

MECHANISMS OF HIGH TEMPERATURE CORROSION: a kinetic approach

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PREFACE

The oxidation of metals is usually a reaction between a gas and a solid which produces a solid reaction product. At first glance, this would seem to be a very simple process, but in actuality, it is considerably more complex. One would think that the reaction product, i.e., the scale that formed on the metal, acts as a physical barrier between the reactants, and thus the reaction should cease after the barrier is established. We know that this is not the case, because transport of matter through the scale causes the reaction to continue. We also know that the scale may not be dense and adherent to the substrate, but it may be cracked, partially spalled, partially detached (wrinkled), or even very porous. In some extreme cases the scale may be a liquid which simply drips from the surface, or it may volatilize at very-high temperatures. Indeed, the reaction between a gas and a metal is very complicated.

The reaction between a single gas and a metal is relatively simple compared to a reaction between a mixed gas (more than one oxidant, e.g., oxygen and sulfur, oxygen and nitrogen, etc.) and a metal. The reaction between a single-oxidant gas (or multiple-oxidant-gases) and alloys is even more complex than reactions involving pure metals.

The first criterion is a thermodynamic one, i.e., does the reaction take place? The thermodynamics of a simple gas-metal reaction are, once again, very simple, but the situation changes markedly when mixed gases and/or alloys are involved.

The numerous details of oxidation have led to thousands of publications over the years and to the writing of a relatively few books on the subject. A list of books apropos to the subject are appended in the present work.

The science of gas-solid reactions, oxidation referred to in the generic sense and which can involve reactions with sulfur, nitrogen, carbon dioxide, water vapor, etc., has evolved greatly over the past forty to fifty years. Numerous symposia and colloquia have been held on the subject and have been widely attended by researchers from all over the world. One of the many factors enabling advancement of our understanding of the field is the creation and evolution of new, sophisticated instruments and techniques which permit a much better analysis of scale compositions and structures.

As seen in the list of books on the subject, the number of works is quite small, and their frequency of publication is sporadic. The early books suffered from lack of extensive data on various metals and alloys, the nonexistence of good experimental equipment, and an emphasis on materials which were important in the era in which the books were written. Many universities now have graduate courses on oxidation, and the availability of texts has been limited. Of the more-recent works, those by Kofstad, Mrowec and Birks & Meier have been very useful.

The present work is an excellent summary of basic principles, the understanding of which is of paramount importance to understand the subject. The book starts with the basics

of thermodynamics, followed by an up-to-date summary of experimental methods, many of which have not been covered in earlier books. The usual topics, such as defect structures in compounds, are covered with great clarity. The book ends with numerous case histories which give a good basis for solving practical problems with the principles provided in the book.

The writers have drawn on their many years of experience in the field and have provided a most-useful book. This work will prove to be an excellent text for graduate courses in oxidation.

D.L. Douglass

Professor Emeritus, UCLA

Editor, Oxidation of Metals

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Chapter 1

THERMODYNAMIC ASPECTS OF HIGH TEMPERATURE CORROSION

1. Thermodynamics of mixtures

1.1. Partial Gibbs free energy, chemical potential

1.1.1. Definition

The Gibbs free energy of a mixture is:

$$G = \sum N_j \bar{G}_j \quad (1.1)$$

where $\bar{G}_j$ is the partial molar free energy of the component j .

In this book, the mixture composition will be expressed using the *mole fraction* of each component, termed N_j , with:

$$N_j = \frac{n_j}{\sum n_j}$$

where n_j is the number of moles of the component j in the mixture.

The double brackets << >>, (()) and [[]] correspond to solid solutions, liquid solutions or gas mixtures, respectively. The pure components will be represented by single brackets <>, () and [].

The natural logarithm (base e) will be referred to as "ln" and the common logarithm (base 10) as "log".

The partial molar Gibbs free energy of the component j , or chemical potential, at constant temperature and pressure, is given by:

$$\mu_j = \bar{G}_j = \left(\frac{\partial G}{\partial n_j} \right)_{T,P,n_k} \quad n_k \neq n_j \quad (1.2)$$

1.1.2. Free energy of mixing

The free energy of mixing, ΔG^m , is defined as the difference between the actual Gibbs energy and its value in an ideal solution:

$$\Delta G^m = \sum N_j (\bar{G}_j - G_j^\circ) = \sum N_j \Delta \bar{G}_j \quad (1.3)$$

where G_j° is the free energy of the pure component j .

1.1.3. Gibbs-Duhem equation

For a small variation in the system composition, at constant temperature and pressure,

the free energy variation dG is given by:

$$dG = \sum \mu_j dn_j. \quad (1.4)$$

$$\text{Since, by definition: } G = \sum n_j \mu_j \quad (1.5)$$

$$\text{we find: } dG = \sum n_j d\mu_j + \sum \mu_j dn_j \quad (1.6)$$

Thus, we can deduce the **Gibbs-Duhem equation**:

$$\sum n_j d\mu_j = 0 \text{ or } \sum N_j d\mu_j = 0. \quad (1.7)$$

1.2. Chemical potential expressions

1.2.1. The concept of Activity

The chemical potential can be expressed as:

$$\mu_j = \mu_j^\circ + R T \ln a_j \quad (1.8)$$

where a_j is the activity of the component j at the temperature T (it should be noted that a_j is a dimensionless quantity) and μ_j° is the standard chemical potential. This last is the chemical potential of the component j in the pure form and in the same physical state as the mixture. The chemical potential is equal to the standard chemical potential for $a_j = 1$.

1.2.2. Gas mixtures

In a gas mixture, the chemical potential of the component j depends on its partial pressure. If the gas is ideal, which is a good approximation at low and modest pressures, say less than 10^2 bar, then the chemical potential of j is given as:

$$\mu_j = \mu_j^\circ + R T \ln P_j \quad (1.9)$$

where P_j is the partial pressure of the component j in the gas mixture, expressed in bar (if P_t is the total pressure of the system, then $P_j = N_j P_t$) and μ_j° represents the chemical potential of the gas j at a pressure $P_j = 1$ bar.

Comment 1: Strictly speaking, we should write, in the case of a gas mixture:

$$\mu_j = \mu_j^\circ + R T \ln \frac{P_j}{P^\circ},$$

where P° (pressure of the standard state) is equal to 1 bar but, in order to lighten the mathematical expressions, the term P° is, generally, omitted. The standard state for a gas, i.e., $P^\circ = 1$ bar, has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) only since 1985: the value $P^\circ = 1$ atm is still found in numerous books.

Comment 2: For pressures higher than, say, 10^2 bar, the gas should no longer be considered ideal and the chemical potential must be written as:

$$\mu_j = \mu_j^\circ + R T \ln \frac{f_j}{P^\circ}$$

where f_j is the fugacity.

1.2.3. Condensed phases

In condensed phases, the activity coefficient γ_j , is defined by the equation:

$$a_j = \gamma_j N_j \quad (1.10)$$

For concentrated solutions of the component j , the solution tends to ideality for the component j and, consequently, the activity of j becomes equal to its mole fraction (**Raoult's law**) :

$$a_j = N_j \quad (1.11)$$

For a very dilute solution of the component j , the activity becomes proportional to the mole fraction and to the activity coefficient γ_j^∞ , which is a constant depending on the temperature and on the nature of the solvent and of the solute (**Henry's law**):

$$a_j = \gamma_j^\infty N_j \quad (1.12)$$

Thus, in a dilute mixture, the solvent tends to obey Raoult's law and the solute, Henry's law.

The variation with composition of the activity of the component j in a binary system is shown schematically in figure 1.1.

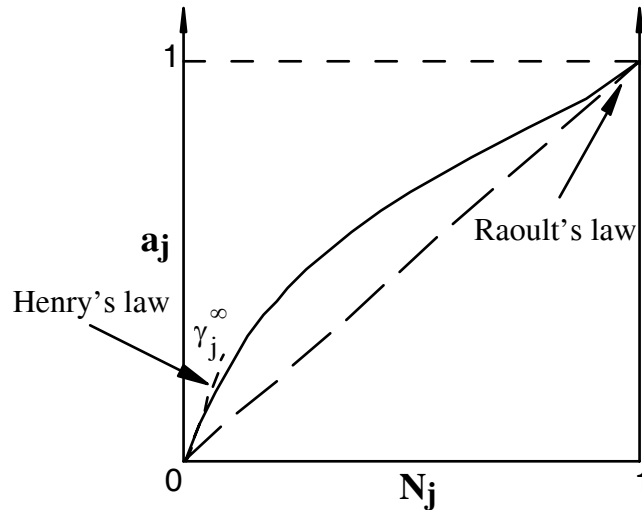


Figure 1.1. Activity of the constituent j vs its mole fraction in a binary system.

Comment: The free energy of mixing can be written as:

$$\Delta G^m = \sum N_j \Delta \bar{G}_j = RT \sum N_j \ln a_j = RT \sum N_j \ln N_j + RT \sum N_j \ln \gamma_j = \Delta G^{\text{id}} + \Delta G^{\text{xs}}$$

The first term in the expression for ΔG^m is the ideal free energy variation (ΔG^{id}). The second term (ΔG^{xs}) is referred to as the free energy of excess which relates to the deviation from an ideal solution.

The activity of the component j depends on the choice of the reference state:

- if the reference state is **the pure component j** in the same physical state as the mixture under consideration, then:

$$\mu_j = \mu_j^\circ + R T \ln a_j \quad (1.13)$$

and a_j tends towards N_j for concentrated solutions of the component j .

- if the reference state is the **infinitely dilute solution** of the component j , the activity h_j tends towards the mole fraction when the latter tends to zero:

$$\mu_j = \mu_j^\infty + R T \ln h_j$$

with $h_j = N_j$ when N_j tends to zero.

If the reference state is the pure component j in the same physical state:

$$\mu_j = \mu_j^\circ + R T \ln a_j$$

with $a_j = \gamma_j^\infty N_j$ when N_j tends to zero.

The activity values in both reference states are linked by the following equation:

$$h_j = \frac{a_j}{\gamma_j^\infty} \quad (1.14)$$

Comment 1: The concentration of an element is often expressed by its weight percent. (Formally, this should be mass % but, historically, the term weight % has been generally used and we shall retain this custom). In these conditions, the reference state is a solution obeying Henry's law and containing 1 wt. % of solute. In the composition range where Henry's law applies:

$$a_j = [\% j]$$

Comment 2: At constant temperature and pressure, we can write:

$$d\mu_j = R T d \ln (\gamma_j N_j)$$

From the Gibbs-Duhem equation ($\sum N_j d\mu_j = 0$) and, so, we obtain:

$$\sum N_j d \ln \gamma_j + \sum N_j d \ln N_j = 0$$

from which, since $\sum N_j = 1$:

$$\sum N_j d \ln \gamma_j = 0 \quad (1.15)$$

1.3. The Equilibrium state

At constant temperature and pressure, a system is at equilibrium when its free energy is a minimum.

- Consider a system consisting of various phases (α , β , γ , ...) which contain a component j ; the chemical potentials of this component, μ_j , in each phase, are equal:

$$\mu_j^\alpha = \mu_j^\beta = \mu_j^\gamma = \dots \quad (1.16)$$

• Consider a chemical reaction in a system involving various components (1, 2, 3, ..., j, ...) contained in different phases (α , β , γ , ..., ϕ , ...); the equilibrium state is characterised by the equation:

$$\sum_j v_j \mu_j^\phi = 0 \quad (1.17)$$

where v_j is the stoichiometric coefficient in the chemical reaction for the component j contained in the phase ϕ . These coefficients have positive values for the products and negative for the reactants. μ_j^ϕ is the chemical potential of the component j contained in the phase ϕ .

Under these conditions, from the expression for the chemical potentials, we obtain:

$$\sum_j v_j \mu_j^\phi = - \ln \left(\frac{\prod_j (a_j^{\phi'})^{v_j}}{\prod_j (a_j^{\phi})^{v_j}} \right) = -RT \ln K \quad (1.18)$$

where $a_j^{\phi'}$ and a_j^{ϕ} are the activities when the reactants and the products are in equilibrium. K is the equilibrium constant for the reaction.

Comments:

- The activities of pure stable solids and liquids are equal to unity.
 - In a sufficiently dilute solution, the solvent activity is generally considered to approach unity.
-

1.4. Variance

The number of degrees of freedom (or variance) of a system is the number of intensive variables which can be altered independently without bringing about the disappearance of a phase or the formation of a new one.

Let us consider a system with c components distributed in ϕ phases and let r be the number of relationships between these components, and, p , the number of intensive variables (temperature, pressure, electric field, magnetic field, etc.) in addition to the mole fractions of the components. The number of degrees of freedom (variance) is given by the equation:

$$v = c + p - \phi - r \quad (1.19)$$

In the case of chemical equilibrium, only temperature, pressure and the mole fractions of the components are, generally, taken into account. Thus, the number of degrees of freedom is given by:

$$v = c + 2 - \phi - r \quad (1.20)$$

Comment: Condensed Phase Rule

For the case of equilibrium between condensed phases, if the equilibrium state is independent of the total pressure, this variable need not be considered and the "reduced" number of degrees of freedom v' is calculated from the equation:

$$v' = c + 1 - \phi - r \quad (1.21)$$

1.5. Pressure dependence of activity in the case of equilibrium between a condensed solution and a gas phase.

Consider two phases, both of which contain a component j . According to the phase rule, we can write:

$$\mu_{(j)} = \mu_{[j]}$$

If the pure component j is chosen as the reference state for the liquid phase, then:

$$\mu_{(j)} - \mu^\circ_{(j)} = \mu_{[j]} - \mu^\circ_{(j)}$$

Let $\mu^*_{[j]}$ be the chemical potential of the pure gas j in equilibrium with the pure liquid (j) at the temperature T . Therefore:

$$\mu_{(j)} - \mu^\circ_{(j)} = R T \ln a_j = \mu_{[j]} - \mu^*_{[j]} + \mu^*_{[j]} - \mu^\circ_{(j)}$$

$\mu^*_{[j]} = \mu^\circ_{(j)}$ since the pure gas $[j]$ is in equilibrium with the pure liquid (j) and, moreover,

$$d\mu_{[j]} = R T d \ln P_j$$

Thus

$$\mu_{[j]} - \mu^*_{[j]} = R T \ln (P_j / P^*_j)$$

P_j and P^*_j are the pressures of j in the gas mixture in equilibrium with the condensed phase and of the pure gas j in equilibrium with the pure liquid, respectively. Thus, we obtain the expression for the activity a_j :

$$a_j = \frac{P_j}{P^*_j} \quad (1.22)$$

1.6. Types of solution

- ideal solution:

An ideal solution is defined as a solution in which all the components obey Raoult's law:

$$a_j = N_j \quad (1.23)$$

For this condition, the free enthalpy of mixing is given by:

$$\Delta G^m = R T \sum N_j \ln N_j = \Delta G^{id} \quad (1.24)$$

- dilute solution:

In a dilute solution, the mutual interactions between the atoms or molecules of the solute can be considered as negligible. Thus, the activity of the component j is a linear function of its mole fraction (Henry's law):

$$a_j = \gamma_j^\infty N_j \quad (1.25)$$

- concentrated solution:

In the case of a binary system, the excess molar free energy is often expressed as a power series such as:

$$\Delta G^{xs} = RT \sum N_j \ln \gamma_j = N_1 N_2 [A_0 + A_1 (N_2 - N_1) + A_2 (N_2 - N_1)^2 + \dots]. \quad (1.26)$$

- simple mixture

In this case, all the coefficients of the series are zero, except A_0 . The excess mixing quantities are symmetric about $N_1 = N_2 = 0.5$. As a result:

$$RT \ln \gamma_j = A_0 (1 - N_j)^2 \quad \text{with } j = 1 \text{ or } 2. \quad (1.27)$$

- regular solution

In such a solution, the mixing is completely random as it is in an ideal solution. The excess molar free energy is, then, equal to the enthalpy of mixing, which is independent of temperature. We find:

$$RT \ln \gamma_j = \Delta \bar{H}_j^m = A_0 (1 - N_j)^2 = \lambda (1 - N_j)^2 \quad (1.28)$$

in which the parameter λ is independent of temperature.

Comment: In a dilute solution, but one insufficiently so in i and j to apply Henry's law, the following equation is often used:

$$\ln \gamma_j = \ln \gamma_j^\infty + \varepsilon_j^j N_j + \varepsilon_j^i N_i \quad (1.29)$$

in which ε_j^j and ε_j^i are Wagner's interaction parameters.

2. Gas – solid equilibrium

2.1. Equilibrium between a metal, a simple gas and the resulting solid

The thermodynamic equilibrium between a metal and a simple reactive gas (O_2 , N_2 , S_2 , etc.) with the consequent formation of a solid phase can be described completely by analytical methods. Nevertheless, the use of graphical methods can provide further useful insights of interest.

Two types of diagrams are commonly used in high temperature corrosion:

- the **free-energy/temperature diagrams**, referred to one mole of oxidising species (Ellingham diagrams) or to one mole of metal,

- the **stability diagrams of condensed phases**, temperature-composition (binary diagrams) or pressure-temperature (isothermal diagrams of stability of condensed phases).

Each of these types of diagram has advantages and, of course, limitations but diverse approaches need to be taken in order to analyse exhaustively the interaction between a metal and gas.

2.1.1. Ellingham diagrams^{1,2,3}

The Ellingham plot is a graphical representation of the standard free energies of oxidation of pure metals versus temperature. The most useful form of representation is to express the quantities in term of **1 mole of the oxidising species**:



At a given temperature T, the standard free energy $\Delta_r G^\circ_T$ of the reaction is:

$$\Delta_r G^\circ_T = \Delta_r H^\circ_T - T \Delta_r S^\circ_T \quad (1.31)$$

where $\Delta_r H^\circ_T$ and $\Delta_r S^\circ_T$ are, respectively, the standard enthalpy and entropy of the reaction.

At equilibrium, we can write:

$$\Delta_r G^\circ_T = -R T \ln K = -R T \ln \left(\frac{a_{\text{M}_\text{m}\text{X}_\text{x}}^{2/x}}{a_{\text{M}}^{2m/x} \cdot P_{\text{X}_2}} \right) \quad (1.32)$$

Assuming that the compound $\text{M}_\text{m}\text{X}_\text{x}$ is stoichiometric and that there is no miscibility between metal and compound, the activities of M and $\text{M}_\text{m}\text{X}_\text{x}$ are taken as unity. Thus:

$$\Delta_r G^\circ_T = R T \ln P_{\text{X}_2} \quad (1.33)$$

In Ellingham diagrams, $\Delta_r G^\circ_T$ (or $R T \ln P_{\text{X}_2}$) is plotted versus temperature for the compounds of a given type, e.g. oxides, sulphides, chlorides, carbides, etc. The standard enthalpy and entropy of formation of the compounds are also considered to be independent of temperature over large temperature ranges (the "Ellingham approximation"). For these conditions:

$$\Delta_r G^\circ_T = \Delta_r H^\circ_{298} - T \Delta_r S^\circ_{298} \quad (1.34)$$

Accordingly, the $\Delta_r G^\circ_T$ values fall on straight lines in the diagram although changes in the slope of the lines occur in the diagram corresponding to phase changes of the metal or the compound. The temperatures at which these phase changes occur are indicated in the diagram by the symbols M (melting point), B (boiling point), S (sublimation point) and T (transition point for allotropic transformation, vitreous transition, etc.). By convention, these letters are contained within a square when they relate to compounds.

Ellingham plots for oxides and sulphides are presented in figure 1.2 and figure 1.3, respectively.

These diagrams are useful in that they allow comparison of the relative stability of two compounds in that the lower the position of the lines on the diagram the more stable is that compound. It will be shown, Section 2.1.2, that diagrams of the same type, but

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

² M. Olette and M.F. Ancey-Moret, *Revue de Métallurgie*, **60**(6) (1963) 569-581.

³ A. Rist, M.F. Ancey-Moret, C. Gatellier and P.V. Riboud, *Techniques de l'Ingénieur*, M 1730 a, 1-20.

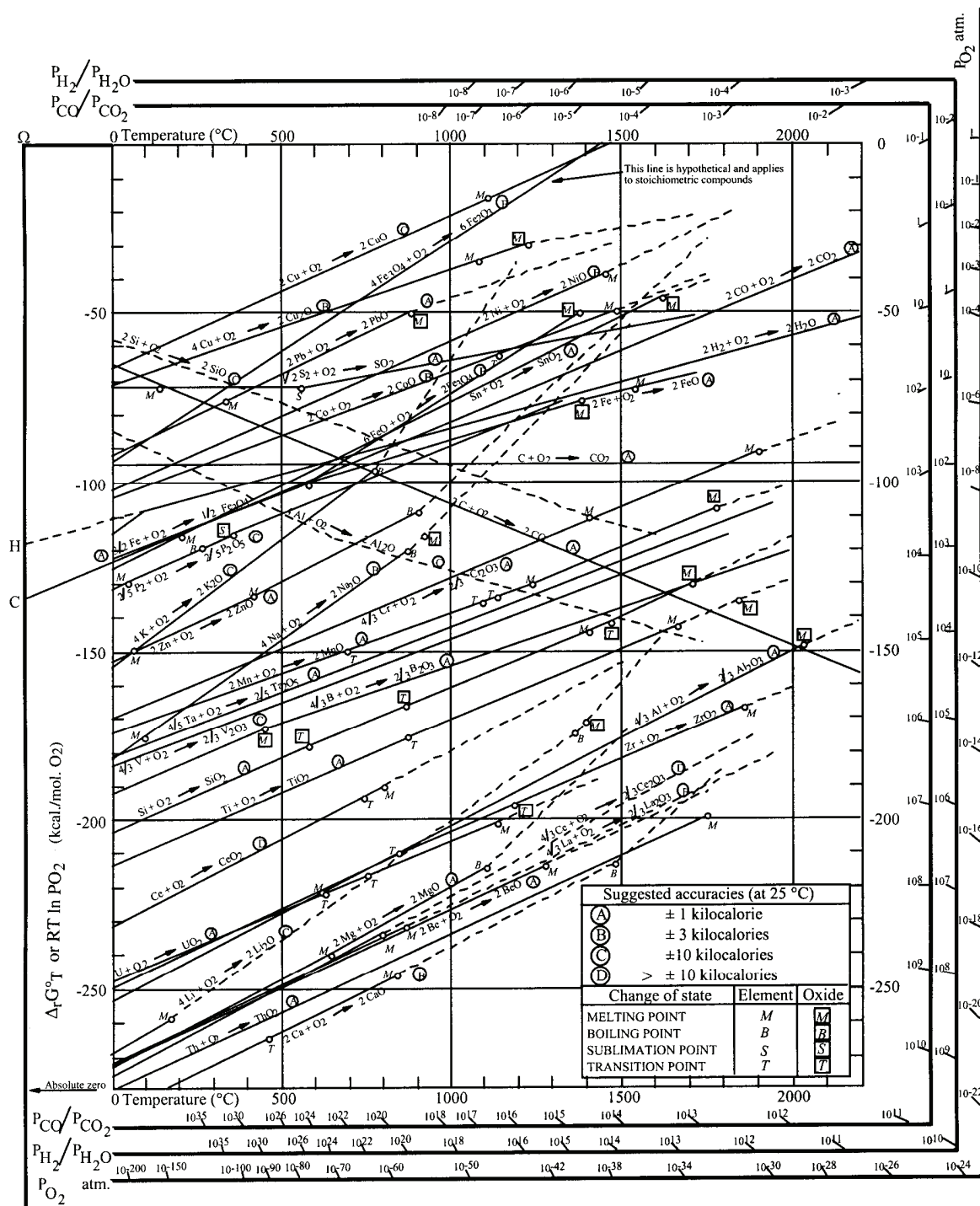


Figure 1.2. Ellingham diagram for oxides of metals (from Richardson et al⁴ and Olette et al²).

⁴ F.D. Richardson and J.H.E. Jeffes, *J. Iron and Steel Inst.*, **160** (1948) 261.

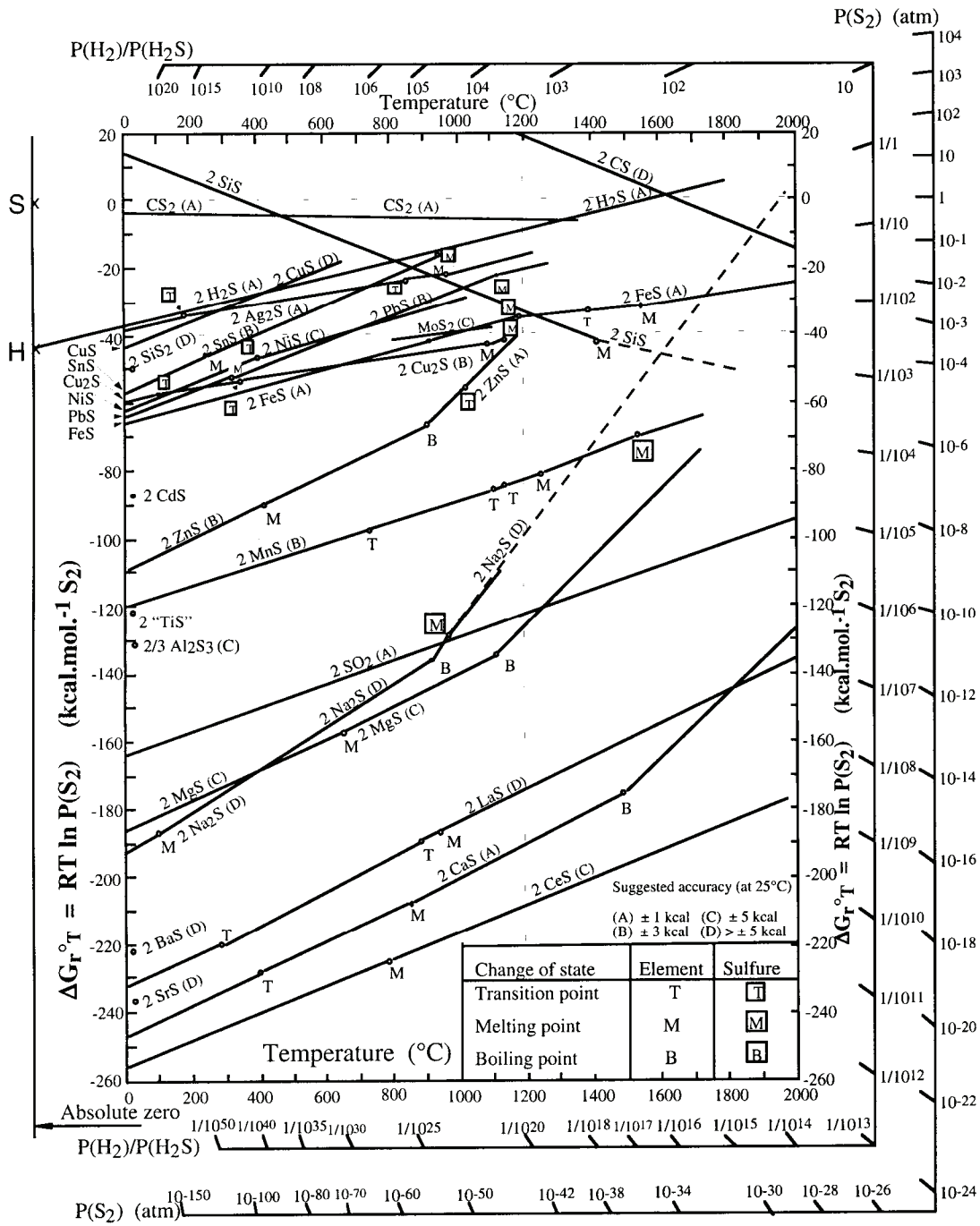


Figure 1.3. Ellingham diagram for sulphides of metals (from Richardson⁵ and Ancy-Moret⁶).

⁵ F.D. Richardson and J.H.E. Jeffes, *J. Iron Steel Inst.*, **171** (1952) 165-175.

⁶ M.F. Ancy-Moret, *Mém. Sci. Rev. Mét.*, **70** (1973) 429-430.

Comment: The units of the original diagrams (ΔG° in kcal.mol.⁻¹, T in °C and P(X₂) in atm) have been intentionally retained in figures 1.2 and 1.3.

In this thermodynamic approach to high temperature corrosion, these diagrams can be used to determine various important parameters. Some examples of their application are given below.

- *Determination of the dissociation temperature of an oxide*

The dissociation temperature of ferric oxide under 1 atm oxygen, according to the following reaction:



is read directly from the diagram, as approximately 1440°C, as that at which the free energy change $\Delta_r G^\circ_T$ becomes zero, i.e. at the intersection of the $\Delta_r G^\circ_T$ - T straight line and the abscissa axis. For temperatures higher than 1440°C, Fe₂O₃ is not stable under an oxygen pressure of 1 atm but, it should be noted that, at lower oxygen pressures, the dissociation temperature is also lower. For example, in a purified inert gas, with a residual oxygen pressure of 10⁻⁶ atm, the dissociation temperature of Fe₂O₃ is reduced to 1050°C. This temperature can be obtained directly from the diagram itself using the logarithmic scale "P_{O₂}" on the right-hand of the diagram. To do this, one only has to draw a straight line passing through the zero point of the diagram (point "Ω" in the upper left-hand corner) and through the point at which P(O₂) = 10⁻⁶ atm. The dissociation temperature then corresponds to the intercept between this straight line and the $\Delta_r G^\circ_T$ - T straight line appropriate to the oxide.

Comment: When a metal can form more than one oxide, it is preferable to plot the variation with temperature of the free energy change associated with the conversion of one mole of metal rather than one mole of oxygen.

- *Determination of the dissociation pressure of an oxide*

The dissociation pressure of wüstite FeO at 1373K can be determined from the $\Delta_r G^\circ_{1373}$ value read on the diagram, i.e. - 84 kcal per mole of oxygen. Using equation (1.33), we obtain the dissociation pressure $P_{\text{dis}} = 4.10^{-14}$ atm. Under an oxygen pressure lower than this, iron will not be oxidised. This dissociation pressure can be obtained directly from the diagram itself using, as previously, the auxiliary logarithmic scale "P_{O₂}" on the right-hand of the diagram. To do this, one has only to draw a straight line passing through

the origin of the diagram (point " Ω ") and through the point at which the Fe-O₂-FeO line intersects the 1100°C (1373 K) temperature line. The intersection point gives the dissociation pressure taking into account that the interpolation between markings on this scale must be made logarithmically.

Comment: The use of these diagrams implies that all the components are in their standard state; in particular, non stoichiometric compounds, frequently, observed at high temperatures, are not taken into account.

• *Stability of a metal in CO/CO₂ or H₂/H₂O mixtures*

As described above in determining the dissociation pressure of an oxide, the critical $P_{\text{CO}}/P_{\text{CO}_2}$ or $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ ratio corresponding to metal stability can be obtained directly from the diagram, using the $P_{\text{CO}}/P_{\text{CO}_2}$ or $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ scales on the right hand side of the diagram. By way of example, consider the case of iron at 1100°C (1373 K) for which the $P_{\text{CO}}/P_{\text{CO}_2}$ ratio is obtained by drawing a straight line from the point "C", on the left hand of the diagram, and through the point representing $\Delta_r G^\circ_{1373}$ for FeO formation. The intersection of this line with the " $P_{\text{CO}}/P_{\text{CO}_2}$ " scale gives the critical CO/CO₂ ratio at the limit of iron stability as 3.

For H₂/H₂O mixtures, the same procedure is carried out but using the point "H" on the left hand side of the diagram as the origin of the straight line. For example, at 1100°C, the critical ratio is equal to 2 for iron and to 6.10^6 for titanium.

Comment: The time necessary to reach equilibrium is not only a function of the oxygen pressure but mainly of the **buffer capacity** of the gas mixture in that the higher the buffer capacity, the shorter the equilibration time. The buffer capacity of a gas mixture, δ , can be defined as the number of moles of gas required to increase the chemical potential by 1 kJ per mole of gas mixture. For a mixture of inert gases with oxygen, the variation of δ with P_{O_2} is linear (figure 1.4). The variation of the buffer capacity of a CO-CO₂-O₂ gas mixture is more complex, however, with, at 900°C, a minimum occurring for oxygen pressure at around 10^{-6} bar and a maximum for oxygen pressure at around 10^{-16} bar (figure 1.4). This maximum corresponds to a $P_{\text{CO}}/P_{\text{CO}_2}$ ratio equal to one. Moreover, it has been shown that, at the same oxygen pressure, the buffer capacity is much lower in a vessel under static conditions than in a circulating inert gas - oxygen mixture.

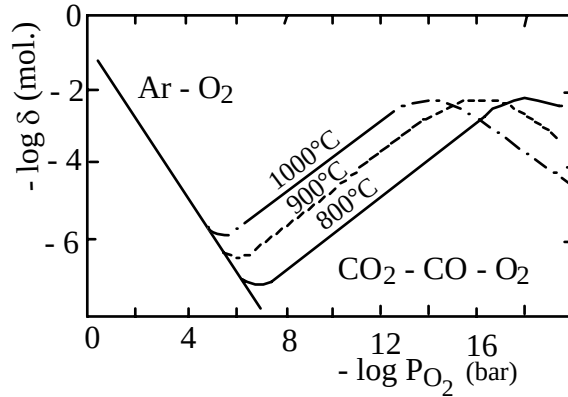
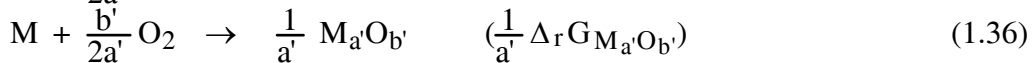


Figure 1.4. Variation of the buffer capacity of Ar-O₂ and CO₂-CO-O₂ mixtures as a function of oxygen partial pressure.

2.1.2. Free energy diagrams related to one mole of metal

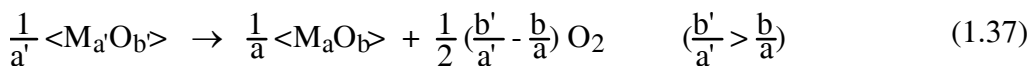
The Ellingham diagrams are very useful for comparing the behaviour of two metals in an oxidising atmosphere but it is not so easy to evaluate from them the relative stability of different oxides of a given metal. In this case, it is more convenient to use the same type of diagrams in which the free energy change corresponds to the conversion of one mole of metal rather than of oxygen.

Let us consider the oxidation reaction of a metal M which is likely to produce two oxides, i.e., M_aO_b and M_{a'}O_{b'} where $(\frac{b'}{a'} > \frac{b}{a})$:



where $\Delta_r G_{M_{a'} O_{b'}}$ and $\Delta_r G_{M_a O_b}$ are the free energies of formation of one mole of each of the respective oxides.

The reactions of the following type:



will take place spontaneously if

$$\frac{1}{a} \Delta_r G_{M_a O_b} < \frac{1}{a'} \Delta_r G_{M_{a'} O_{b'}},$$

noting that:

$$\frac{1}{a} \Delta_r G_{M_a O_b} = \frac{1}{a} \Delta_r G^\circ - \frac{b}{2a} RT \ln P_{O_2}$$

- At constant oxygen partial pressure, we can write for M_aO_b :

$$\frac{1}{a} \Delta_r G_{M_aO_b} = \frac{1}{a} \Delta_r H^\circ - T \left[\frac{1}{a} \Delta_r S^\circ + \frac{b}{2a} R \ln P_{O_2} \right] \quad (1.38)$$

Neglecting the $\Delta_r H^\circ$ and $\Delta_r S^\circ$ variations with temperature, then at constant oxygen partial pressure, the $\frac{1}{a} \Delta_r G$ versus temperature plot is linear (cf. figure 1.5).

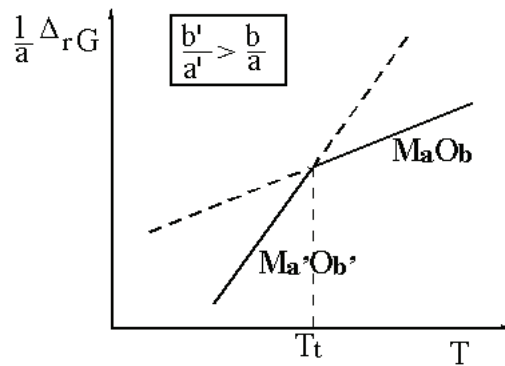


Figure 1.5. Variation, at constant oxygen pressure, of the free energy change for oxidation of one mole of a metal capable of forming both M_aO_b and $M_a'O_b$.

It can readily be appreciated from this diagram that $M_a'O_b$ is stable for temperatures lower than T_t but that M_aO_b is stable for temperatures higher than T_t .

As an example, the diagram dealing with the stability domains of manganese oxides, between 400 and 2000 K, at one bar oxygen pressure is given in figure 1.6. This diagram shows that the temperature domains of thermodynamic stability of the different oxides are: MnO_2 ($T < 780$ K), Mn_2O_3 (780 K $< T < 1265$ K), Mn_3O_4 (1265 K $< T < 1935$ K) and MnO ($T > 1935$ K).

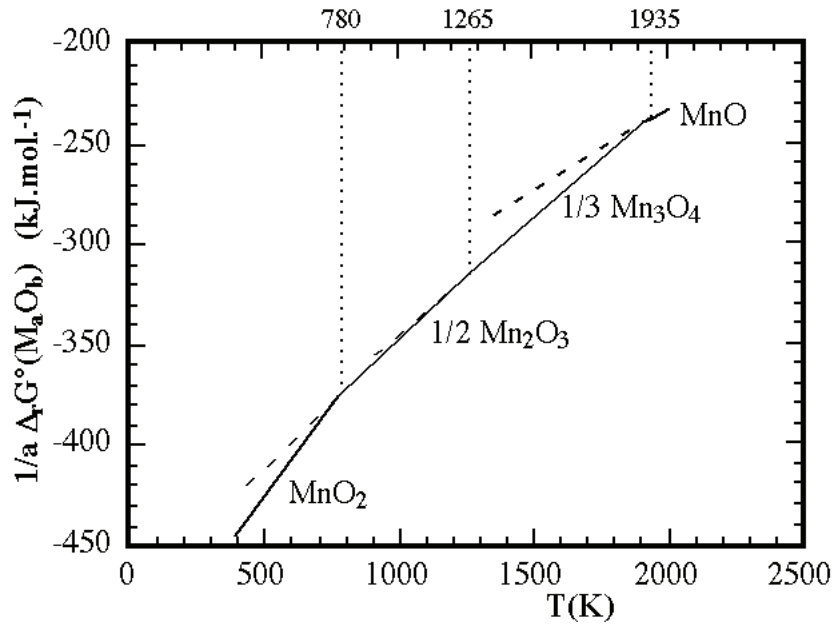


Figure 1.6. Free energy of formation versus temperature of manganese oxides, at one bar oxygen pressure (from the COACH⁷ data bank)

• Under **isothermal conditions**, as illustrated in figure 1.7, for M_aO_b , the relationship between $\frac{1}{a} \Delta_r G$ and $\ln P_{O_2}$ is linear and has a slope of $-\frac{b}{2a} RT$.

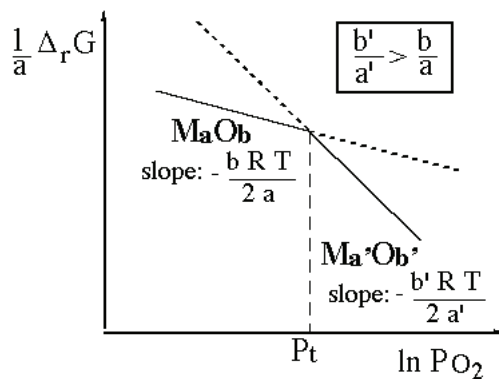


Figure 1.7. Free energy change of oxidation of one mole of a metal M which is capable of forming two oxides, referred to as M_aO_b and $M_{a'}O_{b'}$, under isothermal conditions.

Note that oxides corresponding to the higher oxidation number of the metal are the most stable at high oxygen pressures. Clearly, such diagrams are useful for comparison of the relative stability of oxides under isobaric or isothermal conditions.

⁷ Coach data bank, Thermodata, Saint Martin d'Hères Cedex (France)

2.1.3. Metal - oxygen binary diagrams

If a metal can form several oxides, then discrete oxide layers can develop during high temperature exposure such that the most metal-rich oxide will form in contact with the metal and the most oxygen-rich next to the gas phase. As an example, oxidation of iron can lead to the formation of three oxides: Fe_{1-x}O (wüstite), which, as will be shown in Chapter 3, is a metal-deficient oxide, Fe_3O_4 (magnetite) and Fe_2O_3 (hematite). The section of the Fe-O binary phase diagram, figure 1.8, allows us to predict, on a thermodynamic basis, the most probably occurring oxides as a function of the oxidation temperature. The dotted lines in the diagram represent fixed oxygen pressures. The successive layers observed after oxidation in air of an iron sheet, at 1123 K (850°C), are represented schematically in figure 1.9.

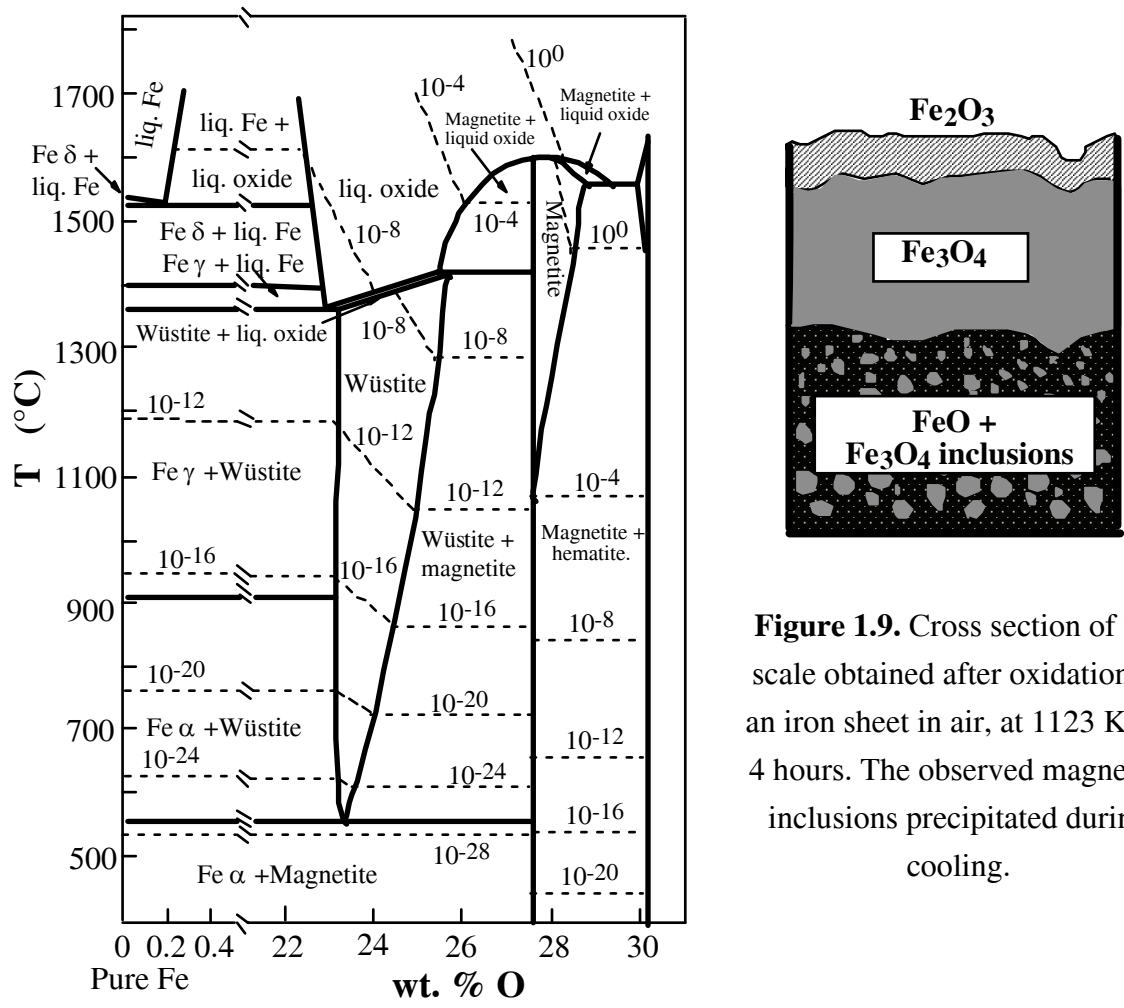


Figure 1.8. A section of the Fe-O phase diagram

Figure 1.9. Cross section of the scale obtained after oxidation of an iron sheet in air, at 1123 K for 4 hours. The observed magnetite inclusions precipitated during cooling.

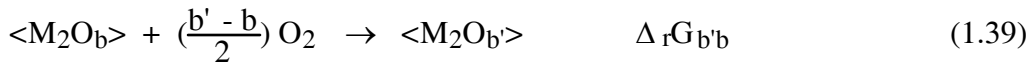
2.1.4. Stability Diagrams of Condensed Phases

These diagrams are used to determine the domains of stability of the condensed phases formed during the oxidation of a metal by a simple gas or a gas mixture.

2.1.4.1. Equilibrium between a simple gas (O_2 , Cl_2 , S_2 , etc.) and two condensed phases without miscibility.

The variance of the system is equal to one since it contains two independent components and three phases. At a given temperature, there is then one and only one equilibrium partial pressure for the system.

Consider the oxidation of M_2O_b into $M_2O_{b'}$ (with $b' > b$) according to the reaction:



The equilibrium oxygen partial pressure is given by:

$$\log P^{eq} = \frac{2}{2,3 R T (b' - b)} \Delta_r G^{\circ}_{b'b} = \frac{2}{2,3 R (b' - b)} \left(\frac{\Delta_r H^{\circ}_{b'b}}{T} - \Delta_r S^{\circ}_{b'b} \right) \quad (1.40)$$

Assuming that the standard enthalpy change and standard entropy of the reactions of type (1.39) are independent of temperature, the Arrhenius plot of P^{eq} is a straight line (see figure 1.10). This line delineates the stability domains of M_2O_b and $M_2O_{b'}$ such that $M_2O_{b'}$ is thermodynamically stable for $P > P^{eq}$ and M_2O_b for $P < P^{eq}$.

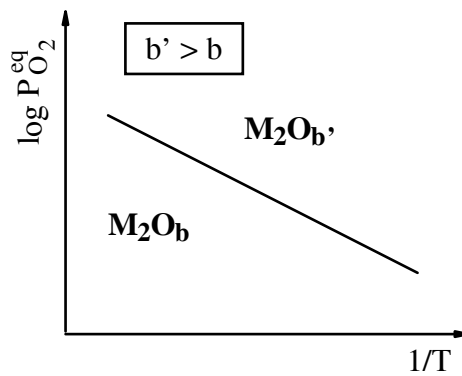


Figure 1.10. Stability domains of M_2O_b and $M_2O_{b'}$

In the case of the formation of several oxides on a metal, it is necessary to consider the equilibria between the successive oxides, in ascending oxidation number. If the corresponding $\log P_{O_2}^{eq} = f\left(\frac{1}{T}\right)$ straight lines do not intersect then the different oxides are stable over the whole temperature range and the lines delineate their stability domains, as shown in figure 1.11, for copper.

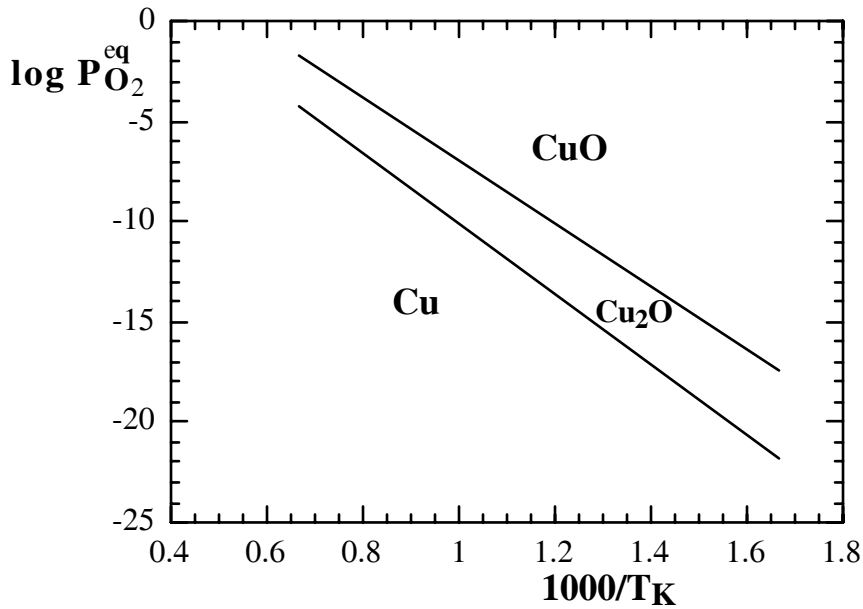
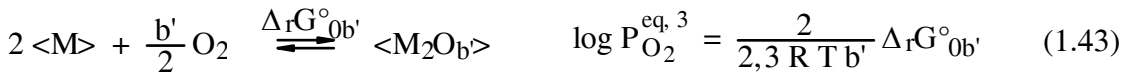
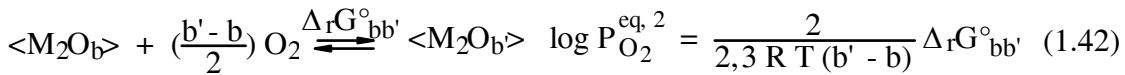
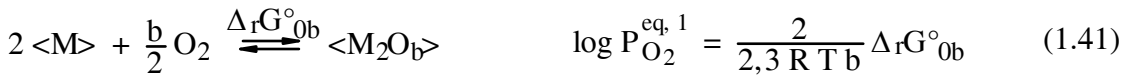


Figure 1.11. Stability domains of Cu_2O and CuO (from the COACH data bank).

In the case that the straight lines intersect, then they define temperature domains within which particular phases are thermodynamically stable. As an example, let us consider a metal M , which is likely to form two oxides, i.e., M_2O_b and $M_2O_{b'}$ (with $b' > b$):



When the $\log P_{\text{O}_2}^{\text{eq}} = f\left(\frac{1}{T}\right)$ straight lines, corresponding to equilibrium reactions (1.41) and (1.42), intersect (point O in figure 1.12) the variance is nil at the point of intersection since there are two independent components and four phases. For $T > T_0$, a stability domain exists for M_2O_b but for temperatures lower than T_0 , it is necessary to consider the equilibrium between M and $M_2O_{b'}$ as given by equation (1.43).

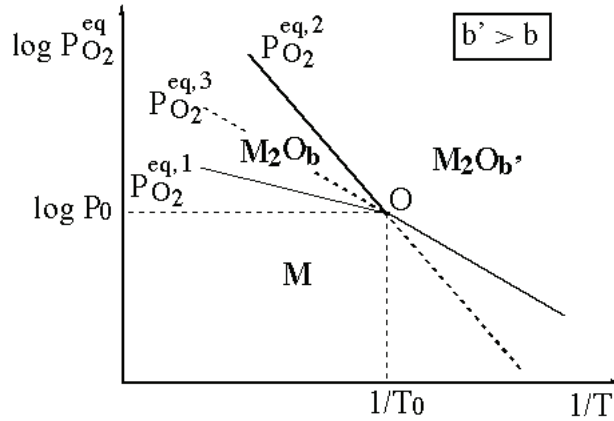
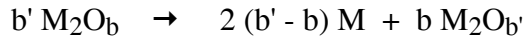


Figure 1.12. Stability domains for the condensed phases $\langle M \rangle$, $\langle M_2O_b \rangle$ and $\langle M_2O_{b'} \rangle$.

Comment 1: For $T < T_0$, M_2O_b disproportionates according to the following reaction:



Comment 2: Since

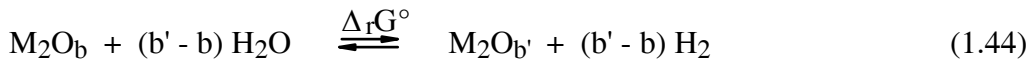
$$\Delta_r G^{\circ}_{0y'} = \Delta_r G^{\circ}_{0y} + \Delta_r G^{\circ}_{yy'}$$

we obtain:

$$b' \log P_{O_2}^{eq,3} = b \log P_{O_2}^{eq,1} + (b' - b) \log P_{O_2}^{eq,2}$$

2.1.4.2. Equilibrium involving gas mixtures such as CO/CO_2 or H_2/H_2O .

Consider a reaction of the type:



The variance of the equilibrium is equal to 2, in this case of condensed phases without miscibility since there are three independent components and three phases in equilibrium. At equilibrium, we have:

$$\Delta_r G^{\circ} = - (b' - b) R T \ln \frac{P_{H_2}}{P_{H_2O}} = - (b' - b) R T \ln \frac{N_{H_2}}{N_{H_2O}} \quad (1.45)$$

where N_{H_2} and N_{H_2O} are the mole fractions of hydrogen and water vapour in the gas mixture, respectively. Assuming that the activities of the condensed phases are unity and that the gases show ideal behaviour, $\Delta_r G^{\circ}$ is independent of the total pressure P and the gas composition is a function of temperature only. Under these conditions, the equilibrium is considered as *pseudo-invariant*.

The stability domains of the condensed phases are represented in N_{H_2} (or N_{H_2O}) versus $f(T)$ plots (Chaudron diagram) or as $\log \frac{P_{H_2}}{P_{H_2O}}$ (or $\log \frac{P_{CO}}{P_{CO_2}} = f\left(\frac{1}{T}\right)^*$. In effect, equation (1.45) can be written as:

* P. Gadelle, *Publications et documents en didactique de la chimie*, April 1985.

$$\log \frac{P_{H_2O}}{P_{H_2}} = \frac{1}{2,3 R (b' - b)} \left[\frac{\Delta_r H^\circ}{T} - \Delta_r S^\circ \right] \quad (1.46)$$

Assuming that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are independent of temperature, $\log \frac{P_{H_2O}}{P_{H_2}}$ is a linear function of $1/T$, as represented in figure 1.13. The straight line marks the boundary between the stability domains of each oxide, i.e., M_2O_b and $M_2O_{b'}$.

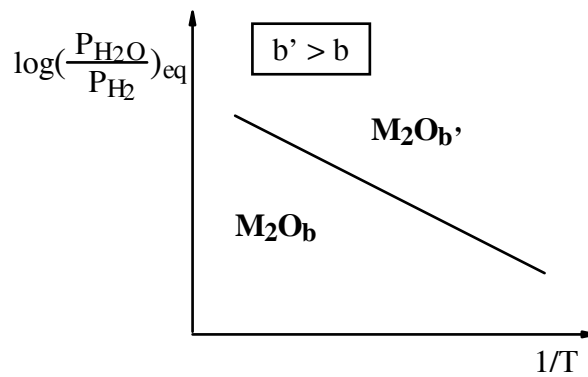


Figure 1.13. Stability domains of M_2O_b and $M_2O_{b'}$ in a H_2/H_2O gas mixture.

