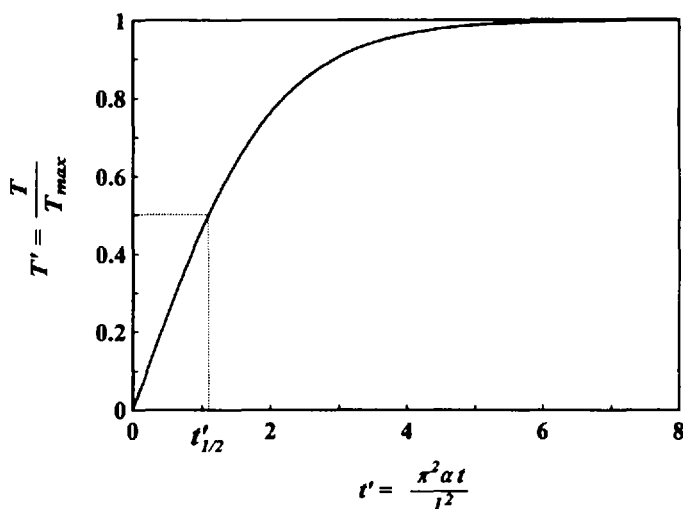


Figure 9.9: Transient temperature response at the specimen back face after laser flash absorption at the the front face.

responding to half the maximum temperature is taken, rather than the time of the maximum temperature, because of the greater clarity in determining its value from the figure. By computer extrapolation at $T'/2$, $t'_{1/2} = 1.09863$.⁶ Hence:

$$\alpha = \frac{(1.09863)l^2}{\pi^2 t_{1/2}}$$

Given that the assumptions of the model have been met experimentally, by determining the time $t_{1/2}$ corresponding to the temperature at half maximum, i.e. $(T_{max} - T_0)/2$, the thermal diffusivity can be determined.

⁶Parker *et al.* [19] determined a different value: $t'_{1/2} = 1.38$.

The temperature rise on the back face is on the order of 5-10°C. The remarkable feature of this technique is that the incident energy on the front face on the specimen need not be known. High speed data acquisition, however, is needed since $t_{\frac{1}{2}}$ is in the 10 ms range. Contemporary data acquisition devices [20] can collect signals at a rate of 10 $\mu\text{s}/\text{value}$. Temperatures can be monitored with low thermal mass thermocouples, but preferentially with sensitive infrared pyrometers.

For the boundary conditions from which the above equation was derived to be valid, the time duration of the flash must be significantly shorter than the time required for temperature rise to appear on the back face. Both pulse lasers and flash lamps are capable of meeting this; the on-time of a flash lamp is on the order of 0.5 ms [21]. It is also necessary that the energy density be uniform across the front face of the specimen.

For the duration of data acquisition, the specimen is under essentially adiabatic conditions. If the energy density to which the specimen is exposed is known, the heat capacity of the specimen can also be determined by this technique after measuring T_m and knowing the specimen density. However, the emittance of the material must be well characterized. This is also true when sensitive infrared detectors are used to measure the temperature of the back face. Thin coatings of carbon-black paint, which are also "black" in the infrared, may be used to give the surfaces near-blackbody behavior. Since it is often difficult to maintain beam uniformity and hence calculate the absorbed radiant flux, the heat capacity is generally determined or calculated by other methods (see section 3.7). Flash diffusivity systems are often used with the specimen in a vacuum chamber, which eliminates gaseous conduction and convection of heat away from the specimen after exposure to the flash, prolonging the adiabatic condition. At elevated temperature it is difficult to maintain adiabatic conditions because of radiation losses.

The energy source of contemporary preference is the pulse

laser, hence the technique is generally referred to as the "laser flash" method for the determination of thermal diffusivity. With the laser, all of the generated energy can be focused on the specimen, instead of emanating radially in all directions. Electron beams have also been used [21].⁷ The specimen holder must be designed to minimize conduction at its contacts. Flash diffusivity has been demonstrated to be effective in measurements over a broad range of thermal diffusivities and with the aid of a stable surrounding furnace chamber, over a broad temperature range. Further, compared to steady state thermal conductivity measurements, the turnover time for results from this apparatus is remarkable. This test requires the smallest specimen size of those described in this chapter (disk, 0.6-1.8 cm diameter and 0.15-0.4 cm thick [14]). Hence, it is the test of choice for the electronic packaging industry.

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⁷Electron beams have the advantage that energy distribution incident on the specimen can be made more uniform.

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Chapter 10

VISCOSITY OF LIQUIDS AND GLASSES

10.1 Background

Viscosity is the resistance of a fluid to flow under an applied load due to internal friction. Its formal definition can be best visualized using Figure 10.1. A viscous fluid resides between

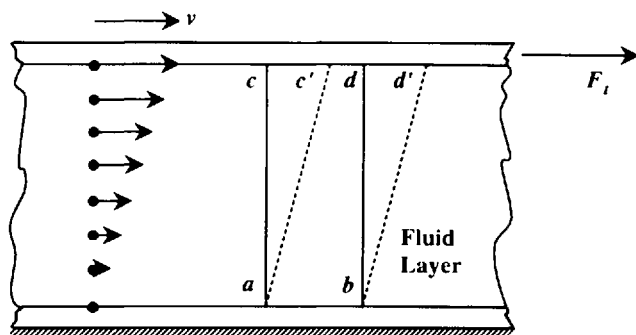


Figure 10.1: Definition of the viscosity of a fluid.

two parallel plates of area A , the inner surfaces of which are separated by a distance x . The lower plate is fixed, while a tangential force is applied to the upper plate. We assume “Newtonian” flow, where the velocity of the fluid between the plates decreases linearly with vertical position. The upper-most edge of the fluid moves at the velocity of the upper plate and the

lower-most edge of the fluid is motionless. This is a laminar flow pattern in which layers of liquid slide over one another, without penetrating into one another, much like the leaves of a book when the book is placed flat on a table and a horizontal force is applied to the top cover.