If several oxides of the same metal can be formed, it is necessary to proceed in the same way as described previously for the case of equilibrium with a simple gas.

The stability domains of iron and iron oxides, i.e., FeO , Fe_2O_3 and Fe_3O_4 , as functions of gas composition and temperature are represented in figures 1.14 and 1.15. Figure 1.14 corresponds to a Chaudron diagram and Figure 1.15 to the plot of $\log \frac{P_{H_2O}}{P_{H_2}}$ (or $\log \frac{P_{CO_2}}{P_{CO}} = f(\frac{1}{T})$).

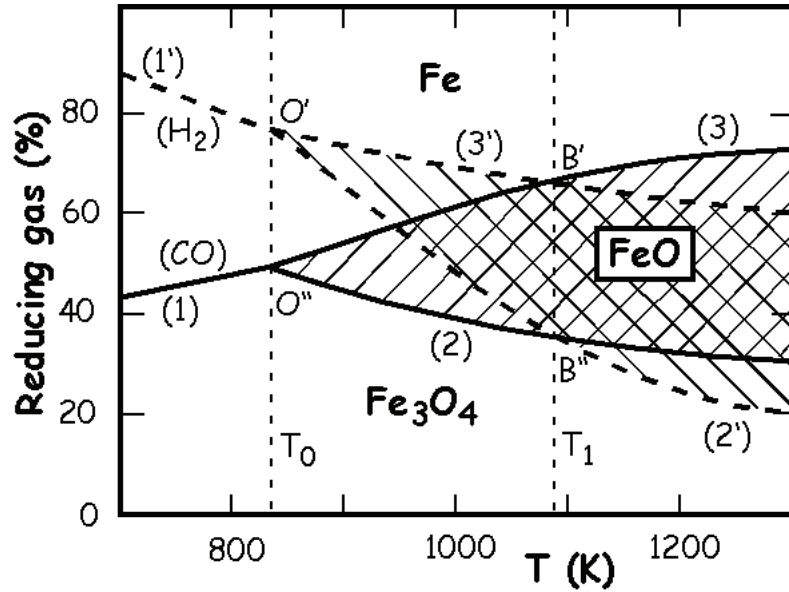


Figure 1.14. Stability domains of iron and iron oxides as functions of temperature and gas composition according to the Chaudron diagram (CO/CO_2 and $\text{H}_2/\text{H}_2\text{O}$ mixtures). The hatched areas indicate the stability domains of FeO according to the gas mixture, i.e., CO/CO_2 or $\text{H}_2/\text{H}_2\text{O}$ (from the COACH data bank).

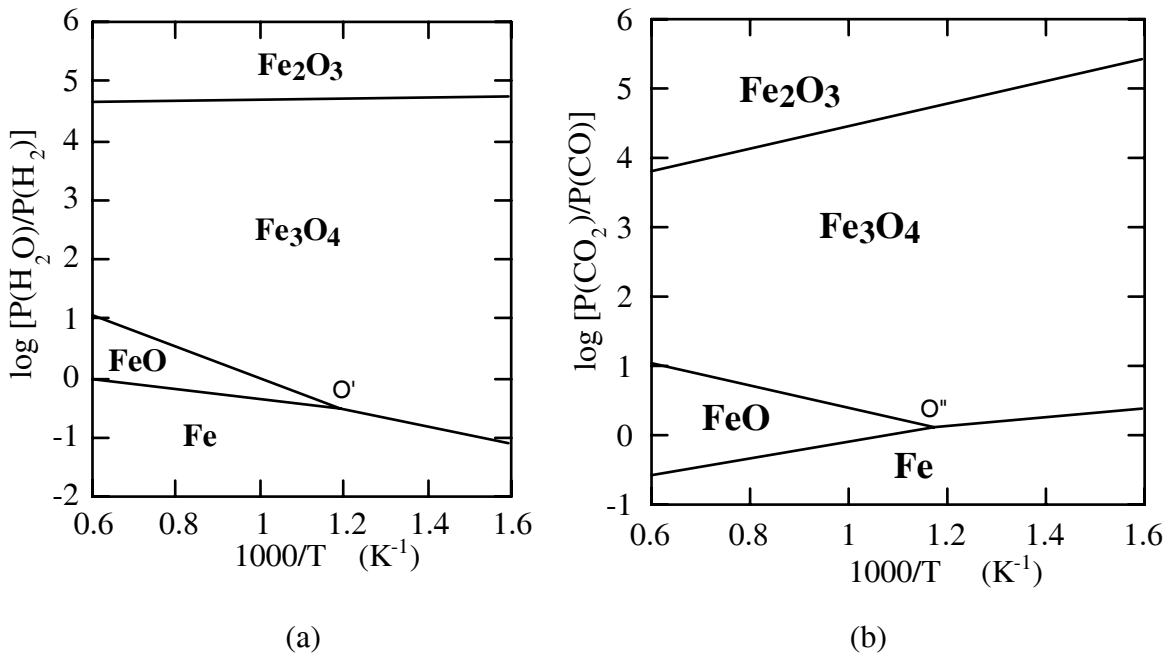
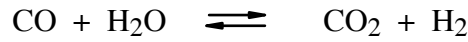


Figure 1.15. Stability domains of iron and iron oxides as functions of temperature and of the $\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$ ratio (Fig. 1.15.a) or of the $\frac{P_{\text{CO}_2}}{P_{\text{CO}}}$ ratio (Fig. 1.15.b) (from the COACH data bank).

Comment 1: Both diagrams exhibit a triple point ($T_0 = 830$ K), O' and O'', respectively, in figure 1.15, corresponding to a pseudo-invariant system, insofar as the pressure is not a factor in the equilibrium since there are three independent components and four phases.

Comment 2: Points B' and B'' in figure 1.14 [intersection of, respectively, the curves (2) and (2') and (3) and (3')] correspond to the inversion temperature of the following equilibrium:



i.e., $T_1 = 1100$ K.

Comment 3: For $T < 1100$ K, CO is more reducing than hydrogen whereas the reverse applies for $T > 1100$ K.

2.2. Solubility of gases in metals

The solubility of diatomic gases such as H_2 , O_2 , N_2 , etc. in metals often plays an important role in their reactivity. Since the dissolved gas is usually in monoatomic form, the overall reaction for solution is:



with the corresponding equilibrium constant:

$$K = \frac{a_{\ll \text{X} \gg}^2}{P_{\text{X}_2}} = \frac{\gamma_{\ll \text{X} \gg}^2 N_{\ll \text{X} \gg}^2}{P_{\text{X}_2}} \quad (1.48)$$

The solubility of these gases is often small and, as a consequence, Henry's law is followed.

At constant temperature, we then obtain Sievert's law:

$$N_{\ll \text{X} \gg \text{sat}} = \frac{K^{1/2} P_{\text{X}_2}^{1/2}}{\gamma_{\ll \text{X} \gg}^\infty} \quad (1.49)$$

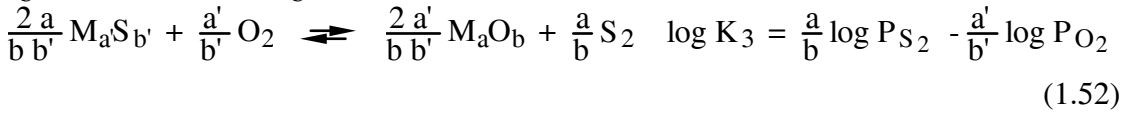
2.3. Equilibrium involving complex atmospheres

Industrial gaseous atmospheres may, in addition to air, consist of complex gases (CO_2 , H_2O , SO_2 , SO_3 , etc.) or mixtures of several gases or contain the gaseous products of corrosion or of the thermal decomposition of corrosion products. In spite of the complexity of corrosion phenomena, the problem can be solved, in some cases, using simple thermodynamic calculations from simplifying hypotheses. In other situations, involving numerous components, it is necessary to use software that minimises the total free energy of the system.

2.3.1. Isothermal stability diagrams of condensed phases

• Simultaneous oxidation and sulphidation of iron⁸

The stability domains of the different phases in thermodynamic equilibrium (metal, oxides, sulphides) are determined from the following equations, with the assumption that the activities of all the condensed phases are unity:



The isobaric straight lines for SO₂ and SO₃ are drawn in figure 1.16 using the equations:



and:

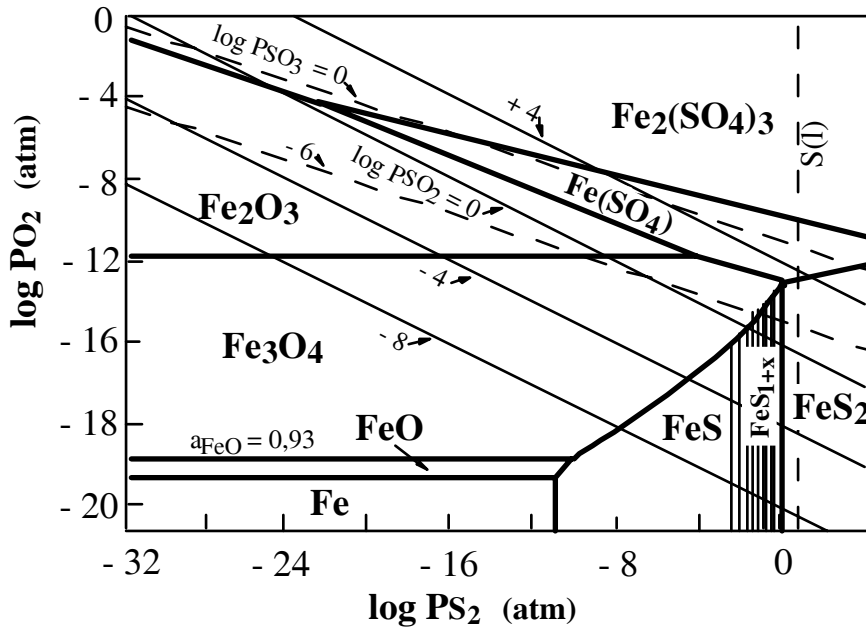


Figure 1.16. Isothermal stability diagram of condensed phases for the oxidation of iron by SO₂, at 953 K (680°C).

As will be shown in exercise 3 of chapter 7 (oxidation of nickel by sulphur dioxide), such a diagram is useful for predicting the scale composition at thermodynamic equilibrium in complex atmospheres. For example, as shown in figure 1.16, the Fe₂O₃ - FeS mixture obtained experimentally by oxidation of iron by SO₂ at 953 K is not in equilibrium with the gas phase.

⁸ A. Yazawa, *Met. Trans. B*, **10 B** (1979) 307-321.

• Si - N - O system⁹

The stability diagram of condensed phases of the Si - N - O system, at 1500 K (1227°C), as a function of the partial pressures of oxygen and nitrogen, is shown in figure 1.17. Dashed lines on the diagram represent the gaseous SiO pressures (in atm.).

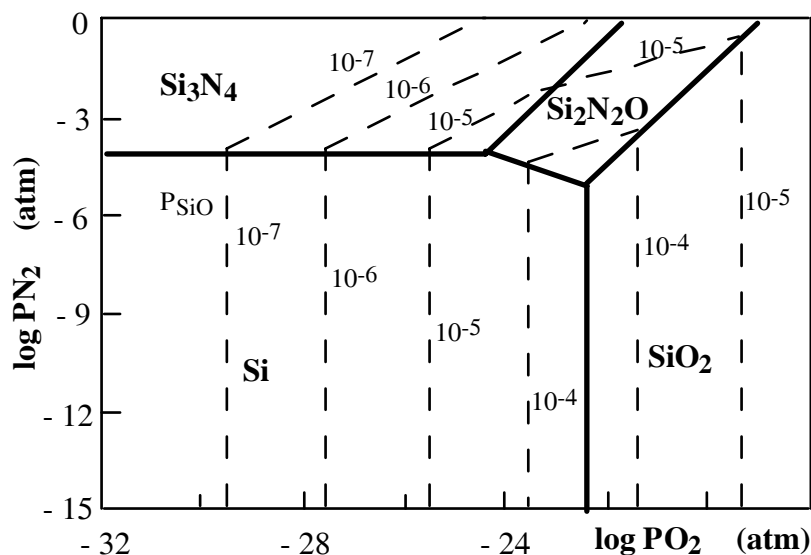


Figure 1.17. Stability diagram of condensed phases in the Si - N - O at 1500 K.

One of the main applications of this diagram is in determining the interfacial reactions occurring during the oxidation of silicon nitride. For example, the diagram shows that the silicon oxynitride is always present at the interface between SiO_2 and Si_3N_4 in industrial processing and, moreover, the oxygen pressure at that interface is there very low. The point of intersection between the dashed lines indicating the $[\text{SiO}]$ pressures and the N_2 pressures for two phase domains allows the calculation to be made of the $P(\text{SiO})/P(\text{N}_2)$ ratio at the solid/solid interfaces.

2.3.2. Free energy minimisation software

In some cases, the gaseous atmosphere can be composed of several tens of components. In these circumstances, special programmes (such as CHEMSAGE/FACTSAGE* and GEMINI§) have been developed to calculate and draw the equilibrium diagrams.

2.4. Gas - alloy equilibrium

In industrial environments, alloys are generally used instead of pure metals. The study of chemical reactivity of an alloy with the surrounding atmosphere requires the

⁹ P. Rocabois, C. Chatillon and C. Bernard, *J. Am. Ceram. Soc.* **79** (1996) 1361-1365.

* G.T.T. - Technologies, Kaiserstraße 100, D-52134 Herzogenrath (Germany).

§ Thermodata - I.N.P.G. - C.N.R.S., BP 66, 38402 Saint Martin d'Hères Cedex (France).

determination of the nature and composition of the phases in equilibrium in the alloy as functions of temperature and global composition. For simple binary or ternary alloys, this information can be obtained from the appropriate phase diagrams which are known for many systems. However, many alloys are more complex, for example, in the case of stainless steels, minute variations of alloying elements can lead to noticeable modifications of the phases present at equilibrium. Even in these cases, guidance on phase stability can be obtained from binary or ternary diagrams, e.g. in stainless steels through the use of empirically determined chromium or nickel equivalents (see section 2.4.1.2).

Comment: It is important to recognise that these diagrams do not allow us to predict the phases likely to be present in non-equilibrium conditions, for example, when rapid changes of temperature take place. Such phases could play an important role in determining the alloy's high temperature corrosion resistance, particularly if the service exposure involved frequent and rapid changes in temperature.

Alloy oxidation can take the simple form of the oxidation of one constituent but is generally more complex, and can involve, for example, the simultaneous oxidation of both metal constituents (in binary alloys), the miscibility of oxides or the formation of a complex oxide (spinel structure, for example). In view of this complexity, thermodynamic analysis, although a desirable prerequisite for high temperature corrosion studies, is not usually sufficient to analyse the behaviour of industrial alloys (binary, ternary, quaternary, etc. alloys) or even of composite materials.

2.4.1. Phase diagrams of mixtures¹⁰

2.4.1.1. Thermodynamics of binary diagrams

It is not the aim of this book to describe exhaustively the method of construction and the interpretation of these diagrams but several typical binary or ternary diagrams of industrial importance will be presented for illustration.

- *Phase rule*

In binary diagrams, where the condensed phase rule is obeyed (see equation 1.21), we observe:

- one-phase domains (liquid phase, solid solution or intermediate phase) with a variance equal to 2; this implies that the temperature and the concentration of one component in the phase may be selected arbitrarily without changing the nature of the phase;

¹⁰ The diagrams have been taken from the book "*Précis de Métallurgie : élaboration, structures-propriétés, normalisation*", J. Barralis and G. Maeder, AFNOR-Nathan, Paris, 1997.

- two-phase domains (liquid + solid, two solids or even two liquids in equilibrium) corresponding to one degree of freedom; for this case, if the temperature is chosen, then the composition of the co-existing phases are fixed;

- at points or lines with zero degrees of freedom, e.g. at a change of state of pure components or of intermediate phases, three phases can exist in equilibrium (eutectic, peritectic, eutectoid, peritectoid reactions, etc.*).

Figure 1.18 shows a simple schematic binary diagram between A and B. It contains a solid solution $\langle\alpha\rangle$, based on component A with a small solubility of the component B, an intermediate phase $\langle\gamma\rangle$, having a large non-stoichiometry domain, and a negligible solubility of component A in B. The diagram shows also two eutectic reactions, one in which α , γ and L (liquid) are in equilibrium, the other involving γ , β and L.

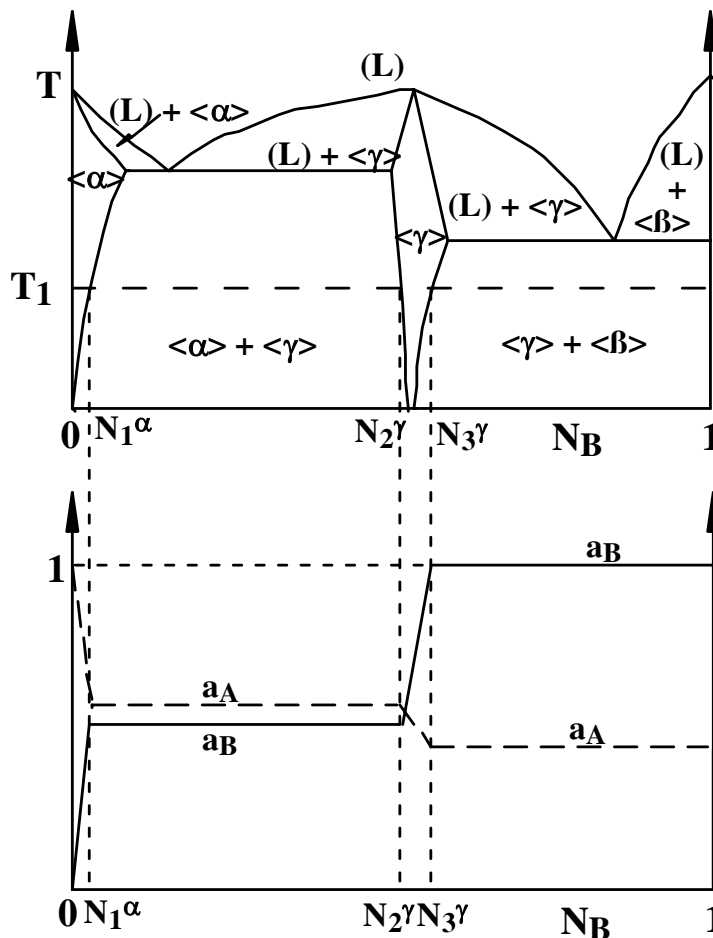


Figure 1.18. Binary diagram exhibiting an intermediate non-stoichiometric phase (upper diagram). The activities of the constituents A and B as a function of the mole fraction of B, at a temperature, T_1 , corresponding to a solid alloy, are shown in the lower diagram.

* The invariant reactions involving liquid phases have a name ending in *-tectic* whilst those occurring completely in the solid state end in *-tectoid*.

At the temperature, T_1 , corresponding to a solid alloy over the entire compositional range, the phases in equilibrium are, successively with increasing N_B :

- solid solution $\langle\alpha\rangle$ for $0 \leq N_B < N_1^\alpha \Rightarrow v = 2$
- a mixture $\langle\alpha\rangle + \langle\gamma\rangle$ for $N_1^\alpha < N_B < N_2^\gamma \Rightarrow v = 1$
- the intermediate phase $\langle\gamma\rangle$ for $N_2^\gamma < N_B < N_3^\gamma \Rightarrow v = 2$
- a mixture $\langle\gamma\rangle + \langle\beta\rangle$ for $N_3^\gamma < N_B < 1 \Rightarrow v = 1$
- the pure solid B, with β structure for $N_B = 1$

Comment: There is a very small domain corresponding to a solid solution of component A in B, referred to as β , invisible on the scale of the diagram.

• Calculation of the activities of the constituents

On the basis of the thermodynamics of mixing reviewed in Section 1, it is possible to determine the variation of the activities of the constituents as a function of alloy composition. The lower diagram of Figure 1.18 shows the activities of the constituents A and B as a function of N_B at the temperature T_1 . For $0 < N_B < N_1^\alpha$, the solubility of the component B in solid solution $\langle\alpha\rangle$ is small and under these conditions a_B varies linearly with N_B . If the $\langle\alpha\rangle$ and $\langle\beta\rangle$ structures are identical, we can write (Henry's law):

$$a'_B = \gamma_B^\infty N_B. \quad (1.55)$$

In the more general case where $\langle\alpha\rangle$ and $\langle\beta\rangle$ structures are different, then, in the $\langle\alpha\rangle$ phase, it is the activity of B referred to pure solid B with α structure that obeys Henry's law:

$$\mu_B = \mu_{\langle B \rangle}^\alpha + RT \ln a_{\langle B \rangle} \quad \text{and} \quad a_{\langle B \rangle} = \gamma_B^\infty N_B \quad (1.56)$$

In the lower diagram of Figure 1.18, the activity of B referred to pure solid B with β structure has been plotted, i.e.:

$$\mu_B = \mu_{\langle B \rangle}^\beta + RT \ln a'_{\langle B \rangle} \quad (1.57)$$

Using equations 1.56 and 1.57, we obtain:

$$a'_{\langle B \rangle} = a_{\langle B \rangle} \exp \left(\frac{\mu_{\langle B \rangle}^\alpha - \mu_{\langle B \rangle}^\beta}{RT} \right) \quad (1.58)$$

and

$$a'_{\langle B \rangle} = \gamma_B^\infty N_B \exp \left(\frac{\mu_{\langle B \rangle}^\alpha - \mu_{\langle B \rangle}^\beta}{RT} \right) \quad (1.59)$$

thus:

$$a'_{\langle B \rangle} = \text{constant} \cdot N_B. \quad (1.60)$$

For $N_1^\alpha < N_B < N_2^\gamma$, both $\langle\alpha\rangle$ and $\langle\gamma\rangle$ phases are in equilibrium, thus:

$$\mu_B(N_1^\alpha) = \mu_B(N_2^\gamma) \quad \text{and} \quad a_B(N_1^\alpha) = a_B(N_2^\gamma) \quad (1.61)$$

The activity of B is, thus, constant over this range of composition.

For $N_3^\gamma < N_B < 1$, $\langle \gamma \rangle$ is in equilibrium with the component B, thus:

$$\mu_B^\gamma(N_3^\gamma) = \mu_B^0 \text{ soit } a_B(N_3^\gamma) = 1 \quad (1.62)$$

and the activity of B is equal to one.

Comment: It can be easily demonstrated that, for a very small mole fraction N_A , the activity of A tends toward zero.

On the pure-B side, with $\langle \beta \rangle$ structure, the activity of A, $a'_{\langle A \rangle}$, referred to pure solid A with the $\langle \alpha \rangle$ structure, obeys the equation:

$$\mu_A = \mu_{\langle A \rangle}^\alpha + RT \ln a'_{\langle A \rangle} \quad (1.63)$$

If $a_{\langle A \rangle}$ is the activity of A referred to pure solid A with the $\langle \beta \rangle$ structure, as the solid solution, we may write:

$$\mu_A = \mu_{\langle A \rangle}^\beta + RT \ln a_{\langle A \rangle} \text{ and } a_{\langle A \rangle} = \gamma_A^\infty N_A \quad (1.64)$$

According to equations (1.63) and (1.64):

$$a'_{\langle A \rangle} = a_{\langle A \rangle} \exp\left(\frac{\mu_{\langle A \rangle}^\beta - \mu_{\langle A \rangle}^\alpha}{RT}\right) \quad (1.65)$$

$$a'_{\langle A \rangle} = \gamma_A^\infty N_A \exp\left(\frac{\mu_{\langle A \rangle}^\beta - \mu_{\langle A \rangle}^\alpha}{RT}\right) \quad (1.66)$$

Thus, when $N_{\langle A \rangle}$ tends towards 0, $a'_{\langle A \rangle}$ also tends towards 0.

• Examples of binary diagrams

Binary diagrams (Fe - Cr, Fe - Ni, etc.) are useful in interpreting the condensed phases in equilibrium as functions of temperature and alloy composition, as illustrated in figures 1.19 and 1.20.

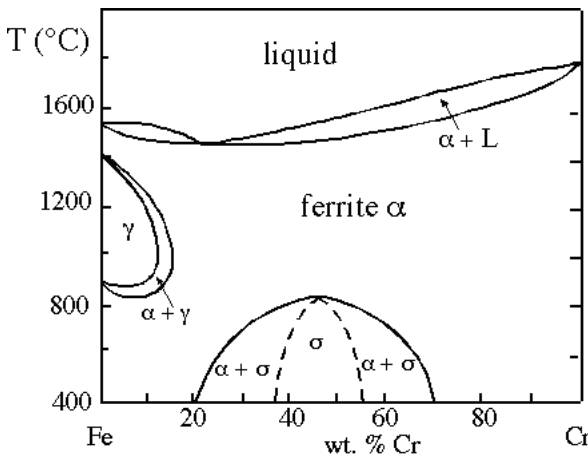


Figure 1.19. Binary diagram of Fe - Cr

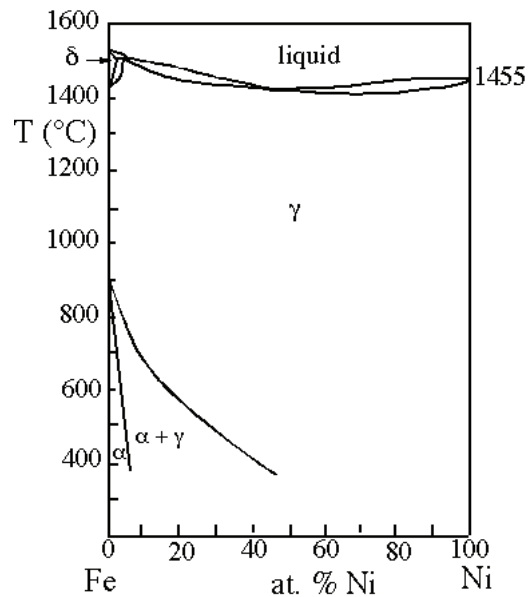


Figure 1.20. Binary diagram of Fe - Ni

Chromium is an important alloying component as far as high temperature corrosion resistance is concerned. It also stabilises the ferritic structure and is called an “ α -stabiliser”. The stability domain of the austenitic solid solution (solid solution γ , with face-centered cubic structure) in the Fe-Cr system is restricted to a loop tangential to ca. 13 wt. % of chromium. Nickel stabilises the austenitic solid solution to the detriment of ferrite and is termed a “ γ -stabiliser”. In practice, a non-equilibrium alloy, having a martensitic structure, is obtained on cooling.

2.4.1.2. Basic thermodynamics of ternary diagrams

In ternary diagrams, the stability domains of phases become volumes rather than just planes as in binary diagrams. The representation of equilibrium in a ternary system therefore requires a three-dimensional diagram in which, generally, alloy compositions are represented in the horizontal plane and temperature along an axis perpendicular to this plane. However, to avoid a three-dimensional layout, it is easier to draw isothermal sections; in some cases, these sections are projected on to a common plane leading to a network of isothermal plots.

Comment: In an isothermal section, the alloy composition is determined at point M by means of an equilateral triangle. The A, B and C mole fractions are obtained by drawing, from point M, parallel straight lines to triangle sides (cf. figure 1.21). Thus:

$$N_A = \frac{ab}{BC}, \quad N_B = \frac{bC}{BC}, \quad N_C = \frac{Ba}{BC}$$

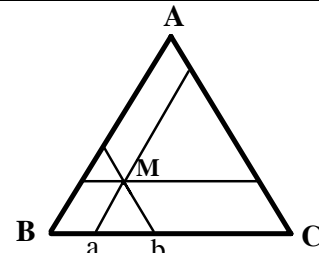


Figure 1.21

For example, figures 1.22 a and b represent equilibrium isothermal sections of the Fe-Ni-Cr ternary diagram, i.e. obtained after slow cooling, for a range of temperature, in the case of Figure 1.22 a, and for 650°C in Figure 1.22 b.

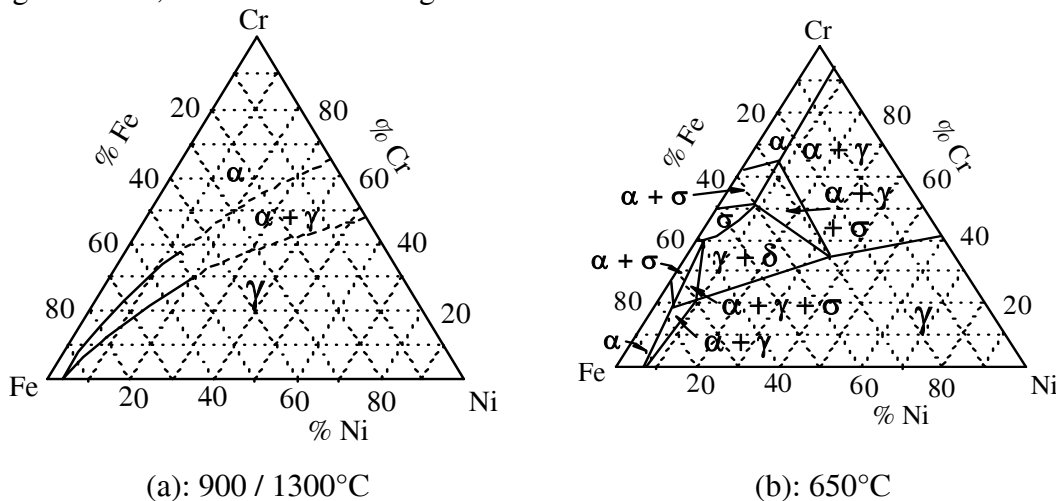


Figure 1.22. Isothermal section of the Fe-Ni-Cr ternary diagram (after slow coolings).

The phases obtained after thermal treatments can also be indicated on isothermal sections for room temperature. By way of example, figure 1.23 shows the composition of ternary alloys Fe - Ni - Cr with 0.1 % of carbon at room temperature after austenisation (1000-1100°C) followed by hyperquenching i.e. very rapid cooling.

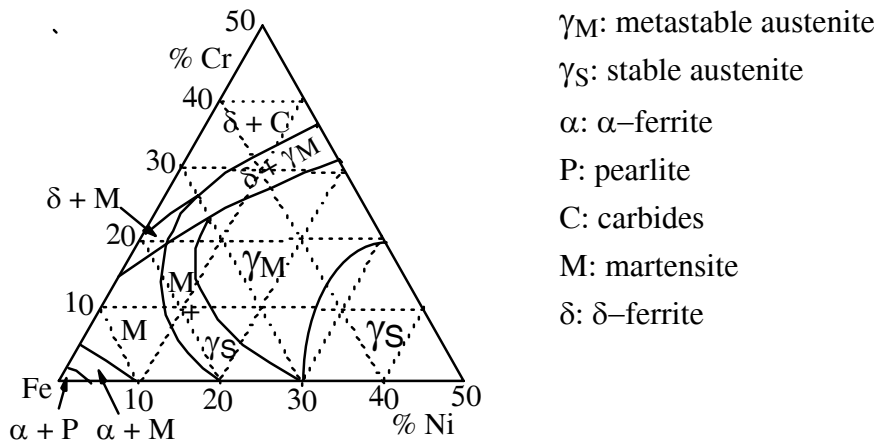


Figure 1.23. Constitution at room temperature of Fe - Ni - Cr ternary alloys with 0.1 % of carbon after hyperquenching.

Nickel- and chromium-based refractory alloys, referred to as "superalloys", contain generally low concentrations of alloying elements (Mo, W, Ti, Y, Ce, Zr, etc.) which can significantly modify the nature of the equilibrium phases. These elements are intended either to improve the mechanical properties of the alloy or to reduce the oxidation rate and improve the adherence of the protective oxide scale. For such materials, the alloy structure can be forecast using the Schaeffler diagram (cf. figure 1.24) where, through the use of empirical formulas, it is possible to take into account the effect of all the alloying elements. Thus, on the Y-axis of the diagram is plotted the equivalent content of " γ - stabilising" elements (i.e., Ni, C, N, Mn, Co, etc.) and on the X-axis the equivalent content of " α -stabilising" elements (i.e., Cr, Mo, Si, Nb, V, Ta, etc.).

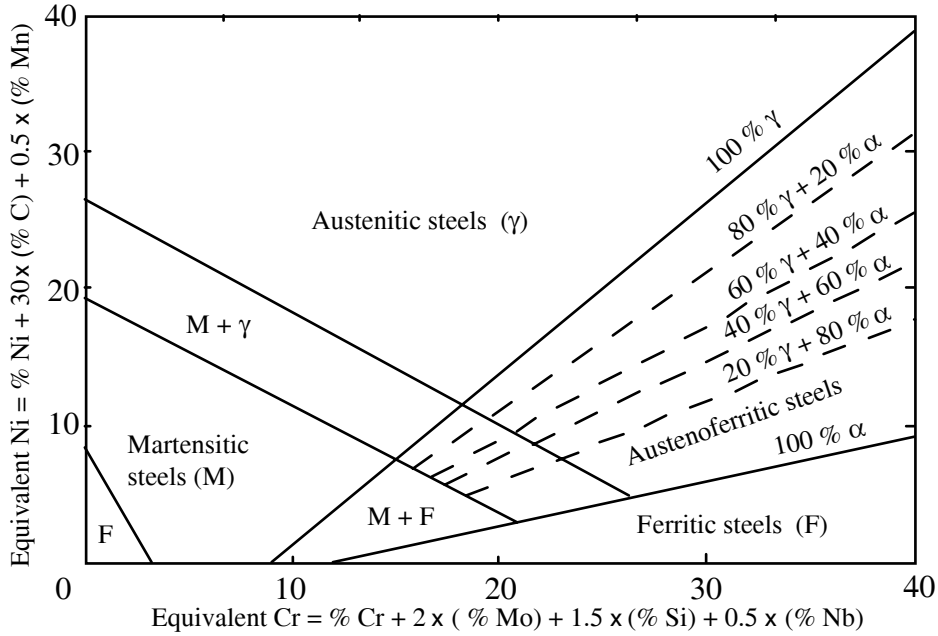


Figure 1.24. Schaeffler diagram for stainless steels.

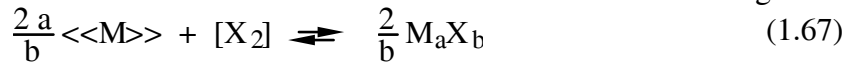
2.4.2. Alloy behaviour in oxidising atmospheres

2.4.2.1. Thermodynamics of gas - alloy interactions

Let us consider a binary alloy MM' in an oxidising atmosphere. The partial pressure corresponding to the stability limit of the metallic phase is a function both of the properties of the alloy and of the compound that is formed.

- *Oxidation only of component M without miscibility of the compound formed*

The equilibrium reaction used in section 2.1 has to be modified according to:

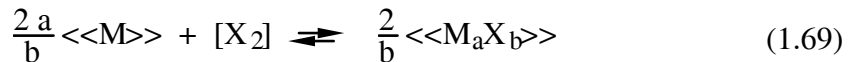


The X_2 pressure in equilibrium with the alloy is a function of the activity of M:

$$\ln P_{X_2} = \frac{\Delta_r G^\circ_T}{RT} - \frac{2a}{b} \ln a_{\ll M \gg} \quad (1.68)$$

- *The compound formed is miscible in another compound*

The equilibrium reaction now becomes:



The X_2 pressure in equilibrium with the alloy is a function of the activity of M and of the compound $M_a X_b$:

$$\ln P_{X_2} = \frac{\Delta_r G^\circ_T}{RT} - \frac{2a}{b} \ln a_{\ll M \gg} + \frac{2}{b} \ln a_{\ll M_a X_b \gg} \quad (1.70)$$

• Binary “alloy – oxygen” diagram

Rather numerous isothermal sections of binary alloy - oxygen systems are available. Figure 1.25 represents the Ni - Cr - O diagram at 1273 K from which it can be seen that three stable oxides are identified: NiO, Cr₂O₃ and the double oxide with spinel structure, NiCr₂O₄.

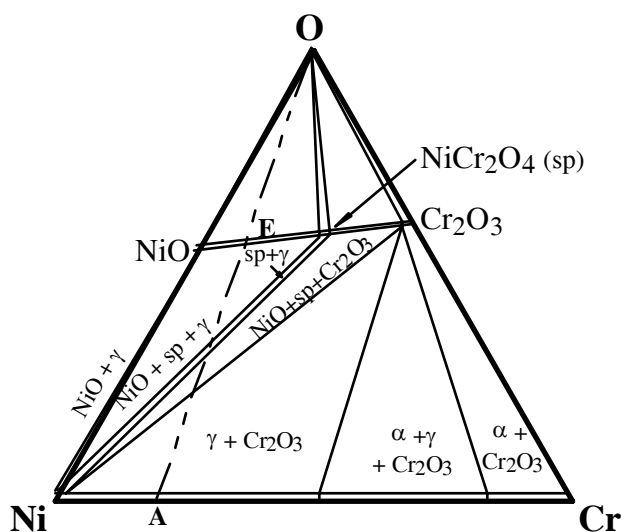


Figure 1.25. Binary alloy - oxygen diagram for Ni - Cr - O at 1273 K (1000°C).

The use of such diagrams alone is, generally, not sufficient to determine the actual oxides formed in practice. However, this diagram together with identification of the phases observed experimentally in the scale allow us to draw onto the ternary diagram the *reaction (or diffusion) path* from point O of the diagram to point A, corresponding to alloy composition.

• Oxide maps

Figure 1.26 indicates on a Ni - Cr - Al diagram, the nature of corrosion scales formed, at 1000°C in oxygen, on alloys which contain these three components. This representation of experimentally observed reactions is often referred to as an "oxide map"¹¹. As shown in figure 1.26, the binary alloys Ni - Al must contain more than 15 % of aluminium to obtain a sufficiently thick protective layer of alumina. With addition of chromium this limit is lowered to ca. 10 %. *It should be emphasised that these diagrams do not reflect equilibrium conditions, and are not equilibrium diagrams, but take into account many kinetic factors.*

¹¹ P. Kofstad, in *High Temperature Corrosion*, Elsevier, London, 1988, p. 372.

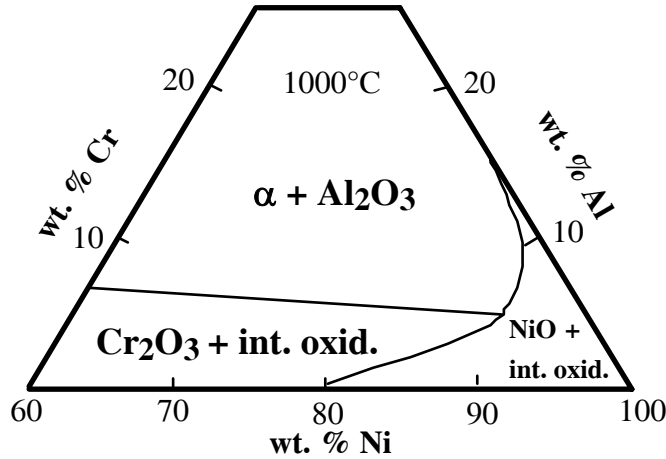


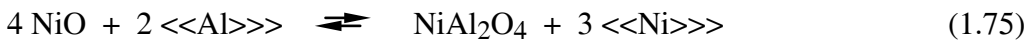
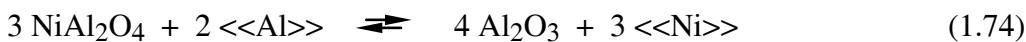
Figure 1.26. Oxide map for Ni - Cr - Al alloys at 1000°C.

2.4.2.2. Stability diagram of condensed phases

In the case of an alloy, it is necessary to calculate from thermodynamic principles the oxide phases in equilibrium with the metallic phase. The same graphical representation can be done in a similar manner as described in the preceding sections. By way of example, Pettit¹² has studied the oxidation of the Ni-Al system in the range 900-1300°C. In the presence of oxygen at high temperatures, the possible reactions that can take place on the surface of the alloy are the following:



As oxidation proceeds, it is necessary to take into account the following exchange reactions:



Application of the mass action law to reactions 1.74 and 1.75 leads to the equilibrium conditions, at 1000°C:

$$(a_{\text{Al}}^2/a_{\text{Ni}}^3)_{\text{eq.}(1.74)} = 10^{-34.3} \quad \text{and} \quad (a_{\text{Al}}^2/a_{\text{Ni}}^3)_{\text{eq.}(1.75)} = 10^{-37.3}$$

It can be assumed that nickel is at unit activity so that the aluminium activity corresponding to equilibrium (1.74) and (1.75) are, respectively, at 1000°C:

$$(a_{\text{Al}})_{\text{eq.}(1.74)} = 10^{-17.2} \quad (a_{\text{Al}})_{\text{eq.}(1.75)} = 10^{-14.6}$$

The corresponding stability diagram of condensed phases is represented in figure 1.27.

¹² F.S. Pettit, *Trans. Met. Soc. AIME*, **239** (1967) 1296-1305.

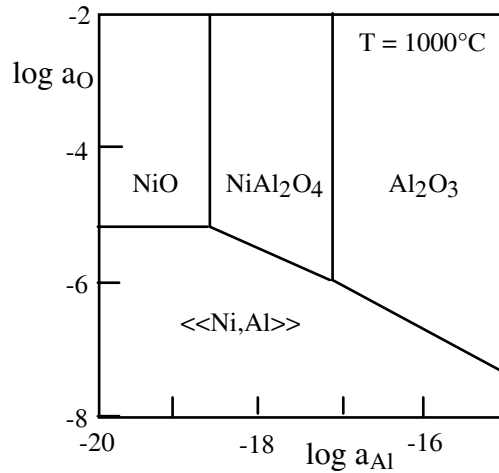


Figure 1.27. Thermodynamic stability diagram of condensed phases on a Ni - Al alloy in oxygen at 1000°C .

This treatment illustrates how restricted are the conditions for the formation of the spinel structure NiAl_2O_4 which can exist at equilibrium only for aluminium contents of less than 1 ppm. In practice, therefore, one should expect to observe only Al_2O_3 or NiO during the oxidation of these alloys. However, this thermodynamic approach is not sufficient to predict which stable oxides actually form and kinetic considerations have also to be taken into account.

Chapter 2

HIGH TEMPERATURE CORROSION: EXPERIMENTAL

1. Scope of high temperature corrosion

It is a widely accepted fact that 25% of steel produced each year is damaged by corrosion but that only a small part of this is caused by high temperature corrosion. However, high temperature corrosion generally occurs in state-of-the-art technologies for which the consequences of failures have a particularly high financial, environmental or human cost.

The technical domains in which high temperature corrosion is of importance can be categorized into five headings:

- thermal machines (internal combustion engines or gas turbines), used for surface, marine and air transportation or for energy conversion (steam or gas turbines), including their inlet and outlet devices (for example, catalytic converters);
- chemical industry, i.e., organic chemistry (steam cracking, catalytic dehydrogenation, chlorination, etc.), inorganic chemistry (soda/chlorine, sulphur, isotopic separation, etc.) or metallurgical industry (roasting, Van Arkel process, thermal and thermomechanical treatments, etc.);
- incineration of domestic or industrial waste;
- electric heating devices (electrical resistances, furnace walls, etc.);
- nuclear engineering (fuel cladding, guiding and lifting systems, liquid metal circuits, etc.).

Besides these purely environmental aspects, high temperature oxidation constitutes a stage of some industrial processes, for example to obtain materials with controlled properties. Thermal oxidation of silicon wafers to obtain a scale of silica (SiO_2) with a thickness less than about 100 nm (grid dielectric) is the basic manufacturing process of integrated MOS transistors. The last stage stripping of stainless steel requires an oxidation step to obtain an appropriate surface state for cold wiredrawing. This operation is generally carried out in a gas oven under complex atmospheres. Similarly, the formation of a bonding layer on steel support structures for catalytic convertors to limit pollution involves an oxidation process. It should also be pointed out that all the thermochemical surface treatment processes (nitriding, carburising, siliciding, boriding), using either chemical vapour deposition techniques or pack-

cementation, are analysed and characterised using the tools and concepts of high temperature corrosion.

Table 2-1 gives several examples of industrial devices working at high temperatures with their maximum temperature of utilisation and expected useful life.

Table 2-1. Typical useful life of various industrial devices.

Useful life	Applications	T _{max} (°C)
several minutes	Rocket engines	2400
	Heat shields of spaceships	1650
10 - 20 h	Superficial coatings of spaceshuttles	1750
100 - 200 h	Ingots moulds in steel works	1350 - 1500
1000 h	Filaments of incandescent lamps	2500
2 000 - 3 000 h	Petrol engines	600 - 800
10000 - 20000 h	Diesel engines	800 - 900
	Resistance heaters in industrial furnaces	1300 - 1600
	Jet engines of passenger aircraft	1050 - 1100
40000 h	Nuclear fuel cladding in PWRs	300 - 350
100000 h	Industrial gas turbines	1000
300000 h	Steam turbines	650

This table clearly shows that the expected performances of these devices can be attained only if high temperature corrosion phenomena are taken into account from the outset, i.e. at the design stage. The improvement of energy conversion efficiencies, which will be one of the key economic factors in technological development in the near future, will accentuate this necessity.

2. Experimental techniques

To understand high temperature corrosion mechanisms, it is necessary to perform careful measurements of corrosion rates as a function of test parameters. In addition to temperature, these will also include the partial pressures of the gaseous reactants and products and the molar fractions of the various alloying elements and impurities. Experimental devices are therefore temperature and pressure controlled. In addition, the corrosion scales formed should be precisely characterised by physical and chemical methods in order to determine their nature, composition, thickness, morphology, adherence and stress state.

2.1. Laboratory testing equipment

2.1.1. Materials

The reaction vessels for studying high temperature corrosion may be horizontal or vertical tubes, depending on the type of measurement required. Pyrex glass can be used up to 450°C only and must be changed to vitreous silica (often improperly called “quartz”) which can then be used up to 1050°C. These glassy materials have the advantage of being transparent to light and of being joined and readily moulded to shape by flame processing. For higher temperatures, ceramic materials such as mullite or alumina should be employed. Metallic reaction vessels are seldom used since they themselves may react with the oxidising gas. For studies of corrosion by fluorine, F₂, or its compounds such as HF, SOF₂ or SO₂F₂, it should be noted that silica glasses are not stable and, similarly, for halogen-carbon reactions where alumina is chlorinated, nickel-based alloys are used. It will also be necessary to use metallic vessels (termed autoclaves) when high-pressure reactions are studied.

2.1.2. Furnaces.

Tubular electric furnaces are of common use in air up to 1250°C with metal wire heating elements (NiCr, FeCrAl, NiCrAl) but, for higher temperatures, these elements have to be protected against oxidation. Heating elements made of SiC or MoSi₂ are self-protecting through the formation of a silica layer and their use extends the temperature range of air furnaces to 1500°C. Tungsten or molybdenum resistance furnaces can be used up to 2500°C, provided they are kept under vacuum to prevent oxide volatilisation.

Reliable measurement of test temperature is of great importance because of the strong dependence of the reaction kinetics on temperature. Several types of thermocouples are available, depending on the temperature range being used:

- NiCr/NiAl (K-type) up to 900 – 1000°C,
- Pt-10%Rh/Pt (S-type) for temperatures up to 1700°C,
- W-Rh/W up to 2500°C.

The higher the maximum temperature for these couples then the lower is their sensitivity. Locating the thermocouple inside the reaction is obviously the best option for accurate temperature measurement but the thermocouple in relation to the specimen within the furnace is of also major importance. A location inside the reactor tube would obviously be best. For particularly corrosive environments, it is sometimes useful to use stainless steel- or Inconel-sheathing, particularly for type K thermocouples. When the thermocouple tip has to be placed outside the reaction vessel, careful calibration measurements have to be performed to map the longitudinal and radial temperature gradients within the furnace. In all cases, effective draught proofing has to be placed at both ends of the furnace, between the reactor and furnace tubes, to avoid air convection currents (see Section 2.2.2.) which would perturb

the temperature distribution within the vessel. The use of such insulation is particularly recommended for vertical furnaces.

2.1.3. Atmospheres

Static or dynamic atmospheres may be used during oxidation testing. For the case of **static atmospheres**, the oxidant, usually a gas, is introduced into the reaction chamber after it has been evacuated and the reaction vessel is then subsequently closed. Such atmospheres are characterised by the total pressure and the molar fraction (partial pressures, in the case of a gas) of each constituent. For the case of **dynamic atmospheres**, the oxidant continuously circulates in the open reaction chamber. The flow rate is then an additional experimental variable and it is necessary to know this as part of the complete characterisation of the oxidation test.

Static atmospheres should be used only when the reactive oxidising species, assumed gaseous for illustration, are in overwhelmingly large concentrations so that the products of reaction do not have any significant effect on the original concentration. In all other cases, only dynamic atmospheres can ensure constant partial pressures of the reacting constituents and control over the build-up of reaction products. Gas flow rates in the range 0.1 to 10 mm.s^{-1} are commonly used but simple mass balance calculations can ensure that the concentration of oxidant is in large excess compared with the amount lost during the reaction. This condition has to be fulfilled to avoid affecting the kinetics of reaction through a limitation on the supply of oxidant. Such a limitation may occur, for example, when very small amounts of highly reactive gases (HCl , SO_2 , ...) are diluted in an inert carrier gas. Experiments conducted at different flow rates can be used usefully to establish whether kinetic limitations apply for particular test conditions.

2.2. Experimental monitoring of oxidation kinetics

2.2.1. Techniques

Kinetic monitoring consists of following as a function of time any parameter that is characteristic of the extent of the reaction. Some fairly common approaches are described below.

Geometrical monitoring uses the thickness of the growing oxide scale or of the recessing metal as a measure of the progress of the reaction. Discontinuous measurements are performed on one or several samples submitted to the same temperature and oxidising environment. The measurement may be destructive (by using optical microscopy or scanning electron microscopy on cross sections), so that one sample is consumed for each data point, or non destructive (by using ellipsometry, Rutherford backscattering, nuclear reaction analysis) so that the same sample may be used for several successive data point

measurements. A continuous geometry-related measurement, seldom used, consists in following the electrical resistance increase of a recessing metallic wire during scaling.

Manometric monitoring can be used when the reaction being studied consumes the gaseous oxidant without any gas release. The decrease of the oxidant pressure in a closed reaction vessel is then used as a monitoring parameter. A highly sensitive pressure transducer must be used to allow experiments to be performed at near-constant pressure. An improved version of the method consists in using two vessels connected by a motorised vane. The first vessel contains the sample where the gas pressure is continuously measured and adjusted to a constant value by repeated small additions from the second vessel. In this latter vessel, the pressure decrease as a function of time is monitored and used as a measure of the progress of the reaction.

Gravimetric monitoring is the most commonly used method and consists of following the mass of the sample as a function of time. This can be done discontinuously by removing the specimen from the furnace, to allow weight measurements at room temperature, and then re-inserting. Continuous measurements are possible using thermobalances (the approach is known as *thermogravimetric monitoring*) of which highly reliable examples are today available, covering a large range of temperature and pressure conditions. It should be pointed out that the choice of the type of gravimetric measurement, continuous or discontinuous, is not without consequence and may influence the kinetic results. Discontinuous monitoring using the same sample imposes thermal cycling, possibly leading to scale degradation and accelerated corrosion (Section 3.2.). This type of monitoring is, however, closer to many industrial service conditions where high temperature parts are generally submitted to thermal cycling. For more academic purposes, the continuous thermogravimetric measurements are preferred in order to understand better the mechanisms of isothermal corrosion.

2.2.2. Thermogravimetry

Two types of thermobalances have been used for thermogravimetric purposes: beam or spring thermobalances.

2.2.2.1. Beam thermobalances

Beam thermobalances are derived from the pivoted-beam laboratory precision scales formerly used for analytical chemistry purposes. At one end of the beam hangs the sample and at the other end are attached an electro-optical displacement detection system and a ferromagnetic re-equilibration cylinder. Any mass variation perturbs the equilibrium of the beam, inducing a signal from the electro-optical system. This signal is amplified and drives the re-equilibration force applied to the ferromagnetic cylinder by an axially-positioned solenoid (Fig. 2.1.). The beam position, therefore, stays, more or less, constant whatever the

mass variation and only the current flowing in the solenoid changes proportionally to these variations. This current is measured and gives the mass changes after a simple calibration procedure. Such a thermobalance may have an accuracy of approximately 50 μg .

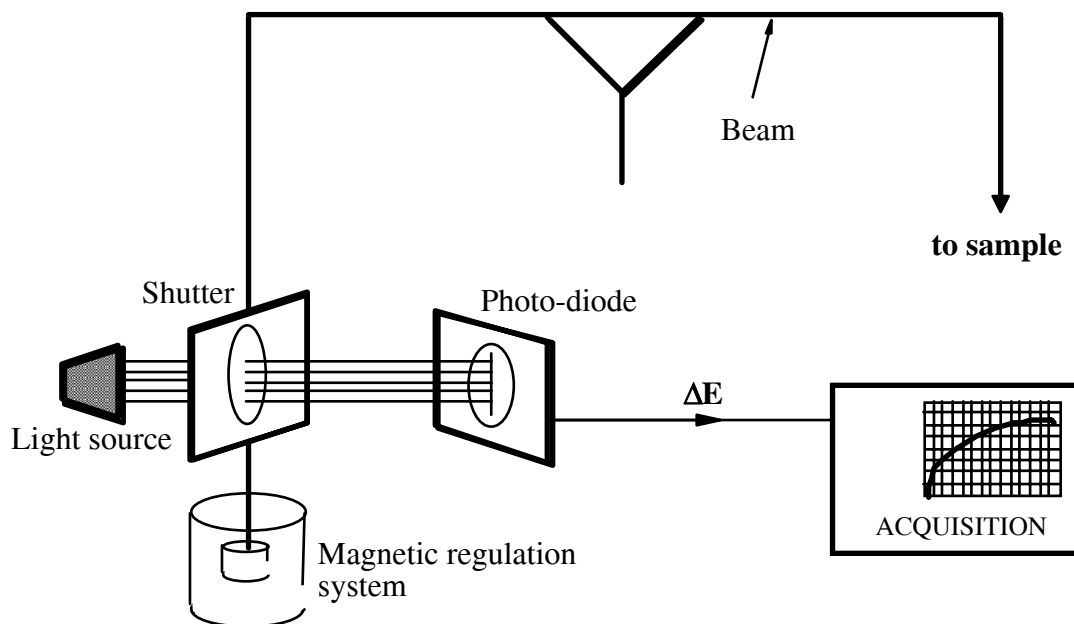


Fig. 2.1. Principle of a beam thermobalance.