The shear stress applied to the top plate via the tangential force is $\tau = F_t/A$. For Newtonian fluids, it is found that the velocity gradient dv/dx is proportional to the shear stress¹, the constant of proportionality being the viscosity of the fluid. Viscosity is thus defined:

$$\eta = \frac{\tau}{dv/dx}$$

A highly viscous fluid is thus one that does not shear rapidly under a large shear stress. Using MKS units, viscosity has units of $[\text{kg}/(\text{m} \cdot \text{s})]$ or Pascal-seconds². Viscosity, in older literature, was expressed using the CGS unit “poise” = $[\text{g}/(\text{cm} \cdot \text{s})]$; $1 \text{ Pa} \cdot \text{s} = 10 \text{ Poise}$.

Powder processing of ceramics and metals, using organic binders to make up a fluid slip of appropriate rheological properties, is greatly concerned with optimizing viscosity behavior for specific applications. The viscosity of glasses is an essential characteristic used to determine temperatures at which glass shapes can be formed, worked, sealed, or machined. It is often continuously monitored for quality and process control during industrial glass fabrication.

The viscosity of a gas increases with temperature due to increased kinetic interaction between molecules, which in turn causes increased “viscous drag”. The viscosity of a liquid decreases with temperature due to increased thermal energy, decreasing the activated barrier for one atom to slip around its neighbors, or perhaps equivalently, the increased thermal en-

¹Note that for solids behaving elastically, the shear strain is proportional to the shear stress. For Newtonian fluids, the shear strain rate (velocity gradient) is proportional to the shear stress.

²Multiplying and dividing $[\text{kg}/(\text{m} \cdot \text{s})]$ by $[\text{m} \cdot \text{s}]$ yields $[\text{kg} \cdot \text{m} \cdot \text{s}/(\text{m}^2 \cdot \text{s}^2)]$ which is equal to $[\text{Pa} \cdot \text{s}]$.

ergy expands atomic distances, permitting more free volume for atoms to slip past their neighbors. The viscosity of oxide glasses demonstrates an exponential decrease with temperature, which often fits well over a broad range to the empirical Fulcher equation:

$$\ln \eta = C + \frac{K}{T - T_0}$$

For the glass industry, temperatures at specific viscosities have traditionally been considered important markers. Figure 10.2 shows these points for various glassy systems. At

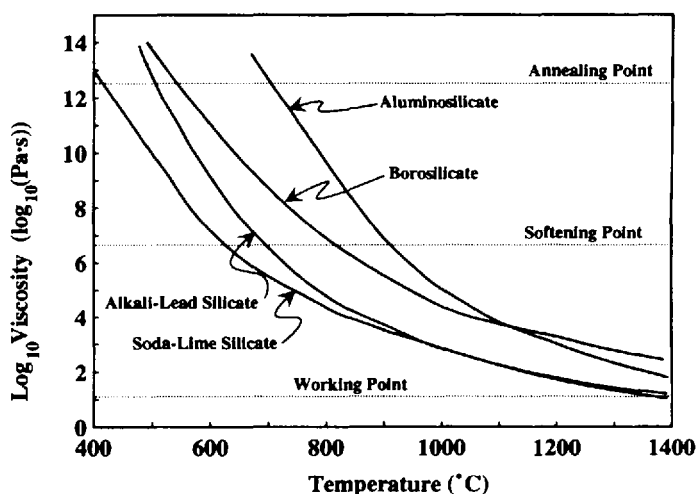


Figure 10.2: Viscosity behavior of various commercially important glass compositions. Approximate compositions in weight percent are—Aluminosilicate: 64 SiO₂, 4.5 B₂O₃, 10.4 Al₂O₃, 8.9 CaO, 10.2 MgO, 1.3 Na₂O, 0.7 K₂O; Borosilicate: 81 SiO₂, 13 B₂O₃, 2 Al₂O₃; Alkali-lead silicate: 77 SiO₂, 1 CaO, 8 PbO, 9 Na₂O, 5 K₂O; Soda-lime silicate: 72.6 SiO₂, 0.8 B₂O₃, 1.7 Al₂O₃, 4.6 CaO, 3.6 MgO, 15.2 Na₂O [2].

least three viscosity/temperature points are needed to determine the constants C , K , and T_0 , from which the entire viscosity/temperature behavior can be known, assuming that the glass follows the Fulcher equation. The viscosity of oxide glasses decreases with the number of non-bridging oxygens e.g. from

introduction of fluxes such as Na_2O into the silicate structure. Although B_2O_3 is a glass network former, it forms a two-dimensional network which lacks the connectivity of a silicate random network. Hence, borosilicate glasses tend to have lower viscosities at any given temperature than high silica (low flux) containing glasses. Alumina can act as a glass former and contribute to the three-dimensional connectivity in an aluminosilicate glass composition. Thus aluminosilicate compositions display a comparatively high viscosity.

When glass is rapidly quenched, the outer portion of the body cools more rapidly than the inner portion, thus more time is permitted for the inner glass to contract, as compared to the outer glass, before the structure becomes too stiff for atomic rearrangement. As a result, stresses exist in the cooled glass from differential contraction. The "strain point" ($\eta \approx 10^{13.5}$ Pa·s) represents a viscosity where the glass is so rigid that internal movement has virtually ceased, and internal stresses can only be relieved after a couple of hours at that temperature. Lower viscosities are generally measured and the strain point is determined by extrapolation, since the glass is too stiff at that temperature. The "annealing point" ($\eta = 10^{12}$ Pa·s) is the temperature at which internal stresses can be relieved in a matter of minutes. This is an important delineation since fabricated glass articles are often re-heated to the annealing temperature in order to relieve these deleterious stresses. The "softening point" is the temperature at which a glass fiber of specific dimensions flows at a specified rate under its own weight. This point refers to a specific experimental test³ (Littleton method [3]) where the viscosity measured with this technique varies with the density and surface tension of the glass. For a standard bottle glass composition, the viscosity is about 4.2×10^6 Pa·s. Glass viscosities at the softening point generally vary from 3×10^6 to 1.5×10^7 Pa·s. The "flow point" ($\eta = 10^4$ Pa·s) is determined

³A rod (fiber) 23.5 cm long and 0.55 to 0.75 mm in diameter elongating at 1 mm/min under its own weight when the upper 10 cm is heated at 5°C/min.

by the time required to completely melt off a short fiber with a light load attached. The “working point” ($\eta = 10^3$ Pa·s) of the glass is determined by measuring the time required for a small platinum/rhodium rod to sink a specified distance in molten glass. The melting point⁴ ($\eta = 10$ Pa·s) represents the appropriate viscosity of molten glass in a glass tank. This would be the state after batch constituent fusion, fining, and homogenization.