Fig. 2.2 gives a schematic view of a typical single-furnace thermobalance of this type used for studying the high temperature corrosion of metals in water vapour. The material for the wire used to hang the sample in the vertical silica reaction tube may be platinum or silica. The electrically heated furnace is also placed vertically and a thermocouple is used to measure the temperature of the reaction vessel. A pumping system can be used to evacuate the reaction vessel down to approximately 10^{-8} bar before starting of the weight change measurement. Vacuum monitoring uses a Pirani-type and an ionisation gauge. The pressure of the reactive gas introduced into the reaction vessel is monitored by a metallic manometer and a piezoresistant deformation gauge. The water-containing vessel is used to control the concentration of water vapour in the equipment.

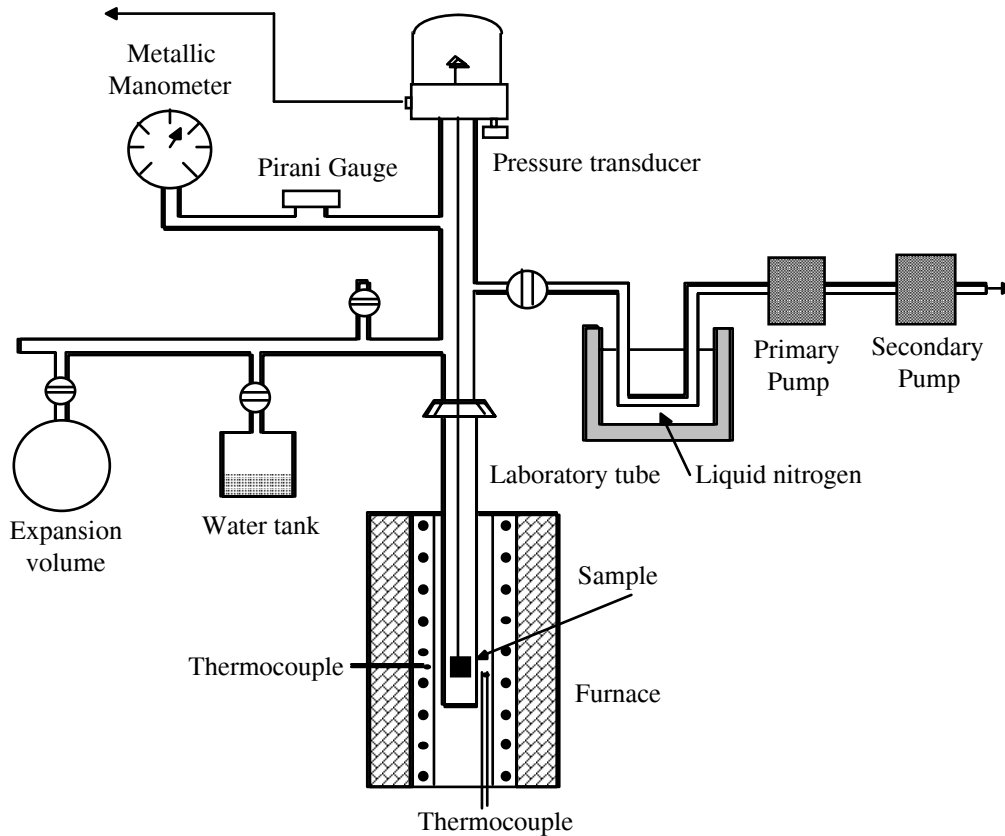


Fig. 2.2. Single-furnace thermobalance used for studying oxidation of metals in water vapour¹

The accuracy of such systems is increased to approximately 10 µg by avoiding the use of knife-edge pivots and allowing the beam to be supported by a torsion wire ribbon and placing the measuring and re-equilibration systems symmetrically at the extreme positions of the beam. To increase the accuracy further towards the microgram range, the physical interactions of the sample with the gas must be taken into account and combated. Three of these interactions are of importance:

- Buoyancy;
- convection forces;
- thermomolecular fluxes.

Buoyancy

Thermogravimetric kinetic measurement will be perturbed and errors introduced in all cases where buoyancy varies with time. To illustrate this, consider a solid of volume V immersed at temperature T in a perfect gas mixture of mean molar mass M at a pressure P . The effect of buoyancy can then be described by:

$$B = \alpha g V M \frac{P}{T} \quad (2.1)$$

¹ Y. Wouters, A. Galerie, J.P. Petit, Solid State Ionics, **104** (1997) 89-96.

where g is the acceleration due to gravity and α the ratio $T^\circ/P^\circ V^\circ$ of the temperature, pressure and molar volume of gases under normal conditions. This relation shows first that buoyancy depends on temperature so that temperature variations during the experiment lead to apparent mass changes but these are easy to calculate. As example, consider a typical rectangular sample with dimensions $20 \times 10 \times 2 \text{ mm}^3$ placed in oxygen. Heating this sample from room temperature to 1000°C will lead to an apparent increase in mass of approximately 0.5 mg. It can be appreciated that, to achieve maximum balance sensitivity under nominally isothermal measurements, care must be taken to ensure a high standard of temperature control of the furnace. For example, with temperature variations of $\pm 3^\circ\text{C}$ near 300°C , the apparent mass variations are of the order of $\pm 2 \text{ }\mu\text{g}$; at higher temperatures, the error in determination of mass is less, e.g. $\pm 0.3 \text{ }\mu\text{g}$ at 1000°C , because of the lower gas density. Buoyancy force variations with the increase of sample volume during oxidation can also be calculated but are generally negligible compared with the accuracy of the thermobalances.

Convection currents

Convection currents² result from the effect of gravity on temperature-induced differences in the specific mass of gas at different locations within the reaction vessel. They become noticeable for pressures greater than 100 – 200 mbar and are manifested by convection loops which can perturb the thermogravimetric measurements.

In open static reaction vessels, the convection loops curl outside the reaction vessel and the well-known chimney effect is observed (Fig. 2.3a.). Such a configuration has to be avoided or one end of the reaction vessel has to be plugged.

In closed static reaction vessels, convection may occur due to radial temperature gradients, as shown schematically in Fig. 2.3b where the sample is envisaged to have a temperature slightly lower than that of the wall of the vessel. The convection loops in this case lead to an apparent mass increase. Near the top of the furnace where strong radial and longitudinal gradients are present, convection phenomena are complex. Such a region (20 cm above the furnace) is subject to turbulence which may be minimised by the use of thin suspension wires having no geometrical irregularities such as asperities or suspension hooks.

² Another type of convection – concentration convection – due to gas composition differences can also be envisaged. In the present application, such a phenomenon is negligible but in the case of liquids, for example near electrode surfaces, diffusional transport is often supplanted by concentration convection in perfectly isothermal conditions.

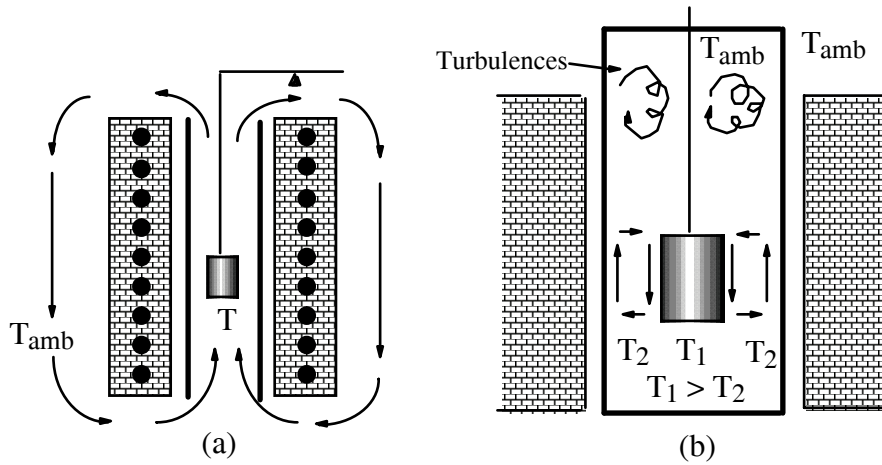


Fig. 2.3. Convection currents in reaction vessels: (a) a vertical open vessel, (b) a closed static vessel.

A semi-quantitative assessment of the importance of these natural thermal gravity convection currents can be obtained through the use of the *Rayleigh* number, Ra . This dimensionless number is defined as:

$$Ra = \frac{g \beta C_p \rho^2 b^3 \Delta T}{\eta K} \quad (2.2)$$

with:

g : the acceleration due to gravity,

β : thermal expansion coefficient of the gas (for a perfect gas: $\beta = 1/T$),

C_p : thermal capacity of the gas at constant pressure,

ρ : density of the gas,

b : length of the non-isothermal zone,

ΔT : temperature difference,

η : dynamic viscosity of the gas,

K : thermal conductivity of the gas.

For low values of the Rayleigh number ($Ra < 40\,000$), natural thermal gravity convection may be neglected. For higher values, convection loops may perturbate thermogravimetric measurements, sometimes creating very strong movements of the sample suspension system and leading to a drastic decrease in accuracy.

In *dynamic reaction vessels*, the imposed gas flow leads to forced convection whose effects are generally greater than those due to natural convection. The flow behaviour within the vessel can then be described by the *Reynolds* number (Re). This dimensionless number is defined as:

$$Re = \frac{\rho u L}{\eta} \quad (2.3)$$

with:

ρ : density of the gas,

u : linear velocity of the gas,

L : characteristic length of the system,

η : dynamic viscosity of the gas, calculated using the following equation:

$$\eta = \frac{1}{3\sqrt{2}\sigma} \sqrt{\frac{8mkT}{\pi}} \quad (2.4)$$

with:

k : Boltzmann's constant,

m : mass of one gas molecule,

T : absolute temperature of the reaction vessel,

σ : mean collisional cross-section of a molecule ($\sigma = 4\pi r^2$ where r is the molecule radius).

When considering this number, it is important to calculate for both the tube (where the tube diameter is used for the characteristic length L) and for the sample (where L is taken as the sample length). The first value then describes the behaviour of the gas in the reaction tube without any sample in it and the second, the perturbation caused by the presence of the sample. With laminar flow in the tube ($Re_{tube} < 2\,000$), the variation of gas velocity across the tube is described by Figure 2.4.

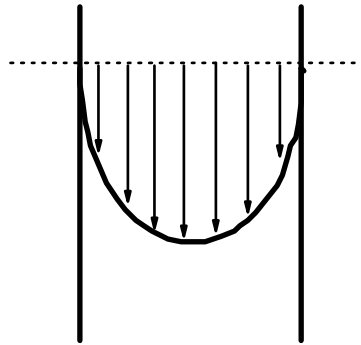


Fig. 2.4. The variation of gas velocity in a cross section of the tube under laminar flow.

For laminar flow along the sample ($Re_{sample} < 10^5$), a boundary diffusion layer of thickness δ is established above the sample surface and mass transport across this layer takes place by diffusion only. The contour of this boundary can be defined by the contour of constant flow rate u_δ :

$$u_\delta = 0.99 u^\infty \quad (2.5)$$

where u^∞ is the remote flow rate in the heart of the gas stream. The thickness of the diffusion boundary layer is given by:

$$\delta = \frac{5L}{\sqrt{\text{Re}}} \quad (2.6)$$

or, using the expression for Re:

$$\delta = 5 \sqrt{\frac{\eta L}{\rho u}}. \quad (2.7)$$

Figure 2.5 shows schematically the variation of the diffusion boundary layer along a vertical sample in a thermobalance where the gas flows downwards.

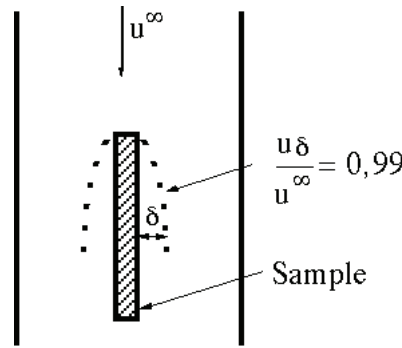


Fig. 2.5. Schematic variation of the boundary layer along a vertical sample of rectangular cross section.

This approach, though of necessity simple, provides insights into the factors that affect the accuracy of the experimental values obtained in thermogravimetric tests. It should be noted though that the values given for the Rayleigh and Reynolds numbers have to be considered as an order of magnitude guide only. For example, a gas flow with a Reynolds number of 2 000 may be turbulent in a tube of high internal roughness, but perfectly laminar in a smooth silica tube.

Thermomolecular fluxes

In contrast to convection forces, which are active at moderate and high gas pressures, thermomolecular fluxes appear at low pressures in the domain where the gas may be considered as a *Knudsen gas*. The term *Knudsen gas* describes a situation where molecules do not collide with each other but only with the vessel wall. Such behaviour obtains for values greater than 1 of the dimensionless *Knudsen number* (Kn):

$$Kn = \frac{\lambda}{d} \quad (2.8)$$

where λ is the mean free path of molecules and d is a characteristic distance, e.g. the tube radius for a cylindrical reaction vessel.

In this *Knudsen* domain, gas pressure relates to temperature according to:

$$\frac{P_2}{P_1} = \sqrt{\frac{T_2}{T_1}} \quad (2.9)$$

Consider a cylindrical sample immersed in a *Knudsen* gas and submitted to a temperature difference $T_2 - T_1$ applied across a horizontal plane whose trace is XY in Fig. 2.6. This sample is then submitted to two resultant *Knudsen* forces:

- a resultant normal *Knudsen* force, F_n , acting on the horizontal circular section (Fig. 2.6a);
- a resultant tangential *Knudsen* force F_t , acting on the vertical surfaces of the cylindrical sample (Fig. 2.6b).

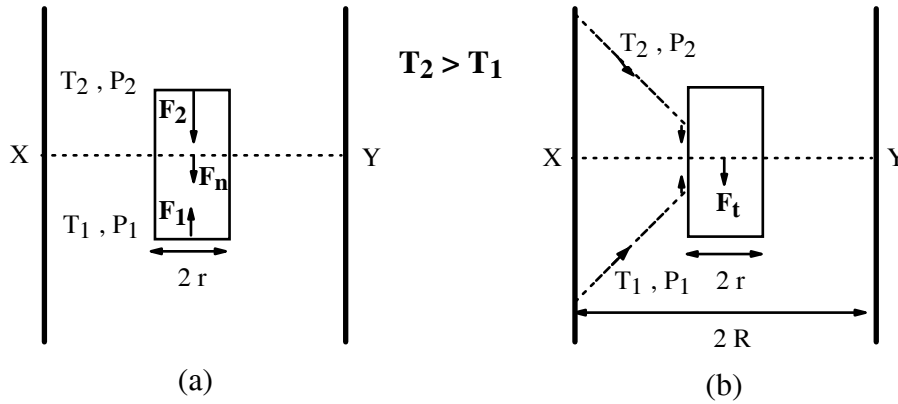


Fig. 2.6. Normal and tangential forces acting on a vertical cylindrical sample submitted to a temperature gradient in a *Knudsen* gas.

Calculation of F_n :

The resultant force F_n arises from the difference in the pressure forces on the two circular bases of the cylinder (Fig. 2.6a):

$$\begin{aligned} F_n &= F_2 - F_1 - (P_2 - P_1) \pi r^2 \\ F_n &= \pi r^2 P_2 \left(1 - \sqrt{\frac{T_1}{T_2}} \right) \end{aligned} \quad (2.10)$$

Calculation of F_t :

The resultant tangential force is due to the difference in the momentum of the molecules hitting the vertical surface of the sample and arriving from the upper (hot) or the lower (cold) part of the reaction vessel (Fig. 2.6b). Such a force was forecast by Maxwell in 1879. It can be expressed by:

$$F_t = \pi r (R - r) P_2 \left(1 - \sqrt{\frac{T_1}{T_2}} \right) \quad (2.11)$$

In the intermediate domain, defined by a *Knudsen* number between 1 and 10^{-5} , normal and tangential forces are the result of a gas flux generated according to the exchange of momentum between molecules. The calculation of these forces is complex but it can be shown that they increase with pressure and pass through a maximum before they decrease. This decrease results from the modification of gas properties and the appearance of a regime where the pressure in a closed isothermal vessel has a unique value.

Table 2.2. describes the different gas-flow phenomena that may perturb thermogravimetric measurements and identifies the domains where they are active.

Table 2.2. Gas-flow regimes where perturbation of thermogravimetric measurements may occur.

Knudsen number	Pressure domain (air, 298 K, R = 5 cm)	Type of gas flow	Observations
$10^4 - 1$	10^{-7} to 10^{-3} mbar	Thermomolecular	Knudsen forces
$1 - 10^{-5}$	10^{-3} to 100 mbar	“Intermediate”	Knudsen forces
$\leq 10^{-5}$	≥ 100 mbar	Convection	Fluctuations around an equilibrium position

In order to limit all the perturbations described above, a symmetrical furnace set-up is particularly efficient. In order to optimise performance, both furnaces are operated as nearly as possible at the same temperature and with the same temperature gradients. Such an arrangement is shown schematically in Fig. 2.7.

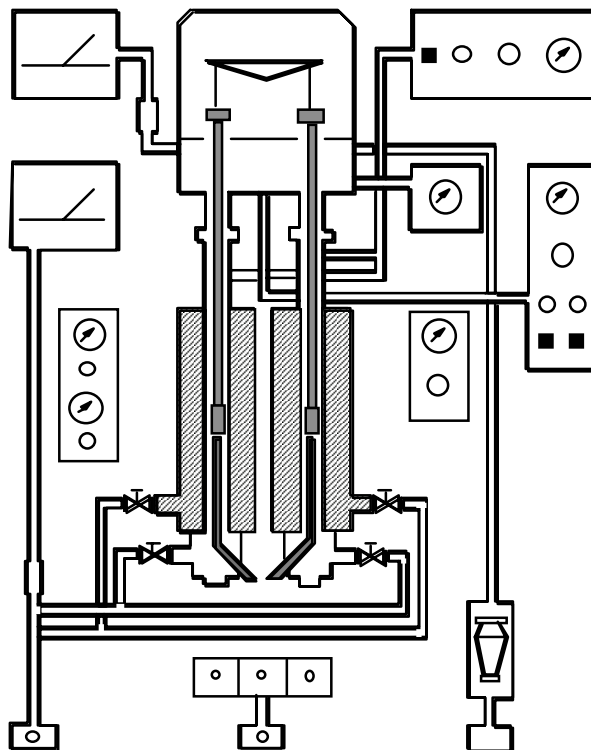


Fig. 2.7. Thermobalance with symmetrical furnaces (Setaram™ type)

2.2.2.2. Spring thermobalances

Spring thermobalances were described as early as 1915 but became well known with the work of McBain (1925) on gas adsorption on solids. The name of this researcher was subsequently associated with all spring thermobalances. Their main attraction is that they can be made entirely in Pyrex or silica glass and therefore can be used with many corrosive environments (chlorine, ammonia, sulphur, ...) without having to protect metallic parts (the beam, for example) by inert gas counter-flows. The measurement is simple and consists in following the elongation of a spring to which the sample is hung. This elongation is proportional to the weight change according to:

$$\Delta m = \frac{1}{k} \Delta l \quad (2.12)$$

where k is the spring constant. This constant is a function of the spring material and geometry and is given by:

$$k = \frac{4 R^3 n}{E r^4} \quad (2.13)$$

where:

R : radius of the spring coil,

n : number of coils,

r : radius of the spring wire,

E : Young's modulus of the spring material.

For a silica spring ($E = 23.5$ GPa) of 100 coils of 1 cm radius, made from a 0.4 mm diameter wire, relation 2.13 gives:

$$k = 10 \text{ m.N}^{-1} = 0.1 \text{ mm.mg}^{-1}$$

Such a value corresponds to a sensibly robust spring of average accuracy, usable for current measurement. The accuracy of the balance therefore relies on the accuracy of measurement of the elongation of the system. With optical cathetometer measurement, having an accuracy of $\pm 10 \mu\text{m}$, mass changes of $\pm 100 \mu\text{g}$ can be resolved. Discontinuous monitoring is, in this case, reasonable but the accuracy can be increased using continuous optical or electromagnetic measurements. Early optical systems projected onto a screen the image of a measurement scale fixed to the spring but modern systems would use a CCD camera with computer imaging analysis. Electromagnetic monitoring uses a differential transformer that follows the displacement of a ferromagnetic cylinder attached to the spring. By this means, a precision of $\pm 25 \mu\text{g}$ can be achieved but even better resolution can be obtained using springs of higher constant.

The limitations of such thermobalances lie in the maximum admissible load and in the influence of temperature. The maximum admissible load is given by:

$$P_{\text{max}} = \frac{2 \ 650 \ \pi \ r^3}{2 \ R} \quad (P \text{ in g and } R \text{ in mm}) \quad (2.14)$$

For the spring described above, it is of the order of 4 g but may be as little as 500 mg for a more accurate spring with a constant of 2 mm.mg^{-1} . The temperature influence arises from the variation of Young's modulus. From equations (2.12) and (2.13), we have:

$$\frac{dl}{l} = - \frac{dE}{E} \quad (2.15)$$

For a silica spring:

$$\frac{1}{E} \frac{dE}{dT} = 1.9 \times 10^{-4}, \quad (2.16)$$

leading to:

$$dl = - 1.9 \times 10^{-4} l \cdot dT$$

For a 1 m long spring, the temperature influence is therefore as high as $200 \mu\text{m.K}^{-1}$. Clearly, therefore, it is of paramount importance for the string to operate at constant temperature. This can be achieved using a double-walled container with temperature-controlled water circulating within the wall space. The overall temperature control can then be excellent, generally ± 0.02 K in the range $35 - 45^\circ\text{C}$.

Figure 2.8 shows an experimental arrangement in which a spring thermobalance is used for measuring the kinetics of metal sulphidation by gaseous carbon disulphide.

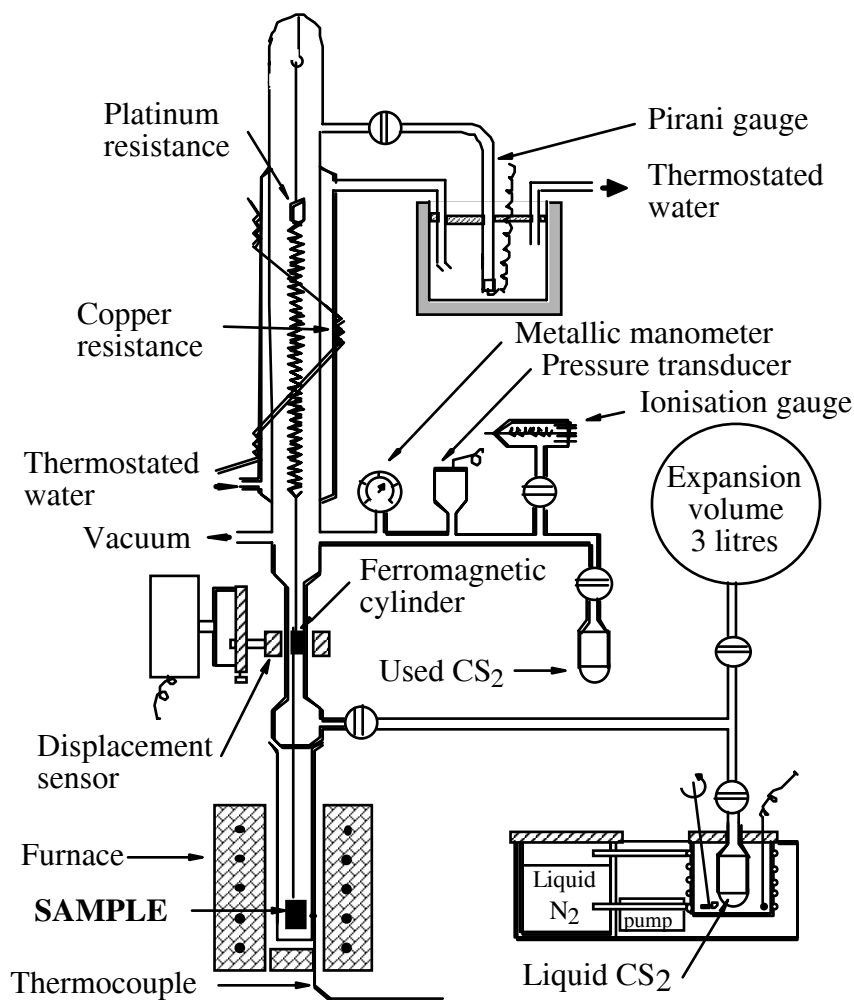


Fig. 2.8. McBain-type spring thermobalance used for metal sulphidation studies with gaseous carbon disulphide³

2.2.3. Thermogravimetric analysis techniques under controlled atmospheres

Precise and extensive thermogravimetric studies require control and monitoring of the gas composition. Laboratory-made designs that achieve this have been coupled to commercially available thermobalances for many years. Volumetric titrating pumps, which were used in the past have now been replaced by mass flowmeters that allow the mixture of several gases with a precise control in the range 1 % - 100 %.

The use of an electrochemical system for the control and monitoring of oxygen partial pressure in a vessel or a flowing gas offers several advantages over other systems because of its sensitivity, ease of control of the oxygen pressure and the ability to produce absolute measurements without reference to other auxiliary techniques such as mass spectrometry,

³ A. Galerie, M. Cailliet, J. Besson, *Progress in Vacuum Microbalance Techniques*, Heyden & Sons Eds., London, **3** (1975) 173-181.

gaseous chromatography, etc. The electrochemical oxygen pump permits the injection or extraction of oxygen into or out of a vessel or a flowing gas. The pump consists of a tube of stabilised zirconia ($\text{ZrO}_2 - \text{Y}_2\text{O}_3$ (9 mol.%)) provided with a platinum coating on both the inner and outer surfaces (see figure 2. 9). The gas flows inside the tube but the external electrode is in direct contact with ambient air. The tube is placed in an electrical resistance furnace so that the middle zone of the pump is in the range 700 - 900°C. This design allows control of the partial pressure of oxygen in several gas mixtures, e.g., oxygen in inert gas, inert gas-CO-CO₂ or inert gas-H₂-H₂O. The partial pressures of the components are controlled by changing a continuous electrical current, I , applied to the electrodes of the pump. For example, in the case of inert gas-oxygen mixtures, the mole fraction of oxygen $N_{\text{O}_2}^0$ in the flowing gas obeys the following equation:

$$N_{\text{O}_2} = N_{\text{O}_2}^0 \pm 0,209 \frac{I}{D} \quad (2.17)$$

where $N_{\text{O}_2}^0$ is the oxygen mole fraction upstream of the pump, D is the gas flowrate (in litres/h TPN) and I is the current (in amps) passing through the zirconia tube. Under these conditions, the oxygen mole fraction can be precisely controlled in the range 1 - 10⁻⁶.

For the case that carbon dioxide is supplied to the gas circuit, the CO and CO₂ partial pressures can be determined by applying a current through the pump according to:

$$P_{\text{CO}} = 0.418 P_t \frac{I}{D} \quad (2.18)$$

$$P_{\text{CO}_2} = P_t \left(N_{\text{CO}_2}^0 - 0.418 P_t \frac{I}{D} \right)$$

where $N_{\text{CO}_2}^0$ is the CO₂ mole fraction upstream of the pump and P_t is the total pressure, in bar. The same design can be used to control the hydrogen and water vapour partial pressures in an inert gas-hydrogen mixture. In this case, the current passing through the pump electrochemically oxidises hydrogen. The calculated equilibrium partial pressures are:

$$P_{\text{H}_2\text{O}} = 0.418 P_t \frac{I}{D} \quad (2.19)$$

$$P_{\text{H}_2} = P_t \left(N_{\text{H}_2}^0 - 0.418 P_t \frac{I}{D} \right)$$

where $N_{\text{H}_2}^0$ is the hydrogen mole fraction upstream of the pump. Using CO-CO₂ or H₂-H₂O mixtures the equilibrium partial pressure can be easily controlled in the 1 - 10⁻²⁷ bar⁴ range.

⁴ A. Caneiro, M. Bonnat and J. Fouletier, *J. Applied Electrochem.*, **11** (1981) 83.

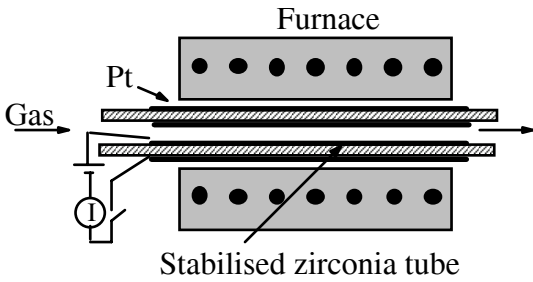


Figure 2. 9. Diagram of the electrochemical oxygen pump.

The partial pressure in a flowing gas can be measured using an oxygen sensor. The most widespread design is the potentiometric zirconia oxygen sensor which consists of a closed-ended stabilised zirconia tube (see figure 2.10). The reference electrode, prepared from platinum paste is in direct contact with the ambient air. The gas to be analysed is brought into contact with the internal electrode using an alumina capillary. The working temperature is measured with a Pt - 10 % Rh / Pt thermocouple placed on the surface of the measuring electrode. The sensor e.m.f. is measured using platinum wires. The equilibrium partial pressure is then obtained from Nernst’s law:

$$\log P_{O_2} = 2.012 \times 10^4 \frac{E}{T} - 0.6985 \tag{2.20}$$

where E is the sensor e.m.f. (in V) and T the temperature (in K).

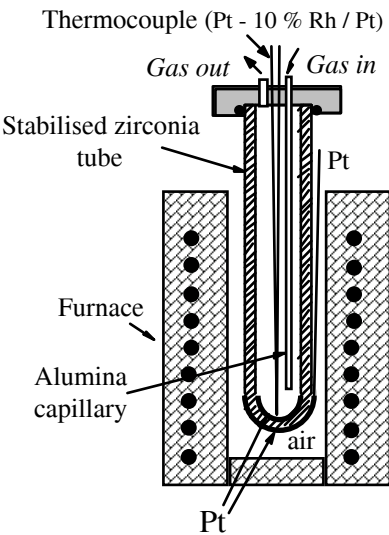


Figure 2.10. Zirconia oxygen sensor

More recently, a potentiometric chlorine sensor has been coupled to a thermobalance.

The design of the electrochemical system, consisting of an oxygen pump and a potentiometric zirconia sensor, coupled to a thermobalance is shown schematically in figure 2.11⁵.

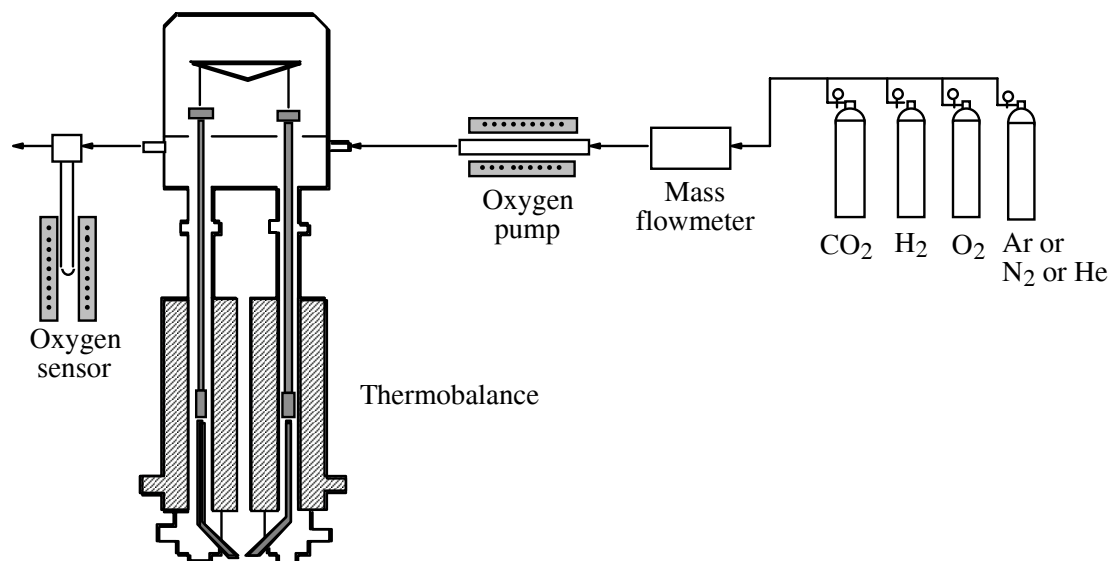


Figure 2.11. Diagram of the experimental set-up coupling an electrochemical system for measurement and regulation of the oxygen pressure with a thermobalance.

2.3. Characterisation of corrosion scales

Characterisation of the scales formed during high temperature oxidation is used to establish their nature, morphology, stress state and adherence. Formerly, techniques used for characterisation were limited to chemical analysis and optical metallography but now numerous physical techniques exist based on interactions between solid matter and beams of particles such as electrons, photons and ions.

2.3.1. Electron-matter interaction and associated techniques

Electron-matter interaction is used in electron microscopes, in scanning (SEM) or transmission (TEM) modes, in the electron microprobe and in the Auger spectrometer. Let us consider an electron beam, with an energy E° , impinging on a solid surface. The different effects generated by such an interaction are summarized in figure 2.12.

⁵ A. Caneiro, P. Bavdaz, J. Fouletier and J.P. Abriata, *Rev. Sci. Instrum.*, **53** (1982) 1072.

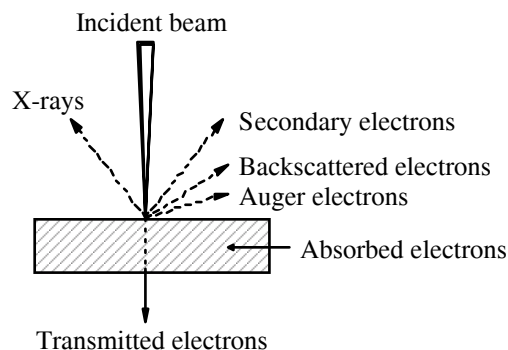


Fig. 2.12. Different responses emitted as a result of the interaction of an electron beam with a solid surface.

In practice, the incident electrons penetrate the specimen, producing a “collision cascade” with the atoms they encounter. The volume of the specimen involved is called the “interaction volume” and is generally pear-shaped (Fig. 2.13).

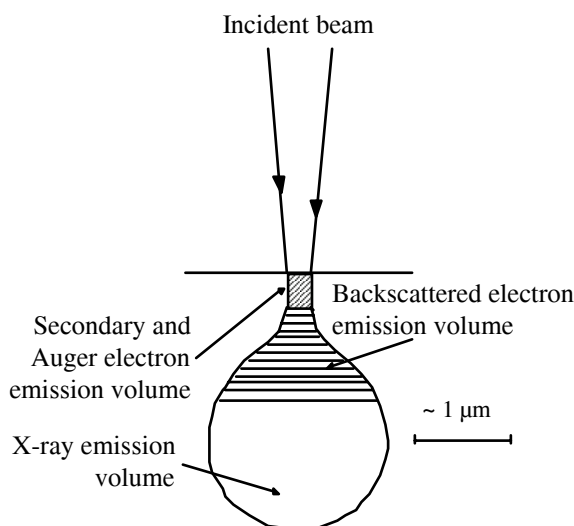


Fig. 2.13. Interaction volume and different zones of emission.

Photons and electrons are emitted from the interaction zone and these can be analysed, in terms of both number and energy, to give useful chemical information.

2.3.1.1. Photonic emission

As they enter the specimen, the energetic incident electrons interact with the atoms, exciting electrons from their deep energy levels to a higher level. Such excited atoms quickly (10^{-16} s) return to their fundamental state by an internal electron transition with emission of a corresponding photon (Fig. 2.14). The wavelength of the emitted photon is therefore directly linked to the nature of the element analysed.

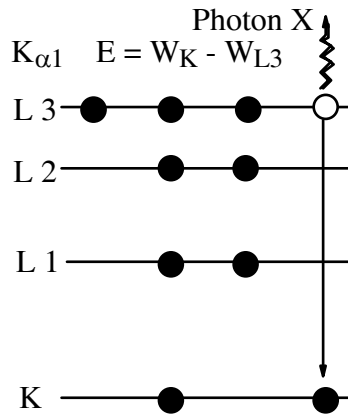


Fig. 2.14: Emission of a photon X by the return of an excited electron to its fundamental state.

It is possible to analyse quantitatively all chemical elements from atomic number $Z = 5$ provided an energetic beam (several keV to tens of keV) is used and a suitable detector is available. In practice, though, only optical wavelength detectors calibrated with careful measurements on standards can provide good quantitative accuracy. This technique is termed “Wavelength Dispersive X-ray analysis” or “WDX” and can be achieved in electron microprobes (*Castaing* microprobes). Through the use of a good spectrometer it may even be possible to observe peak shifts due to differences in the oxidation number of the analysed elements. In contrast, with solid state detectors (“Energy Dispersive X-ray analysis” or “EDX”), only semi-quantitative analysis can be performed but these analyses can be performed very rapidly (a few minutes) and the technique is now a routine capability of most Scanning Electron Microscopes. An example of an EDX spectrum is shown in figure 2.15.

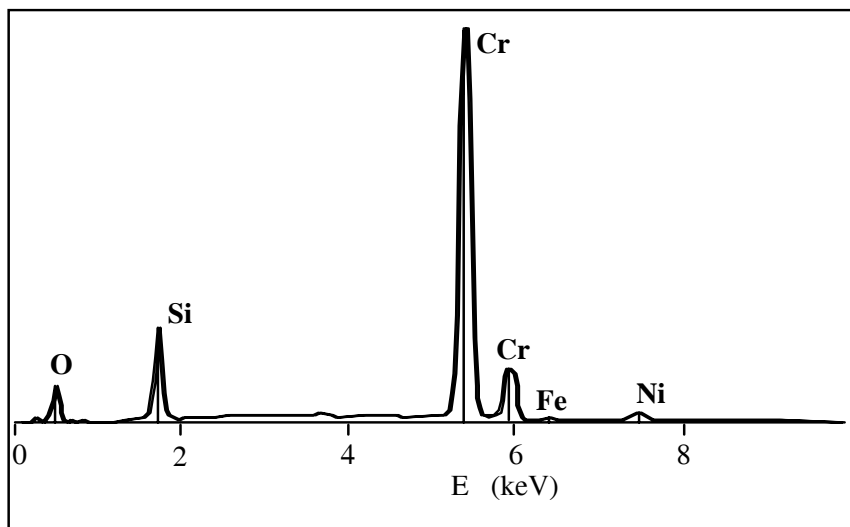


Fig. 2.15. EDX spectrum of the internal part of the scale formed by oxidation of an austenitic stainless steel containing minor addition of Si. The main oxide is Cr_2O_3 but silicon is enriched due to the internal precipitation of SiO_2 .

2.3.1.2. Electronic emission

Figure 2.16 shows the general shape of the energy spectrum of electrons emitted from a solid bombarded by an electron beam. Three types of emitted electrons are observed: backscattered electrons, secondary electrons and Auger electrons.

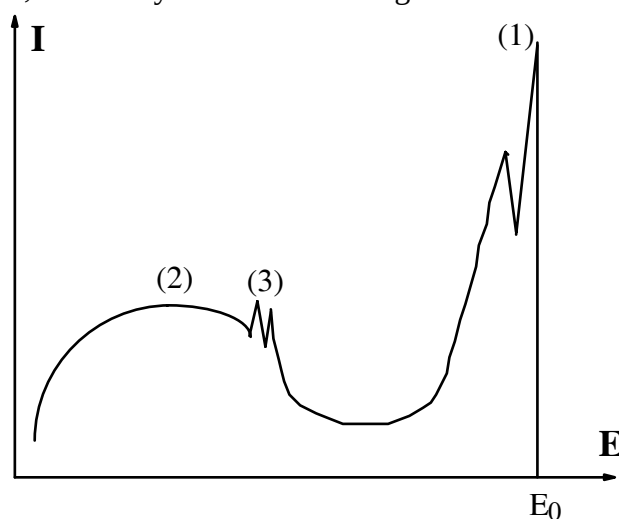


Fig. 2.16. General spectrum (number vs. energy) of emitted electrons from a solid bombarded with a primary electron beam: (1) backscattered electrons, (2) secondary electrons, (3) Auger electrons.

Backscattered electrons result from quasi-elastic collisions with the atoms of the solid. They are very energetic, their energy being directly related to the mass of the atoms they have hit. Energy measurement gives, therefore, information on chemical composition and this can be used in the SEM to obtain composition maps.

Secondary electrons are much less energetic. They are generated in the collision cascade (Figure 2.17) and lose energy on travelling to the surface. Only those electrons produced in the near-surface region can escape the solid, typically with an energy of ~ 50 eV. This energy is greatly influenced by the surface topography and these electrons are generally used to obtain the classical images which have made the SEM popular. Magnifications of 10000 are routinely achievable using secondary electrons.

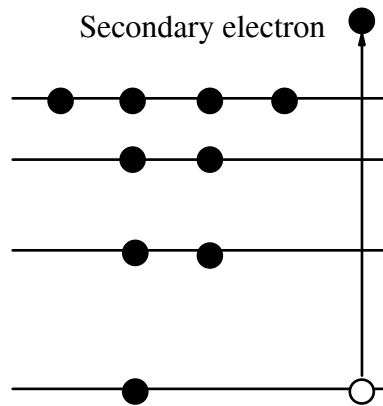


Fig. 2.17. Secondary electron emission under primary electron collision.

Auger electrons result from non-radiative de-excitation which produces an electron rather than a photon. Three energy levels can, therefore, be identified (Fig. 2.18):

- that of the original secondary electron;
- that of the de-excited electron;
- that of the Auger electron produced.

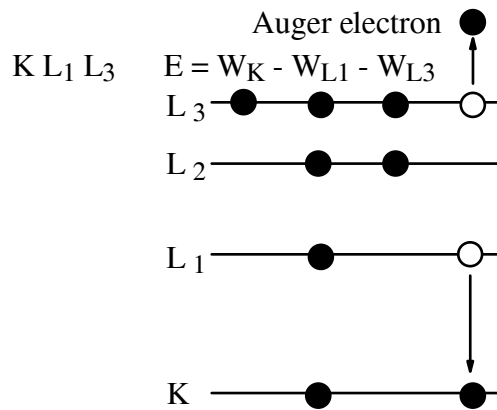


Fig. 2.18. Principle of Auger electron emission.

Auger electrons have very low energy and only those produced at the solid surface can be analysed. Auger spectrometry is therefore classically considered as a surface analysis technique. Moreover, since heavy elements show a very complex Auger spectrum, only light elements are commonly analysed. An interesting feature is the chemical shift due to differences in the oxidation state of the emitting element. Coupling Auger spectrometry with ion beam milling, it is possible to obtain depth concentration profiles up to several 100 to 1000 nanometers (Fig. 2.19).

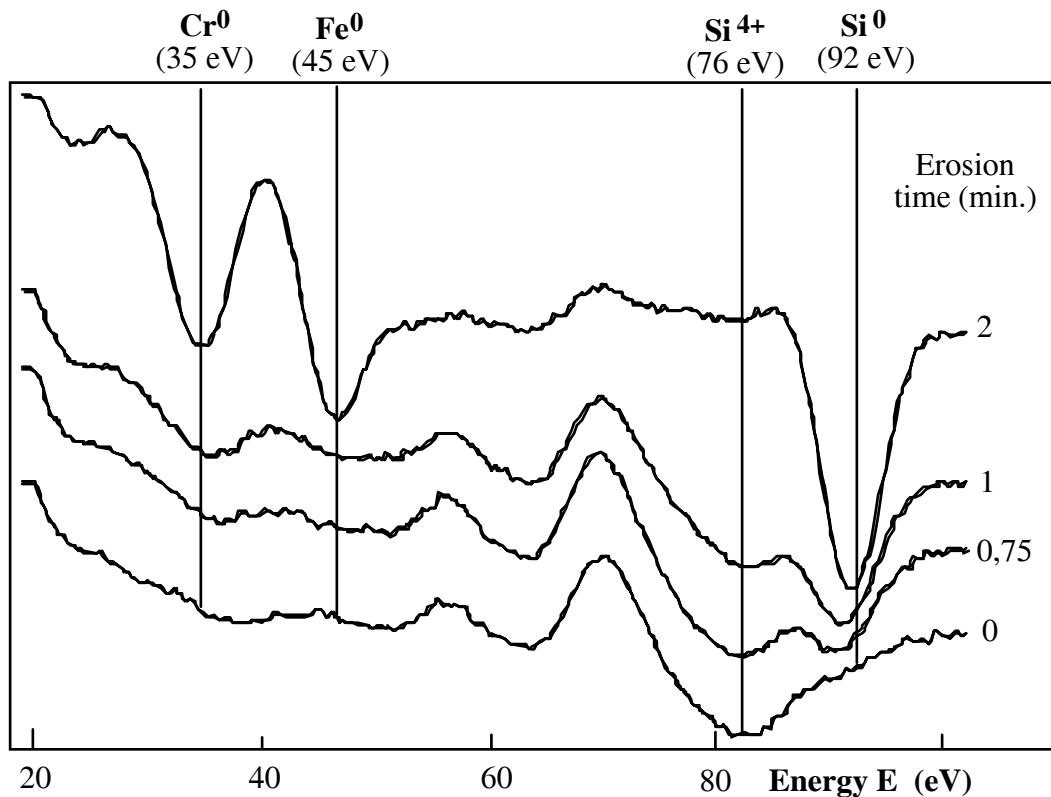


Fig. 2.19. Auger spectrum, in the low energy range, of the surface of a Fe-17Cr-1Si ferritic stainless steel bright-annealed 15 min at 850°C in H_2/H_2O . The differences in the spectrum with sputtering time results from the change from the SiO_2 -covered surface to the bulk material.

Transmitted electrons are used in the Transmission Electron Microscope (TEM). The sample to be analysed by this technique must be thinned by chemical or physical methods down to about 10 nanometers. Magnifications of 10^5 to several millions (high resolution) are possible together with concurrent EDX for chemical analysis and electron diffraction for structural analysis.

2.3.2. Photon-matter interaction and associated techniques

UV or X photons interacting with a solid surface may produce one of the following phenomena:

- fluorescence (emission of light),
- Auger electron emission,
- photoelectron emission,
- refraction,
- diffraction.

The first two are exactly similar to those described in 2.3.1. for electron bombardment. They are used as analytical tools in the X-ray fluorescence spectrometer and in the Photonic Auger

spectrometer. The third exhibits characteristics which make it a very useful tool for performing surface analysis and is the basis of X-ray Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA). The main interest of this technique is that it allows precise measurement of the energy, W , of the electron level from which the photoelectrons are emitted. The emission spectrum exhibits the characteristic peak shape shown in figure 2.20.

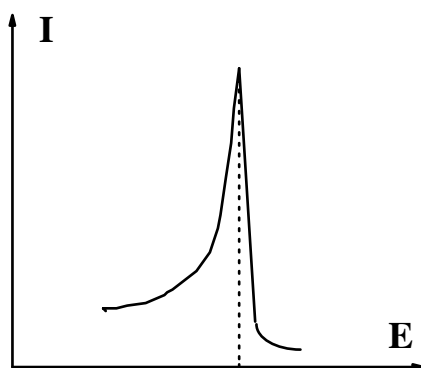


Fig. 2.20. Emission spectrum (intensity versus energy) of the photoelectrons emitted by a given energy level of an atom.

If E_p is the energy of the observed peak, the energy W is given by:

$$W = E_0 - E_p - e\Phi \quad (2.21)$$

where E_0 is the incident photon energy, and $e\Phi$ the work of extraction of the electrons from the solid. Since W is modified by changes in local chemical bonding, the XPS technique gives information on the nature and oxidation state of the analysed elements. As for Auger spectrometry, this technique is limited to the near surface of solids, i.e. to depths in the nanometer range.

Refraction is the deviation of an electromagnetic beam at the interface between two transparent media differing in their refractive index. The phenomenon is governed by Descartes' law.

Diffraction is of a different physical nature and results from the periodicity of the crystalline state. This phenomenon arises when the wavelength of the incident beam* is comparable to the distance between atoms in the solid. The effect of diffraction is identical to reflection (Fig. 2.21) and, for a certain number of angles only, defined by Bragg's law:

* Diffraction is best discussed in terms of the wave nature of the impinging beams and is observed not only with X- and γ -rays but also with electrons and neutrons.

$$\lambda = 2 d_{hkl} \sin \theta \quad (2.22)$$

where λ is the wavelength of the incident beam, d_{hkl} the reticular distance of the family of planes generating the diffraction and θ the diffraction angle (measured in respect to the solid surface).

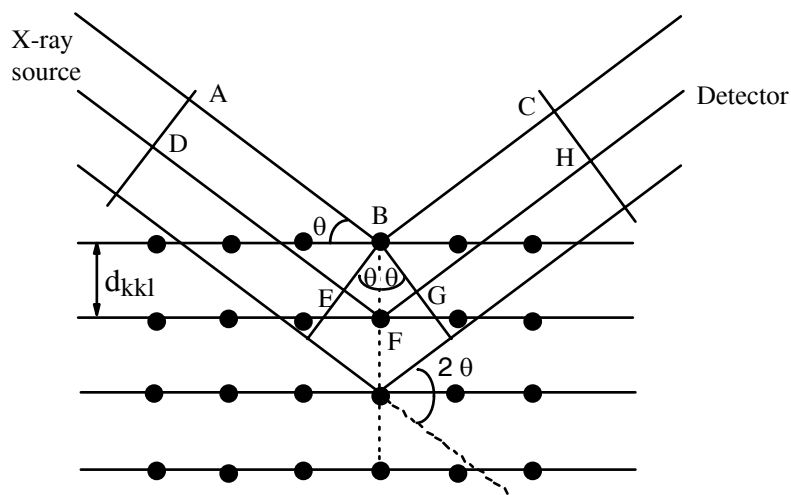


Fig. 2.21. Diffraction by a family of reticular planes with interplane distance d_{hkl} . The path-difference between the two beams ABC and DFH is equal to $EF + FG = 2 d_{hkl} \sin \theta$.

As the interatomic distances of inorganic substances are in the fraction of nanometer range, weak X-rays are particularly suitable for diffraction experiments. The most frequently used beam is produced by electron bombardment of copper (Cu K_α line) in the so-called “X-ray copper tube”.

There are many uses of diffraction such as in the measurement of unknown structures or for the determination of the nature of the phases present in a solid. For this latter purpose, the “powder method” is employed where some members of all families of reticular planes have a statistical probability of being parallel to the surface of the analysed sample. A real powder or a polycrystalline sample is convenient for such an analysis provided that the grain size is much smaller than the area analysed by the beam. Each diffraction peak corresponds here to a family of planes, with position given by Bragg’s law (Eq. 2.22), and its intensity determined by the nature and position of the atoms.

Fig. 2.22 shows the diffraction spectrum of the oxide scale grown on a Ni-Fe-Cr-Si-Mn high-temperature alloy maintained at 900°C in oxygen. The identification of the peaks was made by comparison with the data from the ICDD* (International Center for Diffraction Data) databank. Such an analysis is mainly qualitative and detects products in percentage amounts; generally, neither trace products nor amorphous phases in any amount (vitreous silica in the present example) would be detected.

* formerly JCPDS (Joint Committee on Powder Diffraction Standards)

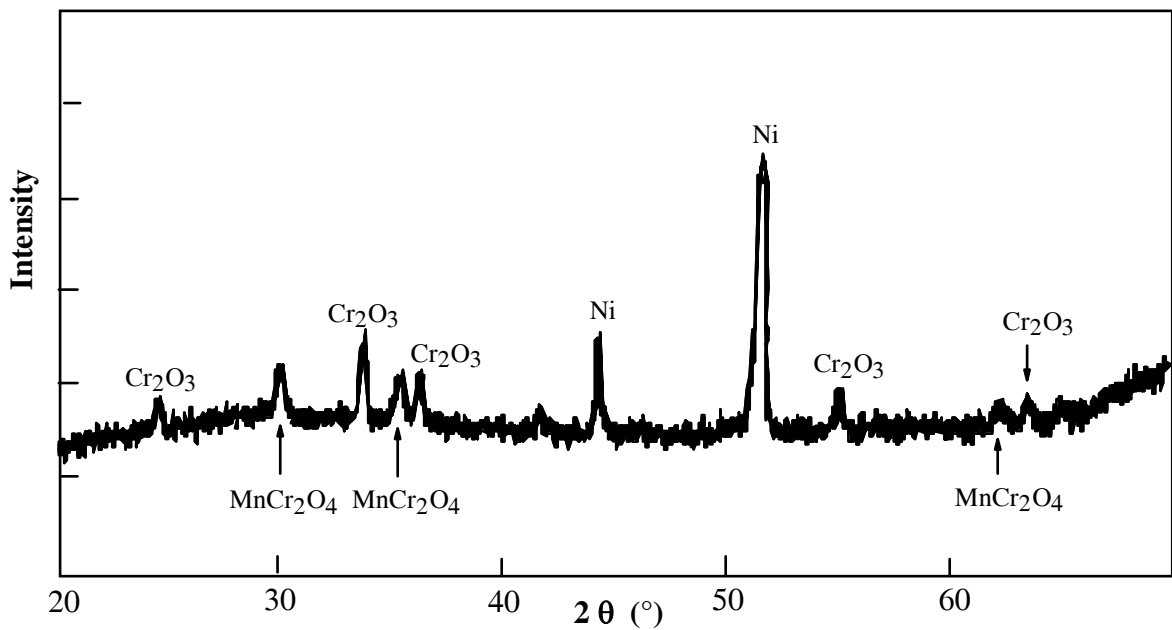


Figure 2.22. X-ray spectrum of the same specimen shown in Figure 2.15 showing that the oxide layer is duplex, consisting of Cr_2O_3 and the spinel MnCr_2O_4 . Amorphous silica does not produce a diffraction peak.

2.3.3. Ion-matter interaction and associated techniques

The bombardment of a solid surface by energetic ions gives rise to the following three phenomena:

- backscattering of incident ions;
- nuclear reactions;
- secondary ion emission.

The relative importance of these phenomena depends on the nature and energy of the incident ions and on the nature of the solid. A particular ion spectroscopy technique is associated with each of these phenomena:

- Rutherford backscattering (RBS);
- nuclear reaction analysis (NRA);
- ion scattering spectroscopy (ISS);
- secondary ion mass spectroscopy (SIMS).

The first two use very energetic ion beams (in the MeV range) whereas the last use lower energies (in the keV range).