Experimental techniques such as those used to measure specific values of viscosity (e.g. softening point) are still in common use, but are not as powerful as those in which a range of viscosities can be measured. Hence, only the Margules (1 to 10^6 Pa·s), parallel plate (10^3 to 10^8), and beam bending viscometers (10^7 to 10^{14} Pa·s) will be discussed here. These devices are manufactured and marketed by Theta Industries.

10.2 Margules Viscometer

As shown in Figure 10.3, a spindle (often made of platinum for high temperature work) is inserted a known depth into a viscous fluid. In one configuration, the crucible (made of the same material as the spindle) is rotated at a known rate and the torque on the spindle applied via the fluid is measured. This is essentially an angular measurement of the definition of viscosity, described in Figure 10.1. In some designs, the crucible is fixed and a spindle is connected through a spring system such that when the spindle rod is rotated, the lag angle of the spindle is related by Hooke’s law to the torque applied to it⁵.

This device is calibrated using NIST standard fluids (oils), where spindles are inserted to a known depth and either the crucible or the spindle is rotated at a known speed. The actual

⁴Glass, of course, does not have a melting point, since at room temperature it maintains a “frozen liquid” structure, which gradually changes to a mobile fluid with increasing temperature.

⁵Such a device is manufactured by Haake Buchler Instruments.

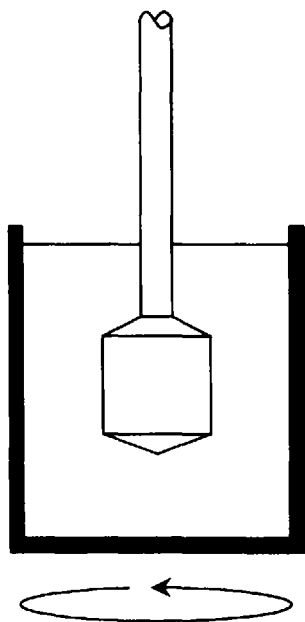


Figure 10.3: Schematic of Margules viscometer.

speed and torque values need not be fundamentally known as long as the output of these values from the instrument are consistent and linearly related to their fundamental units. A calibration constant G can be determined comparing the NIST viscosity data to the ratio of torque S to rotational velocity n :

$$G = \eta \frac{n}{S}$$

The following expression, derived in section 10.3 may be used for absolute measurements of viscosity:

$$\eta = \frac{\Gamma \left[\frac{1}{r_0^2} - \frac{1}{r_1^2} \right]}{4\pi L\omega}$$

where Γ is the measured torque on the spindle, r_0 is the inner radius of the crucible, r_1 is the radius of the spindle, L is the length of the spindle, and ω is the angular velocity of the crucible.

This method works well for viscosities from 1 to 10^3 Pa.s. For somewhat higher viscosities, the torque on the spindle becomes excessive. For these viscosities, a crucible rotation speed is selected so that the spindle lag is near the maximum measurable value. The rotation is then stopped, and the spring loading of the spindle is then allowed to drive the spindle back to its rest point (zero torque). The elapsed time between two selected angles from the rest point is measured during the return. The viscosity is then measured from the following equation [4]:

$$\eta = \frac{K' \Delta t}{\ln(\theta_1/\theta_2)}$$

where Δt is the elapsed time, θ_1 and θ_2 are the selected angles, θ_1 being the larger, and K' is the apparatus constant.

With these two techniques, a complete viscosity curve from about 1 to 10^6 Pa.s can be determined. The greatest potential source of error is from temperature gradients in the tested glass. To avoid spillage, tube furnaces must be mounted vertically, which is a configuration more prone to temperature gradients, yet viscosity varies exponentially with temperature. Minimization of crucible and spindle dimensions will diminish temperature gradients. A correlation between thermocouple junction temperature (often in spring-loaded contact with the bottom of the crucible for the motionless crucible case) and mean glass temperature will also need to be considered.

10.3 Equation for the Rotational Viscometer

While all of the viscosity measurements can be calibrated using well-characterized viscosity standards, the viscosity using these instruments may in fact be calculated from first principles. As an example, a derivation in full is provided for the Margules viscometer:

An element of an elastic solid body under a shear stress deforms as shown in Figure 10.4. The shear strain (deformation)

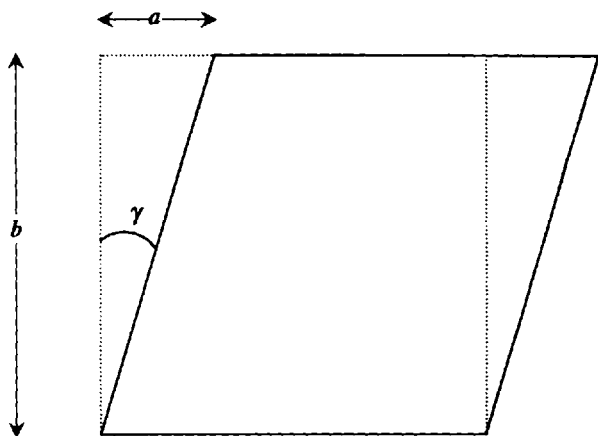


Figure 10.4: Definition of shear strain.

is defined as the ratio of distances a and b . Since $a/b = \tan \gamma$ and for small angles $\tan \gamma = \gamma$, the shear strain is simply the angle γ (in radians).