2.3.3.1. Rutherford backscattering (RBS)

Consider a high-energy beam of light particles, protons (${}^1_1\text{H}$) or α particles (${}^4_2\text{He}$), impinging upon the surface of a thin solid foil. As experimentally demonstrated by Rutherford, a small number only of these particles hit the atoms of the solid and are backscattered by elastic recoil. If their energy is E_0 before and E after the recoil, the kinematic factor describing the backscattering yield is:

$$K = \frac{E}{E_0} \quad (2.23)$$

This factor may be calculated by classical mechanics:

$$K = \left[\frac{\cos \theta + \sqrt{\mu^2 - \sin^2 \theta}}{1 + \mu} \right]^2, \quad (2.24)$$

where μ is the ratio m/M of the masses of the incident ion and of the target atom and θ the angle at which the backscattered ions are collected. Using a multichannel solid detector, the energy of the backscattered ions are analysed to give a spectrum containing discrete peaks corresponding to the elements present in the target solid.

Changing now the thin foil to a semi-infinite solid produces additional backscattered ions recoiled by atoms situated under the surface. These ions exhibit higher energy loss than those backscattered at the surface since they have to penetrate further into the solid and suffer losses both on their inward and outward paths. Their total energy loss is therefore:

$$\Delta E = E_0 - \Delta E_{in} - K(E_0 - \Delta E_{in}) - \Delta E_{out} \quad (2.25)$$

The “in” and “out” energy loss terms can be calculated as a function of recoil depth giving information that permits element profiling. The RBS spectra of semi-infinite solids exhibits, therefore, a sharp front edge corresponding to ions backscattered by surface atoms (energy KE_0) followed by a tail generated by atoms located within the solid. Such a spectrum contains both analytical and in-depth information making RBS a very useful tool for studying thin layers, oxide layers for example, on bulk substrates. The best thickness range is 50 nm to 5 μm with greater sensitivity for heavy elements in light substrates. Fig. 2.23 gives an example of a RBS spectrum showing the information which can be extracted.

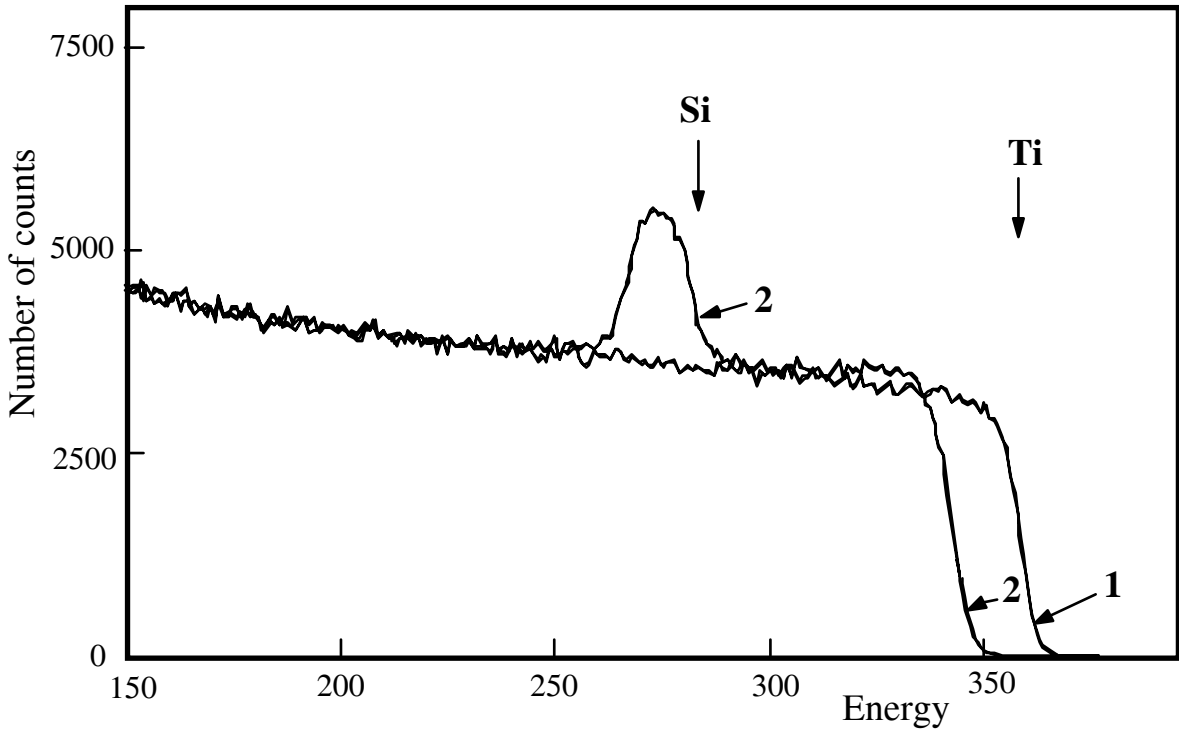
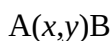


Fig. 2.23 RBS spectra of pure titanium (1) and of titanium covered with 125 nm silicon (2) showing the positions of Ti and Si fronts and the Ti-front shift due to the silicon layer. Spectra obtained with 2 MeV ^4He ions, normal incidence, collection at 165° .

One of the advantages of this technique is that it is non-destructive so that it can be used for repeat analyses on the same sample after different times of oxidation. The main disadvantage is the need for high energy accelerators, generally of the Van de Graaf type, and these are not readily available.

2.3.3.2. Nuclear Reaction Analysis (NRA)

When high energy particles hit atoms in a solid, nuclear reactions may be promoted, emitting new particles, y , different from the incident particle, x , and also exhibiting different energies (lower or higher). In the process, the target nucleus A transforms into another nucleus B . The conventional notation for such a transformation is:



Nuclear reaction analysis is mainly used for detecting light elements like C, N and O, using protons or deuterons (^2_1H). The most popular reactions are $^{16}\text{O}(d, p)^{17}\text{O}$ and $^{18}\text{O}(p, \alpha)^{15}\text{N}$ since these are very suitable for following the oxygen uptake in oxide scales or the development of oxygen diffusion profiles. Like Rutherford backscattering, Nuclear Reaction Analysis is a powerful non destructive tool, limited to 1-2 microns in depth. Lateral

resolution of 1 μm or less can be used for point analyses or mapping in “nuclear microprobes”.

2.3.3.3. Ion Scattering Spectroscopy (ISS)

Using ion beams of much lower energies (0.2 to 2 keV) produced by low cost and easy to use ion guns may generate the same analytical information as RBS but limited to surface atoms. The physical phenomenon is not changed and the expression of the kinematic factor is always given by equation 2.24. The technique is here called Ion Scattered Spectroscopy (ISS) and this is mainly a surface analysis technique, comparable with the electron spectroscopes described above. However, it is possible to obtain depth information by sputtering inward from the specimen surface. The lifetime t_m of the surface monolayer of the solid under ion sputtering is given by:

$$t_m = \frac{C_s}{F_B S} \quad (2.26)$$

where C_s is the surface concentration of the solid (atoms.m^{-2}), F_B is the ion flux of the beam ($\text{ion.m}^{-2}.\text{s}^{-1}$) and S the sputtering yield (number of sputtered atoms/number of incident ions). The first two of these parameters are easy to measure and control but the third is more difficult to evaluate. The sputtering yield is dependent not only on the nature, energy and the angle of incidence of the sputtering ions but also on the nature, crystalline orientation and properties of the bombarded surface. For example, using Ar^+ ions of 1 keV to bombard pure polycrystalline aluminium at 60° incident angle, gives a sputtering yield of about 2. Using a value of $1 \times 10^{19} \text{ atoms.m}^{-2}$ for C_s , a monolayer removal time of 1 second ($t_m = 1$) needs a beam flux of $5 \times 10^{18} \text{ ions.m}^{-2}.\text{s}^{-1}$, corresponding to an ion current of monocharged species of 0.8 A.m^{-2} . Modern ion guns cover a large range of currents from 10^{-5} to 10 A.m^{-2} so that an experimentally convenient choice of sputtering rate can usually be obtained.

2.3.3.4. Secondary Ion Mass Spectroscopy (SIMS)

In addition to the backscattered ions used for obtaining ISS information, secondary ions are generated by the collisions; these ions may be positive or negative and monoatomic (M^+ , C^- , O^-), simple polyatomic (O_2^-) or complex (MO^+). The SIMS technique is based on their collection and analysis with a mass spectrometer.

If the analysis time is less than the monolayer lifetime (“static” SIMS), the technique provides the mass spectrum of the surface layer, with the ion current being directly proportional to the element concentration in that layer. The sensitivity is very high, up to the ppb* (10^{-9}) range. On the other hand, if the beam current is high, leading to rapid surface sputtering ($1\mu\text{m.h}^{-1}$, for example), it is possible to analyse in-depth and to collect

* part per billion

concentration profiles of several selected elements. This analysis mode is called “dynamic” SIMS.

The big advantage of the technique is its high sensitivity for most elements in many materials, including insulating compounds. The profiling mode must be used with care due to the poorly defined relation between sputtering time and depth, particularly in non homogeneous materials such as oxidised metals.

An example of SIMS profiling is given in Fig. 2.24 for the case of the oxidation in oxygen of the binary nitride $\text{Ti}_x\text{Al}_{1-x}\text{N}$ obtained by chemical vapour deposition (see Chap. 6, Section 3.2.1). The figure shows that alumina, Al_2O_3 , is located at the external part of the oxidised scale whereas the internal part consists of a mixture of alumina and titania $\text{Al}_2\text{O}_3 + \text{TiO}_2$.

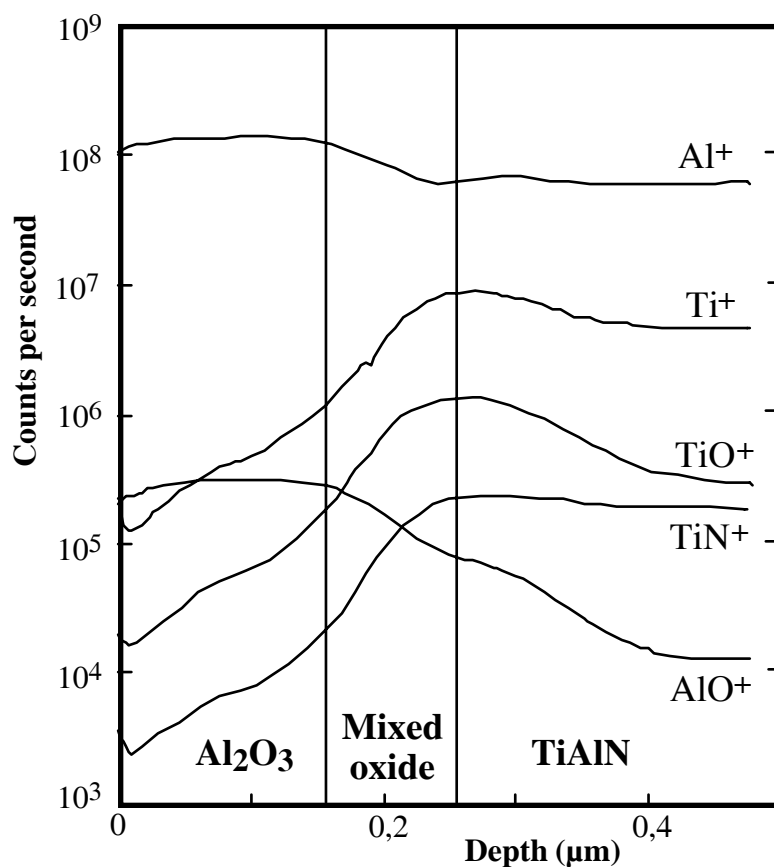


Fig. 2.24. SIMS spectrum as a function of depth of the oxide scale formed by oxidation of TiAlN at 850°C for 150 min using a 4 keV Xe^+ beam at 45° incidence.

2.3.4. Practical aspects

Using the characterisation techniques described above, without forgetting, of course, observation by eye and optical microscopes, all the features of oxide scale growth can be established, including composition, morphology and growth direction. Scale adhesion and oxide stress are also parameters of importance which must be determined.

2.3.4.1. Composition

The phases present in the oxide scales are commonly determined by X-ray diffraction. The technique is non-destructive and is best for scale thicknesses $\geq 1 \mu\text{m}$. For thinner scales, a glancing angle arrangement is used (GAXRD, *glancing angle X-ray diffraction*). For thicker scales, consideration must be given to the maximum penetration of X-rays since, for thick scales, phases at the metal-scale interface may not be observed. For profiling purposes in thin scales, direct experiments (RBS) or successive sputtering (Auger, XPS) are used. In thick scales, successive polishing parallel to the interface with corresponding X-ray diffraction spectra or local EDX measurements on cross- or taper-sections give good results.

2.3.4.2. Morphology

Any assessment of the morphology of oxide scales should begin with naked eye observation of scale homogeneity, its colour and whether obvious pores, cracks, blisters or spallation exist. Optical microscopy on polished cross-sections and scanning electron microscopy on these and on fracture surfaces, polished or not, give information at higher magnifications. Transmission electron microscopy on cross-sections is not as easy a technique due to difficult specimen preparation but it does permit the detection of nanometre precipitates or inclusions, epitaxial features at the metal-scale interface and interface undulation.

2.3.4.3. Growth direction

The direction of growth of the oxide (inward or outward) is a very important indicator of the oxidation mechanism: inward growth is associated with majority transport of oxygen through the scale whereas outward growth is the result of majority cation transport. The dominant process can be determined by three possible ways: two by observing the position of the scale compared with the initial metal surface, the third by observing the location within the scale at which new oxide is formed.

The marker experiment

Described in the thirties⁶, this experiment is based on the observation, after oxidation, of the position of inert markers (powder or thin wires of Pt, Au, SiO_2 , Al_2O_3 , etc.) deposited on the metal surface before oxidation. If the markers exist at the metal-scale interface then the matter transport in the scale is cationic but where the markers are located at the scale-gas interface, the matter transport is probably anionic (Fig. 2.25). Sometimes, the markers may be located at a well-defined intermediate interface, showing that two subscales grow by opposite cationic and anionic transports. For very thin oxide scales where powder and wire deposits are inappropriate, a convenient technique consists in submitting the metal to be oxidised to a

⁶ L. Pfeil, *J. Iron Steel Inst.*, **119** (1929) 501; **183** (1931) 237.

short ion beam sputtering of a non wettable inert substance, most often gold, leading to a deposit of submicron spheroidal markers.

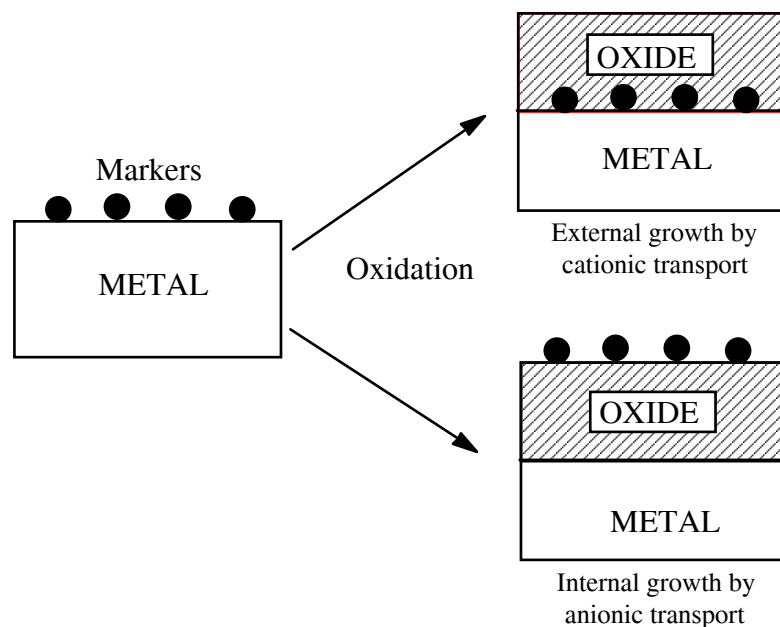


Fig. 2.25. Schematic principle of the inert marker experiment to assess the oxide growth direction.

Total metal consumption

This experiment uses thin metal wires which are totally oxidised. For cationic transport through the oxide, a central hole forms in the specimen with a diameter equivalent to that of the initial wire. In the case of anionic transport, the morphologic features are not so clear, sometimes including porosity, stratification or spallation.

Alternate oxidation in ^{16}O and ^{18}O

Changing, during oxidation, the oxygen atmosphere from natural oxygen predominantly ^{16}O , to ^{18}O and observing, after cooling down, the profiles of both isotopes in the oxide scale, is a convenient method of determining the main transport mechanism in the scale. Possible different ^{18}O distributions that may be observed are shown in Fig. 2.26 together with the associated transport mechanisms. Such a technique may also be used to study the penetration of oxide scales by water vapour with H_2^{18}O as oxidant⁷.

⁷ H. Nickel, Y. Wouters, M. Thiele and J. Quadackers, *J. Anal. Chem.*, **361** (1998) 540-544.

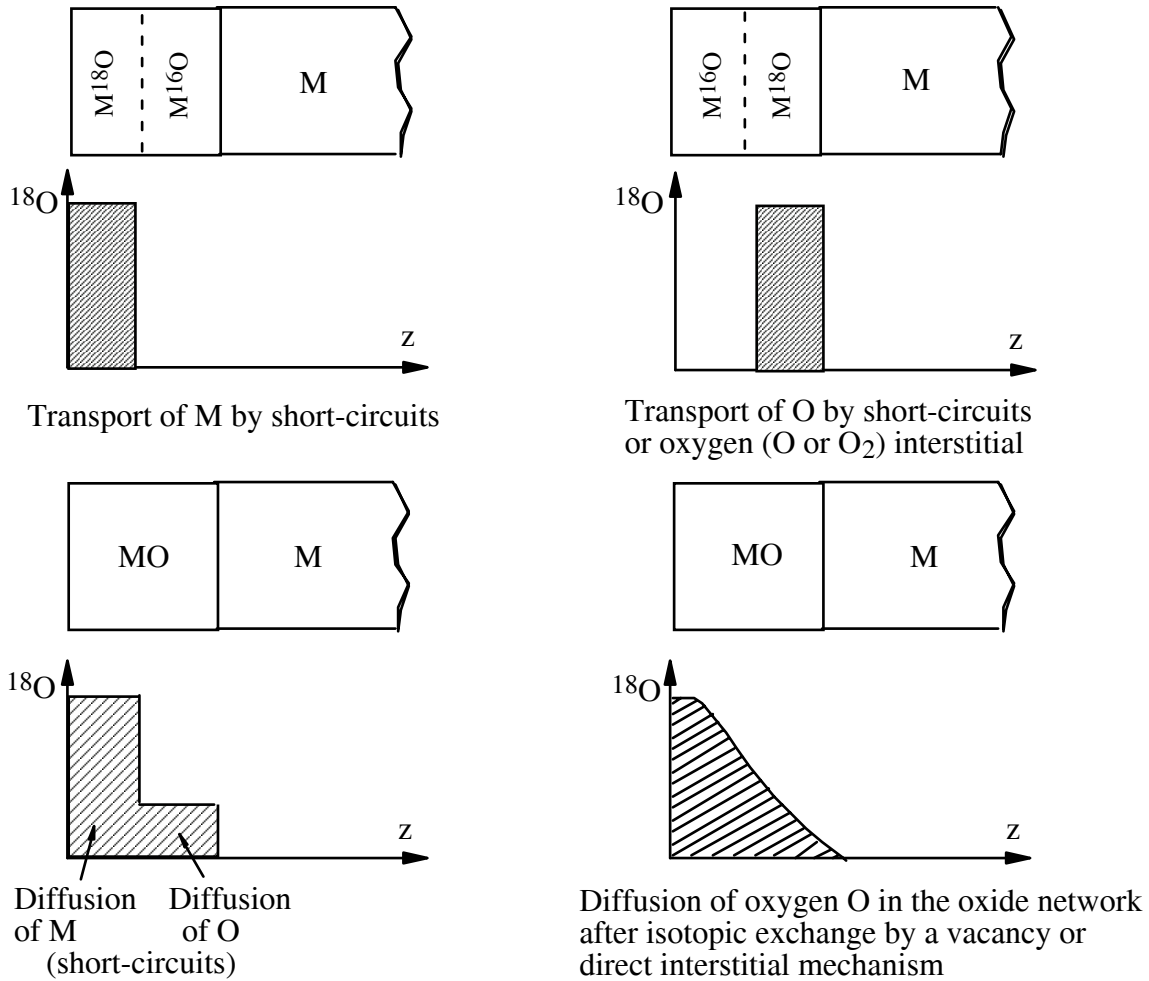


Figure 2.26. Principle of successive oxidations using $^{16}\text{O}_2$ followed by $^{18}\text{O}_2$ ⁸

2.3.4.4. Scale adhesion

Adhesion of oxide scales to their substrate may be qualitatively assessed during microscopic examination, either on the sample surface by examining spalled areas, or on cross-sections by observing the integrity of the metal-scale interface. When no damage is observed, simple tests can be used, consisting, for example, in bending the oxidised sample or using well-described pull-off tests using adhesive tape or a glued metal cylinder. Generating a scratch with a moving Vickers indenter submitted to increasing load also gives good comparative results. In order to make a quantitative determination of the fracture energy of the oxide-metal interface, a more sophisticated technique such as the *blister test*, where the oxide and the metal are forced to separate by a fluid pressure⁹, needs to be used.

⁸ J. Philibert, *Diffusion et Transport de Matière dans les Solides, Monographie de Physique*, Les Editions de Physique, Les Ulis, 1985.

⁹ J. Mougín, M. Dupeux, A. Galerie and L. Antoni, *Mater. Sci. Technol.*, **18** (2002) 1217-1220.

2.3.4.5. Residual stresses

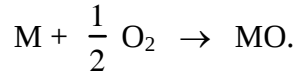
The sign and magnitude of the stresses developed in the oxide layer during its growth (*growth stresses*) can be determined by observing the associated deformation of the specimen. At the macroscopic level, the *bending test* consists of protecting one side of a rectangular thin metal sample and observing the curvature induced by the formation of the scale on the opposite side. At the microscopic level, the changes in the interatomic distances can be accurately measured by X-ray diffraction ($\sin^2\psi$ method) or by Raman spectroscopy. The growth stresses in oxide scales can be as large as 1-2 GPa (compressive), less in the metallic substrate (several tens of MPa), due to the larger thickness and lower creep strength of the metal compared to the oxide.

3. Phenomenological laws

3.1. Rate law, temperature and pressure dependences

3.1.1. Definitions of the reaction rate

Let us consider the oxidation reaction:



The progress, W , of this reaction can be characterised using several definitions of the reaction rate. It can, for example, be defined as the rate of oxygen pick up, $dn_O/A dt$, where dn_O corresponds to the number of moles of oxygen consumed during time dt and A the sample area. From an experimental point of view, though, it is easier to use the sample weight gain Δm . The reaction rate can then be expressed as $d\Delta m/A dt$, where $d\Delta m$ is the weight change occurring during time dt . These expressions are linked by the equation:

$$\frac{dn_O}{dt} = \frac{1}{16} \frac{d\Delta m}{dt} \quad \text{where } \Delta m \text{ is expressed in g.} \quad (2.27)$$

The reaction rate can also be defined as the rate of building of the oxide lattice: $dn_{MO}/A dt$, where dn_{MO} is the number of moles of MO formed during time dt . In this case, it is sensible to characterise the progress of the reaction by the thickness, y , of the scale. Then, if Ω is the volume occupied by one mole of oxide, we can write:

$$\frac{dn_{MO}}{dt} = \frac{1}{\Omega} \frac{dy}{dt}, \quad (2.28)$$

It should be pointed out that the rate of lattice construction $dn_{MO}/A dt$ could be different from that of oxygen pick-up $dn_O/A dt$. As will be discussed later, these rates are identical only when the stationary state is reached.

3.1.2. Rate laws

Integration of the rate equation leads to the **rate law** corresponding to the corrosion process and defines the progress, W , of the reaction with time t . We obtain either an **implicit form**:

$$f(W) = k \cdot t \quad (2.29)$$

where k is the rate constant for the reaction process, or an **explicit form**:

$$W = g(t). \quad (2.30)$$

3.1.3. Temperature and pressure dependences

In any fundamental study of the oxidation mechanism of a metal or an alloy, one of the main factors that needs to be determined is the variation of the oxidation rate with temperature and with the pressure of the oxidising gas. It will be shown in Chapter 4, for example for the case of an oxidation process limited by diffusion within the scale, that the oxidation kinetics are parabolic. The rate constant is independent of the gas pressure if the oxide formed is a n -type semiconductor and proportional to $P^{1/n}$ (n is a positive integer) in the case of a p -type semiconductor.

This type of investigation has sometimes been neglected because of difficulties controlling precisely the gas pressure in thermobalances. However, for some years, it has been possible to couple such thermogravimetric equipment to devices capable of controlling and monitoring the oxygen partial pressure in a gas (e.g. an electrochemical oxygen pump, oxygen sensor). The oxygen pressure can then be precisely controlled between 1 and 10^{-25} bar in gas mixtures, e.g., inert gas-oxygen, CO-CO₂ or H₂-H₂O mixtures (see Section 2.2.3).

The rate constants of the kinetic laws often obey, under constant pressure, an Arrhenius-type equation:

$$k = k^0 \exp\left(-\frac{E_a}{R T}\right) \quad (\text{at given } P) \quad (2.31)$$

where E_a is the apparent activation energy of the process, R the gas constant and T the absolute temperature. The apparent activation energy can be easily determined by plotting $\log k$ as a function of $1/T$ (Fig. 2.27). The slope of the straight line obtained is equal to $-E_a / 2.303 R$.

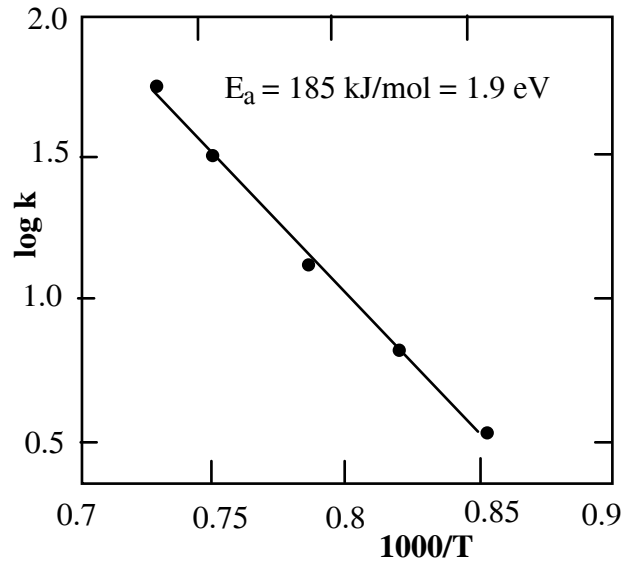


Figure 2.27. Arrhenius plot of the parabolic rate constant for the oxidation of tantalum.

A change in the activation energy could indicate a corresponding change in the limiting process for the corrosion reaction.

3.2. Classification of the different kinetic laws

The main kinetic laws are of linear, parabolic, logarithmic or cubic types but, it should be noted, these are limiting cases and deviations from them are often encountered. In some cases, it is difficult, or even impossible, to obtain such simple kinetic laws from the experimental results.

Observed discrepancies can result from, for example, structural modification of the growing scale or from a variation of its composition in the case of oxidation of impure metals and alloys. The loss of adherence of the scale on the metal surface, at a critical thickness, can also initiate a change in oxidation kinetics. It should also be noted that it is usually assumed that the sample area remains constant during oxidation but this is not strictly true and could explain some discrepancies between theoretical curves and experimental results. In the case of the oxidation of metallic powders, it is necessary to distinguish geometrical from physicochemical contributions but this can be done only in a few cases.

At high temperatures, the oxidation kinetics of numerous metals obey a **parabolic law**:

$$W^2 = k_p t \quad (2.32)$$

where k_p is the parabolic constant*. Such a law corresponds, as will be shown later, to a corrosion rate limited by diffusion through the compact scale that is formed. It is better to

* The parabolic law is sometimes written as $W^2 = 2 k_p t$.

express the parabolic law in the form $W^2 = k_p t$ and not as $W = K_p t^{1/2}$ because, as will be shown in Chapter 4, the constant k_p has a physical meaning whereas K_p does not.

The reaction rate constant may be expressed in different units depending on the actual parameter used to define the progress of the reaction. For example, if the extent of reaction is characterised by the mass gain per unit surface area of the metal during the exposure period, t , the kinetic law is given by: $(\Delta m/A)^2 = k_p t$ and the rate constant is expressed in $\text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$. If the reaction rate is defined by the increase in thickness, y , of the scale, the kinetic law has the form: $y^2 = k'_p t$ and the parabolic rate constant k'_p is expressed in $\text{m}^2 \cdot \text{s}^{-1}$. On the other hand, if the reaction rate is defined by the number of moles of the compound MX formed per unit surface area during the exposure period, t , the kinetic law has the form $(\Delta n_{MX}/A)^2 = k''_p t$. In this case, the rate constant k''_p is expressed in $\text{mol}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$. There is a simple relationship between the rate constants k_p , k'_p and k''_p :

$$k'_p = \Omega^2 k''_p = \left(\frac{\Omega}{M_X} \right)^2 k_p, \quad (2.33)$$

where, Ω is the molar volume of the compound MX and M_X is the atomic weight of the non-metallic element (oxygen, sulphur, etc.).

In some cases, the oxidation rate is constant which means that the **kinetic law** is **linear**:

$$W = k_l t \quad (k_l \text{ is the linear rate constant}). \quad (2.34)$$

As will be shown later, the oxidation rate is, then, governed by an interfacial process such as sorption, reaction at the metal/oxide interface, etc. Using similar nomenclature as for the parabolic rate constants, k_l characterises the reaction measured by the mass gain per unit surface area during time t and k'_l if the rate is defined by the increase in thickness of the growing scale.

The **cubic law** ($W^3 = k_c t$) has been observed during the oxidation of several metals e.g. copper, nickel, zirconium.

Logarithmic laws are observed typically in the case of the oxidation of many metals at low temperatures (generally below 673 K). The initial oxidation rate, corresponding to the growth of oxide layers of thickness generally less than a few tens of nm, is quite rapid and then drops off to low or negligible values. This behaviour can be described by a **direct logarithmic law**:

$$W = k_{\log} \log (a t + 1) \quad (2.35)$$

or by an **inverse logarithmic law**:

$$\frac{1}{W} = B - k_{inv} \log t. \quad (2.36)$$

The evaluation of the kinetic parameters in the case of logarithmic laws is, generally, not very precise and this makes it difficult to validate experimentally proposed mechanisms.

The oxidation rate is frequently found to follow a combination of rate laws. This is the case, for example, when oxidation occurs by two successive mechanisms where one dominates during initial stages and the other after extended periods. In other cases, the rate-determining step changes due to a modification in the nature or the morphology of the growing scale. By way of example, at low temperatures, a logarithmic law followed by a parabolic rate equation can be observed. At high temperature, oxidation reactions are often described by a parabolic rate equation followed by a linear law ("paralinear" regime, see Chapter 5) or a linear rate equation followed by a parabolic law (see Chapter 4, Section 6.4).

3.3. Variation of the kinetic laws with temperature

Typical kinetic laws characteristic of the oxidation of a large number of metals as a function of temperature are given in table 2.3

Table 2.3. Kinetic laws characteristic of the oxidation of several metals as a function of temperature, from Kubaschewski and Hopkins¹⁰

par: parabolic law, *log*: logarithmic law, *lin*: linear law, *cub*: cubic law, *paralin*: paralinear law,

break: "breakaway" corrosion.

T(°C)	200		400		600		800		1000		1200	
Mg	<i>log</i>		<i>par</i>	<i>paralin</i>	<i>lin</i>							
Ca	(<i>log</i>)		<i>par</i>		<i>lin</i>							
Ce	<i>log</i>	<i>log-lin</i>	<i>lin</i>	<i>break</i>								
Th			<i>par</i>	<i>lin</i>	<i>lin</i>							
U			<i>par</i>	<i>paralin</i>	<i>lin</i>							
Ti			<i>log</i>	<i>cub</i>	<i>cub</i>	<i>paralin</i>			<i>paralin</i>			
Zr			<i>log</i>	<i>cub</i>	<i>cub</i>			<i>cub</i>	<i>cub-lin</i>			
Nb			<i>par</i>	<i>par</i>	<i>parlin</i>		<i>lin</i>	<i>lin</i>	<i>break</i>			
Ta	<i>log</i>	<i>inv. log</i>		<i>par</i>	<i>paralin</i>		<i>lin</i>	<i>lin</i>				
Mo			<i>par</i>	<i>paralin</i>	<i>paralin</i>		<i>lin</i>	<i>lin</i>				
W				<i>par</i>	<i>par</i>		<i>paralin</i>	<i>paralin</i>	<i>paralin</i>			
Fe	<i>log</i>	<i>log</i>	<i>par</i>	<i>par</i>	<i>par</i>		<i>par</i>	<i>par</i>	<i>par</i>			
Ni		<i>log</i>	<i>log</i>	<i>cub</i>	<i>par</i>			<i>par</i>	<i>par</i>			
Cu	<i>log</i>	<i>cub</i>	(<i>par</i>)		<i>par</i>		<i>par</i>	<i>par</i>				
Zn		<i>log</i>	<i>log</i>	<i>par</i>	<i>par</i>							
Al	<i>log</i>	<i>inv.log</i>	(<i>log</i>)	<i>par</i>	(<i>asym</i>)	(<i>lin</i>)						
Ge				<i>par</i>	<i>paralin</i>							

¹⁰ O. Kubaschewski and B.E. Hopkins, *Oxidation of Metals and Alloys*, 2nd edition, Butterworth, Londres, 1967.

As an example the kinetic laws characteristic of chromium oxidation are shown in figure 2.28. It can be seen that at 1000°C, a parabolic law is observed but that at 1075°C, the experimental curve is characteristic of the formation of compact scales that crack at a critical thickness due to high mechanical stresses between the metal and the growing scale; at 1200°C, a linear rate equation is observed, with a noticeable increase in corrosion rate.

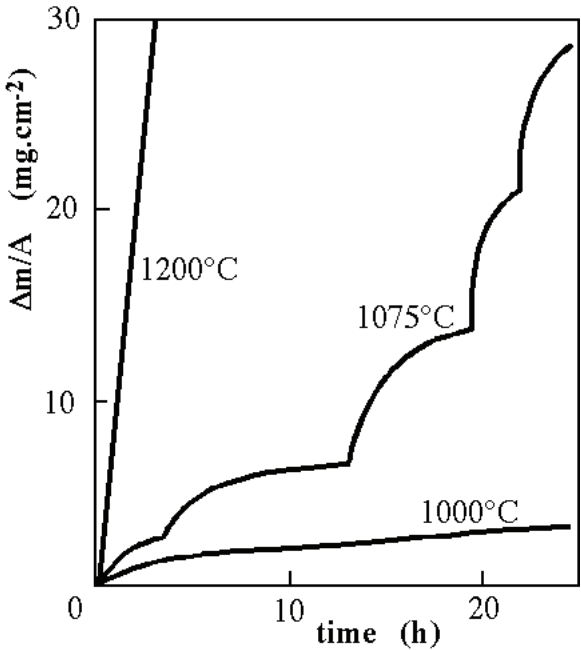


Figure 2.28. Chromium oxidation, between 1000 and 1200 °C, under one bar of oxygen¹¹

3.4. Evolution of the kinetic law with time

Besides the variation of the kinetic laws with temperature, a change of these rate equations with time can sometimes occur. A typical example, characteristic of the changes that may be observed as functions of temperature and time, is given in figure 2.29.

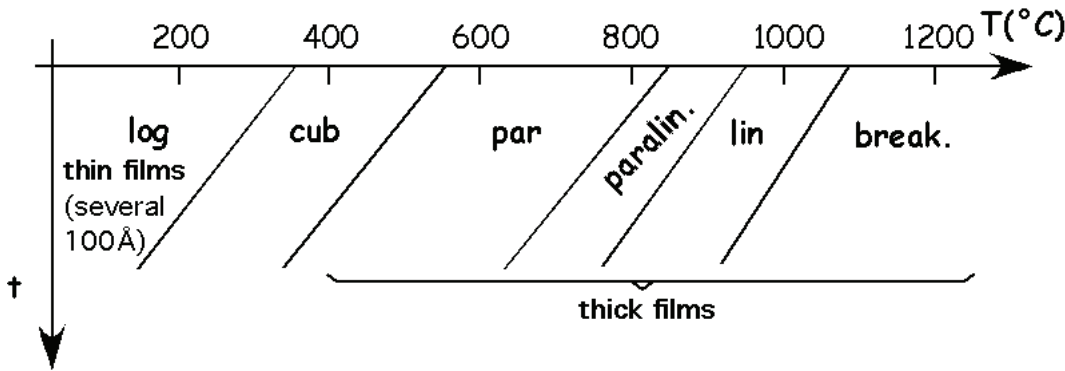


Figure 2.29. Successive kinetic laws observed for the oxidation of a given metal as functions of temperature and time.

¹¹ P. Kofstad, *High-temperature Oxidation of Metals*, John Wiley, New York, 1966, p.235.

It can be seen that at 800°C, for example, the following rate equations are successively observed: parabolic, paralinear and finally linear after extended oxidation.

3.5. Analysis of the experimental data

In many cases, it may be difficult to fit experimental data to simple rate equations but a first approach can be to plot the $W = f(t)$ curve using double-logarithmic coordinates. In the case of a law of type $W^n = k t$, the slope of the straight line then gives the value of n , i.e., 1, 2 and 3 for linear, parabolic and cubic laws, respectively. This technique has the advantage of fitting data over extended oxidation periods. However, taking into account the difficulty of unambiguous interpretation of the results, it is preferable to test the validity of the expected rate equation by plotting W^2 versus time in the case of a suspected parabolic law, W versus t for a linear rate equation or W versus $\log t$ in the case of a logarithmic law, etc.

Some authors, using computer software, fit the data to a third-degree polynomial in W :

$$A W^3 + B W^2 + C W + D = t \quad (2.37)$$

These difficulties in evaluating the proper kinetic law are particularly important in the case of changes in the oxidation behaviour during the corrosion process (see Chapter 3, Section 3.4 and Chapter 5, Section 3).

Comment: The development of software that now allows the rapid fit of the optimum mathematical expression to the experimental data provides a substantial advantage over the use of simple graphical linear transform methods. It should be pointed out that the choice of a fitting technique is of importance since this determines the weight attributed to the experimental data. As an example, homographic transforms of the type $1/r = f(1/P)$ (where r is the reaction rate and P is pressure) lead to fitting constants that depend strongly on the low pressure measurements but these are often obtained with poor accuracy. In these circumstances, unweighted computer fitting has to be preferred. On the other hand, for the interpretation of power laws of the type $W^n = kt$, with $n > 2$, it will be preferable to use a log-log transform so that the value of n can then be obtained as the reciprocal of the slope of the straight line of the $\log W / \log t$ plot. This relationship gives better results than direct computer fitting which assumes power-type kinetics occurring from the onset of oxidation. It is indeed generally observed that the experimental determination of the reaction kinetics in the early stages is difficult.

An elegant method consists in continuously monitoring the kinetic curves with exposure time and calculating for each experimental point, the rate constant appropriate to the expected model. Deviations from this model can then be readily identified¹².

¹² D. Monceau and B. Pieraggi, *Oxid. Met.*, **50** (1998) 477.

Chapter 3

SCALE STRUCTURES

1. Introduction

The ideal crystal is an abstract concept that is used in crystallographic descriptions. In these, the crystal, obtained by oxidation of a metal by a gas, is assumed to have a chemical composition determined by the valency of the constitutive elements. Moreover, this compound is also assumed to have a compact morphology without geometric limitations and a defined crystallographic structure.

In reality, the lattice of an actual crystal always contains imperfections or “defects”. Important properties of the crystal, such as the diffusion of ions, result from the existence of these defects and, as a consequence, mass transport in the scale formed by oxidation can be explained on the basis of its defect chemistry and crystal structure. An understanding of reaction mechanisms in high temperature corrosion requires a precise knowledge of defect structures in solids. Various types of defects may affect scale growth but we shall consider two principal types:

- those that determine the growth of compact scales,
- those that determine the growth of porous scales.

1.1. Defects that determine the growth of a compact scale

These defects represent departures from the perfect crystalline array and various types are described in the following paragraphs.

- **imperfections in the distribution of ions within the lattice**

These imperfections comprise either empty crystallographic sites (*vacancies*) or atoms occupying the interstices between the regular lattice sites (*interstitial atoms*) and are termed *point defects*. Their mole fraction in each sub-lattice, i.e., either the cation or anion sub-lattice, generally does not exceed 10^{-3} - 10^{-2} and is frequently much less. For point defect mole fractions sufficiently high, the defects may associate or cluster to form complex defects such as *extended defects* or aggregates of point defects (*clusters*).

- **displacements in the periodic structure of the crystal in certain directions (dislocations)**

These irregularities are termed *line defects*.

- **regions of lattice mismatch**

These *planar defects* or grain boundaries correspond to the internal interface between grains, i.e. crystals, of different orientation within the polycrystalline structure.

1.2. Defects that determine the growth of a porous scale

During the oxidation of numerous metals, the surface scale can grow in a non-compact manner and contain large, 3-dimensional defects such as cracks and pores. Whereas crystalline defects (point defects, line defects and planar defects) are responsible for the growth of compact scales, these 3-dimensional defects strongly influence the growth of porous layers.

2. Defects responsible for the growth of compact scales

2. 1. Point defects

2.1.1. Point defects and real crystals

The description of a real crystal requires us to take into account structural point defects. A complete development of defect chemistry of inorganic compounds requires a system of notation to describe all the elements of the crystal or "*structural elements*", that is, not only regular crystallographic sites but also lattice imperfections (vacancies, interstitials, substitutional defects, etc.).

2.1.1.1. Structural elements in a real crystal

Two main structural elements can be identified:

- those that involve normal sites of the lattice, either cationic (sites on the cation sub-lattice) or anionic (sites on the anion sub-lattice).
- those that involve interstitial sites corresponding to normally unoccupied positions in a perfect crystal; in this case, the nature of the chemical species forming the interstitial defect defines the sub-lattice (anion or cation) involved in the structural element.

The notation used in the description of the structural element has to give:

- the nature of the sub-lattice involved (normal or interstitial);
- the nature of the chemical species present (or absent) in this sub-lattice;
- the electrical charge carried by the structural element.

The Kröger and Vink notation, recommended by I.U.P.A.C. because of its great simplicity, will be used throughout this book.

• *Representation of structural elements*

Basically, the defect is represented by a main symbol followed by a subscript and a superscript. The main symbol indicates the species concerned, either an atom (represented by its chemical symbol) or a vacancy, and the subscript shows the site on which the species sits (this could be the usual occupant of the site in the perfect crystal, represented by its chemical symbol, or an interstitial site referred to as i). The superscript indicates the effective electrical charge of the defect.

In the case of an oxide MO , structural elements will be described as indicated in table 3.1 (Me and X are impurity atoms dissolved in the crystal, cation and anion, respectively).

Table 3.1. Structural elements in oxides

Structural elements involving regular lattice positions	Normal elements	M on a regular lattice position: M_M O on a regular lattice position : O_O
	Intrinsic defects	Vacant normal cationic site: V_M (M vacancy) Vacant normal anionic site: V_O (O vacancy)
	Extrinsic defects	Me dissolved substitutionally on a regular M site: Me_M X on a regular O site : X_O
Structural elements involving interstitial sites	Intrinsic defects	M on an interstitial site: M_i O on an interstitial site: O_i
	Extrinsic defects	Me on an interstitial site: Me_i X on an interstitial site: X_i

(Note that the anti-sites M_O and O_M do not exist in oxides).

• **Charge on the structural elements**

The *effective charge* of a structural element q_e is the difference between its real charge q_r (i.e. the charge of the species that really occupies the site) and its normal charge q_n , i.e. the charge of the species that would normally occupy the site in a perfect crystal:

$$q_e = q_r - q_n \quad (3.1)$$

In the Kröger-Vink notation, only the effective charge is generally indicated.

Thus, in a crystal MO , a structural element of the cation sub-lattice has a normal charge of + 2 and, consequently, an effective charge equal to zero. This charge is shown as a cross $\times$ (this indication can be omitted) according to $M_M^\times$ or M_M .

Let us consider the formation of an oxygen vacancy by removing an oxygen atom from the crystal. If both electrons of oxygen are localised on a vacant site, the oxygen vacancy will keep two negative charges and, consequently, its effective charge will be zero; it will be written as $V_O^\times$. On the other hand, if the formation of the oxygen vacancy corresponds

to the loss of one or two electrons, the resulting oxygen vacancy will be singly or doubly charged. It will be written as $V_O^\bullet$ or $V_O^{\bullet\bullet}$, respectively, where the dot corresponds to one positive effective charge.

In the Kröger-Vink notation, effective charges are written according to the following notation:

- negative charges as superscript primes '': $O_i^{\prime\prime}, V_M^{\prime\prime}$
- positive charges as superscript dots $\bullet$: $V_O^\bullet, M_i^{\bullet\bullet}$
- effectively neutral defects by a superscript $\times$ (optional): $M_M^\times, X_X$

• **Electronic defects**

These defects may be considered as structural elements. Whatever the electronic structure chosen for the crystal (conduction band model or small polaron hopping model), the electronic defect with negative charge will be written as e' .

Comment: In the case of the hopping model for electrons, the electron may be trapped on particular sites of the cation sub-lattice and can then be written as M_M' .

The electronic defect with positive charge will be written $h^\bullet$. This defect corresponds to the removal of an electron from a regular site of the cation sub-lattice and can also be written as $M_M^\bullet$.

2.1.1.2. Representation of a real crystal

Structural elements that can be present in a crystal MO are shown in figure 3.1. In this figure, Me corresponds to a trivalent impurity dissolved in the crystal.

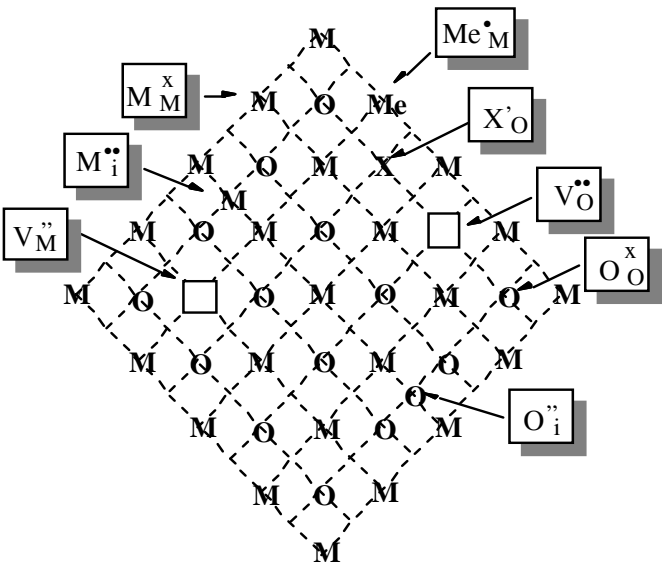


Figure 3.1. Structural elements in an oxide (Kröger-Vink notation).

2.1.1.3. Rules for writing defect reactions in a real crystal

Three rules must be followed in writing defect equilibrium reactions:

- *electroneutrality* of the total charges of the structural elements, i.e. involving normal charges, actual charges and effective charges); it should be noted that only two of these electroneutrality equations are independent;
- *mass balance*, i.e., the number of atoms of each chemical species involved in the defect reaction must be the same before and after the defect formation;
- *ratio of regular lattice sites*, i.e. the ratio of the number of regular cation and anion sites in an ionic crystal is constant, i.e. for a crystal M_pX_q :

$$\frac{\text{number of M sites}}{\text{number of X sites}} = \frac{p}{q}$$

Comment 1: With regard to the conservation of the ratio of regular lattice sites involving the electroneutrality of the actual charges on defects, only the electroneutrality for effective charges needs to be checked.

Comment 2: Conventionally, equilibrium reactions are written in the direction of defect creation.

Following these rules, it is possible to write equilibrium reactions involving a real crystal. These fall into two categories:

1. *Equilibrium reactions that occur internally without involving the external environment*

These thermal equilibria induce atomic and electronic disorder. As these point defects do not change the overall composition, they are also referred to as stoichiometric defects.

- **Frenkel disorder** (figure 3.2)

When an atom is transferred from a regular site to an interstitial one, a vacancy is left behind on the regular site, leading to a Frenkel defect pair. This defect reaction, for cationic disorder, can be written:

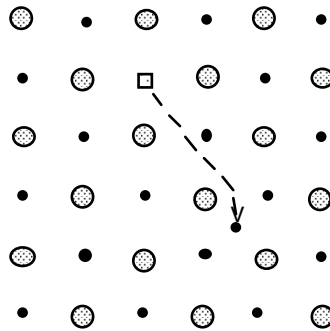


Figure 3.2: Frenkel disorder

Frenkel disorder usually occurs in the cation sub-lattice, rather than in the anion sub-lattice, because cations are usually smaller than anions.

• *Schottky disorder* (figure 3.3)

Ions on the cation and anion sub-lattices can leave their regular positions and diffuse towards the crystal surface or to other sinks such as grain boundaries and dislocations. The formation of the Schottky defect pairs can be written as:



where "zero" designates the perfect crystal.

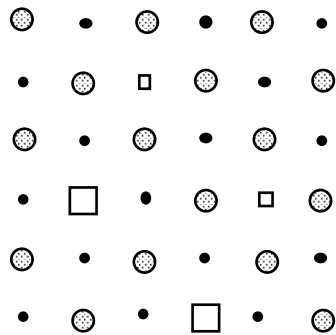


Figure 3.3. Schottky disorder

• *Electronic disorder*

The reaction to produce electronic defects may be represented by the excitation of an electron e' from the valence state to the conduction band, producing a "quasi-free" electron and an electron hole $h^\bullet$ according to:

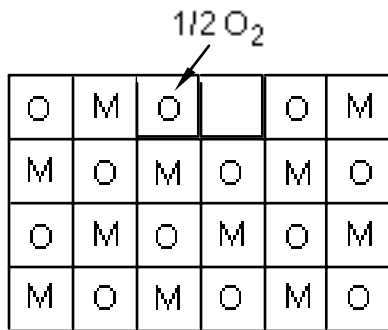


2. *External equilibria involving mass exchange with the environment*

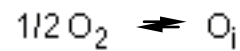
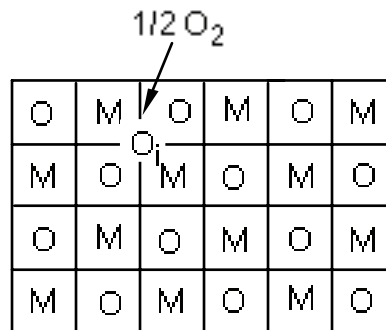
These equilibria involve the normal components of the crystal, such as O or M, so that the reactions can lead to a modification of the crystal stoichiometry. Let us consider the equilibrium of an oxide under an oxygen atmosphere. According to the crystal point defect structure, the following exchange equilibria may be written:

a) Introduction of oxygen into the crystal[§]

- with formation of a new construction unit
- without formation of a new construction unit

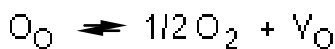
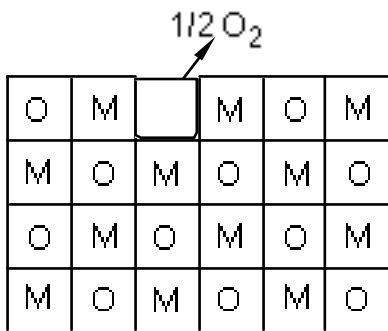


or

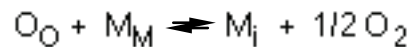
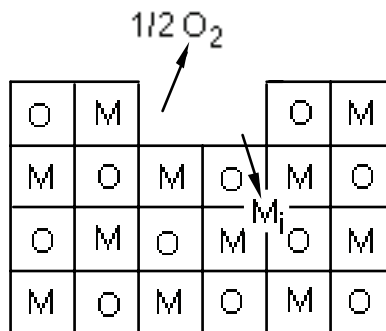


b) Loss of oxygen from the crystal

- without destruction of a construction unit
- with destruction of a construction unit



or



Depending on the experimental conditions (pressure, temperature), the crystal can become nonstoichiometric.

2.1.1.4. Thermodynamics of defect equilibria

The real crystal will be considered as an ideal solution of point defects in a perfect crystal and will be considered appropriate for defect mole fractions less than 10^{-2} . The equilibrium constants will then be evaluated assuming that the activities of atoms on their normal lattice positions can be considered as unity and the activities of point defects will be approximated by their concentrations.

Comment: Throughout this book, the defect concentrations, indicated by a double bracket [], are expressed as the number of moles per mole of compound.

[§] A *construction unit* represents the smallest module necessary to build the lattice.

2.1.2. Point defects and stoichiometry

Generally, metal compounds exhibit noticeable deviations from the exact stoichiometric composition M_aX_b defined by the valence of their components. These compounds are designated as *nonstoichiometric*. However, for some compounds (such as halides) the deviation from stoichiometric composition remains negligible, whatever the experimental conditions. These compounds are termed *stoichiometric*.

2.1.2.1. Nonstoichiometric compounds

Most oxides and sulphides are nonstoichiometric compounds. From a macroscopic viewpoint, two alternative classes of compounds can then be considered:

- (i) The first kind are those for which

$$\frac{\text{atom number of M}}{\text{atom number of X}} > \frac{a}{b}$$

These compounds may be arbitrarily characterised by one or other of the general formulae: $M_{a+x}X_b$ or $M_aX_{b-x'}$.

- (ii) The second kind are those for which

$$\frac{\text{atom number of M}}{\text{atom number of X}} < \frac{a}{b}$$

In the same way, these compounds may be arbitrarily characterised by one or other of the formulae: $M_{a-x}X_b$ or $M_aX_{b+x'}$.

In these formulae, x (or x') is defined as the deviation from stoichiometry in comparison with the stoichiometric composition M_aX_b . From a crystallographic point of view, it is possible to interpret these deviations from stoichiometry by assuming the formation of vacancies or interstitials in one or the other sub-lattices. The required crystal electroneutrality may then be obtained by the formation of an equivalent number of electronic defects. Nevertheless, it should be remembered that, in such an interpretation, the deviation from stoichiometry (x or x') needs to be small, say $\leq 10^{-2}$ but this condition is fulfilled for a great number of oxides and sulphides. However, this ideal approach cannot be applied to several metal-deficient oxides or sulphides ($Fe_{1-x}O$, $Fe_{1-x}S$, $Cu_{2-x}S$, etc.) and several oxygen-deficient oxides of refractory metals (TiO_{2-x} , Nb_2O_{5-x} , MoO_{3-x} , WO_{3-x} , etc.) for which deviations from stoichiometry may be higher than 10^{-1} . As the deviation from stoichiometry increases, point defects interact and it is necessary to consider complex defect formation such as defect clusters and extended defects.

In the following section, interactions between point defects will be neglected and the crystal will be considered as an ideal solution of defects in a perfect crystal.