If we expose a cylindrical elastic solid to a torsional stress, then we would expect a distortion in an element of the body as shown in Figure 10.5, where dimensions are depicted in cylindrical coordinates r and θ . The system is simplified to two dimensions. We wish to determine the shear strain caused by moving the differential element $ABCD$ (of dimensions dr and $d\theta$) to $A'B'C'D'$. Moving point A to point A' involves shifting the point radially by g_r and tangentially by g_θ . Moving point D to point D' involves shifting the point radially by g_r plus a distance corresponding to how the radial displacement changes with angle, $\partial g_r / \partial \theta$, multiplied by $d\theta$. Hence, moving point D involves a radial shift of $g_r + \frac{\partial g_r}{\partial \theta} d\theta$. Similarly, moving point D to point D' involves shifting the point tangentially by $g_\theta + \frac{\partial g_\theta}{\partial r} dr$.

In order to determine the shear strain incurred by the element, we must determine the change in angle between AD and

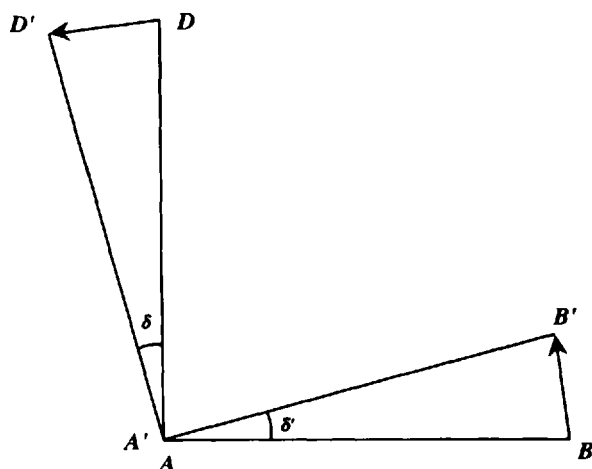


Figure 10.6: Angles between differential elements before and after shear strain.

For elastic bodies, the shear stress is related to the shear strain by the shear modulus. For viscous fluids, the shear stress is related to the shear strain *rate* by the viscosity. We note that for laminar viscous flow in a Margules viscometer (Figure 10.7), radial fluid displacement is zero ($g_r = 0$). Thus, differentiating with respect to time:

$$\dot{\gamma} = \frac{dv_\theta}{dr} - \frac{v_\theta}{r} = \frac{\tau}{\eta}$$

where $\dot{\gamma} = d\gamma/dt$, $v_\theta = dg_\theta/dt$, and τ is the shear stress exerted on the spindle (radius r_0) through the viscous fluid by the rotating crucible (radius r_1). Recognizing that:

$$\frac{d}{dr} \left(\frac{v_\theta}{r} \right) = \frac{1}{r} \left(\frac{dv_\theta}{dr} - \frac{v_\theta}{r} \right)$$

substituting:

$$\frac{d(v_\theta/r)}{dr} = \frac{d\omega}{dr} = \frac{\tau}{\eta r}$$

where ω is the angular velocity ($v_\theta = \omega r$).

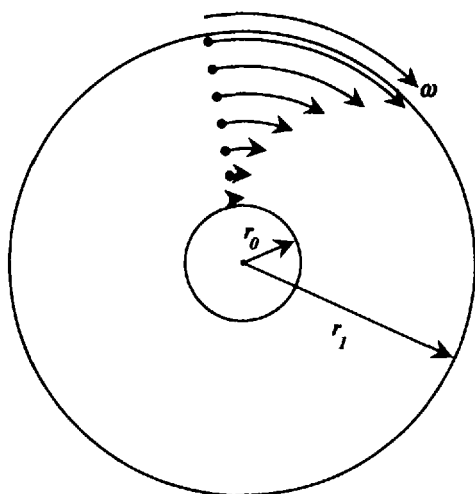


Figure 10.7: Two concentric cylinders with a viscous fluid between: Margules viscometer.

The torque at any given point is the radial distance r multiplied by the tangential force (shear stress multiplied by the cylindrical area):

$$\Gamma = r\tau(2\pi rL)$$

Substituting for shear stress:

$$\frac{d\omega}{dr} = \frac{\Gamma}{2\pi L\eta r^3}$$

Integrating from r_0 to r_1 and rearranging:

$$\eta = \frac{\Gamma \left[\frac{1}{r_0^2} - \frac{1}{r_1^2} \right]}{4\pi L\omega}$$

Even with this equation, the “end effects” associated with the conical bottom end of the cylinder and the shaft extending from the top of the cylinder must be accounted for [5][6]. The longer the cylinder, the less significant the error introduced by the end effects will be. Hence, by testing a fluid using cylinders of equal radius but increasing lengths the “apparent viscosity”

as determined by the above equation will approach the correct viscosity. By plotting apparent viscosity versus reciprocal spindle length, an extrapolation to zero reciprocal spindle length (infinite spindle length) will yield the absolute viscosity of the fluid. Such an extrapolation was used on commercial castor oil in Figure 10.8. From the extrapolated absolute viscosity,

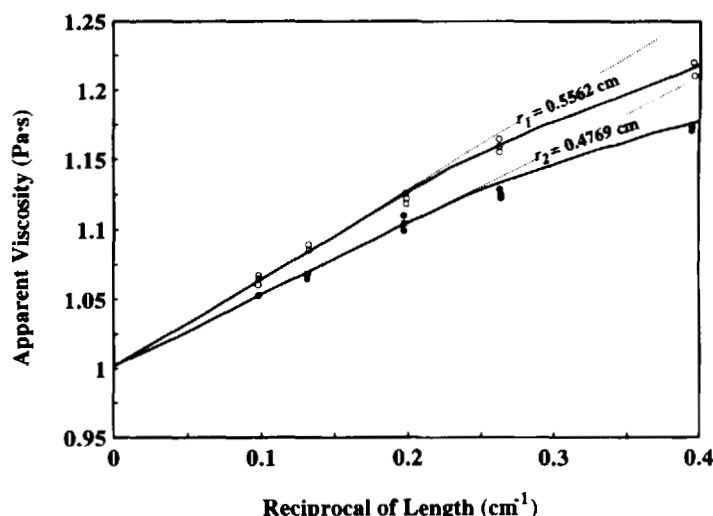


Figure 10.8: Apparent viscosities of castor oil using two spindle radii at a series of lengths [6].

an additional length can be added to the length of a spindle of finite dimensions as a calibration factor, accounting for end effects. Using this “effective length” in the above expression for viscosity will yield absolute viscosities for all viscous fluids using that spindle.

10.4 High Viscosity Measurement

10.4.1 Parallel Plate Viscometer

As shown in Figure 10.9, the parallel plate viscometer involves measuring the rate of compression of a fluid between two paral-

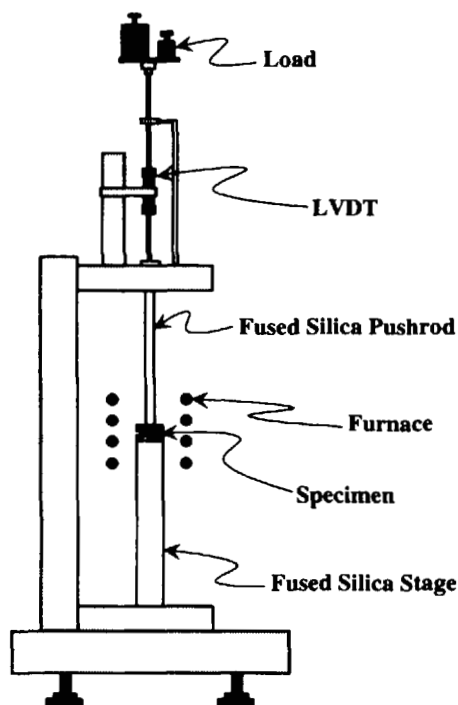


Figure 10.9: Schematic of a parallel plate viscometer.

parallel plates under a known load. Viscosities in a range bracketing the softening point, 10^4 to 10^8 , Pa·s can be measured. As can be seen in the figure, the load is provided in the form of a mass on a platform, transferred to the specimen through a pushrod assembly. The compression of the cylindrical specimen is detected by an LVDT, transducing the motion of the magnet which is part of the pushrod assembly.

As with dilatometry, specimen sizes are relatively large. As a result, temperature gradients within the specimen become a concern, especially considering the exponential temperature dependence of viscosity. The two parallel plates are usually

made out of thin alumina substrates,⁶ and the contact material to the fused silica pushrod and to the fused silica stage is generally a metallic alloy (inconel), whose comparatively high thermal conductivity acts to minimize radial specimen temperature gradients. A cylindrical inconel jacket between the specimen and the furnace windings is also used in an effort to minimize heat flow non-uniformity in the region of the specimen.

A second fused silica pushrod can be placed in rigid contact with the inconel stage and LVDT housing. This is a configuration similar to the double pushrod dilatometer wherein the expansion of the stage moves the LVDT housing. The expansion of the inconel on the pushrod and thin alumina substrates would still not be compensated for. The viscosity can be determined by the following expression [8][9][10]:

$$\eta = \frac{2\pi Mgh^5}{3V \frac{dh}{dt} (2\pi h^3 + V)}$$

where M is the applied load, g is gravitational acceleration, h is the height of the specimen, and V is the volume of the specimen. The fifth power dependence on h makes the accuracy of this dimensional measurement of greatest importance to the accuracy of viscosity measurement.

Viscosities are generally determined by heating to an isothermal temperature of interest and holding, measuring h and dh/dt as a function of time. Only moderate heating schedules to the isothermal temperature are needed, as long as the load is not applied until the isothermal portion is reached. Slow approach ramps have the advantage that temperature gradients in the specimen at the beginning of the measurements can be

⁶The wetting characteristics between the glass and the substrate are important since for the assumption of a Newtonian fluid to be valid, no slip between the top surface of the glass and the substrate can occur. Alumina substrates appear to satisfy these conditions for silicate glasses [11]. Another expression has been derived for conditions of perfect slip [7] which can be experimentally approached by using graphite powder as lubricant at the glass-pushrod interface.

kept at a minimum. While the specimen volume remains constant, its dimensions do not. As the specimen compresses, its cross-sectional area increases. Hence, dh/dt will not be constant with time. However, the viscosity as determined by the above equation should be constant with time. The instantaneous slope of the specimen compression dh/dt can be determined via the techniques described in section 4.2. Isothermal measurements have the advantage of eliminating the effects of pushrod expansion. If the specimen compression is acceptably slow, viscosity measurements at a series of temperatures with the same specimen are feasible using a step-wise temperature schedule.

The parallel plate viscometer does not require fiber formation in order to determine the softening point of glass. This is advantageous when the glass has a high devitrification tendency. The test takes on the order of two hours, which has a time advantage over rotating spindle techniques in the higher viscosity ranges. Viscosity values of 10^5 to 10^9 Pa·s can be measured using this technique [11].

10.4.2 Beam Bending Viscometer

The beam bending viscometer is depicted in Figure 10.10. A glass beam of uniform cross section is extended across an alumina muffle. Using a sapphire or fused silica hook, a load is applied at the center of the beam. The deformation rate of the center of the beam is measured, and the viscosity is determined by [12]:

$$\eta = \frac{gS^3}{2.4I_c v} \left(M + \frac{\rho AS}{1.6} \right)$$

where S is the span of the glass beam between supports in centimeters, I_c is the cross-sectional moment of inertia of the test beam, in cm^4 , v is the midpoint deflection rate (cm/min), A is the cross sectional area of the beam (cm^2), ρ is the density of the glass (gm/cm^3), and M is the applied load. This

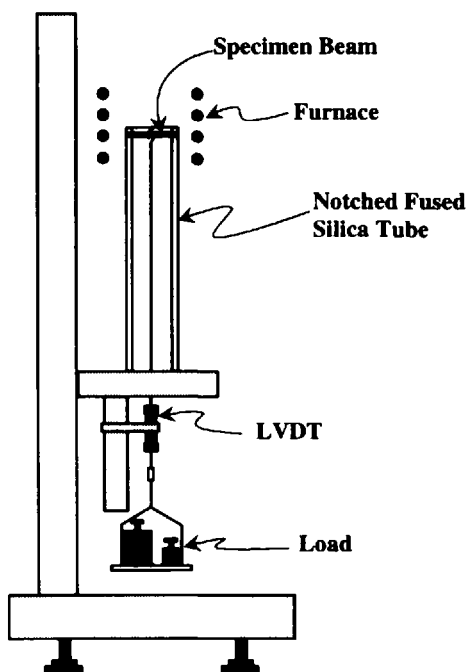


Figure 10.10: Schematic of the beam bending viscometer.

viscometer is useful for measurement of the highest range of viscosities.