Example: TiO_{2-x} (a compound with anion vacancies)

Comment: The crystal could alternatively be described as $\text{Ti}_{1+x}\text{O}_2$ but TiO_{2-x} corresponds better to the actual crystal structure. This type of formulation will be used systematically in the following if point defects involve only one of the crystal sub-lattices.

• **Schematic illustration of the TiO_{2-x} crystal** (figure 3.4)

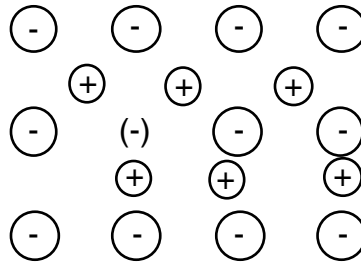


Figure 3.4. Two-dimensional representation of the nonstoichiometric TiO_{2-x} crystal.

• **Vacancy ionisation**

The transfer of an oxygen atom from a regular site on the lattice to the gas phase induces an electron excess localised on the vacant site. These electrons introduce local electron states which may lie within the band gap; as a consequence, they may be more easily excited to a state in the conduction band (band conduction model) or to unoccupied atomic orbitals of neighbouring atoms (hopping electron model).

Whatever the model chosen for TiO_{2-x} , the oxygen vacancy is an electron donor and the oxide behaves as a n-type semi-conductor. The electron transfers lead to the following ionisation equilibria:



• **Crystal equilibrium under an oxygen atmosphere**



• **Variation of the deviation from stoichiometry x with the oxygen pressure P_{O_2}**

In accord with the earlier discussion, the deviation from stoichiometry, x , may be defined as:

$$x = [V_O] + [V_O^\bullet] + [V_O^{\bullet\bullet}]$$

where the vacancy concentrations are expressed in number of moles of defects per mole of oxide. For sufficiently high values of x , intrinsic ionic and electronic disorder can be neglected. The stoichiometry of the crystal can then be related to the oxygen pressure P_{O_2} which can be considered as an independent parameter. x can then be obtained as the solution of a system of non linear equations consisting of 5 equations and 5 unknowns:

- definition of x :	$x = [V_O] + [V_O^\bullet] + [V_O^{\bullet\bullet}]$	(3.10)
- electroneutrality:	$[e'] = [V_O^\bullet] + 2[V_O^{\bullet\bullet}]$	(3.11)
- mass action laws:	$[V_O] = K_{V_O^x} \cdot P_{O_2}^{-1/2}$	(3.12)
	$[V_O^\bullet] \cdot [e'] = K_{V_O^\bullet} \cdot P_{O_2}^{-1/2}$	(3.13)
	$[V_O^{\bullet\bullet}] \cdot [e']^2 = K_{V_O^{\bullet\bullet}} \cdot P_{O_2}^{-1/2}$	(3.14)

This system of equations does not permit a general analytical solution but the equations may be solved for certain limiting conditions:

- predominantly neutral vacancies V_O :	$x = [V_O] = K_{V_O^x} \cdot P_{O_2}^{-1/2}$
- predominantly singly ionised vacancies $V_O^\bullet$:	$x = [V_O^\bullet] = (K_{V_O^\bullet})^{1/2} \cdot P_{O_2}^{-1/4}$
- predominantly doubly ionised vacancies $V_O^{\bullet\bullet}$:	$x = [V_O^{\bullet\bullet}] = \left(\frac{K_{V_O^{\bullet\bullet}}}{4}\right)^{1/3} \cdot P_{O_2}^{-1/6}$

In brief, for an oxide MO with oxygen vacancies, the deviation from stoichiometry decreases with increasing oxygen pressure according to a $P_{O_2}^{-1/n}$ law, where n depends exclusively on the degree of ionisation of the vacancies ($2 \leq n \leq 6$).

The same approach can be applied to nonstoichiometric compounds with cation interstitials ($Zn_{1+x}O$ -type oxide), with cation vacancies ($Cu_{2-x}O$ -type oxide) or with oxygen interstitials (UO_{2+x} -type oxide). The deviation from stoichiometry, as a function of the oxygen pressure, varies according to the predominant point defect as shown in table 3.3.

Table 3.3. Deviation from stoichiometry x in nonstoichiometric oxides M_aO_b , as a function of oxygen pressure, according to the nature and degree of ionisation, z , of the predominant point defect.

Predominant point defect		type of conductivity	x variation with P_{O_2}	M_2O	MO	MO_2
anion point defect	$O_i^{z'}$	p	$\propto P_{O_2}^{1/n}$	$2 \leq n \leq 6$ $0 \leq z \leq 2$		
	$V_O^{z\bullet}$	n	$\propto P_{O_2}^{-1/n}$			
cation point defect	$M_i^{z\bullet}$	n	$\propto P_{O_2}^{-1/n}$	$4 \leq n \leq 8$	$2 \leq n \leq 6$	$1 \leq n \leq 5$
	$V_M^{z'}$	p	$\propto P_{O_2}^{1/n}$	$0 \leq z \leq 1$	$0 \leq z \leq 2$	$0 \leq z \leq 4$

2.1.2.2. Stoichiometric compounds

Alkali halides, silver halides and several oxides (Al_2O_3 , MgO , etc.) are stoichiometric compounds. From a structural point of view, the compounds are characterised by the existence of two types of point defects inducing an intrinsic *atomic disorder*.

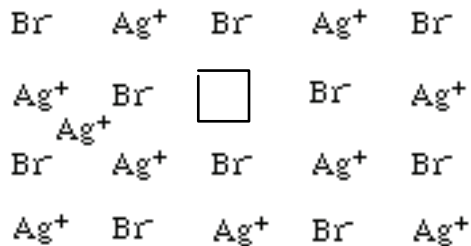
The electroneutrality condition is ensured without the need for electronic defects, the concentration of which is negligible. Thus, ionic conductivity is likely to be an important part of the total conductivity. Two limiting cases can be considered:

- only one sub-lattice is involved,
- both sub-lattices are involved.

• *Frenkel disorder (example: AgBr):*

There exists both vacancies and interstitials of silver.

- Lattice representation



- Internal equilibrium within the crystal

The formation of Frenkel defect pairs in the cation sub-lattice may be written:



The condition that stoichiometry exists requires that:

$$[\text{Ag}_i^\bullet] = [V_{\text{Ag}}].$$

If the concentration of electronic defects is negligible, this condition becomes identified with the electroneutrality equation:

$$[\text{Ag}_i^\bullet] + [h^\bullet] = [V_{\text{Ag}}] + [e'].$$

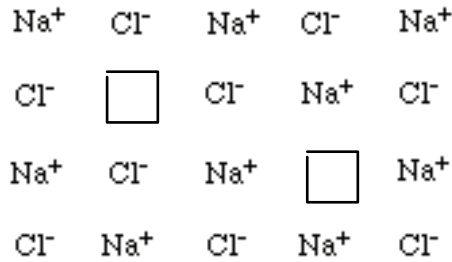
In these conditions, the vacancy and interstitial concentrations are equal to the square root of the Frenkel equilibrium constant K_F :

$$[\text{Ag}_i^\bullet] = [V_{\text{Ag}}] = K_F^{1/2}.$$

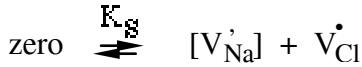
• Schottky disorder (example: NaCl):

Vacancies of both chlorine and sodium exist.

- Lattice representation



The identical chlorine and sodium vacancy concentrations are governed by the Schottky disorder equilibrium according to:



with : $[V_{\text{Cl}}] = [V_{\text{Na}}] = K_S^{1/2}$

where "zero" designates a perfect crystal and K_S is the Schottky equilibrium constant.

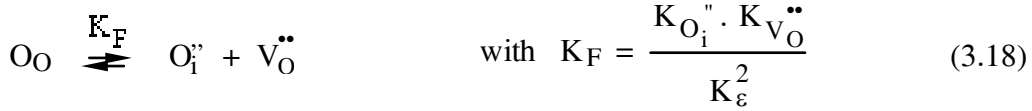
2.1.2.3. Defect model in compounds containing several types of defects. Brouwer approximation of majority defects.

As an example, let us consider the case of an oxide containing in its anion sub-lattice both vacancies and interstitials which will be considered doubly charged, for the sake of simplicity. The equilibrium reaction between the crystal and the oxygen atmosphere may then be written as:





Comment: Combining equilibria (3.15) to (3.17) gives the equilibrium for formation of a **Frenkel defect pair** as:



The variation of defect concentration with P_{O_2} may be obtained by solving the following system of non linear equations (three mass action laws applied to equilibrium (3.15), (3.16), (3.17) and the electroneutrality equation within the crystal):

$$K_{\text{O}_\text{i}''} = [\text{O}_\text{i}''] \cdot [h^{\bullet}]^2 \cdot P_{\text{O}_2}^{-1/2} \quad (3.19)$$

$$K_{\text{V}_\text{O}^{\bullet\bullet}} = [\text{V}_\text{O}^{\bullet\bullet}] \cdot [e']^2 \cdot P_{\text{O}_2}^{1/2} \quad (3.20)$$

$$K_{\varepsilon} = [h^{\bullet}] \cdot [e'] \quad (3.22)$$

$$2 [\text{O}_\text{i}''] + [e'] = 2 [\text{V}_\text{O}^{\bullet\bullet}] + [h^{\bullet}] \quad (3.23)$$

Comment: The concentrations of free electrons $[e']$ and electron holes $[h^{\bullet}]$ are generally designated as n and p , respectively.

This system of equations does not permit an analytical solution but we shall use the *Brouwer approximation** method that allows us to obtain simple solutions in limiting cases.

In this method, domains of oxygen partial pressure are considered for which one of the concentrations on each side of the electroneutrality equation (3.23) is so dominant as to make the other negligible. In each of these pressure domains, the system of equations may then be easily solved.

Two limiting cases may be considered:

- oxides in which an ionic disorder is predominant at the stoichiometric composition; in this case, $K_F \gg K_{\varepsilon}$;
- oxides in which an electronic disorder is predominant at the stoichiometric composition; in this case, $K_F \ll K_{\varepsilon}$.

* C. Brouwer, *Philips Res. Rep.*, **9** (1954) 366.

1. Case of an oxide in which ionic disorder is predominant at the stoichiometric composition

Three oxygen pressure domains may be considered:

- high oxygen pressures : $2 [O_i'] \cong [h^\bullet]$
- low oxygen pressures : $[e'] \cong 2 [V_O^{\bullet\bullet}]$
- intermediate oxygen pressures : $[O_i'] \cong [V_O^{\bullet\bullet}]$

In each of these pressure domains, the variation of the respective predominant defect concentration with oxygen pressure can then be readily approximated and their variation with P_{O_2} is shown in the "Brouwer Diagram" of figure 3.5 (note that logarithmic axes are used in this diagram).

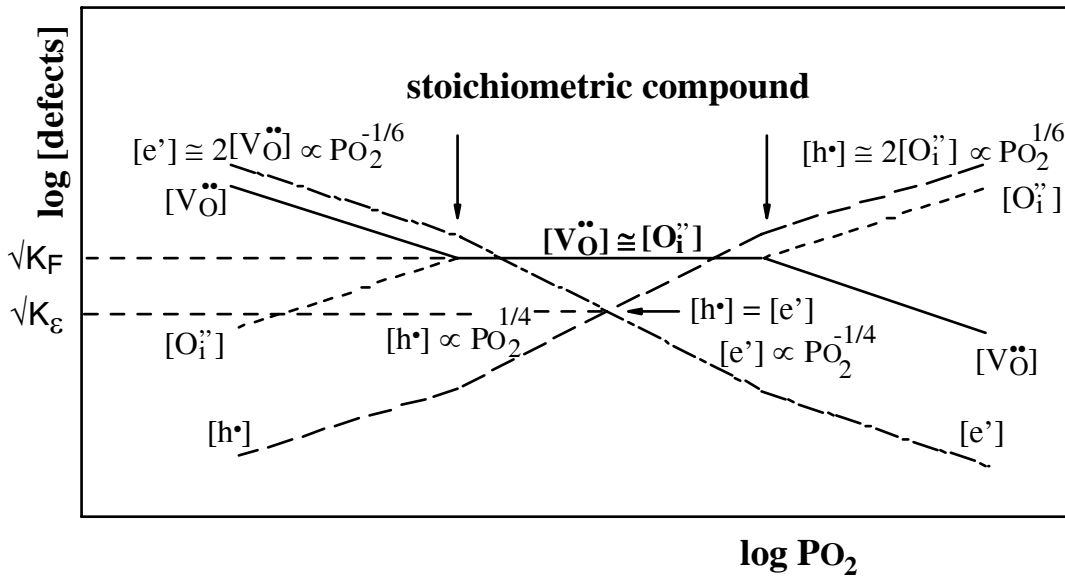


Figure 3.5. Schematic representation of concentrations of oxygen point defects and electronic defects as a function of oxygen pressure: ionic disorder is assumed to predominate at the stoichiometric composition ($K_F \gg K_E$). This diagram is often referred to as a "Brouwer diagram".

2. Case of an oxide in which electronic disorder is predominant at the stoichiometric composition

Three oxygen pressure domains may be considered:

- high oxygen pressures : $2 [O_i'] \cong [h^\bullet]$
- low oxygen pressures : $[e'] \cong 2 [V_O^{\bullet\bullet}]$
- intermediate oxygen pressures : $[e'] \cong [h^\bullet]$

The variation of defect concentrations with oxygen pressure are given, again using logarithmic scales, in figure 3.6.

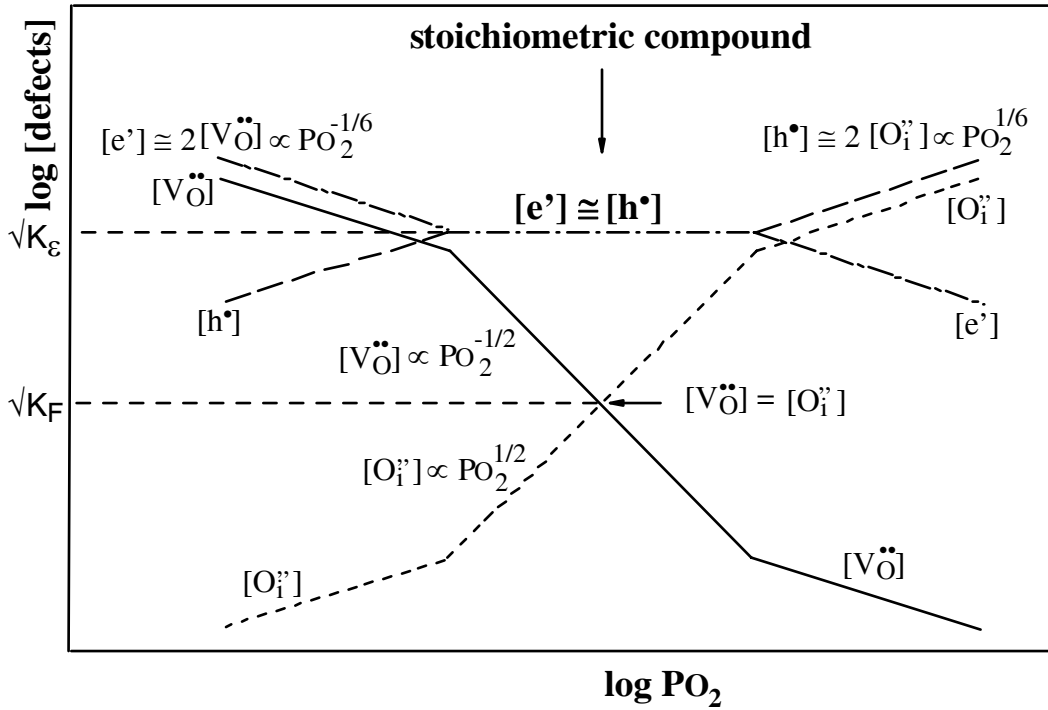


Figure 3.6. Schematic representation of the concentrations of oxygen point defects and electronic defects as a function of oxygen pressure. Electronic disorder is assumed to predominate at the stoichiometric composition ($K_F \ll K_E$).

In the preceding sections, only the majority ionic or electronic defects in the crystal have been considered but the model can take into account all the defects present in the crystal whether they are predominant or in the minority. Brouwer diagrams allow us to understand why some compounds exhibit a quasi-stoichiometric behaviour over a wide pressure domain (see, e.g. the Brouwer diagram for $K_F \gg K_E$ shown as figure 3.5). Moreover, these diagrams show that the distinction between stoichiometric and nonstoichiometric compounds is artificial in that a nonstoichiometric compound may become stoichiometric (or the reverse) according to the experimental conditions. The diagrams will be used for the interpretation of complex corrosion mechanisms involving stoichiometry changes across the scale from its external surface to its interface with the metal (see Chapter 4).

2. 1. 3. Point defects and mass transport

2.1.3.1. Diffusion mechanisms

Intragranular or volume diffusion in crystalline compounds takes place through crystal imperfections and mainly through the movement of point defects. Several types of mechanisms may be considered, as shown schematically in Figure 3.7 but mass transport generally occurs by hopping mechanisms from a well defined site of the crystal into another adjacent site.

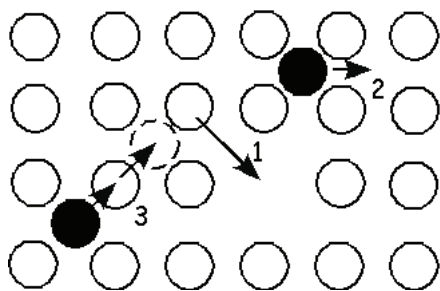


Figure 3.7. Schematic illustration of transport mechanisms in crystalline solids

- 1) Vacancy diffusion
- 2) Interstitial diffusion
- 3) Interstitialcy diffusion

Comment 1: The vacancy diffusion mechanism corresponds to the jump of an atom from its regular site into an adjacent unoccupied site. In this case, the atoms move in the direction opposite to that of the vacancies.

Comment 2: Diffusion occurs by an interstitial mechanism if an atom moves from an interstitial site into one of its neighbouring interstitial sites. This mechanism will apply mainly to the cationic sub-lattice.

Comment 3: In the interstitialcy mechanism, an interstitial atom pushes one of its nearest neighbouring atoms on a regular lattice position into another interstitial position and occupies the site of the displaced atom.

2.1.3.2. Self-diffusion coefficient of a component in a compound M_aX_b and the diffusion coefficient of the lattice defects responsible.

Let us consider a 1-dimensional flux of particles (atoms, ions, point defects or electrons) in the Ox direction. Let $C(x, t)$ be the defect concentrations (number of particles per unit volume) at the coordinate x and at time t . In a chemical potential gradient and without an electrical potential gradient or other type of driving force, a flux, J , of particles occurs, in the Ox direction:

$$J = - \frac{CD}{RT} \frac{\partial \mu}{\partial x} \quad (\text{generalised Fick's law}) \quad (3.24)$$

where D is the diffusion coefficient of the particle.

Comment 1: In the case of an ideal system (infinitely dilute solution), we can write:

$$\frac{\partial \mu}{\partial x} = RT \frac{\partial \log C}{\partial x} = \frac{RT}{C} \frac{\partial C}{\partial x}$$

Then, the diffusion flux becomes:

$$J = -D \frac{\partial C}{\partial x} \quad (3.25)$$

Comment 2: Note that, generally, the chemical potential should also incorporate the work done by or against the local hydrostatic stress if the creation or migration of the point defect produces local volume changes.

Comment 3: Under an additional electrical potential gradient, the particle flux would obey the following general equation:

$$J = -\frac{CD}{RT} \frac{\partial \tilde{\mu}}{\partial x} \quad (3.26)$$

where $\tilde{\mu}$, termed the electrochemical potential, is related to the chemical potential μ by the equation:

$$\tilde{\mu} = \mu \pm z F \phi \quad (3.27)$$

z is the particle charge number, F the Faraday constant, ϕ the electric potential and $\pm z F$ the electric charge.

- Macroscopic approach: self-diffusion coefficient D_j of component j

Let us consider a homogeneous chemical system composed of a binary compound M_aX_b . Both sub-lattices may be considered as independent (the ion movements within one sub-lattice produce displacements of ions only in that sub-lattice). M or X diffusion in the compound M_aX_b is termed *self-diffusion*.

Let J_j be the diffusion flux of component j at the coordinate x , in the Ox direction. In the absence of an electrical potential gradient, the self-diffusion coefficient D_j of component j will obey the following equation:

$$J_j = -\frac{C_j D_j}{RT} \frac{\partial \mu_j}{\partial x} \quad (3.28)$$

C_j is the concentration of component j .

- Structural approach: diffusion coefficient D_δ of the defect δ responsible for lattice diffusion of the component j

The compound described in the previous section may be considered as a solution of point defects in a perfect crystal. Let δ be a defect in the sub-lattice j ; this defect has a

charge z^* or z' . To lighten the mathematical expressions, this charge will be indicated only if necessary.

Let J_δ be the flux of the defect, δ , in the j sub-lattice, at the coordinate x and in the absence of an electric field. The diffusion coefficient D_δ of the defect δ is defined by equation:

$$J_\delta = -\frac{C_\delta D_\delta}{RT} \frac{\partial \mu_\delta}{\partial x} \quad (3.29)$$

where C_δ is the concentration of the defect δ .

- Relation between D_j and D_δ

Whatever the chosen approach, macroscopic or structural, the fluxes of particles, at the coordinate x , must obey the following equations:

$$J_j = J_\delta \quad \text{for an interstitial diffusion mechanism}$$

$$J_j = -J_\delta \quad \text{for a vacancy mechanism.}$$

For example, let us consider the case of cation diffusion by means of a vacancy mechanism. The relationship between the fluxes in opposite directions leads to:

$$-\frac{C_M D_M}{RT} \frac{\partial \mu_M}{\partial x} = \frac{C_{V_M} D_{V_M}}{RT} \frac{\partial \mu_{V_M}}{\partial x} \quad (3.30)$$

Moreover, the chemical potential μ_M and μ_{V_M} are linked by:

$$\partial \mu_M = -\partial \mu_{V_M}$$

Let us examine the equilibrium reaction between gaseous metal M_{gas} and the crystal $M_a X_b$ using both approaches (macroscopic and structural) :



Thus, we may write:

$$\mu_{M_{\text{gaz}}} = \mu_{M_{\langle\langle M_a X_b \rangle\rangle}} = \mu_{M_M} - \mu_{V_M}$$

or, by definition :

$$\mu_{M_{\langle\langle M_a X_b \rangle\rangle}} = \mu_M$$

Then:

$$\mu_M = \mu_{M_M} - \mu_{V_M}$$

and, considering μ_{M_M} as a constant : $\partial \mu_M = -\partial \mu_{V_M}$

we may deduce:

$$C_M D_M = C_{V_M} D_{V_M}$$

This demonstration could be generalised to an anion vacancy mechanism and to an interstitial type mechanism (cation or anion interstitials).

As a general rule, the relationship between D_j and D_δ may be written as:

$$C_\delta D_\delta = C_j D_j$$

or:

$$D_j = \frac{C_\delta}{C_j} D_\delta$$

If N_δ is the mole fraction of defects δ in the j sub-lattice, we may write:

$$D_j = N_\delta D_\delta \quad \text{since} \quad N_\delta = \frac{C_\delta}{C_\delta + C_j} \cong \frac{C_\delta}{C_j} \quad (3.31)$$

This relationship shows that the self-diffusion of component j is proportional to the mole fraction of defects δ contained in the j sub-lattice.

Comment: *Correlation factor*

In practice, the determination of the self-diffusion coefficient of component j (D_j) is carried out by means of marked components or *tracers* (radioactive or not). Let D_j^* be the tracer diffusion coefficient. D_j^* is related to D_j through the correlation coefficient f (with $f \leq 1$):

$$D_j^* = f D_j.$$

2.1.3.3. Pressure dependence of the self-diffusion coefficient

Let us consider a nonstoichiometric oxide containing only one type of defect (vacancy or interstitial) in at least one of its sub-lattices; for example, an oxide exhibiting defects in its cation sub-lattice. Let D_M be the self-diffusion coefficient of the component M . In agreement with equation 3.31 and, depending on the type of defect present in this sub-lattice, we can write either

$$D_M = N_{V_M} D_{V_M} \text{ (cationic vacancy)}$$

or

$$D_M = N_{M_i} D_{M_i} \text{ (interstitial)}.$$

In both cases, evidently, the self-diffusion coefficient D_M of component M varies with oxygen pressure in the same way as does the concentration (mole fraction) of the defect present in the cation sub-lattice.

It should be noted that similar considerations also apply to the presence of defects, even minority defects, in the anion sub-lattice. Thus, if D_O is the self-diffusion coefficient of the component O , D_O will vary with the oxygen pressure again in the same manner as does the mole fraction of the defects present in the anion sub-lattice (see equation 3.31).

• ***Oxides with defects predominantly in one sub-lattice***

It should be pointed out that if the concentration of defects contained in one of the sub-lattices, j , is very much greater than that of defects in the other sub-lattice, their mole fraction is equal to the stoichiometry ratio x of the oxide. Then, the variation with oxygen pressure of the stoichiometry ratio x and of the self-diffusion coefficient D_j of component j are identical.

Table 3.4 shows the dependence on oxygen partial pressure, based on table 3.3, of the self-diffusion coefficients D_O (for the case that anion defects are predominant in the oxide) and D_M (for the case that cation defects are predominant).

Table 3.4. Pressure dependence of the self-diffusion coefficient D_O (predominant anion defects) and D_M (predominant cation defects) in an oxide M_aX_b according to the degree, z , of ionisation of the defect.

Self-diffusion coefficient D_j	Sub-lattice containing the majority defects	Major defects	$D_j = f(P_{O_2})$	M_2O	MO	MO_2
D_O	X sub-lattice (anions)	$O_i^{z'}$	$D_j \propto P_{O_2}^{1/n}$	$2 \leq n \leq 6$ $0 \leq z \leq 2$		
		$V_O^{z\bullet}$	$D_j \propto P_{O_2}^{-1/n}$			
D_M	M sub-lattice (cations)	$M_i^{z\bullet}$	$D_j \propto P_{O_2}^{-1/n}$	$4 \leq n \leq 8$	$2 \leq n \leq 6$	$1 \leq n \leq 5$
		$V_M^{z'}$	$D_j \propto P_{O_2}^{1/n}$	$0 \leq z \leq 1$	$0 \leq z \leq 2$	$0 \leq z \leq 4$

Comment 1: In the case of minority defects, the determination of the oxygen pressure dependence of the diffusion coefficient of the component of the relevant sub-lattice requires solution of the whole system of equations involving the minority defect concentrations.

Comment 2: A comparison of the self-diffusion coefficients of anions and of cations may allow identification of the component which provides the majority of mass transport within the crystal. Thus, nonstoichiometric oxides such as NiO, FeO, Cu_2O contain metal vacancies; this observation is in agreement with the order of magnitude of the diffusion coefficients, i.e., $D_M \gg D_O$ ($D_M/D_O \approx 10^2$ to 10^4). In contrast, in some oxides such as TiO_2 , that have an oxygen deficit, it has been observed that $D_O \approx D_{Ti}$. This result is not in contradiction with the assumption of several authors who postulate that both oxygen vacancies and titanium interstitials are simultaneously present in this oxide.

Comment 3: A given defect may have various degrees of ionisation. Assuming that the diffusion coefficient of the defect D_δ is independent of its charge, the diffusion coefficient D_j may be defined as:

$$D_j = \sum N_\delta D_\delta = D_\delta \sum N_\delta \quad (3.32)$$

2. 1. 4. Point defects and electrical conductivity in ionic crystals

It should be pointed out, and will be shown later, that even if the conductivity of ionic crystals is linked to the existence of point defects, the electrical transport does not necessarily occur by means of these point defects.

2.1.4.1. Definition

The electrical conductivity due to a charge carrier is given by:

$$\sigma = C U z F \quad (3.33)$$

where C is the molar concentration of charge carriers per unit volume and U is the electrical mobility (expressed in $\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$). The mobility U corresponds to the velocity of the charged particles under an electric field equal to unity.

• Partial conductivities

When several particles contribute to electrical conduction, a partial conductivity σ_p may be defined for each of the mobile particles. The total conductivity σ_t is then given by:

$$\sigma_t = \sum \sigma_p \quad (3.34)$$

In ionic crystals, the total conductivity σ_t is generally written in terms of ionic and electronic conductivities, as:

$$\sigma_t = \sigma_{\text{ionic}} + \sigma_{\text{electronic}} \quad (3.35)$$

2.1.4.2. Nernst - Einstein relationship

The ionic contribution of the component j to the total electrical conductivity may be determined from both structural and macroscopic approaches.

• Structural approach

In a crystal, the charge carriers are electronic defects (e' , $h^\bullet$) and ionic defects ($\delta^{z\bullet}$, $\delta^{z'}$). The flux of these defects, with a degree z ($z \neq 0$) of ionisation, in the Ox direction, under an electric field and in the absence of a chemical potential gradient may be written, for a positively charged defect, as:

$$J_\delta = - z F \frac{C_\delta D_\delta}{R T} \frac{\partial \phi}{\partial x} \quad (3.36)$$

From the definition of the electrical mobility U_δ , we obtain:

$$J_\delta = - C_\delta U_\delta \frac{\partial \phi}{\partial x} \quad (3.37)$$

then:

$$D_\delta = U_\delta \frac{R T}{z F} \quad (3.38)$$

Let σ_δ be the partial conductivity relevant to the defect δ :

$$\sigma_{\delta} = z F C_{\delta} U_{\delta} = z^2 F^2 \frac{C_{\delta} D_{\delta}}{R T} \quad (3.39)$$

• **Macroscopic approach**

If σ_j is the contribution to the total conductivity of the charged species j , we can write:

$$\sigma_j = \sigma_{\delta} \quad (3.40)$$

Substituting equation 3.39 in equation 3.40, we have:

$$\sigma_j = z^2 F^2 \frac{C_{\delta} D_{\delta}}{R T} \quad (3.41)$$

$$\text{Since } C_{\delta} D_{\delta} = C_j D_j \quad (3.42)$$

we obtain the **NERNST-EINSTEIN** equation:

$$\sigma_j = z^2 F^2 \frac{C_j D_j}{R T} \quad (3.43)$$

In this equation, σ_j is the ionic contribution of species of type j to the total conductivity, D_j is the self-diffusion coefficient of particles j and C_j is the volume concentration of regular sites in the sub-lattice that contain species j .

2.1.4.3. Oxygen pressure dependence of the conductivity of a crystalline oxide

• **Nonstoichiometric crystal**

Even for the case that a concentration of neutral defects is predominant, we will assume that the oxide always contains ionised defects. Let $\delta^{z'}$ (p-type semi-conductor) or $\delta^{z\bullet}$ (n-type semi-conductor) be the predominant **ionised** defect with a degree z ($z \neq 0$) of ionisation and ε be the electronic defect (e' or $h^{\bullet}$). The predominant defect and the relevant electroneutrality equation for both types of semi-conductors are given in table 3.5.

Table 3.5. Predominant charged defects

type of semi-conductor	predominant charged defects		electroneutrality equation
	ionic	electronic	
n-type semi-conductor	$\delta^{z\bullet}$	e'	$z C_{\delta} = C_{\varepsilon}$
p-type semi-conductor	$\delta^{z'}$	$h^{\bullet}$	$z C_{\delta} = C_{\varepsilon}$

Then, the conductivity may be written:

$$\sigma_t = z F C_{\delta} U_{\delta} + z F C_{\varepsilon} U_{\varepsilon} = z F C_{\delta} (U_{\delta} + U_{\varepsilon}) \quad (3.44)$$

where U_{δ} and U_{ε} are, respectively, the electrical mobilities of the ionic and electronic defects. Since the mobility of electronic defects is much higher than that of point defects ($U_{\varepsilon} \gg U_{\delta}$), then

$$\sigma_t = z F C_{\delta} U_{\varepsilon} \quad (3.45)$$

This expression shows that:

- the total electrical conductivity is essentially electronic,
- the conductivity varies with oxygen pressure in the same way as does the concentration of the predominant ionised defect (although the current is carried by electronic defects).

It should be pointed out that, if the crystal exhibits an oxygen pressure domain within which neutral point defects predominate, the pressure dependence of the electrical conductivity will differ from that exhibited by the stoichiometry ratio x . The dependence on oxygen pressure of x and σ , respectively, are given in table 3.6 for the case of an oxide M_aO_{b-x} containing oxygen vacancies.

Table 3.6. Comparative oxygen pressure dependences of the deviation from stoichiometry, x , and the electrical conductivity, σ , according to the charge on the predominant defect (nonstoichiometric oxide with oxygen vacancies).

predominant point defects	$V_O^{\bullet\bullet}$	$V_O^{\bullet}$	$V_O^{\times}$
x	$\propto P_{O_2}^{-1/6}$	$\propto P_{O_2}^{-1/4}$	$\propto P_{O_2}^{-1/2}$
σ	$\propto P_{O_2}^{-1/6}$	$\propto P_{O_2}^{-1/4}$	$\propto P_{O_2}^{-1/n} *$

* The hypothesis of predominant neutral defects in the lattice does not rule out the existence of ionised point defects (the n value depends on the degree of ionisation of the **predominant ionised defect**):

- if $[V_O^{\times}] \gg [V_O^{\bullet}] \gg [V_O^{\bullet\bullet}]$, then: $\sigma \propto P_{O_2}^{-1/4}$
- if $[V_O^{\times}] \gg [V_O^{\bullet\bullet}] \gg [V_O^{\bullet}]$, then: $\sigma \propto P_{O_2}^{-1/6}$

• General case

Let us consider the case of an oxide exhibiting an anionic Frenkel disorder. Two limiting cases may be considered according to the respective values of the K_E and K_F constants (see section 2.1.2.3).

a) $K_E \gg K_F$

The oxide conductivity is predominantly electronic over the whole oxygen pressure range (figure 3.8).

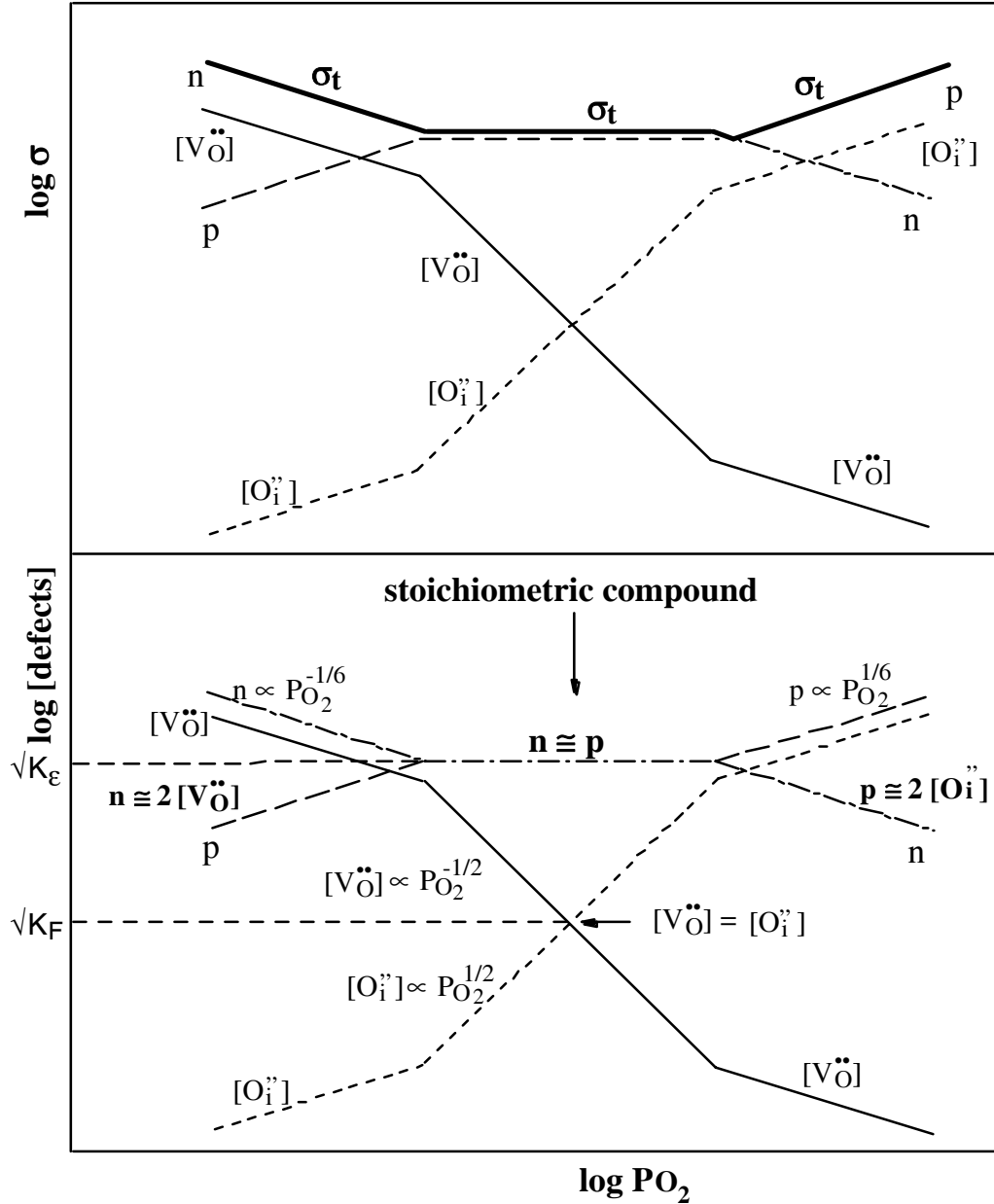


Figure 3. 8. Electrical conductivity as a function of the oxygen partial pressure for a compound exhibiting predominantly electronic conductivity.

In the central pressure domain, corresponding to $[e'] \approx [h^*]$ (or $n \approx p$), the oxygen pressure has no effect on the conductivity.

b) $K_E \ll K_F$

Ionic conductivity may be an important part of the total conductivity over a wide oxygen pressure range. In the pressure domain where the oxide is mainly an ionic conductor, the electrical conductivity is independent of the oxygen pressure (figure 3.9).

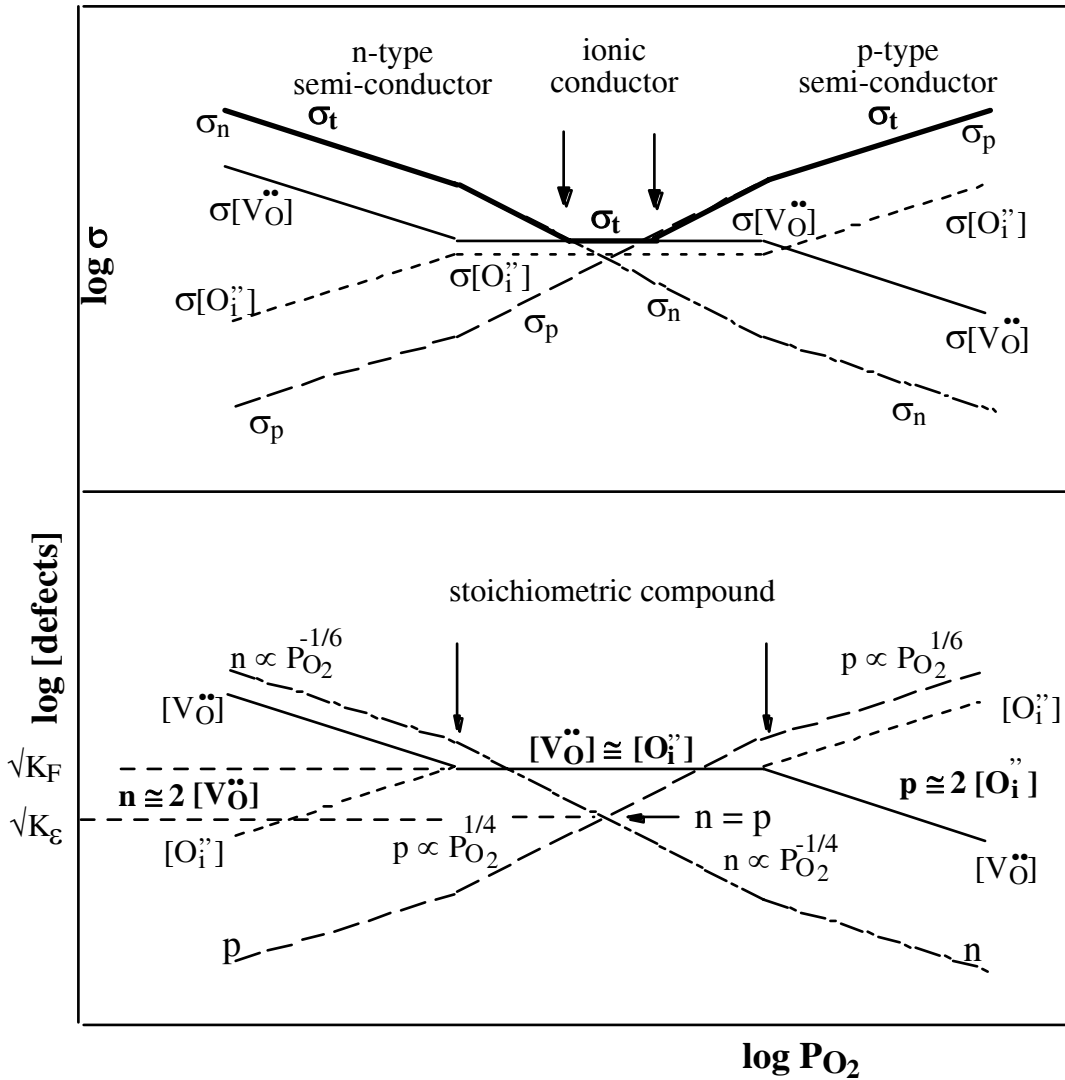


Figure 3. 9. Electrical conductivity as a function of the oxygen partial pressure for a compound exhibiting predominantly ionic conductivity over a defined pressure range.

2.1.4.4. Temperature dependence of the conductivity

The temperature dependence of the conductivity is determined by both the charge carrier mobility and concentration terms.

• Charge carrier mobility

- ionic defects

When ion movements involve jumps between definite sites of the crystal, an energy barrier ΔG_m has to be overcome. The defect mobility then increases strongly with temperature according to an exponential law (*activated process*):

$$U_\delta = U_\delta^0 \exp \left(- \frac{\Delta G_m}{RT} \right) \quad (3.46)$$

ΔG_m is the free energy of migration of the defect.

- electronic defects

The temperature dependence of electron mobility is a function of the electronic structure of the crystal. Two alternative electronic conduction mechanisms can be distinguished in ceramic materials.

At low temperatures, the migration of electrons can be explained by reference to the band model. In this, the electrons or holes are not localised at any specific sites in the lattice but are distributed in more or less narrow bands. The band width decreases with temperature and, simultaneously, the electronic mobility decreases with increasing temperature according to a $T^{-3/2}$ law until the model ceases to have physical significance.

At high temperatures, electron mobility can be described by a hopping model. In this model it is assumed that electrons move by jumps from site to site, between localised energy levels, according to a "small polaron" mechanism. The electron movement is an activated process and the electronic mobility obeys the following equation:

$$U_{\varepsilon} = U_{\varepsilon}^0 \exp \left(- \frac{E_{\varepsilon}}{R T} \right) \quad (3.47)$$

where E_{ε} is the overall activation energy for polaron migration in the periodic field within the crystal.

It is interesting to note that the determination of the variation of the electronic mobility with temperature may allow us to identify the migration mechanism of electrons in the lattice.

• **Charge carrier concentration**

Whatever the nature of the charge carrier (ionic or electronic defects), their concentration increases with temperature according to:

$$[\text{defect}] = [\text{defect}]_0 \exp \left(- \frac{\Delta G_f}{R T} \right) \quad (3.48)$$

ΔG_f is the free energy of formation of the defects.

• **Conductivity**

Whatever the nature of the conduction mechanism, the electrical conductivity is proportional to the product of the drift mobility and the charge-carrier concentration, which varies exponentially with temperature. The crystal conductivity is always an increasing function of temperature due to the predominance of the exponential increase in the number of charge carriers. This characteristic differentiates covalent/ionic compounds from metallic conductors that exhibit a decrease of the electrical conductivity with temperature.

2.2. Clusters and extended defects

It is clear that the structural model of crystals based on the presence of single point defects cannot apply for oxides with large deviations from stoichiometry, say with molar fractions larger than 10^{-2} . In this case, the point defects are likely to associate to form complex defects, either clusters or extended defects. Recent experimental techniques such as neutron diffraction, electron microscopy or Mössbauer spectroscopy together with computer modelling have greatly contributed to the understanding of this phenomenon.

2.2.1. Clusters

Clusters are aggregates of defects which form as a result of strong coulombic interactions between point or electronic defects having opposite charges. Thus, in the case of wüstite, Fe_{1-x}O , a grossly metal deficient oxide ($0.05 < x < 0.15$), experimental studies (neutron diffraction) have shown that, in addition to iron vacancies, (V_{Fe}''), interstitial atoms ($\text{Fe}_i^{\bullet\bullet}$) would be present in the crystal. The crystal structure could be explained by the formation of "elementary units" termed "clusters" that contain an interstitial iron surrounded by 4 iron vacancies with tetrahedral packing, as illustrated in figure 3.10. In this cluster unit, the ratio of iron vacancies to interstitials is about 4/1, thus, it is termed 4:1.

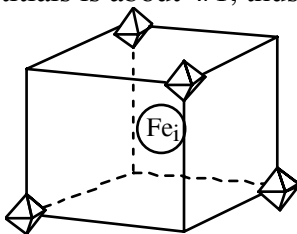
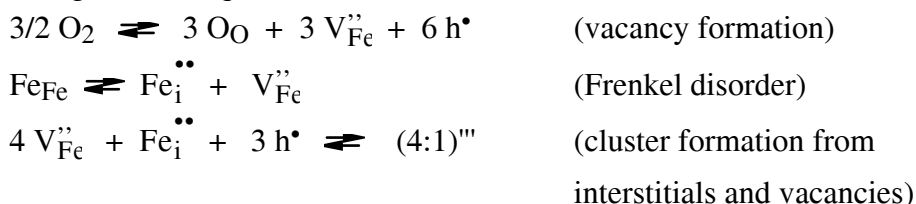
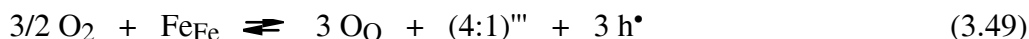


Figure 3.10. Schematic illustration of the (4:1) defect cluster, from Kofstad¹.

The formation of a (4:1) complex defect in the crystal may be explained in terms of the following internal equilibria:



In this example, it is assumed that metal vacancies and interstitials are doubly charged and that the defect cluster has three effective negative charges. The combination of these three equilibria leads to the overall reaction for formation of a (4:1) cluster:



It should be pointed out that more complex units (6:2 or 8:3, etc.) may be formed by the sharing of faces, edges or corners of the (4:1) units (see figure 3.11).

¹ P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science, Londres, 1988, p. 56.

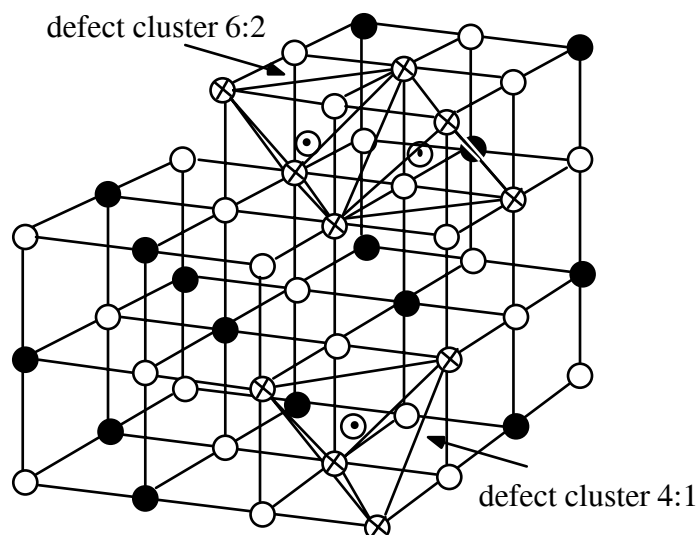


Figure 3.11. Example of 4:1 and 6:2 clusters in an oxide, from Agullo-Lopez et al.². Numbers 4 and 1 correspond, respectively, to four cationic vacancies V_M'' ($\otimes$) and to the central interstitial ion $M_i^{\bullet\bullet}$ ($\odot$). Regular lattice sites are O_O ($\circ$) and M_M ($\bullet$).

Clusters may also be formed in oxides with the fluorite structure exhibiting a large oxygen excess, written as MO_{2+x} ; in UO_{2+x} , for example, the stoichiometry ratio x may reach 0.15. Recent studies, using neutron diffraction and electron paramagnetic resonance, have shown that the nonstoichiometry is not only due to unassociated interstitial oxygen but also to the formation of complex defects within which the ratio of oxygen interstitials to oxygen vacancies is about 2. Each excess interstitial oxygen ion displaces two of the neighbouring oxygen ions into interstitial positions and leaves behind two vacancies on the regular sites. As illustrated in figure 3.12, a 2:1:2 complex defect could be produced by the formation of two oxygen vacancies and two oxygen interstitials by displacement of two oxygen atoms from their regular positions together with one oxygen interstitial atom. These complex defects may also associate to form larger units such as (2:2:2) clusters.

² F. Agullo-Lopez, C.R.A. Catlow and P.D. Townsend, *Point defects in materials*, Academic Press, Londres, 1988, p. 11.

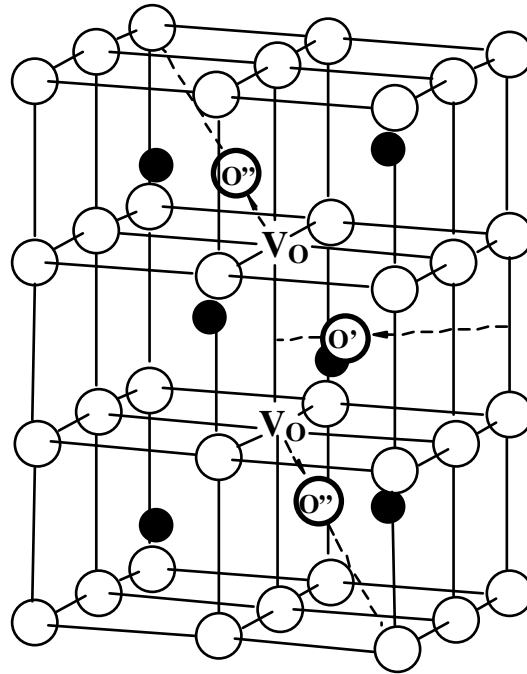


Figure 3.12. Schematic representation of the (2:1:2) defect cluster, from Mrowec³.

2.2.2. Extended defects

These defects result from the long distance ordering of point defects, leading to their elimination by shear of the crystal to form planar defects. In the case of an oxide such as TiO_2 , which is oxygen deficient, the oxygen vacancies or metal interstitials could be eliminated or ordered with the formation of the homologous series of oxides of TiO_2 , with composition $\text{Ti}_n\text{O}_{2n-1}$, (with values of n from 4 to 38), referred to as Magneli phases.

2.2.3. Complex defects and diffusion

The diffusion mechanisms in oxides exhibiting large deviations from stoichiometric composition, and thus containing complex defects, are not currently fully understood. According to several authors, these complex defects would coexist in a dynamic equilibrium with single point defects. For these conditions, diffusion mechanisms may exclusively involve the diffusion of single defects. According to other authors, the clusters, at least the smallest, could move as units. The diffusion mechanisms could involve simultaneous displacement of several species such as interstitials or vacancies.

2. 3 Short-circuit diffusion

As diffusion along line and surface defects, including dislocations, grain boundaries, internal and external surfaces, etc., is generally more rapid than lattice diffusion, they are termed high diffusivity or easy diffusion paths. This type of diffusion is often called "short-circuit diffusion".

³ S. Mrowec, *Defects and diffusion in solids*, Elsevier Scientific Publishing Company, New York, 1980, p. 131.

2.3.1. Linear defects

Recall that an edge dislocation is a linear imperfection of the lattice that may be regarded as an extra plane of atoms inserted partway into the crystal between two other complete planes. The dislocation is characterised by an axis (the linear edge of the half-plane) and the Burgers vector that defines the magnitude and direction of the slip displacement. As an example, figure 3.13 shows an edge dislocation in an ionocovalent crystal M_aX_b formed by insertion into the crystal of two adjacent half-planes belonging, respectively, to the anion and cation sub-lattices.

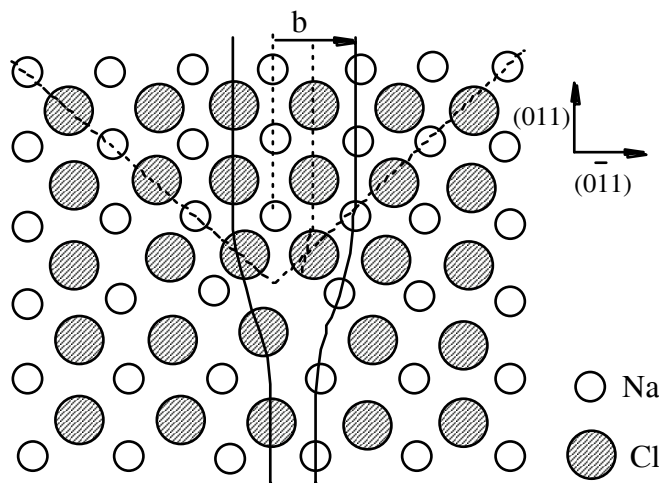


Figure 3.13. Edge dislocation in sodium chloride crystal, from Mrowec ⁴.

Along this line defect, due to local distortions, the coulombic interactions would be less strong than in the bulk crystal and, consequently, diffusion will occur more readily.

2.3.2. Planar defects: grain boundaries

Metal oxidation leads to the formation of one (or several) polycrystalline phase(s). Obviously, the junction between two adjacent crystalline lattices, the interfacial or grain boundary, corresponds to a region of lattice mismatch and consequently, of imperfections in the periodic crystal structure. Whatever the model chosen for the description of the grain boundary structure (boundaries with low or high misorientation), these boundaries constitute transition zones that are more or less disordered. Not surprisingly, diffusion of atoms is more easy in these zones.

The contribution of grain boundary diffusion to the total diffusion flux decreases as the temperature increases for two main reasons:

- the grain size is larger, the higher the temperature because of grain growth;
- the activation energy for grain-boundary diffusion is less than that for intra-crystalline diffusion (from 20 to 30 % smaller).