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Appendix A

INSTRUMENTATION VENDORS

A.1 Thermoanalytical Instrumentation

1. Anter Laboratories, Inc., Unitherm Division, 1700 Universal Road, Pittsburgh, PA 15235-3998. Phone: (412) 795-6410.
2. Cahn Instruments, Inc., 16207 S. Carmenita Road, Cerritos, CA 90701. Phone: (213) 926-3378.
3. Haake Buchler Instruments, Inc., 244-T Saddle River Rd., Saddle Brook, NJ, 07662. Phone: (201) 843-2320.
4. Harrop Industries, Inc, 3470 East Fifth Avenue, Columbus, OH, 43219-1797. Phone: (614) 231-3621.
5. Innovative Thermal Systems, 3916 Chaucer Wood, NE, Atlanta, GA, 30319. Phone (404) 894-6075.
6. Linseis Inc., P.O. Box 666, Princeton Jct., NJ. Phone: (800) 732-6733.
7. Mettler Instrument Corp., Box 71, Hightstown, NJ 08520-0071. Phone: (609) 448-3000.
8. Mitsubishi International Corp., 200 E. Howard St., Des Plaines, IL 60018. Phone: (708) 298-9320.

9. Netzsch-Gerätebau GmbH, D-8672 Selb, Wittelsbacherstr. 42, P.O. Box 1460. Phone: (09287) 881-0. USA Representative: Netzsch Inc., 119 Pickering Way, Exton, PA 19341-1393. Phone: (215) 363-8010.
10. Edward Orton Jr. Ceramic Foundation, P.O. Box 460, Westerville, OH 43081. Phone: (800) 999-5442.
11. Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0993. Phone: (800) 762-4002.
12. Polymer Laboratories, Thermal Sciences Division, Amherst Fields Research Park, 160 Old Farm Road, Amherst, MA 01002. Phone: (413) 253-9554.
13. Seiko Instruments USA, Scientific Instruments Division, 2990 W. Lomita Blvd., Torrance, CA 90505. Phone: (310) 517-7880.
14. Setaram, 160, boulevard de la Republique, 92210 Saint-Cloud, France. Phone (1) 47 71 68 33. USA Representative: Astra Scientific International, Inc., 1961 Concourse Drive, San Jose, CA 95161-1088. Phone: (408) 433-3800.
15. TA Instruments, Inc., 109 Lukens Drive, P.O. Box 311, New Castle, DE 19720-0311. Phone: (302) 427-4000.
16. Theta Industries, 26 Valley Road, Port Washington, NY, 11050. Phone: (516) 883-4088.
17. Ulvac Sinku-Riko, Inc., 300, Hakusan-cho, Midori-ku, Yokohama, 226, Japan. Phone: 81-45-931-2221.

A.2 Furnace Controllers and SCR's

1. Barber-Coleman Co., Industrial Instruments Division, 1354 Clifford Ave., Loves Park, IL, 61132. Phone (815) 877-0241

2. Eurotherm Corporation, 11485 Sunset Hills Road, Reston, VA 22090-5286. Phone (703) 471-4870.
3. Leeds and Northrop, a unit of General Signal, 351 Sumneytown Pike, Box 2000, North Wales, PA 19454. Phone (215) 699-2000.

A.3 Heating Elements

1. Kanthal Corp., Furnace Products Division, P.O. Box 502, S-73401 Hallstahammar, Sweden, Phone: 46 220 21600, USA Address: 119 Wooster St., Bethel, CT 06801. Phone: (203) 744-1440.
2. Deltech Inc., 750 W. 39th Ave., Denver, CO, 80216. Phone: (303) 433-5939.
3. Carborundum Company, Electric Products Division, P.O. Box 664, Niagara Falls, NY 14302. Phone: (716) 278-6241.

A.4 Optical Pyrometers

1. Ircon, Infrared Measurement Division of Square D Company, 7301 North Caldwell Ave., Niles, IL 60648. Phone: (800) 323-7660.
2. Omega Engineering, Inc., P.O. Box 2284, Stamford, CT 06906. Phone: (800)872-9436.

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Appendix B

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INDEX

- α - β quartz transformation, 63
- A/D converters, 105
- absolute minima using Simplex, 152
- absolute zero temperature, 4
- accidental specimen melting, 175
- activation energy, 63, 150
- adiabatic conditions, 246
- advanced applications of DTA/TG, 143
- alumina-silica system, 58
- aluminosilicate glasses, 254
- amorphous materials (see glasses)
- amplification of transducer signals, 105
- annealing point, 254
- Anter Laboratories, 228
- apparent viscosity, 261
- Archimedes' principle, 116
- Arrhenius equation, 67, 149
- atmospheric effects on DTA, 81
- atmospheric transmittance, 223
- attractive atomic forces, 168
- automatic control systems, 28
- auxiliary heaters, 241
- axial heat flow, 241
- β -quartz structure, 179
- back-up insulation, 232
- band gap, 11
- baseline shift, 77
- beam bending viscometer, 265
- beam splitter, 192
- best fit line, 95
- binary numbers, 106
- bits, 106
- blackbody definition, 205
- blackbody cavity, 205
- boiling, 54
- bonding related to expansion, 169
- Borchardt and Daniels, 46
- borosilicate glasses, 254
- brightness temperature, 214
- buoyancy effects, 116
- Cahn, 21
- Cahn microbalance, 111
- calcium carbonate (calcite), 57, 126
- calcium oxalate, 120
- calibration
 - dilatometry, 173
 - disappearing filament pyrometer, 211
 - energy, 49
 - temperature, 49, 99
 - thermogravimetry, 118
- calorimeter, 232
- calorimeter method, 231
- calorimetric measurements, 44, 48, 216
- calorimetric method for spectral emissivity determination, 216
- Carnot engine, 4

- casing: dilatometry, 169, 173, 175
- castor oil, 262
- Celsius, 4
- centigrade, 4
- central heater, 228
- centroid, 146
- coefficient of expansion, 98
 - linear, 165
 - volume, 166
- cold junction compensation, 17
- commercial thermocouples, 18
- compensating lead-wire, 17
- compensator plate, 192
- computer modeling, 144
- conduction, 199
- conduction band, 11
- constant force dilatometer, 177
- constantan disk DTA, 72
- contact resistance, 204
- contraction, 146
- control thermocouple, 37
- convection, 199, 203
- convolution theorem, 235
- core: LVDT, 171
- corrosive gases: effect on TG, 113
- creep, 179
- critical temperature, 64
- cryogenic furnaces, 22
- Curie temperature, 64, 119
- Curie temperature calibration for TG, 119
- cut and weight method, 91
- data
 - acquisition, 105
 - derivatives, 95
 - extrapolation, 104
 - subtraction, 74, 102
- dead band, 29
- Debye temperature, 70, 169
- decomposition, 56
 - kinetics using TG, 159
 - model, 148
 - reactions, 81
- deconvolution, 143
- Deltech, 22
- derivative control, 30
- derivative thermogravimetry, 114
- deviations from ideality: hot wire method, 237
- differential scanning calorimeter, 1, 37
- differential thermal analysis, 1, 35
- differential thermocouple, 35
- diffusion equation for flash diffusivity, 243
- digital
 - data acquisition, 105
 - filter, 107
- digital displacement transducer, 173
- dilatometric softening point, 182
- dilatometry, 1, 165
- dilution, 75
- dipole moments, 65
- disappearing filament pyrometry, 211
- dispersion toughened ceramics, 182
- displasive transformations, 63
- dolomite, 36, 114, 126
- DSC mode, 53
- DTA/DSC calibration, 49
- dual pushrod dilatometer, 171
- dust and smoke, 218
- effective length, 262
- effective thermal conductivity, 203
- electron thermal conductivity, 203
- electron beams, 247
- emissivity, 208
- emittance, 209
- end effects: viscosity, 261
- endothermic transformations, 36
- energy, 2
- energy calibration, 49
- enthalpy, 43
- enthalpy of melting versus boiling, 56
- Euler's constant, 236
- exact differentials, 3
- exit gas bubbling, 113

- exothermic transformations, 36
- expansion, 146
- expansion polynomials, 174
- experimental concerns
 - dilatometry, 175
 - DTA/DSC, 80
 - TG, 111
- exponential decay, 51
- 4-20 mA current instruction, 24
- Fahrenheit, 4
- false contraction, 176
- feldspar, 126
- ferromagnetic, 26
- ferromagnetic materials, 64
- ferromagnetic/paramagnetic transformation in nickel, 66
- film conductance, 204
- first exponential integral, 236
- first law of thermodynamics, 2
- first order reaction, 149, 159
- first order transitions, 63
- Fizeau fringes, 191
- flash duration, 246
- flash method, 242
- flow point, 254
- forced convection, 203
- Fourier's law, 200
- fraction transformed, experimental determination, 45
- free convection, 204
- free electron model, 12
- Fulcher equation, 253
- furnace feedback control, 23
- furnaces, 19
- gas
 - corrosive: effect on TG, 113
 - evolution, 83
 - reactions with, using DTA, 80
 - viscosity, 252
- gas flow tube
 - centering: effect on DTA, 72
 - diameter: effect on TG, 115
- gate current, 23
- gauge block, 173
- glass
 - aluminosilicate, 254
 - batch fusion, 125
 - borosilicate, 254
 - cadmium-germanium-arsenide, 62
 - ceramics, 179
 - DTA trace, 40
 - spectral transmittance, 222
 - thermal conductivity, 202
 - to metal seals, 184
 - transformation temperature, 182
- gold, 214
- graphite heating elements, 22
- grey filter, 212
- greybody, 208
- guard bricks, 231
- guarded hot-plate method, 240
- guards: calorimeter method, 232
- Haake Buchler, 255
- Haidinger fringes, 191
- half-maximum temperature, 245
- Hall effect device, 238
- hanging cable method, 121
- Harrop, 21, 120
- heat, 2
- heat capacity, 44, 246
 - baseline shifts in DTA, 70, 75, 76
 - change at T_g , 183
- heat conduction equation, 234
- heat to energy relation, 44
- heat transfer, 199
- heat-flux differential scanning calorimeter, 40
- heated capillary, 125
- heating rate, 85
 - dilatometry, 175
 - DTA, 85
 - TG, 115
- higher order transitions, 63
- horizontal gas flow: TG, 118

- hot strip method, 240
- hot wire
 - method, 234
 - temperature by resistance, 239
- impedance matching, 27
- indium, 85
- induction heating, 210
- inexact differentials, 3
- infinite heat capacity, 63
- infrared heating furnace, 22
- infrared pyrometry, 220
- instrument design
 - differential scanning calorimetry, 38, 74
 - differential thermal analysis, 35, 74
 - dilatometry, 169
 - thermogravimetry, 112, 113
- integral control, 30
- interference from thin films, 191
- interferometry, 165, 186
- interferometry: fundamental equation, 191
- internal energy, 2
- Iron, 223
- irreversible transformations, 60
- isothermal crystallization, 67
- Johnson-Mehl-Avrami equation, 66
- Kanthal, 20, 22
- Kelvin, 4
- kinetic barrier, 63
- kinetics of transformations, 60
- kyanite, 165
- lag, 71
- lambda transitions, 64
- Laplace transforms, 235
- laser flash, 247
- latent heat
 - fusion, 53
 - transformations, 64
- law of intermediate elements, 14
- law of successive potentials, 15
- least squares, 95
- LeChatelier's principle, 50
- light interference, 187
- linear variable differential transformer (LVDT), 171
- local minima, 152
- magnesium carbonate, 81
- manipulation of data, 91
- Margules viscometer, 255
- martensitic transformations, 63
- mass spectrometry, 122
- mean atomic distance, 169
- mean free path, 203
- mechanism constant, 67
- melting, 49
 - model, 146
 - related to expansion, 169
 - standards, 49, 102
- metals: thermal conductivity, 203
- metastability, 63
- Michelson interferometer, 191
- micrometer, 173
- model solid state transformations, 179
- molybdenum disilicide heating elements, 21
- monochromatic light, 192
- mullite, 58
- negative coefficient of resistance, 10
- Netzsch, 21, 122
- Newtonian flow, 204, 251
- Newton's law of cooling, 204
- nichrome wire, 20
- nickel block DTA, 72
- null balance, 39
- numerical integration, 91
- on-off control, 29
- on-off oscillation, 29
- optical DTA, 60
- Orton, 6, 21