The effective diffusion coefficient may be defined by the Hart equation:

$$D_{\text{eff}} = f D_{\text{gb}} + (1 - f) D_{\text{v}}$$

⁴ S. Mrowec, *Defects and Diffusion in Solids*, Elsevier Scientific Publishing Company, New York, 1980, p. 25.

where f is the volume fraction of short-circuit paths, D_V the lattice diffusion coefficient and D_{gb} the short-circuit diffusion coefficient. The temperature dependence of the apparent diffusion coefficient D_{eff} of a component of a crystal may be schematised as illustrated in figure 3.14.

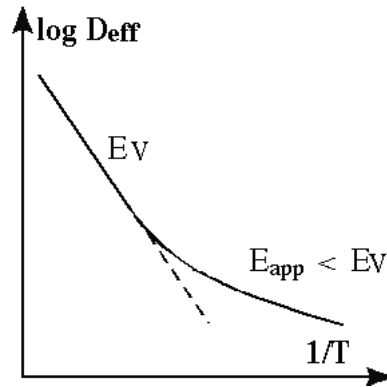


Figure 3.14. Temperature dependence of the effective diffusion coefficient.

D_{eff} may be identified with D_V , the intracrystalline diffusion coefficient, at high temperatures but, at low temperatures, the short-circuit contribution to diffusion can become significant. In general, in accordance with Tamann's empirical law, grain boundary diffusion would be expected to dominate at lower temperatures, say below a transition temperature of between $1/2$ to $2/3$ of the absolute melting temperature of the crystal. Conversely, the contribution made by short circuit diffusion processes will be negligible at higher temperatures.

3. Defects responsible for growth of porous scales

Stress generation in the oxide layer and the underlying metal may cause through-scale cracking, spalling of the oxide, stratification phenomena, or even detachment of the scale. These phenomena lead to loss of protective properties and faster degradation of metals and alloys. The sources of stress may be either internal (scale growth) or external (mechanical and/or thermal stresses). Often, due to mechanical stresses, a porous layer may develop after the oxide scale has reached a critical thickness,.

The two main sources of stress are **growth stresses**, which develop during isothermal formation of the scale, and **thermal stresses**, which arise from differential thermal expansion between the oxide scale and the metal or alloy during temperature changes.

3.1. Growth stresses

Observed stresses depend on the oxidation mechanism and on the physicochemical properties of the alloy and of the oxide. The most important causes of growth stresses are^{5,6} : the volume difference between the oxide and the metal (Pilling and Bedworth rule), the oxidation mechanism (for example, internal or external oxidation of alloys), oxygen dissolution in alloys, epitaxial constraints, physicochemical changes in the alloy or scale during the growth, specimen geometry, etc. The complexity of the phenomena involved impedes the complete analysis in this book of the various stress generation and relief mechanisms. However, their main features will be summarised without mathematical development.

3.1.1. PILLING and BEDWORTH rule⁷

Pilling and Bedworth suggested that oxides could be divided into two main classes according to the ratio between the molar volume of the oxide and that of the metal from which it is formed. This is termed the "Pilling-Bedworth ratio" (PBR) defined as:

$$\text{PBR} = \frac{\frac{1}{a} V_{\text{eq}}(\text{M}_a\text{O}_b)}{V_{\text{eq}}(\text{M})} \quad (3.50)$$

It was argued that if the PBR was less than 1, the growth stresses would be tensile and the oxide would crack and not cover the entire metal surface. As indicated in table 3.7, alkali and alkaline earth metals belong to this class of materials. On the other hand, if the PBR was higher than 1, compressive stresses would develop and the oxide could be protective, at least during the early stages of oxidation. The majority of metals fall into this category (table 3.7)

Table 3.7. Pilling-Bedworth ratios for some metal-oxygen systems.

Oxide	K ₂ O	CaO	MgO	CeO ₂	Na ₂ O	CdO	Al ₂ O ₃	ZnO	ZrO ₂
PBR	0,45	0,64	0,8	0,90	0,97	1,21	1,28	1,55	1,56
Oxide	Cu ₂ O	NiO	FeO	TiO ₂	CoO	SiO ₂	Cr ₂ O ₃	Ta ₂ O ₅	Nb ₂ O ₅
PBR	1,64	1,65	1,7	1,73	1,86	1,9	2,07	2,5	2,7

We now know that the Pilling and Bedworth rule regarding protective behaviour exhibits several exceptions. Important examples are tantalum or niobium where, even though the PBR is substantially larger than unity, cracks develop in the oxide scale after extended exposure and these produce non-protective conditions. Whereas the Pilling and Bedworth

⁵ G. Béranger, A.M. Huntz and B. Pieraggi, in *Corrosion des matériaux à haute température*, G. Béranger, J.C. Colson and F. Dabosi eds., Les Éditions du C.N.R.S., Les Ulis (France), 1987, pp. 227-269.

⁶ P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science, Londres, 1988, pp. 206-277.

⁷ N.B. Pilling and R.E. Bedworth, *J. Inst. Met.*, **1** (1923) 529.

paper was a significant advance at the time, it is now recognised that the approach was incomplete and that the influence of the difference between the molar volume of metal and oxide depends on the oxide growth mechanism (see section 3.1.2).

3.1.2. *Influence of the oxide growth mechanism*

For an oxide exhibiting electronic conductivity and if the scale grows at the gas-oxide interface as a consequence of cation diffusion, it is now recognised that the stresses will be small even for high PBR values because the newly-formed oxide grows into free space. On the other hand, if the scale is formed at the metal-oxide interface, as a consequence of anion diffusion, the stresses may be very high provided the Pilling-Bedworth ratio is larger than unity (the case for titanium or silicon, for example).

For an oxide exhibiting ionic conductivity, oxide growth occurs by counter-current diffusion of both cations and anions. In this case, during oxide growth, deformation and then cracking are often observed within the scale. This phenomenon has been observed, for example, during the oxidation of chromium at temperatures higher than 1050°C. It has been ascribed to large growth stresses resulting from the formation and growth of new oxide along pre-existing oxide grain boundaries that constitute short-circuit paths for diffusion.

3.1.3. *Oxygen dissolution in alloys*

Oxygen dissolution in metals or alloys may cause large stresses to be developed as a result of generally anisotropic lattice expansion. It is especially the case when the oxygen solubility is high (titanium, zirconium, niobium, tantalum).

3.1.4. *Epitaxial stresses*

The lattice parameter difference between metal and oxide may induce stresses at least during initial oxidation or at low oxidation temperatures. It has been shown that the epitaxial stresses, and even the resulting deformation, can then be very important. As the scale thickens, the epitaxial constraints are reduced.

In the case of the formation of multi-layered scales, epitaxial relationships between the metal and one of the oxides formed, can lead to the favoured growth of this oxide. A typical example is given by iron oxidation (see Figure 3.15) where, for temperatures below 910°C, a crystallographic relationship exists between FeO and the α -Fe (bcc) lattices (figure 3.15 a). In this situation, an atom of the metal may cross the metal-oxide interface without discontinuity and become incorporated into the oxide lattice. For temperatures higher than 910°C, there is no dimensional relationship between the lattice parameters of γ -iron (fcc) and FeO. In these conditions, the wüstite (FeO) layer thickens more slowly than Fe₂O₃ and Fe₃O₄ (figure 3.15 b).

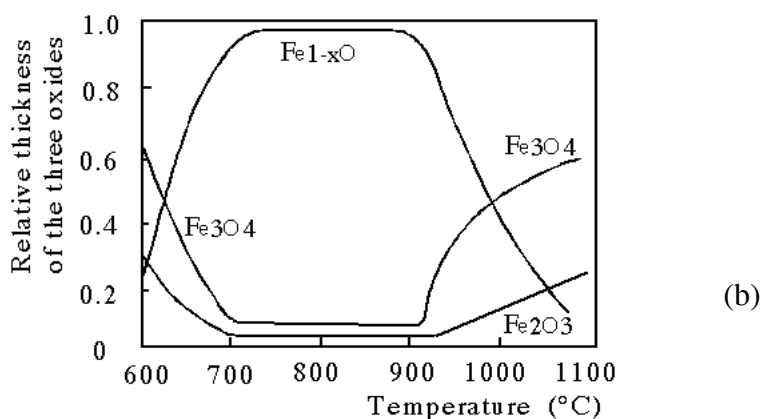
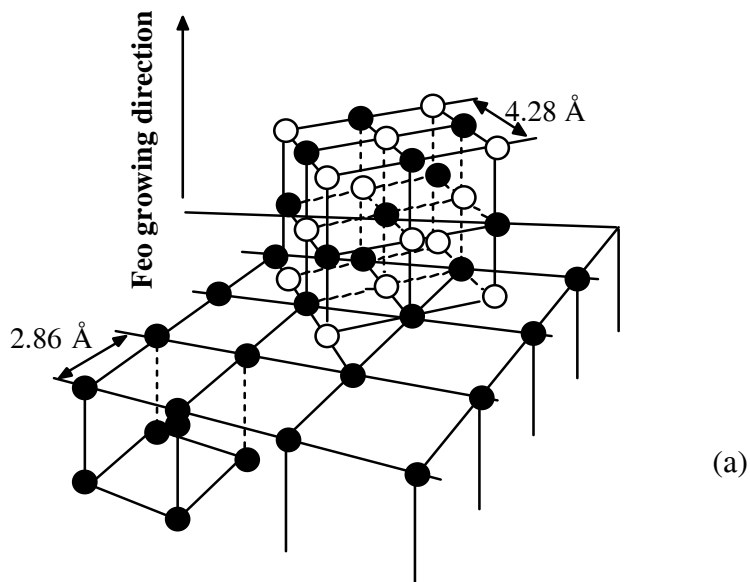


Figure 3.15. (a) Epitaxial relationship between the lattices of Fe_{1-x}O (wüstite) and of $\alpha\text{-Fe}$.
 (b) Relative thicknesses of the oxide layers as a function of oxidation temperature (from⁸)

3.1.5. Physicochemical modifications

During alloy oxidation (see chapter 6), selective oxidation of a component induces concentration gradients in the alloy sub-surface. Internal oxidation will lead to the formation of inclusions of oxides and this could result in significant stresses. If the oxide formed exhibits a large deviation from stoichiometry, significant variations of its lattice parameter may be observed within the oxide layer.

In the case of formation of several oxides, large stresses may develop; for example, in the case of copper oxidation to form Cu_2O and CuO or of iron oxidation to form FeO , Fe_3O_4 or Fe_2O_3 . It has been suggested that recrystallisation of the oxide during its growth may affect the magnitude of the growth stress. Phase transformation of the oxide, may also cause stresses in the scale. A typical example is the oxidation of zirconium or Zircaloy (Zr-Sn-Fe

⁸ P. Lacombe and F. Dabosi, in *Corrosion des matériaux à haute température*, G. Béranger, J.C. Colson and F. Dabosi eds., Les Editions du C.N.R.S., Les Ulis (France), 1987, pp. 11-56.

alloy) for which ZrO_2 changes from the monoclinic to the tetragonal structure between 1000 and 1200°C corresponding to an 8 % volume change.

In some cases, the metal or alloy oxidation leads to the formation of a volatile phase which is, obviously, non-protective. This phenomenon may be observed during the oxidation of alloys containing chromium, molybdenum or tungsten.

3.1.6. Specimen geometry

The stress level depends on the geometry of the specimens, the local curvature and, especially on the nature of the ionic defects that control mass transport within the scale. For example, when oxide forms by cation migration on concave surfaces, a decrease in the compressive stresses is observed due to the retreat of the underlying metal. Tensile stresses may even be generated resulting in loss of oxide adherence. Figure 3.16 illustrates this effect during the oxidation of an iron wire at 750°C. By contrast, the compressive stresses increase in the scale in the case of anion diffusion and compressive shear cracks may also form within the scale at the oxidation temperature but without loss of adherence.

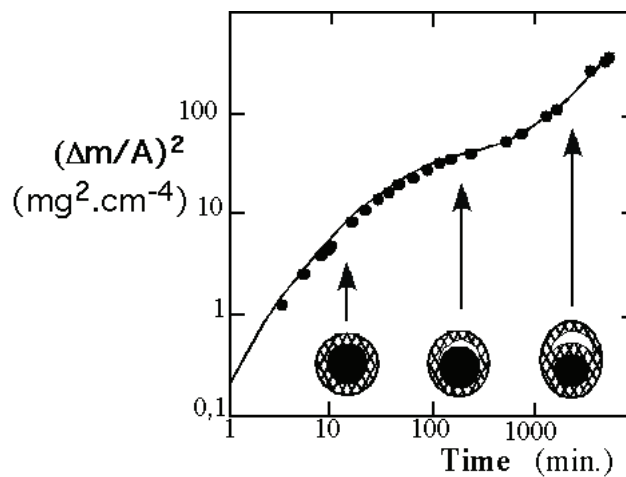


Figure 3.16. Effects of loss of adherence of the oxide scale on the kinetics of oxidation of an iron wire in oxygen ($\phi = 0.48$ mm) at 715°C, from Engell and Wever⁹.

3. 2. Thermal stresses

In most applications, high temperature alloys are subjected to temperature fluctuations even under nominally isothermal conditions. In this case, though, the resultant stresses in the oxide layer, resulting from the difference in the thermal expansion coefficients of the metal and oxide (see Table 3.8), are small and may be neglected. This will not be the case, however, for large thermal cycles or during cooling to room temperature when large stresses, perhaps of order 1 GPa, are produced in the oxide layer. Metals have, generally, a higher

⁹ H.J. Engell and F. Wever, *Acta Metall.*, **5** (1957) 695.

coefficient of thermal expansion than oxides (Table 3.8) and, consequently, tensile stresses are induced in the oxide scale on heating and compressive stresses during cooling.

Tableau 3.8. Linear coefficients of thermal expansion of metals and oxides

System	Oxide: $10^6 \cdot \alpha_{ox}$	Metal: $10^6 \cdot \alpha_M$	Ratio: $\frac{\alpha_M}{\alpha_{ox}}$
Fe/FeO	12,2	15,3	1,25
Fe/Fe ₂ O ₃	14,9	15,3	1,03
Ni/NiO	17,1	17,3	1,03
Co/CoO	15,0	14,0	0,93
Cr/Cr ₂ O ₃	7,3	9,5	1,30
Cu/Cu ₂ O	4,3	18,6	4,32
Cu/CuO	9,3	18,6	2,0

Assuming elastic behaviour of both materials and a flat metal surface, the average magnitude of the in-plane thermal stress developed in the oxide may be expressed by the following simplified equation:

$$\sigma_{ox} = \frac{E_{ox} \cdot \Delta T \cdot (\alpha_M - \alpha_{ox})}{1 + 2 \frac{E_{ox}}{E_M} \cdot \frac{e_{ox}}{e_M}} \quad (3.51)$$

where E_{ox} and E_M are, respectively, the oxide and metal Young's modulus, α_{ox} and α_M are the coefficient of thermal expansion, e_{ox} and e_M the oxide and metal thicknesses and ΔT the temperature change (negative for a temperature drop). As can be seen, assuming that the various coefficients are independent of temperature, the magnitude of the stress is proportional to ΔT and to the difference in thermal expansion coefficients (see figure 3.17).

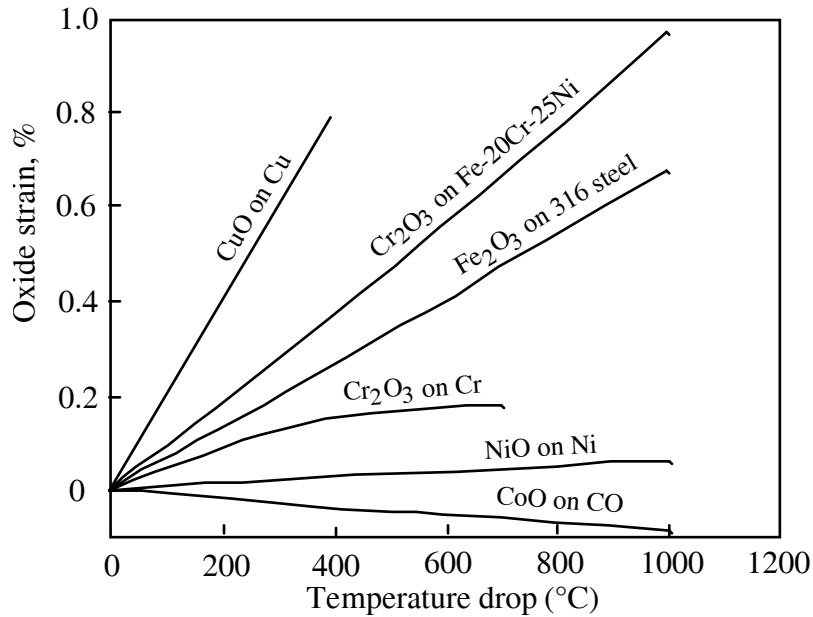


Figure 3.17. Oxide strains as a function of the temperature drop from the oxidation temperature¹⁰.

When the cooling rate is high, the stresses cannot be accommodated and cracking in the scale or even its detachment may be observed.

3.3. Degradation mechanisms

Growth stresses and thermal stresses may be relieved through various mechanisms that could operate simultaneously:

- plastic deformation of the oxide scale,
- plastic deformation of the metal substrate,
- spalling of the oxide from the alloy,
- cracking of the scale.

When plastic deformation is not sufficient for stress relief, cracking may develop in the scale. It is the more efficient relaxation mechanism but will result in a sudden increase in corrosion rate. The metal oxidation may exhibit repeated regular sequences of cracking and healing of the scale (see oxidation of chromium, Chapter 2).

Under *tensile stresses* (heating to temperatures higher than the oxidation temperature or over convex regions of a non-planar surface) cracks appear as soon as the elastic fracture strain is reached. This critical value will be significantly less than 1% even at high temperatures.

Under *compressive stresses*, the degradation leads to spallation and the mechanisms are more complex. Two processes are necessary to produce spalling: transverse cracking through the oxide and decohesion along the metal-oxide interface. Two routes to spallation

¹⁰ H.E. Evans, *Int. Mater. Rev.*, **40** (1995) 1-40.

have been identified: the case corresponding to a low cohesive strength of the oxide and a high adhesive strength of the scale on the substrate surface (route 1: cracking of the oxide before decohesion) and the case corresponding to a high cohesive strength of the oxide and poor adhesion of the oxide to the metal (route 2: decohesion before metal cracking). Figure 3.18 illustrates these two distinct mechanisms.

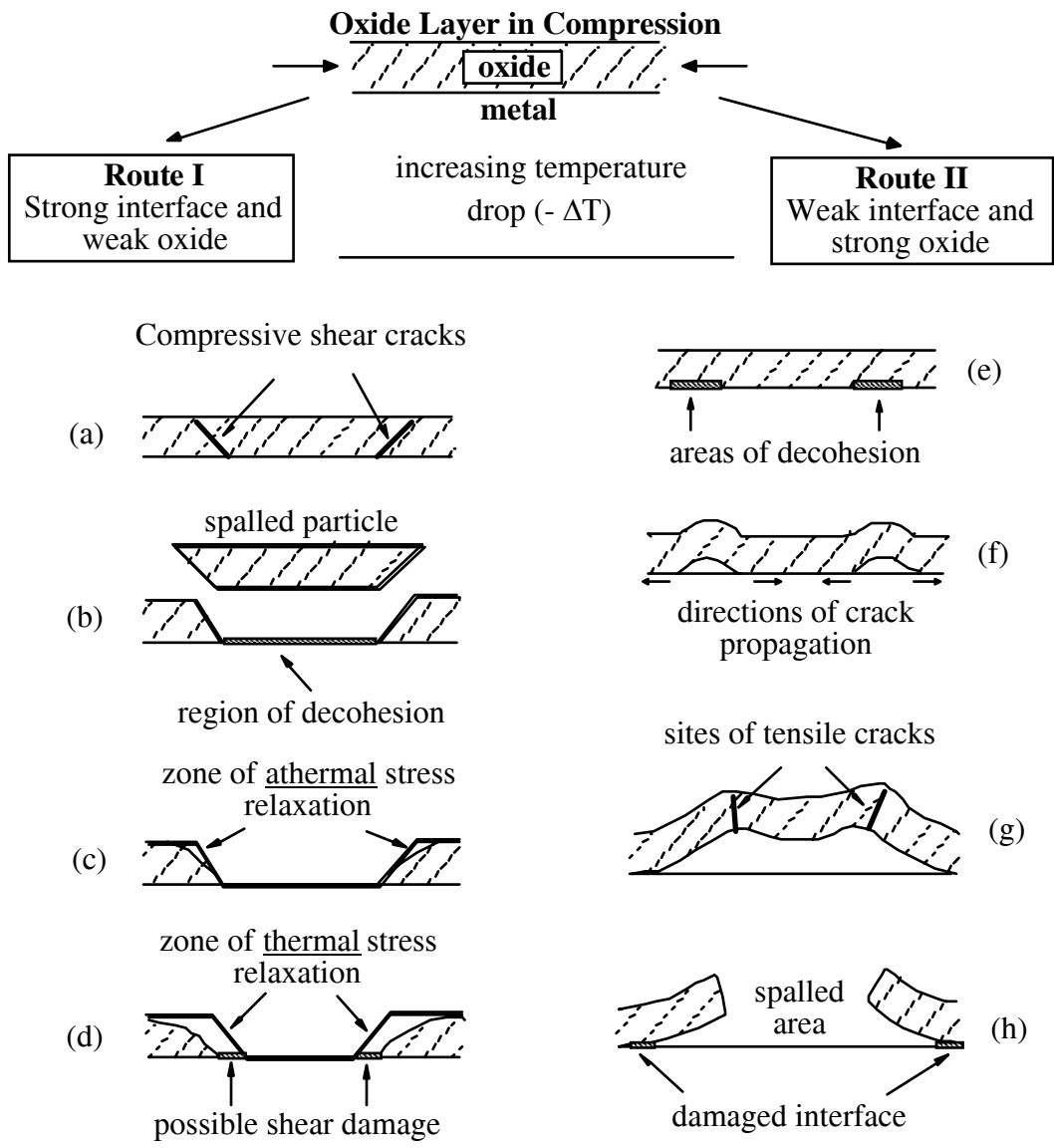


Figure 3.18. Cracking and spallation caused by compressive oxide stresses, from Evans¹⁰.

3.4. Formation of a porous layer

The formation of a porous layer may result from cracking of an initially protective oxide scale, due to mechanical stresses, or to the direct formation of a porous scale (oxides for which the PBR is less than unity).

Generally, the formation of a porous scale is characterised by:

- a linear rate law (see chapter 4),
- a large specific area of the scale: in the case of a compact scale, the specific area is below $10^{-2} \text{ m}^2 \cdot \text{g}^{-1}$ but it may reach several tens of $\text{m}^2 \cdot \text{g}^{-1}$ in the case of a porous layer.

The formation of a porous layer may have various consequences on the oxidation rate:

- in some cases, the growth rate of fissures is sufficiently low so that the oxide may be rebuilt until a new critical value is reached when cracking again occurs; the observed rate law has been shown schematically in figure 2.28 of chapter 2 ($T = 1075^\circ\text{C}$).
- in other cases, the oxide thickens parabolically until a critical thickness at which the scale becomes non-protective due to a high rate of fissure development; this catastrophic process is termed "breakaway oxidation" and the overall kinetics are illustrated in figure 3.19.

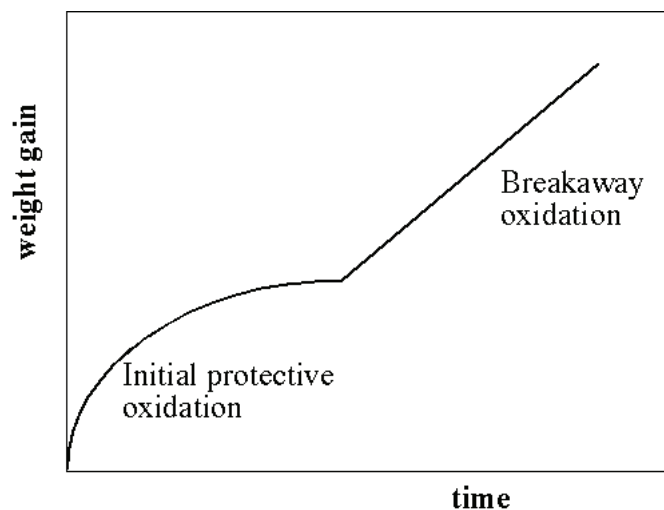


Figure 3.19. Schematic illustration of the kinetics of breakaway oxidation.

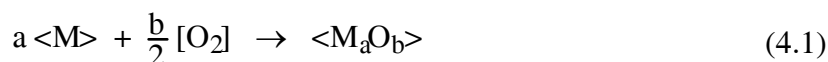
- In the case of the formation of multi-layered scales, a continuous variation of the kinetic oxidation law may be observed with, for example, an initial parabolic law followed by a linear oxidation at a critical thickness of the scale. This mechanism (Loriers-Haycock model) will be described in chapter 5.

Chapter 4

KINETIC APPROACH TO HIGH TEMPERATURE CORROSION: Growth of a compact scale

1. Introduction

The overall oxidation reaction of a metal M may be written as:



This reaction leads to the formation of a solid oxide scale M_aO_b , as illustrated in figure 4.1, and can proceed only if diffusion of matter (oxygen or metal) occurs through the oxide film.

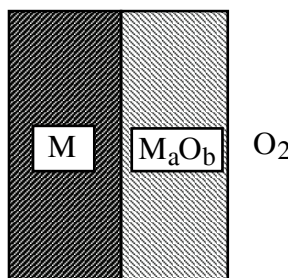


Figure 4.1. Schematic illustration of formation of a compact oxide scale M_aO_b .

The reaction mechanism is complex and results from a series of elementary steps. The nature of these elementary steps depends on the structure of the scale formed. Two limiting cases will be studied:

- the scale formed is porous and mass transport (in this case, exclusively oxygen) occurs by gas diffusion,
- the scale formed is compact and mass transport occurs by means of solid-state diffusion.

The oxidation mechanism, in the latter case, consists of a succession of at least four basic fundamental processes:

- oxygen *adsorption* on the oxide M_aO_b ,
- an external elementary step corresponding to an exchange of matter between the adsorbed phase and the oxide M_aO_b , which we shall term an *external semi-reaction*,

- transport of matter through the oxide scale M_aO_b by *solid-state diffusion* of one or both of the reactants, i.e. metal or oxygen,
- an internal elementary step corresponding to an exchange of matter between oxide and metal M, which we shall term an *internal semi-reaction*.

In addition to these four basic stages, other steps may occur:

- gas phase diffusion (in the case of oxidation by a complex gas such as CO_2 , H_2O , etc.) leading to the release of gas,
- diffusion processes within the metallic phase (for example in the case of oxygen dissolution in the metal or during the oxidation of alloys).

Moreover, it should be pointed out that, in the most general case where mass transport is envisaged to occur by the migration of charged species (ionised point defects), the oxidation mechanism is all the more complex because electrical transport must occur simultaneously with the mass transport. We shall take this general process into account here and adopt the conventional approach to the analysis of the reaction kinetics, i.e.:

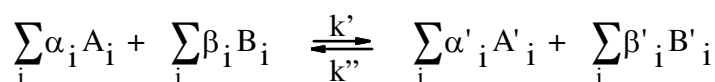
- formulation of the elementary steps,
- calculation of the rate of these elementary steps,
- derivation of the system of differential equations allowing calculation of the reaction rate,
- use of the quasi steady-state approximation to solve the system analytically.

2. Formulation of the elementary steps

2.1. Elementary steps at interphases*

Let a chemical elementary step be a local reversible reaction that occurs without the formation of a distinct intermediate product, i.e., the reaction proceeds in a single step, and let an interphase elementary step be a chemical process involving matter exchange between two distinct phases. The main difficulty encountered for the formulation of these steps relates to the conditions required for the application of classical theories (Eyring theory) for the calculation of the step rates.

Let A and B be two condensed phases in contact and let us consider a chemical reaction at the interface A/B, according to:



where A_i , B_i and A'_i , B'_i are, respectively, the reactant and product species in solution in phases A and B, respectively. Let $[A_i]$, $[B_i]$, $[A'_i]$ and $[B'_i]$ be the concentrations of each species in their phase (number of moles per mole of solvent). These concentrations are proportional to their mole fractions. If all the species show ideal behaviour in their respective

* We reserve the use of the term "interface" for contact between condensed phases.

phase, in other words if their activity equates to their mole fraction, and if the reaction proceeds in a single step, then applying Eyring's theory¹ of absolute rates leads to the following expression:

$$v = k' \prod_i [A_i]^{\alpha_i} [B_i]^{\beta_i} - k'' \prod_i [A'_i]^{\alpha'_i} [B'_i]^{\beta'_i}$$

where k' and k'' are, respectively, the forward and reverse rate constants of the elementary steps. They are functions only of temperature.

Thus, we will have to choose, for the adsorbed phase as well as for the oxide, structural models that exhibit ideal behaviour for the reacting species in their own phase. Moreover, we will assume that the theory of absolute rates can, under these conditions, be extended to heterogeneous elementary steps involving matter exchange between two different phases.

Comment 1: Rate expression and deviation from equilibrium

When the elementary step is in equilibrium, its rate is zero. Thus, if K is the corresponding equilibrium constant, we obtain:

$$\left(\frac{\prod_i [A'_i]^{\alpha'_i} [B'_i]^{\beta'_i}}{\prod_i [A_i]^{\alpha_i} [B_i]^{\beta_i}} \right)_{eq} = \frac{k'}{k''} = K$$

The ratio of the forward over the reverse rate constants can be identified as the equilibrium constant and, consequently, the reaction rate can be expressed as functions of the rate constant of the direct process only and of a term expressing a deviation from equilibrium, according to:

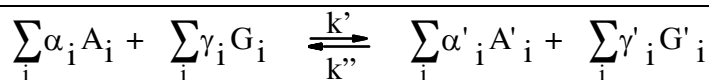
$$v = k' \left(\prod_i [A_i]^{\alpha_i} [B_i]^{\beta_i} - \frac{1}{K} \prod_i [A'_i]^{\alpha'_i} [B'_i]^{\beta'_i} \right)$$

We will use this formulation systematically.

Comment 2: Such an expression can be easily transposed to the case of an elementary step involving gaseous species G_i and G'_i , belonging to a gaseous phase G , assuming that these species demonstrate ideal behaviour, i.e. that the activities are proportional to their partial pressures P_{G_i} and $P_{G'_i}$.

Let us consider, for example, the elementary step described by the interphase reaction:

¹ S. Glasstone, K.J. Laidler and H. Eyring, *Theory of Rate Process*, Mc Graw-Hill, Booth Company, New York, 1941.



where A is a condensed phase and G is a gaseous phase. Provided that the species show ideal behavior in their respective phase, applying Eyring's theory then leads to the following expression for the reaction rate:

$$v = k' \left(\prod_i [A_i]^{\alpha_i} [p_{G_i}]^{\gamma_i} - \frac{1}{K} \prod_i [A'_i]^{\alpha'_i} [p_{G'_i}]^{\gamma'_i} \right)$$

2.1.1. Sorption process

It should be recalled that adsorption is the process whereby gas atoms or molecules adhere to the surface of a solid.

2.1.1.1. Sorption phenomena

On a solid surface, the atomic environment is modified in comparison with that in the bulk. The resulting imbalance of the forces in the surface of solids produces attractive forces for gas molecules or atoms. The phenomenon of adsorption can then produce an excess of gas atoms or molecules on the surface compared with the concentration in the adjacent gas phase. For adsorption to occur spontaneously, the process must produce a decrease in free energy but, since there is also a decrease in system entropy, adsorption is always an exothermic process. Consequently, the amount of adsorbed gas at equilibrium at constant pressure (the "adsorption isobar") decreases with increasing temperature.

Depending on the nature of the forces involved, adsorption processes may be classified as physical adsorption (also termed as van der Waals adsorption or physisorption) or chemical adsorption, usually abbreviated to chemisorption (see table 4.1). Physisorption generally occurs at temperatures close to gas liquefaction. The binding forces are of the van der Waals type. The electronic structure of adsorbed molecules is not much changed and the phenomenon is reversible. Physical adsorption is not a specific process in the sense that gas atoms or molecules are not adsorbed on specific atoms of the solid surface. Thus, surface concentration is only a function of temperature and gas pressure. As shown in figure 4.2 (curve (a)), the potential energy goes through a minimum Φ_ϕ for the equilibrium position, r_ϕ , of the adsorbed molecule or atom.

Table 4.1. Main criteria that allow us to distinguish between physical and chemical adsorption.

Characteristics	Physical adsorption	Chemical adsorption
Binding forces	van der Waals forces	electron transfer between adsorbant and adsorbate
Specificity	not specific	specific
Reversibility	reversible	generally, not reversible except at high temperature
Heat of adsorption (kJ.mol ⁻¹)	10 - 20	40 – 600
Activation energy (kJ.mol ⁻¹)	spontaneous phenomenon, no activation energy	20 – 80
Number of adsorbed layers	may be higher than 1	≤ 1

Chemical adsorption involves an exchange of electrons between gas molecules and the solid. Chemisorption is more specific in nature than is physisorption. The energy of chemisorption is of the same order as that of the binding energies of molecules (several tens to several hundreds of kJ) and is much greater than that for physisorption which is of the same order of magnitude as the heat of liquefaction (see figure 4.2 (curve (b))).

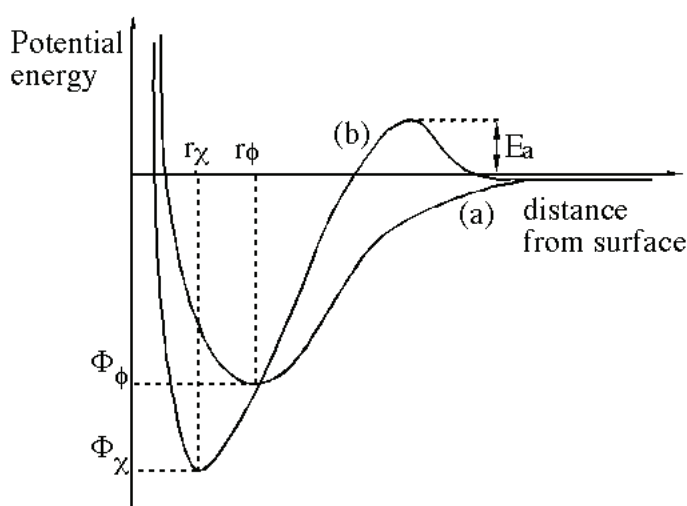


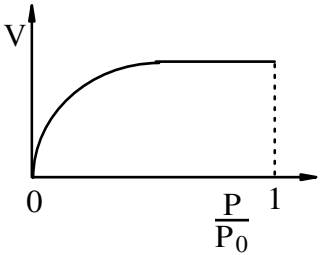
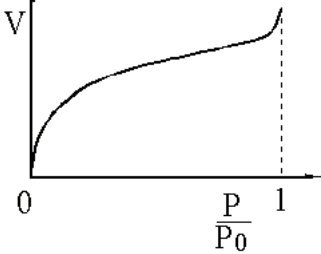
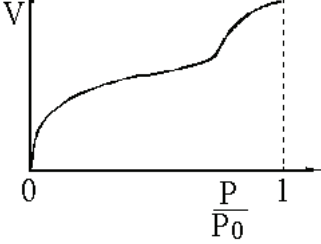
Figure 4.2. Change of potential energy of a gas on approaching a solid surface for the case of physical adsorption (curve (a)) and of chemical adsorption (curve (b)).

Physisorption is generally quasi instantaneous while chemisorption proceeds often slowly, involving an activation energy E_a . Thus, the chemical adsorption rate becomes appreciable only at sufficiently high temperature.

A large number of theories and models have been proposed to explain the shape of adsorption isotherms that represent the variation of adsorbed volume as a function of gas pressure or of the $\frac{P}{P_0}$ ratio (P_0 is the saturation vapour pressure at the experimental temperature). The description of monolayer adsorption can be made using as variable the fraction of the available adsorption sites which are occupied by adsorbed atoms or molecules $\theta = \frac{s}{s_0}$ where s_0 is the number of adsorption sites that are initially available* per surface area unit and s , the number of occupied surface sites per surface area unit (thus, θ is the fraction of occupied sites).

The three main shapes of isotherms observed in the case of physisorption are shown in Table 4.2. Type 1 corresponds to monomolecular adsorption ("Langmuir" type curve), type 2 corresponds to multimolecular adsorption (B.E.T. isotherm), whereas the third type corresponds to adsorption on porous substrates for which gas condensation in the pores is observed for pressures close to gas liquefaction.

Table 4.2. Main types of physisorption isotherms.

Isotherm types	Isotherm equations	Isotherm shapes
Type 1 Langmuir type isotherm Monomolecular adsorption	$\frac{V}{V_m} = \theta_{eq} = \frac{K_a P}{1 + K_a P}$ P : pressure of gas G V_m: volume corresponding to an adsorbed monolayer	
Type 2 Sigmoid curve Multimolecular adsorption	$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1)}{V_m C} \frac{P}{P_0}$ C : constant	
Type 3 Porous substrate	Complex	

* In the case of oxygen adsorption on an oxide, these sites can be assumed to be metallic ions on the solid surface.

In the most widespread model (Langmuir isotherm²) it is assumed that molecules are adsorbed on to definite surface sites without creation of a new adsorption site: the amount adsorbed is confined to a monomolecular layer. Isotherm equation development is based on the following assumptions:

- *the adsorbed molecules are localised,*
- *only one molecule or atom can be adsorbed on each site of the surface,*
- *every site on the surface has the same energy of adsorption which does not depend on the number of adsorbed molecules already present on the surface.*

Adsorption isotherm equations are established in section 2.1.1.2 for the case of dissociative and non-dissociative adsorption.

Other models have been proposed to take into account the variation of adsorption energy with the fraction of adsorbant surface covered with adsorbate. This variation is generally observed and is ascribed to surface heterogeneity, to adsorbate-adsorbant interactions and to heterogeneity induced by adsorption. Freundlich assumes an exponential decrease of adsorption energy with covering factor θ . For these conditions, the isotherm equation can be written in the form:

$$V = K \cdot P^n \quad (n < 1)$$

The Temkin isotherm is based on the assumption of a linear decrease of the adsorption energy with fractional surface coverage θ . The corresponding isotherm equation can be expressed as:

$$\frac{V}{V_m} = \theta_{eq} = a \log(b \cdot P) \quad a \text{ and } b \text{ are constants}$$

The multimolecular adsorption theory, developed by Brunauer, Emmett and Teller³, known as the BET theory, is an extension of the Langmuir model. The basic assumptions are the following:

- *when an atom or a molecule is adsorbed, a new adsorption site is created so that successive layers can be formed*
- *the energies of adsorption of the bare solid surface and in the second and succeeding layers of adsorbate are identical and equal to the heat of liquefaction of the adsorbate.*

The main application is to the measurement of the specific surface of solids.

Chemisorption involves partial electronic transfer between adsorbed molecules and the substrate. The solid surface appears inhomogeneous and exhibits specific "active" sites on which chemisorption takes place preferentially.

² I. Langmuir, *J. Am. Chem. Soc.*, **40** (1918) 1361.

³ S. Brunauer, P.H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60** (1938) 309.

The transition between physical and chemical adsorption is continuous. Figure 4.3 shows the variation of the amount of adsorbed gas on a metal as a function of temperature (adsorption isobar). At very low temperature, physisorption predominates. When temperature is increased, the amount of adsorbed gas by chemisorption increases because it is an activated process; the isobar curve passes through a maximum because chemisorption is an exothermic phenomenon.

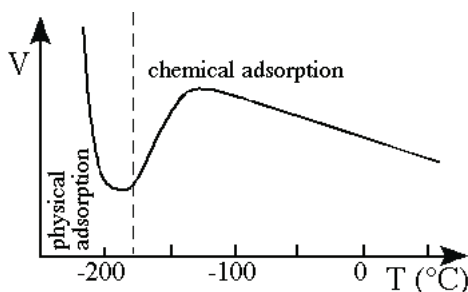


Figure 4.3. Adsorption isobar.

The main applications of chemisorption is to catalysis, gas sensors and interfacial electrochemistry.

Only chemisorption, prevalent at high temperatures and involving chemical bonding, will be considered in this book. It can be thought that high temperature corrosion proper begins when the process proceeds beyond one monolayer,.

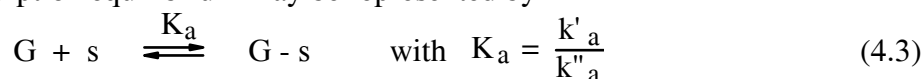
2.1.1.2. A model of the chemisorbed phase

In the following, the adsorbed phase will be considered as a 2-dimensional solution (i.e. sorption of a monolayer) of free surface sites, s , and of occupied sites leading to the formation of a superficial compound referred to as $G-s$, where G is a particle of the gas phase. Such a solution may be considered as **ideal** since it is assumed that no interaction occurs between the free and occupied sites. The sorption process may then be described by an equation representing the balance between two opposite reactions with rate constants k'_a and k''_a , respectively:



• Calculation of the fractional surface coverage at equilibrium θ^{eq}

The sorption equilibrium may be represented by:



K_a denotes the equilibrium constant of the elementary step of sorption.

Under these conditions, if P denotes the partial pressure of the G species, θ^{eq} the fractional surface coverage, the law of mass action applied to the equilibrium leads to:

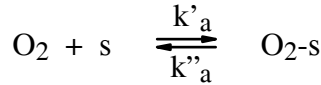
$$\frac{\theta^{eq}}{1 - \theta^{eq}} = K_a P \quad \text{from this expression, we obtain:} \quad \theta^{eq} = \frac{K_a P}{1 + K_a P} \quad (4.4)$$

indicating that the sorption is governed by the Langmuir equation.

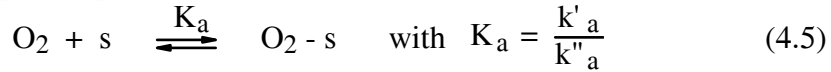
• **Generalisation to the case of the chemisorption of a diatomic gas (O_2 , for example)**

Two hypotheses may be considered:

a) *Dissociation does not occur on chemisorption*



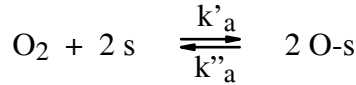
The chemisorption equilibrium may be written:



The mass action law applied to the sorption equilibrium leads to:

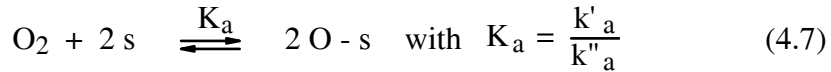
$$\theta^{eq} = \frac{K_a P_{O_2}}{1 + K_a P_{O_2}} \quad (4.6)$$

b) *Dissociation occurs on chemisorption* (likely at high temperature)



where O-s is an atomically chemisorbed oxygen

K_a will be the equilibrium chemisorption constant:



θ^{eq} can be calculated from the law of mass action:

$$\theta^{eq} = \frac{\sqrt{K_a P_{O_2}}}{1 + \sqrt{K_a P_{O_2}}} \quad (4.8)$$

Comment: However, it should be pointed out, that more sophisticated models have been developed but do not appear easy to use. By contrast, the model proposed here satisfies the ideality criteria and, consequently, offers two advantages:

- first, it leads from a thermodynamical approach to the classical expression of the Langmuir isotherm,

- second, it leads, from the application of classical rate theories, to a formulation of the sorption rate which corresponds to the Langmuir isotherm at equilibrium, i.e. where the sorption rate is equal to zero.

2.1.2. Interfacial processes

For the sake of simplicity, we shall consider a system M/MO/O₂, consisting of a gaseous phase O₂, a metal M and an oxide MO. We define the external and internal elementary steps as the insertion of oxygen at the external interface and the insertion of metal at the internal interface during the construction of the oxide lattice. The proposed model to account for these transfers of matter uses the concept of point defects. The oxide MO will be considered as an ideal solution of point defects in a perfect crystal. The interface will be considered as planar, without macroscopic defects, and the transfers of matter as unidirectional*.

The formulation of the interfacial elementary steps is shown schematically in Table 4.3. They depend on the nature of the point defects likely to be present in the oxide lattice. For the sake of simplicity, we make the assumption that only one defect is predominant in the lattice, with a degree, z , of ionisation where z is an integer between 0 and 2 (for the case that the oxide MO is a semiconductor). Thus, the predominant defect will be either the metal vacancy $V_M^{z'}$ or the oxygen interstitial $O_i^{z'}$ for the case of a p-type semi-conductor and either the oxygen vacancy $V_O^{z\bullet}$ or the metal interstitial $M_i^{z\bullet}$ for the case of a n-type semiconductor.

As shown in Table 4.3, each elementary step is represented by a balance equation of two opposite reactions with rate constants k'_e and k''_e (external elementary step) and k'_i and k''_i (internal elementary step).

Table 4.3. Formulation of the elementary interfacial steps according to the nature of the predominant defects present in the MO oxide lattice.

* More sophisticated models, using a microscopic approach, have been proposed (Pierragi and Rapp). Such an approach, which is not easy to develop analytically, is beyond the scope of this book.

MO p-type semi-conductor		
<i>defect</i>	<i>external elementary step</i>	<i>internal elementary step</i>
O_i	$O-s \xrightleftharpoons[k''_e]{k'_e} O_i^{z'} + z h^\bullet + s$	$\langle M \rangle + O_i^{z'} + z h^\bullet \xrightleftharpoons[k''_i]{k'_i} O_O + M_M$
V_M	$O-s \xrightleftharpoons[k''_e]{k'_e} O_O + V_M^{z'} + z h^\bullet + s$	$V_M^{z'} + z h^\bullet + \langle M \rangle \xrightleftharpoons[k''_i]{k'_i} M_M$

MO n-type semi-conductor		
<i>defect</i>	<i>external elementary step</i>	<i>internal elementary step</i>
M_i	$O-s + M_i^{z\bullet} + z e' \xrightleftharpoons[k''_e]{k'_e} O_O + M_M + s$	$\langle M \rangle \xrightleftharpoons[k''_i]{k'_i} M_i^{z\bullet} + z e'$
V_O	$O-s + V_O^{z\bullet} + z e' \xrightleftharpoons[k''_e]{k'_e} O_O + s$	$\langle M \rangle \xrightleftharpoons[k''_i]{k'_i} M_M + V_O^{z\bullet} + z e'$

Comment 1: With a **p**-type semi-conductor, the defects are generated at the EXTERNAL interface and with a **n**-type semi-conductor, at the INTERNAL interface.

Comment 2: The lattice is built at the interface where the construction unit* is generated, either at the internal interface (anionic diffusion) or the external one (cationic diffusion).

2.2. Diffusional processes

In a thick, growing oxide scale, an electric field can be present. Indeed, due to the difference between ionic and electronic point defect mobilities, a volumetric distribution of charge, a “space charge”, can be set up within the growing scale. Thus, in the case of the simultaneous diffusion of an interstitial cation and an electronic defect from the internal

* The construction unit has been defined in Chapter 3, section 2.1.2.1 as the smallest module that can be used to build the oxide lattice.

interface towards the external one, a positive space charge can appear in contact with the metal balanced by a negative space charge localised near the external interface. This charge distribution induces, at any point within the scale, an electric field that both accelerates the positively charged ionic defects and slows down the negatively charged electronic defects until no net electrical current flows through the scale. Consequently, as illustrated in figure 4.4, stationary concentration profiles of both positive and negative charges are established in the MO scale.

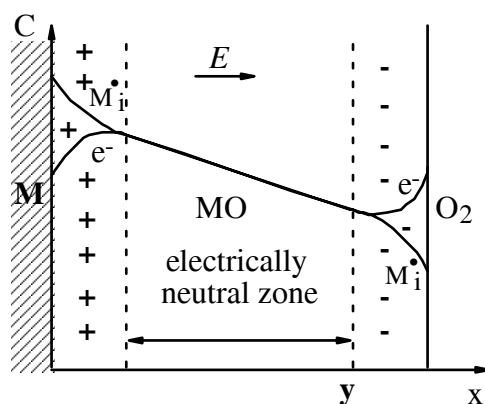


Figure 4.4. Concentration profiles of metallic and electronic defects in a growing oxide scale (n-type semi-conductor).

Following Wagner^{4*}, we will make the assumption that the electrically neutral zone extends over practically all of the scale thickness, i.e. the space charge is localised close to each interface.

3. Calculation of the reaction rate of the elementary steps

In the following, we shall use the following parameters:

dn_{O-s} , is the number of O-s particles formed by adsorption per unit area during the time dt ,
 dn_e and dn_i are the numbers of defects formed at unit area of the external and internal interfaces, respectively, during the time dt . Ω is the volume of one mole of oxide and C_δ is the concentration of point defects, δ , per unit volume.

The defect concentrations expressed using a double square bracket $[]$ notation will always be expressed in number of moles per mole of the compound (see Chapter 3)*. In the following, the notation $[]_e$ or $[]_i$ will indicate these concentrations at the external and internal interfaces, respectively. The notations $[]_e^{eq}$ and $[]_i^{eq}$ correspond to these concentrations at thermodynamic equilibrium.

⁴ C. Wagner, *Z. Phys. Chem. Abt.*, **B 21** (1933) 25 ; *Z. Elektrochem.*, **39** (1933) 543.

* C_δ and $[\delta]$ are linked by the relationship: $C_\delta = \frac{[\delta]}{\Omega}$

3.1. Interphase processes

We will assume, based on Eyring's theory generalised to heterogeneous processes, that **the reaction order of the elementary reactions with regard to each reacting species is equal to the stoichiometric coefficient of that species** and that this order is zero with regard to the constituents that play the role of solvent (normal elements in the oxide lattice and in the metallic phase). We shall adopt, for the formulation of rate equations, expressions involving a term representing the deviation from equilibrium; this is the classical approach to the thermodynamics of irreversible processes (cf. section 2.1).

3.1.1. Sorption process

We will assume in the following a dissociative oxygen sorption process** that is second order in relation to the sorption sites:



where k'_a and k''_a are the direct and reverse rate constants and $K_a = \frac{k'_a}{k''_a}$ the sorption equilibrium constant. The rate of the sorption process is given by the equation:

$$\frac{dn_{\text{O-s}}}{dt} = k'_a (1 - \theta)^2 P_{\text{O}_2} - k''_a \theta^2 \quad (4.10)$$

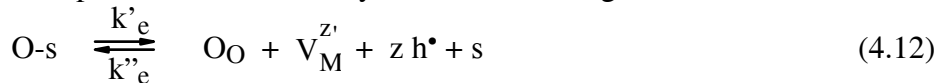
This rate can also be expressed using the rate constant k'_a only:

$$\frac{dn_{\text{O-s}}}{dt} = k'_a \left[(1 - \theta)^2 P_{\text{O}_2} - \frac{\theta^2}{K_a} \right] = k'_a \frac{\theta^2}{K_a} \left[\left(\frac{1 - \theta}{\theta} \right)^2 K_a P_{\text{O}_2} - 1 \right] \quad (4.11)$$

with $K_a P_{\text{O}_2} = \left(\frac{\theta_{\text{eq}}}{1 - \theta_{\text{eq}}} \right)^2$

3.1.2. External elementary process

In the case of a p-type semiconducting oxide that contains **metal vacancies** and using the formulation adopted for the elementary reaction occurring at the external surface:



where k'_e and k''_e are the direct and reverse rate constants and $K_e = \frac{k'_e}{k''_e}$ the corresponding equilibrium constant. The external reaction rate is given by the following:

$$\frac{dn_e}{dt} = k'_e \theta - k''_e [V_{\text{M}}^{z'}]_e ([h^\bullet]_e)^z (1 - \theta) \quad (4.13)$$

This can be expressed, taking into account the electroneutrality equation:

$$z [V_{\text{M}}^{z'}]_e = [h^\bullet]_e$$

** In the case of a heteroatomic gas, this hypothesis is not necessarily justified.

and using the rate constant k'_e only, as:

$$\frac{dn_e}{dt} = k'_e \theta \left[1 - \frac{z^z}{K_e} ([V_M^{z'}]_e)^{z+1} \left(\frac{1-\theta}{\theta} \right) \right] \quad (4.14)$$

Under equilibrium conditions, for a given value of θ , we have:

$$K_e = z^z ([V_M^{z'}]_e^{eq})^{z+1} \left(\frac{1-\theta}{\theta} \right) \quad (4.15)$$

Substituting equation 4.15 into equation 4.14, we have for the rate equation:

$$\frac{dn_e}{dt} = k'_e \theta \left[1 - \left(\frac{[V_M^{z'}]_e}{[V_M^{z'}]_e^{eq}} \right)^{z+1} \right] \quad \text{avec} \quad [V_M^{z'}]_e^{eq} = \left[\frac{1}{z^z} K_e \left(\frac{\theta}{1-\theta} \right) \right]^{1/(z+1)} \quad (4.16)$$

3.1.3. Generalisation

More generally, the expressions for the rates of the interphase processes (for the examples of the formation of p-type or n-type semiconductor oxides) are given in Table 4.4.

Table 4.4. Expressions for the rates of the elementary interphase processes: calculations made for the cases of formation of an oxide with metal vacancies (p-type semi-conduction) and with oxygen vacancies (n-type semi-conduction).

$K_e = \frac{k'_e}{k''_e}$ and $K_i = \frac{k'_i}{k''_i}$ are the equilibrium constants of the interfacial elementary steps at the external and internal interfaces, respectively.

Comment: The previous calculations are easy to transpose for the case of the formation of an oxide with oxygen excess (p-type semi-conduction) or with metal excess (n-type semi-conduction).