- pan floating, 115
- parallel plate viscometer, 262
- parallel ramping, 30
- parallel wire method, 240
- paramagnetic materials, 64
- particle packing, 81
- particle size, 81
 - effect on reaction path, 138
 - glass batch fusion, 128
- path independence, 3
- Pauli exclusion principle, 10
- peak shape, 51
- Perkin-Elmer, 9, 40, 53
- phase diagrams, 58
- phase equilibria, 58
- phonon heat transfer, 201
- photo-cell detector, 112
- photon conductivity, 203
- Planck's blackbody equation, 206
- platinum
 - disk DTA, 72
 - furnace windings, 21
 - resistance temperature detector, 9
 - taut band, 111
- poise, 252
- Polymer Laboratories, 121, 122
- polymorphic transformations, 63
- polynomial regression, 99
- popcorn, 159
- post-type DTA, 72
- potential well for vibrating atoms, 169
- power transformers, 26
- power transistors, 238
- power-compensated DSC, 37, 61, 62
- power-compensated vs. heat-flux DSC, 62
- primary
 - LVDT, 172
 - transformer, 25
- proportional integral derivative control, 27
 - derivative control, 30
 - integral control, 30
 - proportional control, 29
- pushrod, 169
- pushrod force: dilatometry, 177
- pyrometric cones, 5
- pyrometry, 299, 210
- quartz, 126
- radial heat flow, 227
- radiation, 199, 205
- rate constant, 149
- rate controlled sintering, 185
- reaction order, 160
- reactions with gases: DTA/DSC, 80
- reconstructive transformations, 63
- recrystallization, 83
- reference mass, 75
- reflection, 146
- repulsive atomic forces, 168
- resistance temperature transducers, 9
- resolution: interferometry, 194
- reversible transformations, 49
- rigid body rotation, 259
- rotating sector disk, 212
- rotational viscometer, 255
- S-shaped curve, 46
- sample dimensions, 85
- sample mass, 61, 75, 81
- sapphire, 202
- sapphire light guides, 220
- scaling, 146
- second order transitions, 64
- secondary
 - LVDT, 172
 - transformer, 26
- secondary heater, 241
- Seebeck voltage, 14
- Seiko, 121
- self-adjusting controllers, 32
- self-feeding reactions, 61

- semiconductor, 10
- semiconductor-controlled rectifiers (SCR), 24
- servo mechanism, 112
- Setaram, 120, 121
- setpoint temperature, 29
- setting PID constants, 32
- shear strain, 258
- shrinkage rate controlled sintering, 185
- siderite, 81
- signal noise filtering, 106
- silicon carbide heating elements, 21
- Simplex algorithm, 144
- simultaneous thermal analysis, 120
- single pushrod dilatometer, 169
- single wavelength assumption, 214
- sintering, 185
- smoothing data, 99
- soda ash, 126
- soda-lime-silica glass: spectral transmittance, 221
- sodium disilicate, 133
- sodium metasilicate, 135
- softening point, 254
- solid state detectors, 221
- specific heat
 - definition, 45
 - experimental determination, 79
- spectral emissivity
 - definition, 207
 - experimental determination, 214
- spectral radiancy, 207
- spectral radiancy pyrometer, 211
- spindle, 255
- stabilized zirconia, 180
- state functions, 3
- steady state heat transfer, 200
- Stefan-Boltzmann constant, 207
- step down transformer, 26
- step up transformer, 27
- Stephan's law, 210
- strain hardening, 83
- strain point, 254
- stroke: LVDT, 176
- superimposed DTA and TG, 128
- superposition principle, 143
- suspended wire calibration for TG, 118
- TA Instruments, 21, 40, 73, 117
- target tubes, 220
- temperature, 2,3
 - anomaly, type B thermocouples, 19
 - calibration, 49, 99
 - gradients, 85, 118
 - lag in DTA/DSC, 71
- theoretical origins of thermal expansion, 168
- thermal conductivity, 200
 - measurement, 227
 - gases, 200
- thermal diffusivity, 200
- thermal energy, 3, 70
- thermal expansion
 - matching, 184
 - reference point, 165
- thermal Ohm's law, 5, 200
- thermal shock, 179
- thermistor, 10
- thermocouple, 12
 - cold junction compensation, 17
 - commercial, 18
 - compensating lead-wire, 17
 - control, 37
 - junction beads, forming, 19
 - placement: TG, 115, 118
 - polarity determination, 19
 - polynomials, 15, 99
 - shielding, 115
- thermodilatometric analysis, 179
- thermodynamic constants, 42
- thermodynamic data from DTA, 46
- thermogravimetric analysis, 1, 111
- thermomechanical analysis, 179
- thermometer, 3

- thermopile, 219
- Theta Industries, 171, 178, 255
- three zone furnace, 231
- thyristor, 23
- total radiation pyrometry, 218
- transformation
 - models, 144
 - onset determination, 40
 - toughened zirconia, 180
- trapezoidal method of integration, 92
- triac, 23
- true expansion, 171
- tungsten lamps, 220
- two-color pyrometry, 216
- two-slit experiment, 187
- Ulvac/Sinku-Rico, 22, 194
- unmatched total heat capacity in DTA/DSC, 70
- vacuum atmosphere: TG, 118
- valence band, 11
- vertical dilatometers, 177
- viscosity: definition, 251
- viscosity of liquids and glasses, 251
- visual acuity, 214
- water, 54
- wavelength selection: infrared pyrometry, 221
- Wein's displacement law, 205
- x-ray diffraction, 60, 127
- zero crossover, 24
- zirconia
 - heating elements, 22
 - refractories, 179
 - transformation toughened, 180