Interphase		p-type semi-conductor	n-type semi-conductor
sorption		$\text{O}_2 + 2s \xrightleftharpoons[k''_a]{k'_a} 2\text{O} \cdot s$ $\frac{dn_{\text{O} \cdot s}}{dt} = k'_a \frac{\theta^2}{K_a} \left[\left(\frac{1-\theta}{\theta} \right)^2 K_a P_{\text{O}_2} - 1 \right]$ with $K_a P_{\text{O}_2} = \left(\frac{\theta_{\text{eq}}}{1-\theta_{\text{eq}}} \right)^2$	
Interfaces	external semi-reaction	$\text{O} \cdot s \xrightleftharpoons[k''_e]{k'_e} \text{O}_\text{O} + V_{\text{M}}^{z'} + z h^\bullet + s$ $\frac{dn_e}{dt} = k'_e \theta \left[1 - \left(\frac{[V_{\text{M}}^{z'}]_e}{[V_{\text{M}}^{z'}]_{\text{eq}}} \right)^{z+1} \right]$ with $[V_{\text{M}}^{z'}]_{\text{eq}} = \left[\frac{1}{z^z} K_e \left(\frac{\theta}{1-\theta} \right) \right]^{1/(z+1)}$	$\text{O} \cdot s + V_{\text{O}}^{z\bullet} + z e' \xrightleftharpoons[k''_e]{k'_e} \text{O}_\text{O} + s$ $-\frac{dn_e}{dt} = z^z k'_e \theta \left[([V_{\text{O}}^{z\bullet}]_e)^{z+1} - ([V_{\text{O}}^{z\bullet}]_{\text{eq}})^{z+1} \right]$ with $[V_{\text{O}}^{z\bullet}]_{\text{eq}} = \left[\frac{1}{z^z} \frac{1}{K_e} \left(\frac{1-\theta}{\theta} \right) \right]^{1/(z+1)}$
	internal semi-reaction	$V_{\text{M}}^{z'} + z h^\bullet + \langle M \rangle \xrightleftharpoons[k''_i]{k'_i} M_{\text{M}}$ $-\frac{dn_i}{dt} = z^z k'_i \left[([V_{\text{M}}^{z'}]_i)^{z+1} - ([V_{\text{M}}^{z'}]_{\text{eq}})^{z+1} \right]$ with $[V_{\text{M}}^{z'}]_{\text{eq}} = \left(\frac{1}{z^z} \frac{1}{K_i} \right)^{1/(z+1)}$	$\langle M \rangle \xrightleftharpoons[k''_i]{k'_i} M_{\text{M}} + V_{\text{O}}^{z\bullet} + z e'$ $\frac{dn_i}{dt} = k'_i \left[1 - \left(\frac{[V_{\text{O}}^{z\bullet}]_i}{[V_{\text{O}}^{z\bullet}]_{\text{eq}}} \right)^{z+1} \right]$ with $[V_{\text{O}}^{z\bullet}]_{\text{eq}} = \left(\frac{1}{z^z} K_i \right)^{1/(z+1)}$

3.2 Diffusion: particle fluxes

Taking into account the possible electric potential gradient through the scale, the particle fluxes will be given by the following expressions (see Chapter 3, section 2.1.3).

• **Flux J_z of defects δ of degree of ionisation z (charge $\pm z F$)**

$$J_z = - D_\delta \left[\frac{\partial C_\delta}{\partial x} \pm \frac{z F}{RT} C_\delta \frac{\partial \phi}{\partial x} \right] \quad (4.17)$$

$$J_z = - \left[D_\delta \frac{\partial C_\delta}{\partial x} \pm C_\delta u_\delta \frac{\partial \phi}{\partial x} \right] \quad (4.18)$$

In these expressions, C_δ is the volume concentration of point defects with z degree of ionisation, D_δ is their diffusion coefficient, u_δ is the electric mobility of these charge carriers and ϕ the electric potential at the coordinate x . A positive sign (+) has to be used if the defects are positively charged and a negative sign (-) for negatively charged defects.

• **Fluxes J_ε of electronic defects (electrons or electron holes)**

$$J_\varepsilon = - D_\varepsilon \left[\frac{\partial C_\varepsilon}{\partial x} \pm \frac{F}{RT} C_\varepsilon \frac{\partial \phi}{\partial x} \right] \quad (4.19)$$

$$J_\varepsilon = - \left[D_\varepsilon \frac{\partial C_\varepsilon}{\partial x} \pm C_\varepsilon u_\varepsilon \frac{\partial \phi}{\partial x} \right] \quad (4.20)$$

In these expressions, C_ε is the volume concentration of electronic defects, D_ε and u_ε are, respectively, the diffusion coefficient and the electric mobility of the electronic defects and ϕ is the electric potential at the coordinate x . The sign (-) has to be used if the electronic defect is an electron and (+) if an electron hole.

4. General system of equations

We have given the rate expressions of the elementary steps in a form involving the deviation from equilibrium, that is to say within the framework of the thermodynamics of irreversible processes (a consequence of the assumption of ideality of the phases considered). The general system of equations relating to the growth of an oxide scale MO can then be established by expressing the mass balance at both sides of each interphase, in the adsorbed phase and within the scale.

4.1. Case of p-type semi-conduction

As an example, consider the case of a metal-deficient oxide for which we shall assume that the predominant defect is the metal vacancy $V_M^{z'}$, with a degree of ionisation, z ,

equal to 0, 1 or 2. Let $D_{V_M^{z'}}$ and D_h be, respectively, the diffusion coefficients of the ionic and electronic defects, $U_{V_M^{z'}}$ and U_h their electric mobilities and $J_{V_M^{z'}}$ and J_h the respective fluxes.

If $\frac{\partial \phi}{\partial x}$ is the electric field set up at the coordinate x by the electric space charges in

the growing scale, the system of differential equations obtained is:

$$x = 0 \quad s_0 \frac{d\theta}{dt} = k_a \frac{\theta^2}{K_a} \left[\left(\frac{1-\theta}{\theta} \right)^2 K_a P_{O_2} - 1 \right] - k_e \theta \left[1 - \left(\frac{[V_M^{z'}]_e}{[V_M^{z'}]_{eq}} \right)^{z+1} \right] \quad (4.21)$$

$$a \frac{d[V_M^{z'}]_e}{dt} = k_e \theta \left[1 - \left(\frac{[V_M^{z'}]_e}{[V_M^{z'}]_{eq}} \right)^{z+1} \right] - (J_{V_M^{z'}})_{x=0} \quad (4.22)$$

$$0 < x < y \quad J_{V_M^{z'}} = -\frac{1}{\Omega} \left(D_{V_M^{z'}} \frac{\partial [V_M^{z'}]}{\partial x} - [V_M^{z'}] U_{V_M^{z'}} \frac{\partial \phi}{\partial x} \right) \quad (4.23)$$

$$\frac{\partial [V_M^{z'}]}{\partial t} = -\frac{\partial J_{V_M^{z'}}}{\partial x} \quad (4.24)$$

$$J_h = -\frac{1}{\Omega} \left(D_h \frac{\partial [h]}{\partial x} + [h] U_h \frac{\partial \phi}{\partial x} \right) \quad (4.25)$$

$$\frac{\partial [h]}{\partial t} = -\frac{\partial J_h}{\partial x} \quad (4.26)$$

$$x = y \quad a \frac{d[V_M^{z'}]_i}{dt} = -z^z k_i \left[([V_M^{z'}]_i)^{z+1} - ([V_M^{z'}]_{eq})^{z+1} \right] + (J_{V_M^{z'}})_{x=y} \quad (4.27)$$

Comment: The origin of the x -coordinate is chosen as the external interface and the x -axis direction corresponds to the direction of particle diffusion. a is a parameter used for homogenisation of the units and corresponds to an atomic dimension.

4.2. Case of n -type semi-conduction

As an example, we shall deal with the case of an oxygen deficient oxide but an oxide with metal excess can be treated similarly. We will assume, in the following, that only one defect is predominant, i.e., the metal vacancy $V_O^{z\bullet}$, with a degree of ionisation, z , equal to 0, 1 or 2. Let $D_{V_O^{z\bullet}}$ and D_h be, respectively, the diffusion coefficients of the ionic and electronic defects, $U_{V_O^{z\bullet}}$ and U_e , their electric mobilities and $J_{V_O^{z\bullet}}$ and J_e their respective fluxes.

If $\frac{\partial \phi}{\partial x}$ is the electric field set up at the coordinate x by the electric space charges in

the growing scale, the system of differential equations obtained is:

$$x = y \quad s_0 \frac{d\theta}{dt} = k_a' \frac{\theta^2}{K_a} \left[\left(\frac{1-\theta}{\theta} \right)^2 K_a P_{O_2} - 1 \right] - z^z k_e' \theta \left[([V_O^{z\bullet}]_e)^{z+1} - ([V_O^{z\bullet}]_e^{eq})^{z+1} \right] \quad (4.28)$$

$$a \frac{d[V_O^{z\bullet}]_e}{dt} = -z^z k_e' \theta \left[([V_O^{z\bullet}]_e)^{z+1} - ([V_O^{z\bullet}]_e^{eq})^{z+1} \right] + (J_{V_O^{z\bullet}})_{x=y} \quad (4.29)$$

$$0 < x < y \quad J_{V_O^{z\bullet}} = -\frac{1}{\Omega} (D_{V_O^{z\bullet}} \frac{\partial [V_O^{z\bullet}]}{\partial x} + [V_O^{z\bullet}] U_{V_O^{z\bullet}} \frac{\partial \phi}{\partial x}) \quad (4.30)$$

$$\frac{\partial [V_O^{z\bullet}]}{\partial t} = -\frac{\partial J_{V_O^{z\bullet}}}{\partial x} \quad (4.31)$$

$$J_e = -\frac{1}{\Omega} (D_e \frac{\partial [e']}{\partial x} - [e'] U_e \frac{\partial \phi}{\partial x}) \quad (4.32)$$

$$\frac{\partial [e']}{\partial t} = -\frac{\partial J_e}{\partial x} \quad (4.33)$$

$$x = 0 \quad a \frac{d[V_O^{z\bullet}]_i}{dt} = k_i' \left[1 - \frac{([V_O^{z\bullet}]_i)^{z+1}}{[V_O^{z\bullet}]_i^{eq}} \right] - (J_{V_O^{z\bullet}})_{x=0} \quad (4.34)$$

Comment: The origin of the x-coordinate is here chosen as the internal interface and the x-axis direction corresponds to the direction of the particle diffusion.

Comment: In both cases, the origin of the x-coordinate is chosen as the interface at which the defects are generated and the x-axis direction corresponds to the direction of the defect diffusion. As a consequence, the fluxes are always positive.

4.3. Expression for the equilibrium pressure $P_{O_2}^{eq}$ of the M/MO/O₂ system as a function of the interfacial equilibrium constants

If $P_{O_2}^{eq}$ is the equilibrium oxygen pressure of the M/MO/O₂ system, the rates of all the elementary steps are zero at this pressure. Moreover, there is no net flux of matter through the scale. In other words, all the interphase elementary steps are at equilibrium and there is neither an electric potential gradient through the scale nor a concentration gradient. We can then write for this oxygen pressure $P_{O_2}^{eq}$, whatever the type of conduction, at the adsorbed phase/gas phase interface:

$$\left(\frac{1-\theta}{\theta} \right)^2 K_a P_{O_2}^{eq} = 1 \quad (4.35)$$

- For the case of p-type semi-conduction, at the interfaces:

$$[V_M^{z'}]_e = [V_M^{z'}]_e^{eq} = \left[\frac{1}{z^z} K_e \frac{\theta^{eq}}{(1 - \theta^{eq})} \right]^{1/(z+1)} = \left[\frac{1}{z^z} K_e \sqrt{K_a P_{O_2}^{eq}} \right]^{1/(z+1)} \quad (4.36)$$

$$[V_M^{z'}]_i = [V_M^{z'}]_i^{eq} = \left[\frac{1}{z^z} \frac{1}{K_i} \right]^{1/(z+1)} \quad (4.37)$$

- For the case of n-type semi-conduction, at the interfaces:

$$[V_O^{z\bullet}]_e = [V_O^{z\bullet}]_e^{eq} = \left[\frac{1}{z^z} \frac{1}{K_e} \frac{(1 - \theta^{eq})}{\theta^{eq}} \right]^{1/(z+1)} = \left[\frac{1}{z^z} \frac{1}{K_e \sqrt{K_a P_{O_2}^{eq}}} \right]^{1/(z+1)} \quad (4.38)$$

$$[V_O^{z\bullet}]_i = [V_O^{z\bullet}]_i^{eq} = \left[\frac{1}{z^z} K_i \right]^{1/(z+1)} \quad (4.39)$$

The condition that there is no concentration gradient leads then, whatever the type of conduction, to the equation:

$$P_{O_2}^{eq} = \frac{1}{K_a K_e^2 K_i^2} \quad (4.40)$$

4.4. Simplified system under steady state approximation

The systems of differential equations given above can not be solved analytically. However, it is possible to make the simplifying assumption that the concentrations tend to become time independent, i.e. a quasi steady state develops. On this basis, the differential equations can be considerably simplified as shown in Table 4.5 for the adsorbed phase, at the interfaces and within the scale ($0 < x < y$).

Table 4.5. Simplified differential equations arising from the assumption of quasi steady state conditions. The origin of the x-coordinate is chosen as that interface at which the defects are generated.

Place	p-type semi-conduction	n-type semi-conduction
Adsorbed phase	$x = 0 \quad \frac{d\theta}{dt} = 0$	$x = y \quad \frac{d\theta}{dt} = 0$
External interface within the scale	$x = 0 \quad \frac{d[V_M^{z'}]_e}{dt} = 0$	$x = y \quad \frac{d[V_O^{z\bullet}]_e}{dt} = 0$
Internal interface within the scale	$x = y \quad \frac{d[V_M^{z'}]_i}{dt} = 0$	$x = 0 \quad \frac{d[V_O^{z\bullet}]_i}{dt} = 0$
Within the scale $0 < x < y$	$\frac{\partial[V_M^{z'}]}{\partial t} = -\frac{\partial J_{V_M^{z'}}}{\partial x} = 0$ conservation of flux: $(J_{V_M^{z'}})_0 = (J_{V_M^{z'}})_y$	$\frac{\partial[V_O^{z\bullet}]}{\partial t} = -\frac{\partial J_{V_O^{z\bullet}}}{\partial x} = 0$ conservation of flux: $(J_{V_O^{z\bullet}})_0 = (J_{V_O^{z\bullet}})_y$

The implementation of these relationships to the differential systems previously established shows that, under the quasi steady state hypothesis, the rates of all the elementary steps are equal. The common value of this rate is simply the reaction rate, $\frac{1}{\Omega} \frac{dy}{dt}$.

Under this steady state approximation, the differential systems describing the scale growth have then the following simplified forms:

- For the case of p-type semi-conduction

$$\frac{1}{\Omega} \frac{dy}{dt} = k_a' \frac{\theta^2}{K_a} \left[\left(\frac{1-\theta}{\theta} \right)^2 K_a P_{O_2} - 1 \right] = k_e' \theta \left[1 - \left(\frac{[V_M^{z'}]_e}{[V_M^{z'}]_{eq}} \right)^{z+1} \right] = J_{V_M^{z'}} = z^z k_i' \left[([V_M^{z'}]_i)^{z+1} - ([V_M^{z'}]_{eq})^{z+1} \right] \quad (4.41)$$

- For the case of n-type semi-conduction

$$\frac{1}{\Omega} \frac{dy}{dt} = k_a' \frac{\theta^2}{K_a} \left[\left(\frac{1-\theta}{\theta} \right)^2 K_a P_{O_2} - 1 \right] = z^z k_e' \theta \left[([V_O^{z\bullet}]_e)^{z+1} - ([V_O^{z\bullet}]_{eq})^{z+1} \right] = J_{V_O^{z\bullet}} = k_i' \left[1 - \left(\frac{[V_O^{z\bullet}]_i}{[V_O^{z\bullet}]_{eq}} \right)^{z+1} \right] \quad (4.42)$$

Inspection of these systems leads to a number of comments.

1. If one of the rate constants or the diffusion coefficient has a finite value, all the other constants having very large values, we deal with what is called a *pure regime*. In all other cases, the regime will be called a *"mixed regime"*.

2. *In the case of a pure regime*, all the processes other than the limiting one equilibrate. In effect, the rate constants for these processes are infinite. However, for all these processes, the rate equation, determined as a function of the deviation from equilibrium, must produce a finite value of this rate common to all the processes. This expression has necessarily an indefinite form ($\infty \times 0$), which can be interpreted as there being no deviation from equilibrium.

3. *In the case of a pure regime*, only the rate constant of the limiting step determines the overall reaction rate. Therefore, the reaction rate becomes identified with that of the limiting step. However, it is not correct to write, as it sometimes is, that the slowest of the elementary steps controls the overall reaction rate.

4. *In the case of a pure regime*, a quasi steady state is obtained from the outset of the reaction since all the processes, other than the limiting step, equilibrate.

5. *In the case of a mixed regime*, a transient stage is first observed during which the rates of all the elementary steps tend to become equal. Theoretically, the steady state is obtained after an infinite time but, in practice, the transient period is less than the duration of the experiment.

In the following, we shall study in detail the pure regimes (interphases and diffusional regimes). We shall also describe a few simple mixed regimes.

5. Overall reaction rate limited by one of the elementary chemical steps

5.1 Reaction rate limited by interphase processes

We will obtain the kinetic law and the pressure law for each pure regime with the following assumptions:

1. the rate constants other than that of the limiting step have infinite values;
2. the diffusion coefficients of the point defects and particularly that of the electronic defects are also infinite ($D_E \gg D_\delta$); this second hypothesis implies that the ionic and electronic concentration gradients are zero, as well as the electric potential gradient within the scale (see equations 4.17 and 4.19); then the concentrations are constant within the scale and there is no electric field in this layer.

5.1.1. Reaction rate governed by the sorption process

By definition: k'_a has a finite value and $\theta \neq \theta^{eq}$. The reaction rate becomes identified with the rate of the sorption process:

$$\frac{1}{\Omega} \frac{dy}{dt} = k'_a \frac{\theta^2}{K_a} \left[\left(\frac{1-\theta}{\theta} \right)^2 K_a P_{O_2} - 1 \right] \quad (4.43)$$

The fraction, θ , of the surface that is covered is determined by the equilibrium equations at both interfaces and within the scale (equilibrium concentration values are taken from table 4.4):

- For the case of p-type semi-conduction:

$$[V_M^{z'}]_e = [V_M^{z'}]_e^{eq} = \left[\frac{1}{z^z} K_e \left(\frac{\theta}{1-\theta} \right) \right]^{1/(z+1)} \quad \text{at the external interface}$$

$$[V_M^{z'}]_e = [V_M^{z'}]_i \quad \text{within the layer}$$

$$[V_M^{z'}]_i = [V_M^{z'}]_i^{eq} = \left[\frac{1}{z^z} \frac{1}{K_i} \right]^{1/(z+1)} \quad \text{at the internal interface}$$

It follows that:

$$[V_M^{z'}]_e^{eq} = [V_M^{z'}]_i^{eq} \quad \text{or} \quad K_e \left(\frac{\theta}{1-\theta} \right) = \frac{1}{K_i} \quad (4.44)$$

- For the case of n-type semi-conduction:

$$[V_O^{z\bullet}]_e = [V_O^{z\bullet}]_e^{eq} = \left[\frac{1}{z^z} \frac{1}{K_e} \left(\frac{1-\theta}{\theta} \right) \right]^{1/(z+1)} \quad \text{at the external interface}$$

$$[V_O^{z\bullet}]_e = [V_O^{z\bullet}]_i \quad \text{within the layer}$$

$$[V_O^{z\bullet}]_i = [V_O^{z\bullet}]_i^{eq} = \left[\frac{1}{z^z} K_i \right]^{1/(z+1)} \quad \text{at the internal interface}$$

It follows that:

$$[V_O^{z\bullet}]_e^{eq} = [V_O^{z\bullet}]_i^{eq} \quad \text{or} \quad \frac{1}{K_e} \left(\frac{1-\theta}{\theta} \right) = K_i \quad (4.45)$$

Finally, whatever the type of conduction, θ can be expressed as:

$$\theta = \frac{1}{1 + K_e K_i} \quad (4.46)$$

and the defect concentration profiles in the scale, according to the type of conduction, are shown in figure 4.5.

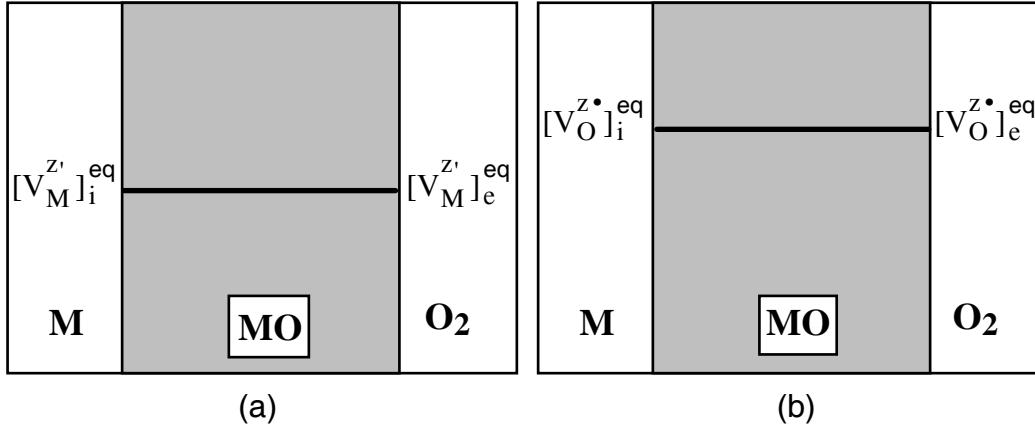


Figure 4.5. Defect concentration profile in the oxide scale for the case of a reaction rate governed by the sorption process

- a) p-type semi-conduction (oxide with metal vacancies),
- b) n-type semi-conduction (oxide with oxygen vacancies).

Replacing θ with this value and, taking into account equation 4.40, $P_{O_2}^{eq} = \frac{1}{K_a K_e^2 K_i^2}$, we obtain:

$$\frac{1}{\Omega} \frac{dy}{dt} = \frac{k'_a}{[1 + \sqrt{K_a P_{O_2}^{eq}}]^2} [P_{O_2} - P_{O_2}^{eq}] \quad (4.47)$$

$$y = \frac{k'_a \Omega}{[1 + \sqrt{K_a P_{O_2}^{eq}}]^2} [P_{O_2} - P_{O_2}^{eq}] t \quad (4.48)$$

$$y = \frac{k'_a \Omega}{[1 + \sqrt{K_a P_{O_2}^{eq}}]^2} P_{O_2} t = k'_1 t \quad \text{if } P_{O_2}^{eq} \ll P_{O_2} \quad (4.49)$$

The rate law is linear:

$$y = k'_1 t \quad (4.50)$$

where the linear rate constant

$$k'_1 = \frac{k'_a \Omega}{[1 + \sqrt{K_a (P_{O_2})^{eq}}]^2} P_{O_2}$$

is proportional to the oxygen pressure.

5.1.2. Overall reaction rate governed by the external chemical process

By definition, in this regime, k'_e has a finite value but all the other rate constants and the diffusion coefficient are infinite. The reaction rate is then identified with the rate of the external process.

5.1.2.1. Case of p-type semi-conduction

The rate equation may be expressed as:

$$\frac{1}{\Omega} \frac{dy}{dt} = k'_e \theta \left[1 - \left(\frac{[V_M^{z'}]_e}{[V_M^{z'}]_{eq}} \right)^{z+1} \right] \quad (4.51)$$

The θ and $[V_M^{z'}]_e$ values are determined from the equilibrium equations in the adsorbed phase, within the oxide scale and at the inner interface, that is:

$$\begin{aligned} \theta &= \theta^{eq} \\ [V_M^{z'}]_i &= [V_M^{z'}]_i^{eq} \\ [V_M^{z'}]_e &= [V_M^{z'}]_i \end{aligned}$$

These conditions lead to:

$$[V_M^{z'}]_e = [V_M^{z'}]_i^{eq} \quad (4.52)$$

The reaction rate is then given by:

$$\frac{1}{\Omega} \frac{dy}{dt} = k'_e \theta^{eq} \left[1 - \left(\frac{[V_M]_i^{eq}}{[V_M]_e^{eq}} \right)^{1/(z+1)} \right] \quad (4.53)$$

with:

$$\theta^{eq} = \frac{\sqrt{K_a P_{O_2}}}{1 + \sqrt{K_a P_{O_2}}} \quad (4.54)$$

$$[V_M^{z'}]_e^{eq} = \left[\frac{1}{z} K_e \frac{\theta^{eq}}{1 - \theta^{eq}} \right]^{1/(z+1)} = \left[\frac{1}{z} K_e \sqrt{K_a P_{O_2}} \right]^{1/(z+1)} \quad (4.55)$$

$$[V_M^{z'}]_i^{eq} = \left[\frac{1}{z} \frac{1}{K_i} \right]^{1/(z+1)} \quad (4.56)$$

This last concentration may be rewritten, taking into account equation 4.40:

$$[V_M^{z'}]_i^{eq} = \left[\frac{1}{z} K_e \sqrt{K_a P_{O_2}^{eq}} \right]^{1/(z+1)} < [V_M^{z'}]_e^{eq} \quad (4.57)$$

The defect concentration profile in the oxide scale is shown schematically in figure 4.6.

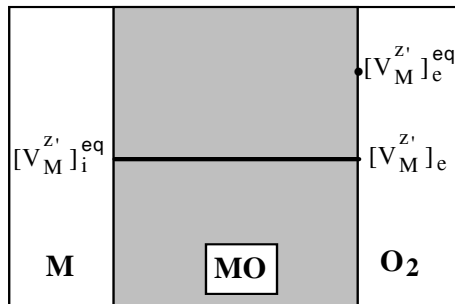


Figure 4.6. Concentration profile of metal vacancies $V_M^{z'}$ in the growing oxide scale for the case of a reaction rate governed by the external chemical process.

Substituting θ^{eq} , $[V_M^{z'}]_i^{eq}$ and $[V_M^{z'}]_e^{eq}$ by their values expressed as a function of the oxygen pressure, we obtain, for the rate equation:

$$\frac{1}{\Omega} \frac{dy}{dt} = k'_e \frac{\sqrt{K_a P_{O_2}}}{1 + \sqrt{K_a P_{O_2}}} \left(1 - \sqrt{\frac{P_{O_2}^{eq}}{P_{O_2}}}\right)$$

or, by integration:

$$y = \left(\Omega k'_e \sqrt{K_a} \frac{\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}}}{1 + \sqrt{K_a P_{O_2}}} \right) t \quad (4.58)$$

The kinetic law is then linear with the linear rate constant proportional to $\sqrt{P_{O_2}}$. In general, $P_{O_2} \gg P_{O_2}^{eq}$ and, so, equation 4.58 may then be simplified.

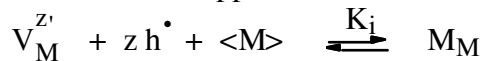
Comment 1: Comparison of the following expressions:

$$[V_M^{z'}]_i^{eq} = \left[\frac{1}{z} K_e \sqrt{K_a P_{O_2}^{eq}} \right]^{1/(z+1)} \quad (\text{equation 4.57})$$

$$\text{and } [V_M^{z'}]_e^{eq} = \left[\frac{1}{z} K_e \sqrt{K_a P_{O_2}} \right]^{1/(z+1)} \quad (\text{equation 4.55) shows that the oxygen}$$

pressure at the internal interface, when the interfacial equilibrium is achieved, is the dissociation pressure of the oxide in contact with the metal, i.e., $P_{O_2}^{eq}$.

Comment 2: The law of mass action applied to the internal equilibrium:



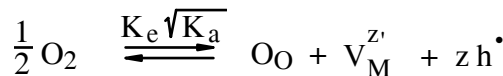
leads to the equation:

$$[V_M^{z'}]_i ([h^\bullet]_i)^z = \frac{1}{K_i}$$

Taking into account equation 4.40, this expression may be rewritten:

$$[V_M^{z'}]_i ([h^\bullet]_i)^z = K_e \sqrt{K_a P_{O_2}^{eq}}$$

Thus, the interfacial internal equilibrium may be considered as the equilibrium for vacancy formation:



under the oxygen pressure $P_{O_2}^{eq}$ for oxide dissociation, that is under the oxygen pressure $(P_{O_2})_i$ at the inner interface.

5.1.2.2. Case of n-type semi-conduction

The rate equation may be expressed as:

$$\frac{1}{\Omega} \frac{dy}{dt} = z^z k_e' \theta \left[([V_O^{\bullet}]_e)^{z+1} - ([V_O^{\bullet}]_e^{\text{eq}})^{z+1} \right] \quad (4.59)$$

The θ and $[V_O^{\bullet}]_e$ values are determined from the equilibrium equations for the adsorbed phase, within the oxide scale and at the inner interface, that is:

$$\begin{aligned} \theta &= \theta^{\text{eq}} \\ [V_O^{\bullet}]_i &= [V_O^{\bullet}]_i^{\text{eq}} \\ [V_O^{\bullet}]_e &= [V_O^{\bullet}]_i \end{aligned}$$

These conditions lead to:

$$[V_O^{\bullet}]_e = [V_O^{\bullet}]_i^{\text{eq}} \quad (4.60)$$

The reaction rate is then given by:

$$\frac{1}{\Omega} \frac{dy}{dt} = z^z k_e' \theta^{\text{eq}} \left[([V_O^{\bullet}]_i^{\text{eq}})^{z+1} - ([V_O^{\bullet}]_e^{\text{eq}})^{z+1} \right] \quad (4.61)$$

with:

$$\theta^{\text{eq}} = \frac{\sqrt{K_a P_{O_2}}}{1 + \sqrt{K_a P_{O_2}}} \quad (4.62)$$

$$[V_O^{\bullet}]_i^{\text{eq}} = \left(\frac{1}{z^z} K_i \right)^{1/(z+1)} \quad (4.63)$$

$$[V_O^{\bullet}]_e^{\text{eq}} = \left[\frac{1}{z^z} K_e \frac{(1 - \theta^{\text{eq}})}{\theta^{\text{eq}}} \right]^{1/(z+1)} = \left[\frac{1}{z^z} \frac{1}{K_e \sqrt{K_a P_{O_2}}} \right]^{1/(z+1)} \quad (4.64)$$

which, taking into account equation 4.40, then becomes:

$$[V_O^{\bullet}]_e^{\text{eq}} = \left[\frac{1}{z^z} K_i \sqrt{\frac{P_{O_2}^{\text{eq}}}{P_{O_2}}} \right]^{1/(z+1)} < [V_O^{\bullet}]_i^{\text{eq}} \quad (4.65)$$

The defect concentration profile in the oxide scale is shown schematically in figure 4.7.

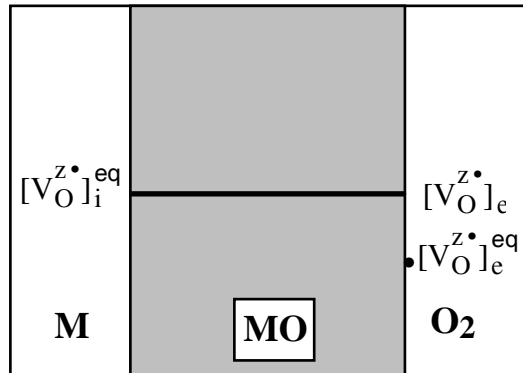


Figure 4.7. Concentration profile of oxygen vacancies $V_O^{\bullet}$ in the growing oxide scale for the case of a reaction rate governed by the external chemical process.

The rate equation may be expressed as a function of the oxygen pressure:

$$\frac{1}{\Omega} \frac{dy}{dt} = k'_e K_i \frac{\sqrt{K_a P_{O_2}}}{1 + \sqrt{K_a P_{O_2}}} \left(1 - \sqrt{\frac{P_{O_2}^{eq}}{P_{O_2}}} \right) \quad (4.66)$$

Then, by integration and neglecting $P_{O_2}^{eq}$ in comparison with P_{O_2} , we obtain:

$$y = \left(\Omega k'_e K_i \frac{\sqrt{K_a P_{O_2}}}{1 + \sqrt{K_a P_{O_2}}} \right) t \quad (4.67)$$

Thus, the rate equation is again linear and an expression of the pressure dependence of the same type as for p-type-semi-conduction is obtained.

Comment 1: The comparison of the expressions obtained previously for $[V_O^{z\bullet}]_i^{eq}$ and $[V_O^{z\bullet}]_e^{eq}$ i.e.

$$[V_O^{z\bullet}]_i^{eq} = \left[\frac{1}{z} K_i \right]^{1/(z+1)} \quad (4.63)$$

and

$$[V_O^{z\bullet}]_e^{eq} = \left[\frac{1}{z} K_i \sqrt{\frac{P_{O_2}^{eq}}{P_{O_2}}} \right]^{1/(z+1)} \quad (4.65)$$

show that the oxygen pressure at the inner interface, when the interfacial equilibrium is reached, is the dissociation oxygen pressure $P_{O_2}^{eq}$ of the oxide in contact with the metal.

Comment 2: The application of the mass-action law to the inner interfacial equilibrium:



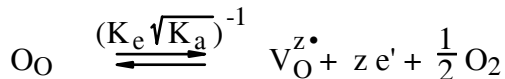
leads to the equation:

$$[V_O^{z\bullet}]_i ([h\dot{]}_i)^z = K_i$$

Taking into account equation 4.40, this expression may be rewritten:

$$[V_O^{z\bullet}]_i ([h\dot{]}_i)^z = \left(K_e \sqrt{K_a P_{O_2}^{eq}} \right)^{-1} \quad (4.68)$$

The consequence is that the inner interfacial equilibrium may be considered as the chemical equilibrium for the formation of the oxygen vacancies $V_O^{z\bullet}$ according to:



under the oxide dissociation pressure $P_{O_2}^{eq}$ existing at the inner interface.

5.1.3. Overall reaction rate governed by the internal chemical process

By definition, in this regime k_i' has a finite value and all the other rate constants and the diffusion coefficient are infinite. The reaction rate then becomes identified with the rate of the internal process.

5.1.3.1. Case of p-type semi-conduction

The rate equation may be expressed as:

$$\frac{1}{\Omega} \frac{dy}{dt} = z^z k_i' \left[([V_M^{z'}]_i)^{z+1} - ([V_M^{z'}]_i^{eq})^{z+1} \right] \quad (4.69)$$

The $[V_M^{z'}]_i$ value is determined from the equilibrium equations in the adsorbed phase, within the oxide scale and at the outer interface, that is:

$$\begin{aligned} \theta &= \theta^{eq} \\ [V_M^{z'}]_e &= [V_M^{z'}]_e^{eq} \\ [V_M^{z'}]_i &= [V_M^{z'}]_e \end{aligned}$$

These conditions lead to:

$$[V_M^{z'}]_i = [V_M^{z'}]_e^{eq} \quad (4.70)$$

The reaction rate is then given by the following equation:

$$\frac{1}{\Omega} \frac{dy}{dt} = z^z k_i' \left[([V_M^{z'}]_e^{eq})^{z+1} - ([V_M^{z'}]_i^{eq})^{z+1} \right] \quad (4.71)$$

The values of $[V_M^{z'}]_e^{eq}$ (equation 4.55) and $[V_M^{z'}]_i^{eq}$ (equation 4.57) have already been calculated in section 4.1.2 (for the case of an oxide with metal vacancies). The situation within the oxide scale is shown schematically in figure 4.8.

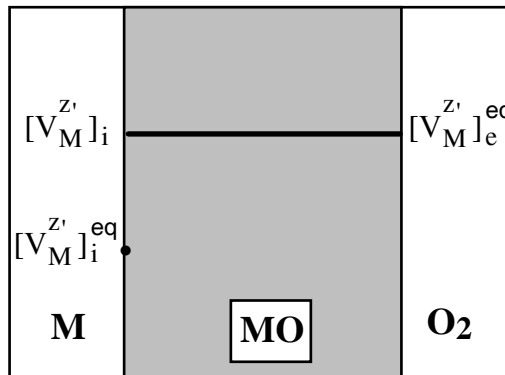


Figure 4.8. Concentration profile of metal vacancies $V_M^{z'}$ in the growing oxide scale for the case of a reaction rate governed by the internal chemical process.

The rate equation may then be expressed as:

$$\frac{1}{\Omega} \frac{dy}{dt} = k_i' K_e \sqrt{K_a} [\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}}] \quad (4.72)$$

By integration and neglecting $P_{O_2}^{eq}$ in comparison with P_{O_2} , we obtain:

$$y = [\Omega k_i' K_e \sqrt{K_a P_{O_2}}] t \quad (4.73)$$

The rate equation is again linear but, in this case, the pressure law is different from section 5.1.2 in that the linear rate constant is proportional to $\sqrt{P_{O_2}}$.

5.1.3.2. Case of n-type semi-conduction

The reaction rate may be expressed as:

$$\frac{1}{\Omega} \frac{dy}{dt} = k_i' \left[1 - \left(\frac{[V_O^{z\bullet}]_i}{[V_O^{z\bullet}]_i^{eq}} \right)^{z+1} \right] \quad (4.74)$$

The $[V_O^{z\bullet}]_i$ value is determined from the equilibrium equations in the adsorbed phase, within the oxide scale and at the outer interface, that is:

$$\begin{aligned} \theta &= \theta^{eq} \\ [V_O^{z\bullet}]_e &= [V_O^{z\bullet}]_e^{eq} \\ [V_O^{z\bullet}]_i &= [V_O^{z\bullet}]_e \end{aligned}$$

These conditions lead to:

$$[V_O^{z\bullet}]_i = [V_O^{z\bullet}]_e^{eq} \quad (4.75)$$

The reaction rate is then given by:

$$\frac{1}{\Omega} \frac{dy}{dt} = k_i' \left[1 - \left(\frac{[V_O^{z\bullet}]_e^{eq}}{[V_O^{z\bullet}]_i^{eq}} \right)^{z+1} \right] \quad (4.76)$$

The values of $[V_O^{z\bullet}]_e^{eq}$ (equation 4.65) and $[V_O^{z\bullet}]_i^{eq}$ (equation 4.63) have already been calculated in section 4.1.2 (for the case of an oxide with oxygen vacancies). The situation within the oxide scale is shown schematically in figure 4.9.

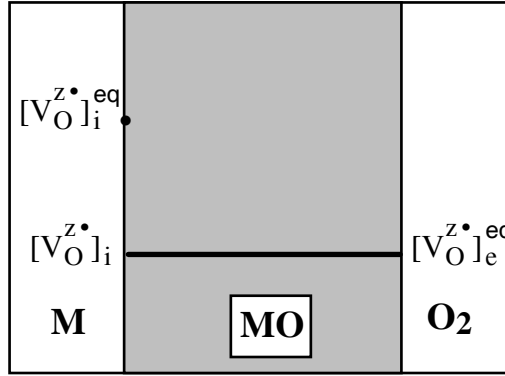


Figure 4.9. Concentration profile of oxygen vacancies $V_O^{z\bullet}$ within the growing oxide scale for the case of a reaction rate governed by the internal chemical process.

The rate equation may then be expressed as a function of the oxygen pressure according to:

$$\frac{1}{\Omega} \frac{dy}{dt} = k_i' \left[1 - \sqrt{\frac{P_{O_2}^{eq}}{P_{O_2}}} \right] \quad (4.77)$$

On integration and neglecting $P_{O_2}^{eq}$ by comparison with P_{O_2} , we obtain:

$$y = \Omega k_i' t \quad (4.78)$$

We obtain yet again a linear law but, in this case, with a rate constant independent of oxygen pressure.

5.1.4. Conclusion

The interphase regimes (sorption, external elementary step, internal elementary step) all lead to linear rate equations but with different types of pressure laws. The results obtained are summarised in Table 4.6.

Table 4.6. Summary of rate equations and pressure laws in the cases of an overall reaction rate governed by an interphase chemical step.

RATE EQUATION	Limiting step		Influence of P_{O_2} on the rate constant	
			<i>p-type semi-cond.</i>	<i>n-type semi-cond.</i>
LINEAR	Interphases	SORPTION PROCESS	proportional to P_{O_2}	
		EXTERNAL CHEMICAL PROCESS	proportional to $\frac{\sqrt{K_a P_{O_2}}}{1 + \sqrt{K_a P_{O_2}}}$	
		INTERNAL CHEMICAL PROCESS	proportional to $\sqrt{P_{O_2}}$	independent of P_{O_2}

It can be appreciated that the determination of the pressure law permits the limiting step to be identified theoretically and, thus, insights into the oxidation mechanism can be obtained.

In practice, the situation is often more complex and the determination of the pressure law may seldom be carried out unambiguously because of uncertainty in determining its domain of validity. As an example, a pressure dependence of the type $\frac{a\sqrt{P_{O_2}}}{1 + b\sqrt{P_{O_2}}}$ may be analysed as a linear function of $\sqrt{P_{O_2}}$ if the range of investigation, at a given temperature, is restricted to low pressures, even if these pressures are appreciably higher than atmospheric pressure. For this to occur, it requires only that $b\sqrt{P_{O_2}} \ll 1$. On the other hand, an observed independence on oxygen pressure can hide the actual relationship if the oxygen pressure used is restricted to too high a range of values, even if these pressures are appreciably smaller than the atmospheric pressure. In this case, $b\sqrt{P_{O_2}} \gg 1$.

To conclude, it should be pointed out that care is necessary when attempting to confirm the nature of the pressure law and it may be necessary to study simultaneously the influence of temperature on the apparent pressure laws.

5.2. Study of diffusion controlled oxidation

Assuming that the values of the rate constants k'_a , k'_e and k'_i for reactions at the phase boundaries are infinite and that the diffusion coefficient D_δ (or the electrical mobility U_δ) of the defect δ is very small, then thermodynamic equilibrium will be established between the oxide and oxygen gas at the oxide/oxygen interface and between the metal and the oxide at the metal/oxide interface.

5.2.1. Scales with predominantly electronic conductivity

It should be recalled from Chapter 3 that such an oxide scale is necessarily a non-stoichiometric compound. For the sake of simplicity, let us consider growth of an oxide scale involving only one type of point defect in its lattice:

- metal vacancies $V_M^{z'}$ or oxygen interstitials $O_i^{z'}$ in p-type oxides,
- oxygen vacancies $V_O^{z''}$ or metal interstitials $M_i^{z''}$ in n-type oxides.

where z is the degree of ionisation of the majority point defect and ranges, in both cases, from 0 to 2.

5.2.1.1. p-type scale

In this case, the predominant defect within the oxide will be either cation vacancies (i.e., $V_M^{z'}$) or anion interstitials (i.e., $O_i^{z'}$). Let us consider, as example, the growth of a metal-deficient oxide with metal ion vacancies $V_M^{z'}$ as the predominant defect (z ranging from 0 to 2). In this case, the reaction rate $\frac{1}{\Omega} \frac{dy}{dt}$ may be identified with the flux of metal vacancies $J_{V_M^{z'}}$.

The equations required to calculate the flux $J_{V_M^{z'}}$ and, consequently, the reaction rate can be obtained from the classical stationary-state and electroneutrality hypotheses (table 4.7). Note that these hypotheses are not entirely compatible⁵ but have the advantage of leading to an analytical solution of the system of differential equations.

⁵ P. Sarrazin and J. Besson, *J. Chim. Phys.*, **1** (1973) 27-32.

Table 4.7. Basic equations necessary for calculation of the reaction rate for the case of diffusion controlled oxidation (oxide MO, p-type semi-conductor).

• **Stationary state:**

$$\frac{\partial [V_M^{z'}]}{\partial t} = - \frac{\partial J_{V_M^{z'}}}{\partial x} \approx 0 \quad \text{conservation of flux} \quad (4.79)$$

$$J_h = z J_{V_M^{z'}} \quad \text{no net current flows through the scale} \quad (4.80)$$

• **Electroneutrality:**

$$[h^\bullet] = z [V_M^{z'}] \quad \text{except near the interphase boundaries} \quad (4.81)$$

• **Flux expressions:**

$$\text{with the condition: } [V_M^{z'}] \cdot U_{V_M^{z'}} \ll [h^\bullet] \cdot U_h$$

$$J_{V_M^{z'}} = - \frac{1}{\Omega} (D_{V_M^{z'}} \frac{\partial [V_M^{z'}]}{\partial x} - [V_M^{z'}] U_{V_M^{z'}} \frac{\partial \phi}{\partial x}) \quad (4.82)$$

$$J_h = - \frac{1}{\Omega} (D_h \frac{\partial [h^\bullet]}{\partial x} + [h^\bullet] U_h \frac{\partial \phi}{\partial x}) \quad (4.83)$$

• **Growth rate of the oxide scale:**

$$\frac{1}{\Omega} \frac{dy}{dt} = J_{V_M^{z'}} \quad (4.84)$$

Eliminating the gradient of potential between equations 4.82 and 4.83, we obtain:

$$\frac{J_{V_M^{z'}}}{[V_M^{z'}] \cdot U_{V_M^{z'}}} + \frac{J_h}{[h^\bullet] \cdot U_h} = - \frac{1}{\Omega} \frac{R T}{z F} \frac{\partial \ln [V_M^{z'}] \cdot [h^\bullet]^z}{\partial x} \quad (4.85)$$

Under the quasi stationary-state assumption, no net current flows through the scale ($J_h = z J_{V_M^{z'}}$), and the point defect flux is everywhere constant, the expression 4.85 becomes:

$$J_{V_M^{z'}} \left(\frac{1}{[V_M^{z'}] \cdot U_{V_M^{z'}}} + \frac{z}{[h^\bullet] \cdot U_h} \right) = - \frac{1}{\Omega} \frac{R T}{z F} \frac{d \ln [V_M^{z'}] \cdot [h^\bullet]^z}{dx} \quad (4.86)$$

Under the conditions:

$$[V_M^{z'}] \cdot U_{V_M^{z'}} \ll [h^\bullet] \cdot U_h \quad (4.87)$$

and using the electroneutrality relationship 4.81, the expression 4.86 becomes:

$$\frac{J_{V_M^{z'}}}{[V_M^{z'}] \cdot U_{V_M^{z'}}} = - \frac{1}{\Omega} \frac{R T}{z F} \frac{d \ln ([V_M^{z'}])^{z+1}}{dx} \quad (4.88)$$

then:

$$J_{V_M^{z'}} = -\frac{1}{\Omega} (z+1) U_{V_M^{z'}} \frac{R T}{z F} \frac{d[V_M^{z'}]}{dx} \quad (4.89)$$

Recalling that:

$$D_{V_M^{z'}} = U_{V_M^{z'}} \frac{R T}{z F} \quad (4.90)$$

we obtain:

$$J_{V_M^{z'}} = -\frac{1}{\Omega} (z+1) D_{V_M^{z'}} \frac{d[V_M^{z'}]}{dx} \quad (4.91)$$

The point defect flux is obtained by solving the differential equation:

$$J_{V_M^{z'}} \int_0^y dx = -\frac{1}{\Omega} (z+1) D_{V_M^{z'}} \int_{[V_M^{z'}]_e^{eq}}^{[V_M^{z'}]_i^{eq}} d[V_M^{z'}] \quad (4.92)$$

Solving this equation, we obtain:

$$J_{V_M^{z'}} = \frac{1}{\Omega} (z+1) D_{V_M^{z'}} \left(\frac{[V_M^{z'}]_e^{eq} - [V_M^{z'}]_i^{eq}}{y} \right) \quad (4.93)$$

where $[V_M^{z'}]_e^{eq}$ and $[V_M^{z'}]_i^{eq}$ denote, respectively, **the equilibrium concentrations** of metal vacancies at the external and internal interfaces* .

Comment 1: Equation 4.93 shows that the values of the defect flux $J_{V_M^{z'}}$ will be higher the greater the charge on the defect by a factor $(z+1)$, where z denotes the degree of ionisation of the point defect. This is an effect of the electric field in the growing scale by producing a space charge due to the different mobilities of the electronic and point defects.

The expression $(z+1) D_{V_M^{z'}}$ is by definition the *chemical diffusion coefficient* because it determines the rate of return to chemical equilibrium of the oxide after excursions in temperature or pressure.

Comment 2: Strictly speaking, when $z = 0$, the calculation should be carried out using the simplified Fick's law.

* Equation 4.92 is valid only when z and $D_{V_M^{z'}}$ are constant throughout the scale. This is generally considered to be the case but may not be so for compounds (e.g. FeO, FeS, etc.) exhibiting large departures from stoichiometry.

• Rate law

Integration of the rate equation:

$$\frac{dy}{dt} = \Omega J_{V_M^{z'}} \quad (4.94)$$

leads to the well known parabolic rate law:

$$y^2 = 2(z+1) D_{V_M^{z'}} ([V_M^{z'}]_e^{eq} - [V_M^{z'}]_i^{eq}) t \quad (4.95)$$

The oxidation rate constant k'_p may be written:

$$k'_p = 2(z+1) D_{V_M^{z'}} ([V_M^{z'}]_e^{eq} - [V_M^{z'}]_i^{eq}) \quad (4.96)$$

and scale growth is determined by the diffusion of the predominant point defects, metal vacancies in this case.

• Oxidation pressure dependence

As demonstrated earlier (see section 5.1.2.1), the interface equilibria may be identified with the formation equilibria of metal ion vacancies $V_M^{z'}$, under the oxygen pressure $(P_{O_2})_e$ at the external interface and $(P_{O_2})_i$ at the inner interface according to:



Following Wagner⁶, we assume that the mass action law:

$$[V_M^{z'}] \cdot [h^\bullet]^z = K_{V_M^{z'}} \cdot P_{O_2}^{1/2} \quad (4.98)$$

may be applied at any point within the scale. Taking into account the electroneutrality condition, relation 4.98 leads to:

$$[V_M^{z'}] = \left(\frac{K_{V_M^{z'}}}{z^z} \right)^{1/(z+1)} \cdot P_{O_2}^{1/2(z+1)} \quad (4.99)$$

$$[h^\bullet] = \left(z K_{V_M^{z'}} \right)^{1/(z+1)} \cdot P_{O_2}^{1/2(z+1)} \quad (4.100)$$

Figure 4.10 shows schematically the concentration of ionic and electronic defects as a function of oxygen pressure P_{O_2} .

⁶ C. Wagner, *Z. Phys. Chem. Abt.*, **B 21** (1933) 25 and *Z. Elektrochem.*, **39** (1933) 543.

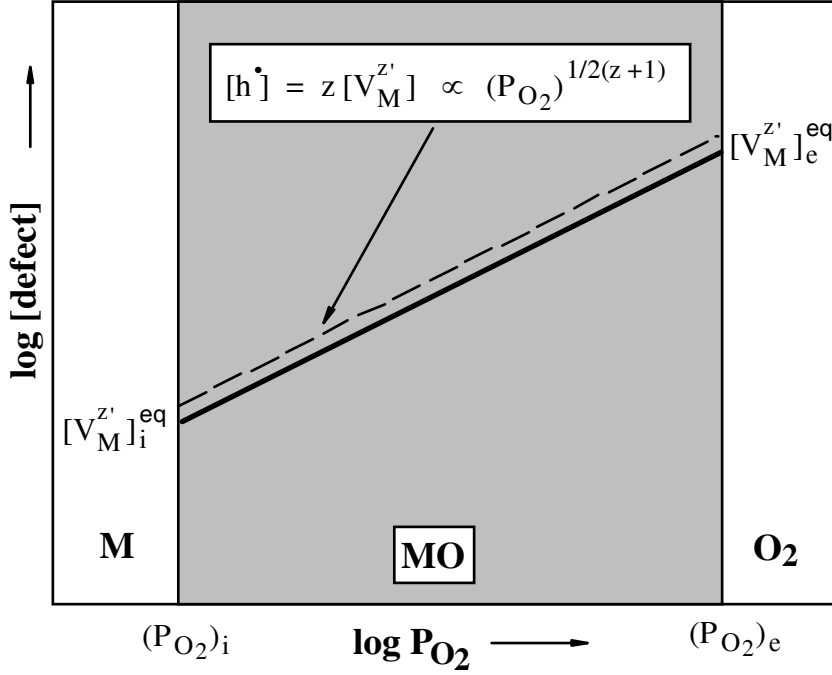


Figure 4.10. Schematic representation of ionic and electronic defect concentrations within the scale as a function of P_{O_2} (logarithmic scales). $(P_{O_2})_e$ and $(P_{O_2})_i$ are the equilibrium oxygen pressures of formation of vacancies at external and internal interfaces, respectively. Interfacial space charges have been neglected.

Inserting into equation (4.96) the expression (4.99) for $[V_M^{z'}]$ as a function of the oxygen pressures $(P_{O_2})_e$ and $(P_{O_2})_i$ at the outer and the inner interfaces, we obtain:

$$k'_p = 2(z+1) D_{V_M^{z'}} \left(\frac{K_{V_M^{z'}}}{z^z} \right)^{1/(z+1)} \left((P_{O_2})_e^{1/2(z+1)} - (P_{O_2})_i^{1/2(z+1)} \right) \quad (4.101)$$

Note that the oxygen pressure $(P_{O_2})_i$ may be identified with the decomposition pressure of MO $P_{O_2}^{eq}$ in equilibrium with the metal M , $(P_{O_2})_e$ is the ambient oxygen pressure and will be termed P_{O_2} . Then, the rate constant k'_p may be rewritten:

$$k'_p = 2(z+1) D_{V_M^{z'}} \left(\frac{K_{V_M^{z'}}}{z^z} \right)^{1/(z+1)} \left(P_{O_2}^{1/2(z+1)} - P_{O_2}^{eq\ 1/2(z+1)} \right) \quad (4.102)$$

Generally $(P_{O_2})_i$ is significantly smaller than P_{O_2} and the expression for k'_p reduces to:

$$k'_p = 2(z+1) D_{V_M^{z'}} \left(\frac{K_{V_M^{z'}}}{z^z} \right)^{1/(z+1)} \cdot P_{O_2}^{1/2(z+1)} \quad (4.103)$$

As shown in this expression, the influence of oxygen pressure on the scaling constant depends on the electrical charge on the predominant defect.

Comment: A similar result is obtained for a scale involving interstitial oxygen $O_i^{z'}$ and, in general, we can write

$$k'_p = 2(z+1) D_{V_M^{z'}} [V_M^{z'}]_e^{eq}$$

• Relation between the parabolic rate constant and the self-diffusion coefficient of the component having the predominant role in matter transport

Since $[V_M^{z'}]_e^{eq}$ denotes the fraction of the metal ion sites that are vacant at the outer interface, the expression:

$$k'_p = 2(z+1) D_{V_M^{z'}} [V_M^{z'}]_e^{eq} \quad (4.105)$$

may be written: $k'_p = 2(z+1) D_M \quad (4.106)$

where D_M is the self-diffusion coefficient of the metal M in the oxide MO at this interface under the pressure P_{O_2} .

Consequently, for a p-type scale, under diffusion controlled oxidation, the self-diffusion coefficient at the outer surface of the component playing the predominant role in matter transport can be calculated from a single measurement of the parabolic rate constant k'_p , if the degree of ionisation of the defects is known. Moreover, the dependence of the self-diffusion coefficient (D_M in the present case) on oxidant pressure P_{O_2} may be deduced from a series of measurements of k'_p at various pressures.

Comment: These properties may be generalised to a more complex oxide scale $M_{2-x}O_b$. In this case:

$$[N_{V_M^{z'}}]_e^{eq} = \frac{x}{2} = \frac{[V_M^{z'}]_e^{eq}}{2} \quad (4.107)$$

and: $k'_p = 4(z+1) D_M \quad (4.108)$

5.2.1.2. n-type scale

These oxides can contain either anionic defects ($V_O^{z\bullet}$) or cationic defects ($M_i^{z\bullet}$). Let us consider, as an illustration, the growth of an oxygen deficient oxide with charged oxygen vacancies $V_O^{z\bullet}$ as the predominant defect (z ranging from zero to 2). It follows also that:

$$[V_O^{z\bullet}] \cdot U_{V_O^{z\bullet}} \ll [e'] \cdot U_e \quad (4.109)$$

and the reaction rate $\frac{1}{\Omega} \frac{dy}{dt}$ is identified with the flux of oxygen vacancies $J_{V_O^{z\bullet}}$. Table 4.8 gives the basic equations required for the calculation of the flux and oxidation rate.

Table 4.8. Basic equations required for the calculation of the oxidation rate for the case of diffusion-controlled oxidation within the n-type MO oxide.

• **Stationary state:**

$$\frac{\partial[V_O^{\bullet z}]}{\partial t} = -\frac{\partial J_{V_O^{\bullet z}}}{\partial x} \approx 0$$

conservation of flux within the growing oxide scale (4.110)

$$J_e = z J_{V_O^{\bullet z}}$$

no net current flows through the scale (4.111)

• **Electroneutrality:**

$$[e'] = z [V_O^{\bullet z}]$$

except near the interphase boundaries (4.112)

• **Flux expressions:**

with the condition: $[V_O^{\bullet z}] \cdot U_{V_O^{\bullet z}} \ll [e'] \cdot U_e$ (4.113)

$$J_{V_O^{\bullet z}} = -\frac{1}{\Omega} (D_{V_O^{\bullet z}} \frac{\partial [V_O^{\bullet z}]}{\partial x} + [V_O^{\bullet z}] U_{V_O^{\bullet z}} \frac{\partial \phi}{\partial x})$$

(4.114)

$$J_e = -\frac{1}{\Omega} (D_e \frac{\partial [e']}{\partial x} - [e'] U_e \frac{\partial \phi}{\partial x})$$

(4.115)

• **Growth rate of the oxide scale (thickness: y):**

$$\frac{1}{\Omega} \frac{dy}{dt} = J_{V_O^{\bullet z}}$$

(4.116)

On eliminating the electrical potential in equations 4.114 and 4.115, we obtain:

$$\frac{J_{V_O^{\bullet z}}}{[V_O^{\bullet z}] \cdot U_{V_O^{\bullet z}}} + \frac{J_e}{[e'] \cdot U_e} = -\frac{1}{\Omega} \frac{R T}{z F} \frac{\partial \ln[V_O^{\bullet z}] \cdot [e']^z}{\partial x}$$

(4.117)

Assuming that, in the quasi-stationary state, no net current flows through the scale and that the point defect flux is constant over the whole scale, equation 4.117 becomes:

$$J_{V_O^{\bullet z}} \left(\frac{1}{[V_O^{\bullet z}] \cdot U_{V_O^{\bullet z}}} + \frac{z}{[e'] \cdot U_e} \right) = -\frac{1}{\Omega} \frac{R T}{z F} \frac{d \ln[V_O^{\bullet z}] \cdot [e']^z}{dx}$$

(4.118)

Recalling that for the n-type scale:

$$[V_O^{\bullet z}] \cdot U_{V_O^{\bullet z}} \ll [e'] \cdot U_e$$

expression 4.118 may then be written:

$$\frac{J_{V_O^{\bullet z}}}{[V_O^{\bullet z}] \cdot U_{V_O^{\bullet z}}} = -\frac{1}{\Omega} \frac{R T}{z F} \frac{d \ln[V_O^{\bullet z}] \cdot [e']^z}{dx}$$

(4.119)

Taking into account the electroneutrality condition 4.112, equation 4.119 becomes:

$$\frac{J_{V_O^{z\bullet}}}{[V_O^{z\bullet}] \cdot U_{V_O^{z\bullet}}} = -\frac{1}{\Omega} (z+1) \frac{RT}{zF} \frac{d \ln[V_O^{z\bullet}]}{dx} \quad (4.120)$$

Using the classical equation $D_{V_O^{z\bullet}} = U_{V_O^{z\bullet}} \frac{RT}{zF}$, relation 4.120 becomes:

$$J_{V_O^{z\bullet}} = -\frac{1}{\Omega} (z+1) D_{V_O^{z\bullet}} \frac{d[V_O^{z\bullet}]}{dx} \quad (4.121)$$

Integrating this equation from the inner to the outer interfaces, we obtain:

$$J_{V_O^{z\bullet}} = \frac{1}{\Omega} (z+1) D_{V_O^{z\bullet}} \left(\frac{[V_O^{z\bullet}]_i^{\text{eq}} - [V_O^{z\bullet}]_e^{\text{eq}}}{y} \right) \quad (4.122)$$

where $[V_O^{z\bullet}]_i^{\text{eq}}$ and $[V_O^{z\bullet}]_e^{\text{eq}}$ denote, respectively, the **equilibrium concentrations** of oxygen vacancies at the external and internal interfaces.

Comment: As for p-type scales, when the degree of ionisation of the predominant point defects is different from zero, the flux $J_{V_O^{z\bullet}}$ is enhanced by a factor $(z+1)$.

• Rate law

Integration of the rate equation $\frac{dy}{dt} = \Omega J_{V_O^{z\bullet}}$ leads to the parabolic rate law:

$$y^2 = 2(z+1) D_{V_O^{z\bullet}} ([V_O^{z\bullet}]_i^{\text{eq}} - [V_O^{z\bullet}]_e^{\text{eq}}) \cdot t \quad (4.123)$$

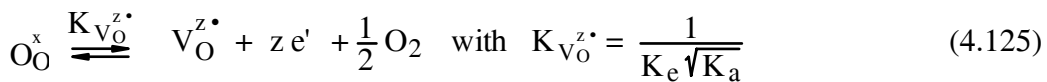
The oxidation rate constant k'_p may be written:

$$k'_p = 2(z+1) D_{V_O^{z\bullet}} ([V_O^{z\bullet}]_i^{\text{eq}} - [V_O^{z\bullet}]_e^{\text{eq}}) \quad (4.124)$$

The rate-determining step is the diffusion of point defects within the growing scale.

• Oxidation pressure dependence

The interface equilibria* may be identified with the equilibrium for the formation of oxygen vacancies $V_O^{z\bullet}$ at the oxygen partial pressure $(P_{O_2})_i$ at the inner interface and $(P_{O_2})_e$ at the outer interface, according to:



Following Wagner, the mass action law may be applied at any point of the scale and leads to:

$$[V_O^{z\bullet}] \cdot [e']^z = K_{V_O^{z\bullet}} P_{O_2}^{-1/2} \quad (4.126)$$

Taking into account the electroneutrality condition, it is possible to express the concentrations of ionic and electronic defects as a function of oxygen pressure:

* see section 5.1.2.2, n-type semi-conduction, Comment 2.

$$[V_O^{z\bullet}] = \left(\frac{K_{V_O^{z\bullet}}}{z^z}\right)^{1/(z+1)} \cdot P_{O_2}^{-1/2(z+1)} \quad (4.127)$$

$$[e'] = \left(z K_{V_O^{z\bullet}}\right)^{1/(z+1)} \cdot P_{O_2}^{-1/2(z+1)} \quad (4.128)$$

A graphical representation of the ionic and electronic defect concentrations across the scale as a function of oxygen pressure P_{O_2} is given in figure 4.11.

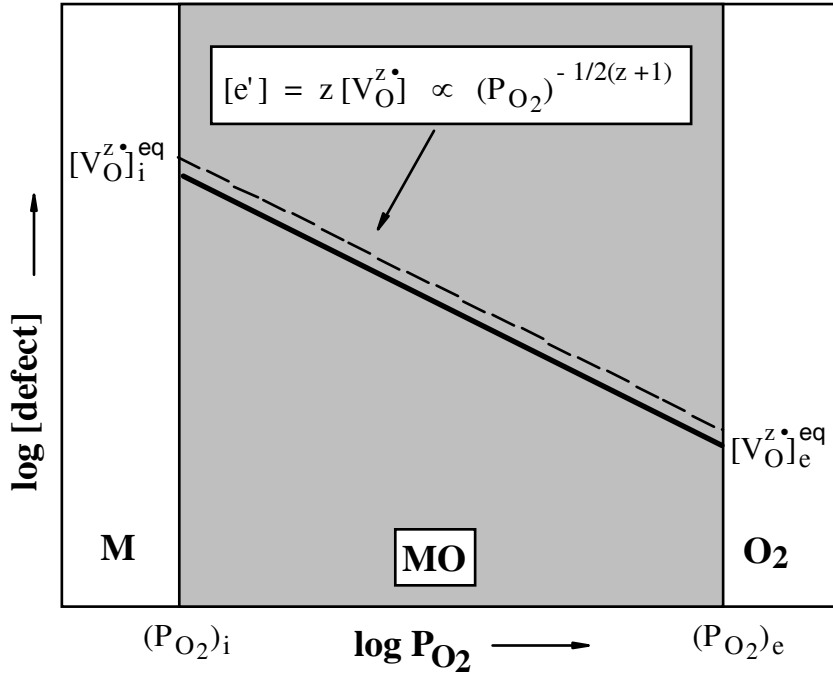


Figure 4.11. Schematic representation of the concentrations in the oxide scale of ionic and electronic defects (logarithmic scales). $(P_{O_2})_e$ and $(P_{O_2})_i$ are the equilibrium oxygen pressures of formation of oxygen vacancies at the external and internal interfaces, respectively. Interfacial space charges have been neglected.

By inserting the expressions for $[V_O^{z\bullet}]$ as a function of the pressures $(P_{O_2})_e$ and $(P_{O_2})_i$ at the outer and inner interfaces, we obtain for the parabolic constant k'_p :

$$k'_p = 2(z+1) D_{V_O^{z\bullet}} \left(\frac{K_{V_O^{z\bullet}}}{z^z}\right)^{1/(z+1)} \left((P_{O_2})_i^{-1/2(z+1)} - (P_{O_2})_e^{-1/2(z+1)} \right) \quad (4.129)$$

The oxygen pressure $(P_{O_2})_i$ is, of course, the decomposition pressure $P_{O_2}^{eq}$ of MO in equilibrium with the metal M and $(P_{O_2})_e$ is the ambient oxygen pressure P_{O_2} . The rate constant k'_p may then be written:

$$k'_p = 2(z+1) D_{V_O^{z\bullet}} \left(\frac{K_{V_O^{z\bullet}}}{z^z}\right)^{1/(z+1)} \left(P_{O_2}^{eq}^{-1/2(z+1)} - P_{O_2}^{-1/2(z+1)} \right) \quad (4.130)$$

Generally, $(P_{O_2})_i$ is much smaller than $(P_{O_2})_e$ and the expression for k'_p can be simplified to:

$$k'_p = 2(z+1) D_{V_O^{z\bullet}} \left(\frac{K_{V_O^{z\bullet}}}{z^z} \right)^{1/(z+1)} P_{O_2}^{eq - 1/2(z+1)} \quad (4.131)$$

This equation shows that the parabolic rate constant k'_p does not depend on the ambient oxygen pressure. This result differs from that found for the growth of p-type scales.

Comment 1: We can adopt, for k'_p , a reduced form of expression 4.124:

$$k'_p = 2(z+1) D_{V_O^{z\bullet}} [V_O^{z\bullet}]_i^{eq} \quad (4.132)$$

Comment 2: A comparable result may be obtained for scales involving interstitial metal ions $M_i^{z\bullet}$.

• Relation between the parabolic rate constant and the self-diffusion coefficient of the component having the predominant role in matter transport

Since $[V_O^{z\bullet}]_i^{eq}$ denotes the fraction of oxygen ion sites that are vacant at the inner interface, expression 4.132 may be written:

$$k'_p = 2(z+1) D_O \quad (4.133)$$

where D_O is the self-diffusion coefficient of oxygen in the oxide MO at this interface under the pressure $P_{O_2}^{eq}$, i.e. the dissociation pressure of the oxide.

Consequently, for n-type scales, measurement of the parabolic rate constant permits determination of the self-diffusion coefficient of the rate-controlling species but only at the pressure $P_{O_2}^{eq}$. It does not provide information of the dependence of the diffusion coefficient on the external oxygen pressure P_{O_2} . This result differs from that obtained for the growth of p-type scales.

5.2.2. Scales with predominantly ionic conductivity

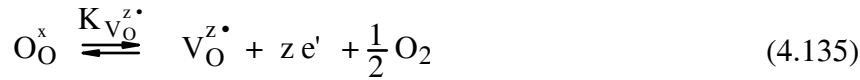
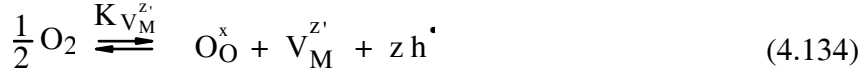
We have seen in Chapter 3 that such a scale is necessarily a *stoichiometric compound*. Even if most oxides are electronic semi-conductors, oxidation of some metals (Al, for example) may still result in an oxide scale exhibiting significant ionic conductivity.

For the sake of simplicity, let us consider the growth of a hypothetical oxide MO with essentially ionic conductivity throughout the whole scale* thickness. We shall suppose that this oxide contains both oxygen vacancies $V_O^{z\bullet}$ and metal ion vacancies $V_M^{z'}$, i.e., Schottky

* Such a hypothesis would be quite conceivable in the case of halides (such as AgX, NaX or CdX₂) which are stoichiometric compounds over a wide range of pressure and temperature.

disorder. It will be assumed that both oxygen vacancies and metal ion vacancies have the same degree of ionisation, z , and that this is greater than zero.

For *diffusion-controlled oxidation*, thermodynamic equilibria are established between the oxide and oxygen gas at the oxide/oxygen interface and between the metal and the oxide at the metal/oxide interface. In other words, the interface equilibria may be identified with the formation equilibria of metal ion vacancies and oxygen vacancies under the oxygen pressure $(P_{O_2})_e$ at the external interface and $(P_{O_2})_i$ at the inner interface, according to:



It will be necessary to take into account the intrinsic equilibrium of electronic defects:



At any point in the scale, applying the law of mass action to the formation of ionic and electronic defects leads to:

$$[V_M^{z'}] \cdot [h^\bullet]^z = K_{V_M^{z'}} \cdot P_{O_2}^{1/2} \quad (4.137)$$

$$[V_O^{z\bullet}] \cdot [e']^z = K_{V_O^{z\bullet}} \cdot P_{O_2}^{-1/2} \quad (4.138)$$

Approximating the electroneutrality condition by:

$$[V_M^{z'}] \cong [V_O^{z\bullet}]$$

the concentrations of ionic and electronic defects are then given by ($z \neq 0$):

$$[V_M^{z'}] \cong [V_O^{z\bullet}] = \sqrt{\frac{K_{V_M^{z'}} \cdot K_{V_O^{z\bullet}}}{K_\varepsilon^z}} = \sqrt{K_S} \quad (4.139)$$

$$[h^\bullet] = \sqrt{K_\varepsilon} \left(\frac{K_{V_M^{z'}}}{K_{V_O^{z\bullet}}} \right)^{1/2z} \cdot P_{O_2}^{1/2z} \quad (4.140)$$

$$[e'] = \sqrt{K_\varepsilon} \left(\frac{K_{V_M^{z'}}}{K_{V_O^{z\bullet}}} \right)^{-1/2z} \cdot P_{O_2}^{-1/2z} \quad (4.141)$$

where K_S is the Schottky disorder equilibrium constant.

The variation, as a function of oxygen pressure, of these defect concentrations across the scale are given in figure 4.12.

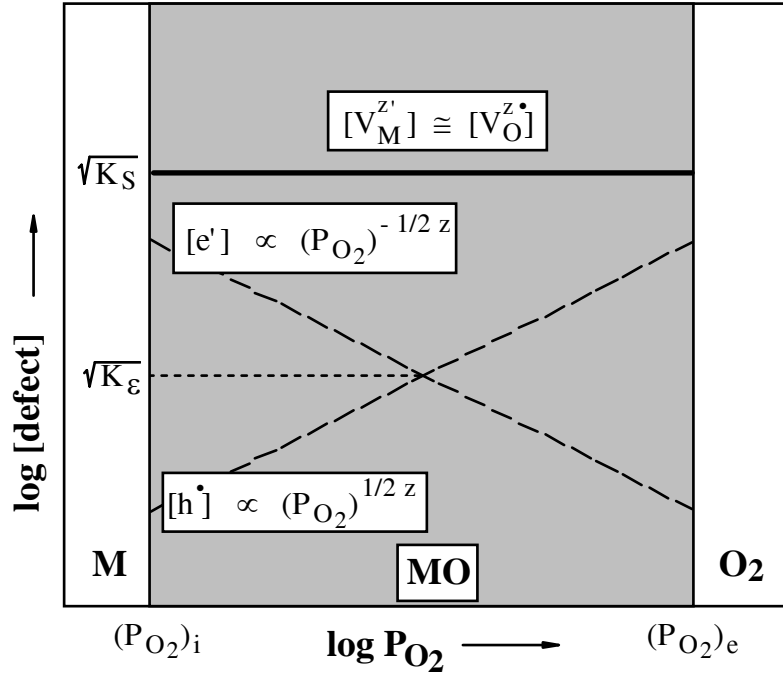


Figure 4.12. Schematic representation of the concentration of ionic and electronic defects as a function of oxygen pressure P_{O_2} in a metal oxide with predominantly ionic conductivity (logarithmic scales).

• Calculation of the total flux of defects

The origin of the x-axis will be taken at the inner interface, M/MO, between metal and oxide so that x increases towards the outer oxide interface with the gas. With this convention, the outward flux of oxygen vacancies is positive and the inward flux of metal vacancies, negative:

$$J_{V_O^{z\bullet}} > 0 \text{ and } J_{V_M^{z'}} < 0.$$

Table 4.9, shows the equations required for calculation of the oxidation rate ($z \neq 0$).

Table 4.9. Equations required for the calculation of oxidation rate for the case of diffusion controlled oxidation (oxide MO, ionic conductor).

• Stationary State:		
<i>Conservation of</i>	$\frac{\partial J_{V_O^{z\bullet}}}{\partial x} \approx 0$	(4.142)
<i>flux of defects</i>	$\frac{\partial J_{V_M^{z'}}}{\partial x} \approx 0$	(4.143)
<i>in the growing scale</i>	$\frac{\partial J_e}{\partial x} \approx 0$	(4.144)
	$\frac{\partial J_h}{\partial x} \approx 0$	(4.145)
<i>No net current through the scale:</i>		
	$z J_{V_O^{z\bullet}} + J_h = z J_{V_M^{z'}} + J_e$	(4.146)
• Electroneutrality:		
	$z [V_O^{z\bullet}] + [h\dot{\bullet}] = [e'] + z [V_M^{z'}] \Rightarrow [V_O^{z\bullet}] = [V_M^{z'}] = \sqrt{K_S}$	
	$[h\dot{\bullet}] \text{ and } [e'] \text{ negligible}$	<i>stoichiometric compound</i>
• Flux expressions:		
<i>with the convention : $[V_M^{z'}] \cdot U_{V_M^{z'}} + [V_O^{z\bullet}] \cdot U_{V_O^{z\bullet}} \gg [h\dot{\bullet}] \cdot U_h + [e'] \cdot U_e$</i>		
	$J_{V_O^{z\bullet}} = -\frac{1}{\Omega} [V_O^{z\bullet}] \cdot U_{V_O^{z\bullet}} \cdot \frac{\partial \phi}{\partial x}$	(4.147)
	$J_{V_M^{z'}} = \frac{1}{\Omega} [V_M^{z'}] \cdot U_{V_M^{z'}} \cdot \frac{\partial \phi}{\partial x}$	(4.148)
	$J_e = -\frac{1}{\Omega} (D_e \frac{\partial [e']}{\partial x} - [e'] \cdot U_e \frac{\partial \phi}{\partial x})$	(4.149)
	$J_h = -\frac{1}{\Omega} (D_h \frac{\partial [h\dot{\bullet}]}{\partial x} + [h\dot{\bullet}] \cdot U_h \frac{\partial \phi}{\partial x})$	(4.150)
• Growth rate of the oxide scale (thickness: y):		
	$\frac{1}{\Omega} \frac{dy}{dt} = J_{V_O^{z\bullet}} - J_{V_M^{z'}}$	(4.151)

These expressions for the ionic defect fluxes may be simplified by assuming that the concentration gradient of these species within the growing scale is negligible. Then, taking into account the electroneutrality condition:

$$[V_M^{z'}] \equiv [V_O^{z\bullet}]$$

and assuming that, in the quasi-stationary state, no net current flows through the scale, and that flux is conserved:

$$J_{V_O^{z\bullet}} - J_{V_M^{z\bullet}} = \frac{1}{2}(J_e - J_h) \quad (4.152)$$

The problem therefore consists in determining the fluxes of electronic defects. Expressing the electrical potential gradient in function of electronic defect fluxes from equations 4.147, 4.148 and 4.152:

$$\frac{1}{\Omega} \frac{\partial \phi}{\partial x} = - \frac{J_{V_M^{z\bullet}} - J_{V_O^{z\bullet}}}{[V_M^{z\bullet}] \cdot U_{V_M^{z\bullet}} + [V_O^{z\bullet}] \cdot U_{V_O^{z\bullet}}} = \frac{1}{Z} \frac{J_h - J_e}{[V_M^{z\bullet}] \cdot U_{V_M^{z\bullet}} + [V_O^{z\bullet}] \cdot U_{V_O^{z\bullet}}} \quad (4.153)$$

By inserting the expression for the potential gradient $\frac{\partial \phi}{\partial x}$ in the flux equations 4.149 and 4.150, we obtain:

$$(J_e - J_h) \left(1 + \frac{1}{Z} \frac{[h\bullet] \cdot U_h + [e'] \cdot U_e}{[V_M^{z\bullet}] \cdot U_{V_M^{z\bullet}} + [V_O^{z\bullet}] \cdot U_{V_O^{z\bullet}}} \right) = - \frac{1}{\Omega} \left(\frac{D_e d[e']}{dx} - \frac{D_h d[h\bullet]}{dx} \right) \quad (4.154)$$

Recalling that the conductivity is predominantly ionic, we can write:

$$[V_M^{z\bullet}] \cdot U_{V_M^{z\bullet}} + [V_O^{z\bullet}] \cdot U_{V_O^{z\bullet}} \gg [h\bullet] \cdot U_h + [e'] \cdot U_e$$

and equation 4.154 may be simplified to become:

$$(J_e - J_h) = - \frac{1}{\Omega} \left(\frac{D_e d[e']}{dx} - \frac{D_h d[h\bullet]}{dx} \right) \quad (4.155)$$

This equation may be rewritten, introducing the *electrical mobility* U_e and U_h of electronic defects:

$$J_{V_O^{z\bullet}} - J_{V_M^{z\bullet}} = - \frac{1}{\Omega} \frac{RT}{zF} \left(\frac{U_e d[e']}{dx} - \frac{U_h d[h\bullet]}{dx} \right) \quad (4.156)$$

• Electrons are ultra-minority defects within the scale

This limiting condition may be expressed as $[e'] \ll [h\bullet]$, for all x ($0 \leq x \leq y$). The situation in the scale is depicted in figure 4.13.

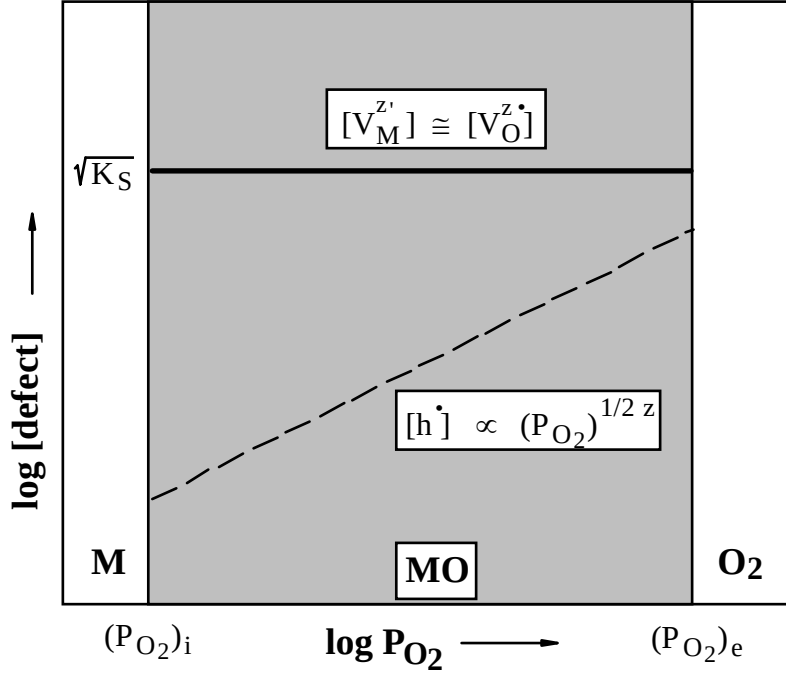


Figure 4.13. Schematic representation of the concentrations of $V_M^{z'}$, $V_O^{z\bullet}$ and $h^\bullet$ as a function of oxygen pressure P_{O_2} in a metal oxide with predominantly ionic conductivity (electrons are ultra-minority defects).

The total point defect flux $J_{V_O^{z\bullet}} - J_{V_M^{z'}}$ may be obtained by solving the differential equation:

$$J_{V_O^{z\bullet}} - J_{V_M^{z'}} = \frac{1}{\Omega} \frac{RT}{zF} U_h \frac{d[h^\bullet]}{dx} \quad (4.157)$$

Integrating this equation over the whole scale (thickness: y), we obtain:

$$J_{V_O^{z\bullet}} - J_{V_M^{z'}} = \frac{1}{\Omega} \frac{RT}{zF} \left(\frac{[h^\bullet]_e^{eq} - [h^\bullet]_i^{eq}}{y} \right) \quad (4.158)$$

- Rate law

The reaction rate $\frac{1}{\Omega} \frac{dy}{dt}$ may be identified with the total point defect flux $J_{V_O^{z\bullet}} - J_{V_M^{z'}}$:

$$\frac{dy}{dt} = \Omega (J_{V_O^{z\bullet}} - J_{V_M^{z'}}) = \frac{RT}{zF} \left(\frac{[h^\bullet]_e^{eq} - [h^\bullet]_i^{eq}}{y} \right) \quad (4.159)$$

Integration of the reaction rate leads to the parabolic rate law:

$$y^2 = \frac{2RT}{zF} U_h ([h^\bullet]_e^{eq} - [h^\bullet]_i^{eq}) \cdot t \quad (4.160)$$

The oxidation rate constant k'_p may then be written:

$$k'_p = \frac{2RT}{zF} U_h ([h^\bullet]_e^{eq} - [h^\bullet]_i^{eq}) \quad (4.161)$$

The rate determining step is the transport of electron holes across the growing scale.

Comment 1: Generally, as will be shown later, the electron hole concentration may be assumed to be negligible at the inner interface. Then, the expression for k'_p reduces to:

$$k'_p = \frac{2RT}{zF} U_h [h]_e^{\bullet \text{eq}} \quad (4.162)$$

Comment 2: In this expression, the parabolic constant k'_p is derived in terms of the electronic conductivity in the scale which, in this case, occurs by the transport of electron holes. For such a compound, electronic conductivity will be much smaller than ionic conductivity, itself very small, and such a scale can exhibit protective properties. The fact that alumina (Al_2O_3) is an ionic conductor over at least part of its phase stability range may suggest that electronic transport across the scale may be rate determining. This assumption is consistent with the fact that the electrical conductivity of alumina is a factor 10^9 less than the electrical conductivity of FeO ⁷.

- Oxidation pressure dependence

Inserting in 4.161 the expression for $[h^\bullet]$ as a function of the oxygen pressures $(P_{\text{O}_2})_e$ and $(P_{\text{O}_2})_i$ at the outer and the inner interfaces, respectively, (relation 4.140), we obtain for the scaling constant k'_p :

$$k'_p = \frac{2RT}{zF} U_h \sqrt{K_\varepsilon} \left(\frac{K_{V_M}^{z_i}}{K_{V_O}^{z_i}} \right)^{1/2z} \left[(P_{\text{O}_2})_e^{1/2z} - (P_{\text{O}_2})_i^{1/2z} \right] \quad (4.163)$$

As seen previously, $(P_{\text{O}_2})_e$ is the ambient oxygen pressure and will be termed P_{O_2} ; $(P_{\text{O}_2})_i$ may be identified with the decomposition pressure $P_{\text{O}_2}^{\text{eq}}$ of MO in equilibrium with the metal M. Recalling that, generally, $P_{\text{O}_2}^{\text{eq}} \ll P_{\text{O}_2}$, the expression of k'_p reduces to:

$$k'_p = \frac{2RT}{zF} U_h \sqrt{K_\varepsilon} \left(\frac{K_{V_M}^{z_i}}{K_{V_O}^{z_i}} \right)^{1/2z} \cdot P_{\text{O}_2}^{1/2z} \quad (4.164)$$

This expression shows that the parabolic rate constant depends on the ambient oxygen pressure. However, the influence of oxygen pressure, in its dependence on the degree of ionisation, z , differs from that found for a p-type scale.

• The electron holes are ultra-minority defects within the scale

This limiting condition may be written as $[h^\bullet] \ll [e']$ for all x ($0 \leq x \leq y$). The situation within the oxide scale is depicted in figure 4.14.

⁷ M.F. Ashby and D.R.H. Jones, "Engineering Materials", Pergamon Press, London, 1st Edition, 1986.

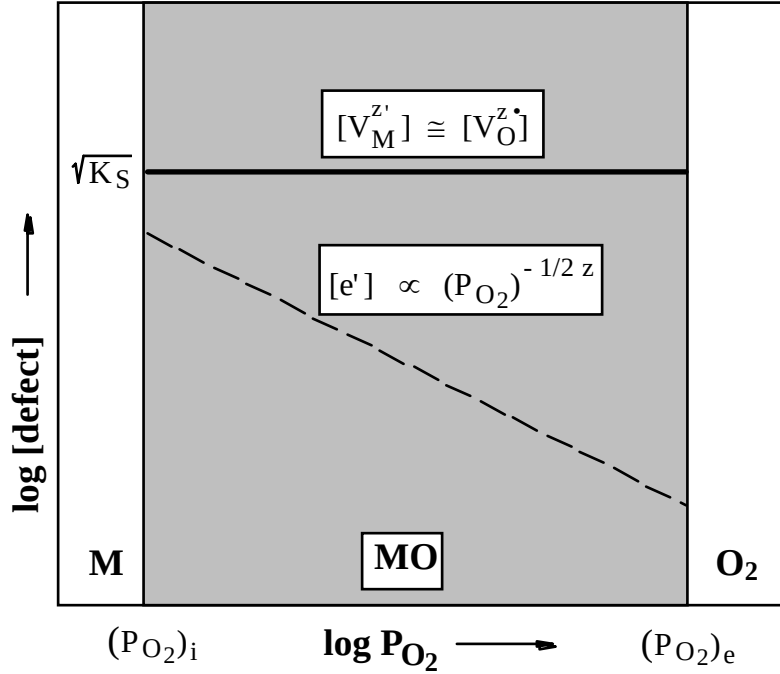


Figure 4.14. Schematic representation of the concentrations of $V_M^{z'}$, V_O^{z*} and e' as a function of oxygen pressure P_{O_2} in a metal oxide with predominantly ionic conductivity (electron holes are assumed to be ultra-minority defects).

Equation 4.156 may be simplified to:

$$J_{V_O^{z*}} - J_{V_M^{z'}} = -\frac{1}{\Omega} \frac{R T}{z F} U_e \frac{d[e']}{dx} \quad (4.165)$$

Integrating over the scale thickness y , the total point defect flux may be expressed as:

$$J_{V_O^{z*}} - J_{V_M^{z'}} = \frac{1}{\Omega} \frac{R T}{z F} \left(\frac{[e']_i^{eq} - [e']_e^{eq}}{y} \right) \quad (4.166)$$

where $[e']_i^{eq}$ and $[e']_e^{eq}$ denote, respectively, the equilibrium concentrations of electrons at the inner and at the outer interfaces.

- Rate law

Integration of the rate equation:

$$\frac{1}{\Omega} \frac{dy}{dt} = J_{V_O^{z*}} - J_{V_M^{z'}}$$

leads to the parabolic rate law:

$$y^2 = \frac{2 R T}{z F} U_e ([e']_i^{eq} - [e']_e^{eq}) \cdot t \quad (4.167)$$

The oxidation rate constant may be written:

$$k'_p = \frac{2 R T}{z F} U_e ([e']_i^{eq} - [e']_e^{eq}) \quad (4.168)$$

The rate determining step is the transport of electrons across the growing scale.

Generally, the electron concentration may be assumed to be negligible at the inner interface. Then, the expression for k'_p reduces to:

$$k'_p = \frac{2 R T}{z F} U_e [e']_i^{eq} \quad (4.169)$$

- Oxidation pressure dependence

Inserting in 4.168 the expression of $[e']$ as a function of the oxygen pressure $(P_{O_2})_i$ at the inner interface and $(P_{O_2})_e$ at the outer interface, we obtain:

$$k'_p = \frac{2RT}{zF} U_e \sqrt{K_\varepsilon} \left(\frac{K_{V_M}^{z'}}{K_{V_O}^{z'}} \right)^{-1/2z} \left[(P_{O_2})_i^{-1/2z} - (P_{O_2})_e^{-1/2z} \right] \quad (4.170)$$

As $(P_{O_2})_i = P_{O_2}^{eq}$ is negligible compared with $P_{O_2} = (P_{O_2})_e$, the expression 4.170 reduces to:

$$k'_p = \frac{2RT}{zF} U_e \sqrt{K_\varepsilon} \left(\frac{K_{V_M}^{z'}}{K_{V_O}^{z'}} \right)^{-1/2z} \cdot P_{O_2}^{eq - 1/2z} \quad (4.171)$$

This expression shows that the parabolic rate constant does not depend on the ambient oxygen pressure. Such a result has been shown earlier for the growth of n-type scales.

5.2.3. Conclusion

For diffusion controlled reactions, the rate of formation of oxide scales follows the parabolic rate law. The influence of oxygen pressure on the scaling constant depends on the relative contributions of electronic and ionic conductivity in the growing scale. It should be pointed out that in the case of formation of a scale exhibiting majority electronic defects, the pressure law depends on the nature of the defects, either electrons or electron holes.

Table 4.10 gives the variation, as a function of ambient oxygen pressure, of both the properties of the scale, formed by oxidation of a metal M, and of the parabolic rate constant, k'_p , for all types of oxides (see sections 2.1.2., 2.1.3 and 2.1.4 of Chapter 3).

In this chapter we have assumed that the same defect structure prevails across the whole scale from the outer to the inner interface. This may be an oversimplified model and more complex situations may exist as the scale thickens. For example, a scale may exhibit p-type conductivity at the outer interface, ionic conductivity in the bulk of the scale, and n-type conductivity at the inner interface (see the Brouwer diagrams of Chapter 3).

Table 4.10. Comparison, as a function of oxygen pressure, of the parabolic rate constant k'_p for oxidation of a metal M to MO with defect dependent properties in the MO oxide.

P_{O_2} : ambient oxygen pressure
 z : degree of ionisation of the predominant defect(s)
 z^* : degree of ionisation of the predominant charged defect(s).

SCALING SYSTEM M / MO / O ₂	non-stoichiometric oxide	Type of electrical conductivity	Scales with predominant electronic conductivity	
			p-type semi-conductor	n-type semi-conductor
		Non-stoichiometry ratio	$\propto P_{O_2}^{1/2(z+1)}$	$\propto P_{O_2}^{-1/2(z+1)}$
		Self-diffusion coefficient **	$\propto P_{O_2}^{1/2(z+1)}$	$\propto P_{O_2}^{-1/2(z+1)}$
		Total conductivity, σ_t	$\propto P_{O_2}^{1/2(z^*+1)}$	$\propto P_{O_2}^{-1/2(z^*+1)}$
		Parabolic constant, k'_p	$\propto P_{O_2}^{1/2(z+1)}$	No oxygen pressure dependence
	stoichiometric oxide	Type of electrical conductivity	Scales with predominant ionic conductivity	
			$h^\bullet$, major electronic defect	e' , major electronic defect
		Total conductivity, σ_t	No oxygen pressure dependence	
		Electronic conductivity, σ_e	$\propto P_{O_2}^{1/2 z}$ $z \neq 0$	$\propto P_{O_2}^{-1/2 z}$ $z \neq 0$
		Parabolic constant, k'_p	$\propto P_{O_2}^{1/2 z}$ $z \neq 0$	No oxygen pressure dependence $z \neq 0$

**Self-diffusion coefficient of the component taking the predominant part in matter transport.

5.3. Growth of scale by short-circuit diffusion

Lattice diffusion will be the dominate process of mass transport at high temperature, provided there is a sufficiently high defect concentration, but mass transport can also occur along dislocations or grain boundaries (see Chapter 3, section 2.3.2). Thus, the overall transport in polycrystalline oxide scales generally results from two fluxes of matter in parallel: an intragranular flux J_V^* and a flux along grain boundaries J_{gb} (see figure 4.15); let D_V and D_{gb} be the corresponding diffusion coefficients.

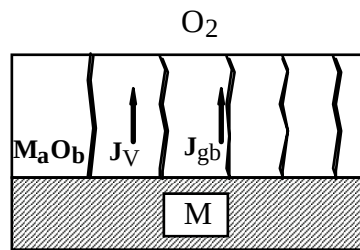


Figure 4.15. Schematic illustration of fluxes of diffusion through the oxide scale.

The significant role of short-circuit diffusion has been underlined in the high temperature corrosion of metals such as Ni, Cu, Cr, Al, etc. It is an important mode of diffusion in the case of scales exhibiting a columnar microstructure but has been observed also in the case of isotropic microstructures.

Figure 4.16 illustrates the role of linear defects (dislocations) and surface defects (grain boundaries) on the oxidation kinetics of nickel. It has been observed that the oxidation rate is higher with cold-worked nickel (abrasion or shot-peening) than with annealed metal. This phenomenon, noticeable at 900°C, becomes less important at temperatures sufficiently high to give rise to grain growth.

* In this section, subscript V refers to volume, whatever the mobile point defect may be (vacancy or interstitial)

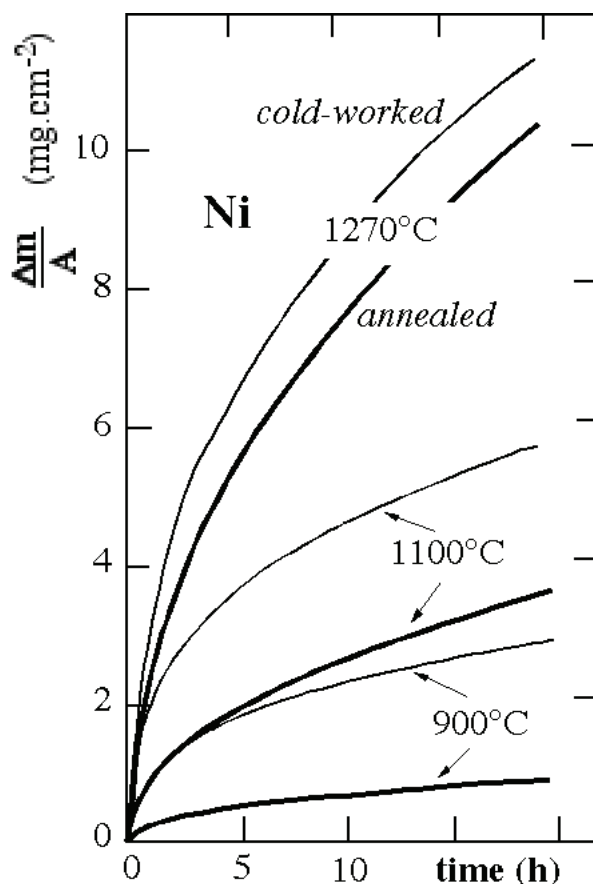


Figure 4.16. Oxidation curves of zone refined nickel after cold-working or annealing, from 900 to 1270°C, from Caplan et al.⁸.

The important role of grain boundaries at low temperatures has been mentioned in Chapter 3 (section 2.3.2). Under these conditions:

- the oxidation rate may be several orders of magnitude higher than the values estimated for oxidation by bulk diffusion,
- the rate equation is not strictly parabolic and the oxidation rate decreases more rapidly with time than for the ideal parabolic law: the instantaneous effective rate constant decreases rapidly with time and approaches a constant value at long times (see figure 4.18).

Semi-empirical models attribute this decrease with time of oxidation rate to grain growth in the oxide scale.

The oxidation rate may be expressed as a function of the effective diffusion coefficient defined in Chapter 3 (section 2.3.2) as:

$$D_{\text{eff}} = f D_{\text{gb}} + (1 - f) D_v \quad (4.172)$$

⁸ D. Caplan, M.J. Graham and M. Cohen, *J. Electrochem. Soc.*, **119** (1972) 1205-1215.

where f is the fraction of diffusion sites located at grain boundaries. The scale growth rate obeys the differential equation:

$$\frac{dy}{dt} = \Omega D_{\text{eff}} \frac{\Delta C}{y} \quad (4.173)$$

where ΔC is the defect concentration difference through the oxide scale and Ω the molar volume of the oxide. Integration of equation 4.173 leads to:

$$y^2 = 2 D_{\text{eff}} \Delta C t = k'_{\text{p(eff)}} t \quad (4.174)$$

where $k'_{\text{p(eff)}}$ is the effective parabolic constant.

Assuming that the oxide is dense and pure and the grains are spherical, it has been demonstrated that the variation with time of grain size obeys the equation⁹:

$$r_t^2 - r_0^2 = K t \quad (4.175)$$

where r_t is the grain radius at time t , r_0 its initial radius and K is a constant, which is a function of, among others, the surface energy of grain boundaries, their thickness and of the diffusion coefficient of matter across the grain boundaries. The fraction of sites per unit area in the grain boundary at time t may be written:

$$f = \frac{2d}{r_t} = \frac{2d}{(K t + r_0^2)^{1/2}} \quad (4.176)$$

where d is the boundary width.

Combining the preceding equations, when $D_{\text{gb}} \gg D_{\text{V}}$ we obtain:

$$y^2 = 2 \Omega D_{\text{V}} \Delta C \int_0^t \left[1 + \frac{D_{\text{gb}}}{D_{\text{V}}} \frac{2d}{(K t + r_0^2)^{1/2}} \right] dt \quad (4.177)$$

which leads to the following rate equation:

$$y^2 = 2 \Omega \Delta C \left[D_{\text{V}} t + 4 D_{\text{gb}} \frac{1}{K} (K t + r_0^2)^{1/2} \right] \quad (4.178)$$

This simple model has been applied with success to the oxidation of nickel single crystals at four temperatures between 500 and 800°C¹⁰. Figure 4.17 shows the mass gain ($\Delta m/A$) per unit area versus time between 500 and 800°C. Clearly, very good agreement has been obtained between the experimental points and equation 4.178.

⁹ J.E. Burke, *Trans. A.I.M.E.*, **180** (1949) 73-91.

¹⁰ N.N. Khoi, W.W. Smeltzer and J.D. Embury, *J. Electrochem. Soc.*, **116** (1975) 1495.

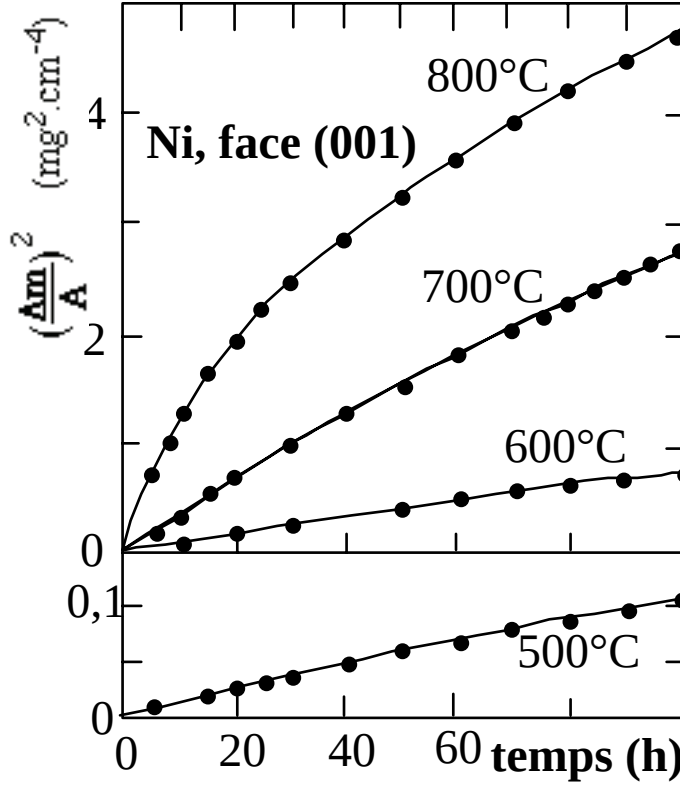


Figure 4.17. Experimental verification of the model of metal oxidation taking into account both bulk and grain boundary diffusion, from Khoi et al.⁹

Black circles represent experimental points and full curves correspond to equation 4.178.

Equation 4.178 may also be written:

$$\frac{d(y^2)}{dt} = k'_{p(\text{eff})} = k'_{p(V)} + f k'_{p(\text{gb})} \quad (4.179)$$

where $k'_{p(\text{eff})}$ is the instantaneous parabolic constant that can be evaluated from the tangents to the oxidation curves $y^2 = f(t)$ at time t , $k'_{p(V)}$ is the parabolic constant resulting from a lattice diffusion rate-limiting step ($k'_{p(V)} = 2 \Omega D_V \Delta C$) and $k'_{p(\text{gb})}$ is the parabolic constant for the case of metal oxidation controlled by grain boundary diffusion ($k'_{p(\text{gb})} = 2 \Omega D_{\text{gb}} \Delta C$).

An example of the role of grain boundary diffusion on the oxidation rate of iron and of iron treated by surface ion implantation of bismuth is given in Chapter 6 (section 3.1.2).

Several authors have evaluated the respective contributions of lattice diffusion and grain boundary diffusion. Figure 4.18 shows results obtained during the oxidation of cold-worked nickel, leading to the formation of a fine grain size in the oxide, and after annealing. The effective instantaneous parabolic rate constant k_{eff} may be calculated using the equation:

$$k_{p(\text{eff})} = 2 \frac{1}{A} \frac{d(\Delta m)}{dt} \frac{(\Delta m)}{A}$$

where Δm is the mass gain at time t and $\frac{d(\Delta m)}{dt}$ is the slope of the mass gain curve at this time.

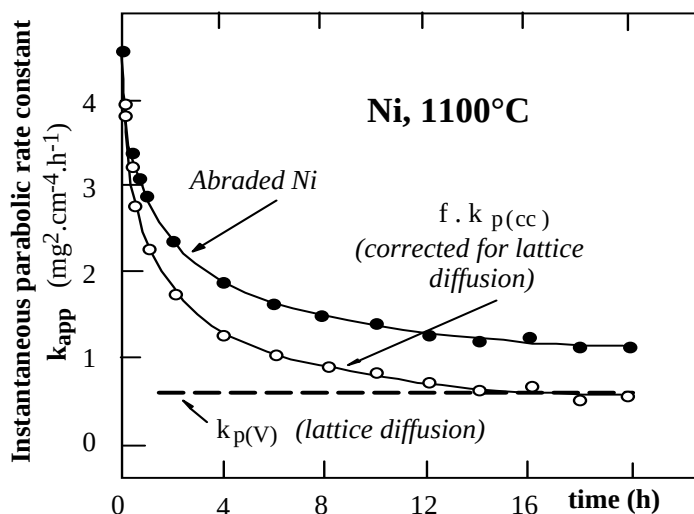


Figure 4.18. Evaluation of relative contributions of lattice diffusion and grain boundary diffusion on the instantaneous parabolic constant applied to the oxidation of cold-worked nickel, at 1100°C, from Graham et al.¹¹.

The gradual increase in oxide grain size during the growth of the scale results in a decrease in the relative contribution of grain boundary short-circuits to the overall mass transport. Further numerical development of this simple model has allowed a grain size distribution, different grain boundary widths or different laws of grain growth to be taken into account.

5.4. Effects of impurities on parabolic oxidation

It is well known that the ionic and electronic defect concentrations in oxide can be modified by introducing small quantities (dopants) of foreign elements with different valences from that of the host-metal cation. So one may expect, for parabolic oxidation of metals controlled by diffusion, a dependence of the oxidation rate on the concentration of foreign elements in the oxide scale. The study of the foreign-element influence has been extensively developed in the literature from Hauffe's original work¹² (Hauffe-Wagner rule) and, more recently by Kofstad^{13,14} and Gesmundo and Viani¹⁵.

We shall present here a new approach to this problem and discuss the validity of previous analyses. Let us consider as an illustration the effect of a higher-valence foreign metal addition on the parabolic growth of a metal-deficient oxide MO with metal ion charged vacancies $V_M^{z'}$ (z ranging from 1 to 2). For the sake of simplicity, let us choose Cr as a

¹¹ M.J. Graham, D. Caplan and M. Cohen, *J. Electrochem. Soc.*, **119** (1972) 1265-1267.

¹² K. Hauffe, *Oxydation von Metallen und Metallegierungen*, Springer, Berlin, 1957.

¹³ P. Kofstad, *Corros. NACE*, 24 (1968) 379.

¹⁴ P. Kofstad, *Nonstoichiometry Diffusion and Electrical Conductivity in Binary Metal Oxides*, J. Wiley, New York, 1972, p. 106.

¹⁵ F. Gesmundo and F. Viani, *J. Electrochem. Soc.*, **128** (1981) 470.

trivalent impurity. Chromium, alloyed to the basic metal, penetrates the MO lattice during oxidation.

This model is based on the following hypotheses:

1. The foreign elements are dissolved substitutionally in the parent oxide as $\text{Cr}_M^\bullet$.
2. The substitutional defects are homogeneously distributed throughout the scale.
3. The chemical equilibria are not modified by the presence of foreign ions.
4. The metal oxidation follows the Wagner oxidation mechanism.

5.4.1. Relation between ionic and electronic fluxes

The equations required to calculate the flux $J_{V_M^{z'}}$, established from classical stationary and electroneutrality hypotheses, are given in table 4.11 (z ranging from 1 to 2). In this table, $J_{V_M^{z'}}$ and J_h denote, respectively, the fluxes of metal ion vacancies and electron holes in the doped oxide (these differ from the fluxes $J_{V_M^{z'}}$ et J_h in the pure oxide), $[V_M^{z'}]$ and $[h^\bullet]$ are the concentrations of ionic and electronic defects in the doped oxide (these differ from the concentrations $[V_M^{z'}]$ and $[h^\bullet]$ in the pure oxide) and α is the concentration of defects $\text{Cr}_M^\bullet$. In the following, α will be considered as a controlled parameter.

Table 4.11. Equations required for the calculation of the oxidation rate in the doped oxide MO with metal ion vacancies $V_M^{z'}$.

• **Stationary State:**

$$\frac{\partial [V_M^{z'}]}{\partial t} = - \frac{\partial J_{V_M^{z'}}}{\partial x} \sim 0$$

conservation of defect flux in the growing scale

$$J_h = z J_{V_M^{z'}}$$

no net current flows through the scale

• **Electroneutrality:**

$$\alpha + [h^\bullet] = z [V_M^{z'}] \quad (4.180)$$

• **Flux expressions:**

$$J_{V_M^{z'}} = - \frac{1}{\Omega} (D_{V_M^{z'}} \frac{\partial [V_M^{z'}]}{\partial x} - [V_M^{z'}] U_{V_M^{z'}} \frac{\partial \phi}{\partial x})$$

$$J_h = - \frac{1}{\Omega} (D_h \frac{\partial [h^\bullet]}{\partial x} + [h^\bullet] U_h \frac{\partial \phi}{\partial x}) \quad (4.181)$$

• **Growth rate of the oxide scale (thickness: y):**

$$\frac{1}{\Omega} \frac{dy}{dt} = J_{V_M^{z'}} \quad (4.182)$$

Tables 4.11 and 4.7 are identical except for the electroneutrality equations 4.180 and 4.81. It follows that the relationship between ionic and electronic fluxes is still valid:

$$J_{V_M^{z'}} \left(\frac{1}{[V_M^{z'}] \cdot U_{V_M^{z'}}} + \frac{z}{[h^\bullet] \cdot U_h} \right) = - \frac{1}{\Omega} \frac{R T}{z F} \frac{d \ln[V_M^{z'}] \cdot [h^\bullet]^z}{dx} \quad (4.183)$$

5.4.2. Situation in the doped oxide scale

For the sake of simplicity*, let us consider a metal deficient oxide with singly charged metal ion vacancies ($z = 1$). Recalling that in the pure oxide (see section 5.2.1.1) the ionic and electronic defect concentrations obey the following relationships:

$$[h^\bullet] = z [V_M^{z'}] \quad (\text{see equation 4.81})$$

$$[V_M^{z'}] \cdot [h^\bullet]^z = K_{V_M^{z'}} \cdot P_{O_2}^{1/2} \quad (\text{see equation 4.98})$$

The resolution of this system of equations (with $z = 1$) leads to:

$$[V_M'] = [h^\bullet] = K_{V_M'}^{1/2} \cdot P_{O_2}^{1/4} \quad (4.184)$$

The situation in the doped oxide is determined by the electroneutrality condition:

$$[h^\bullet] + \alpha = z \cdot [V_M^{z'}] \quad (\text{see equation 4.180})$$

The relationship between ionic and electronic concentrations is still valid:

$$[V_M^{z'}] \cdot [h^\bullet]^z = K_{V_M^{z'}} \cdot P_{O_2}^{1/2} \quad (4.185)$$

The solution of this system of equations, with $z = 1$, leads to:

$$[V_M'] = \frac{1}{2} (\alpha + \sqrt{\alpha^2 + 4 K_{V_M'} \cdot P_{O_2}^{1/2}}) \quad (4.186)$$

and

$$[h^\bullet] = \frac{2 K_{V_M'} \cdot P_{O_2}^{1/2}}{\alpha + \sqrt{\alpha^2 + 4 K_{V_M'} \cdot P_{O_2}^{1/2}}} \quad (4.187)$$

This expression may be rewritten in terms of the ionic defect concentration V_M' in the non-doped oxide:

$$[V_M'] = \frac{1}{2} (\alpha + \sqrt{\alpha^2 + 4 [V_M']^2}) \quad (4.188)$$

$$[h^\bullet] = \frac{2 [V_M']^2}{\alpha + \sqrt{\alpha^2 + 4 [V_M']^2}} \quad (4.189)$$

* For a doped oxide with doubly charged ion metal vacancies, the ionic and electronic defect concentrations cannot be calculated analytically.

The situation in the doped oxide is schematically illustrated in figure 4.19. In this figure, we have superimposed the ionic and electronic defect concentration for a non-doped oxide.

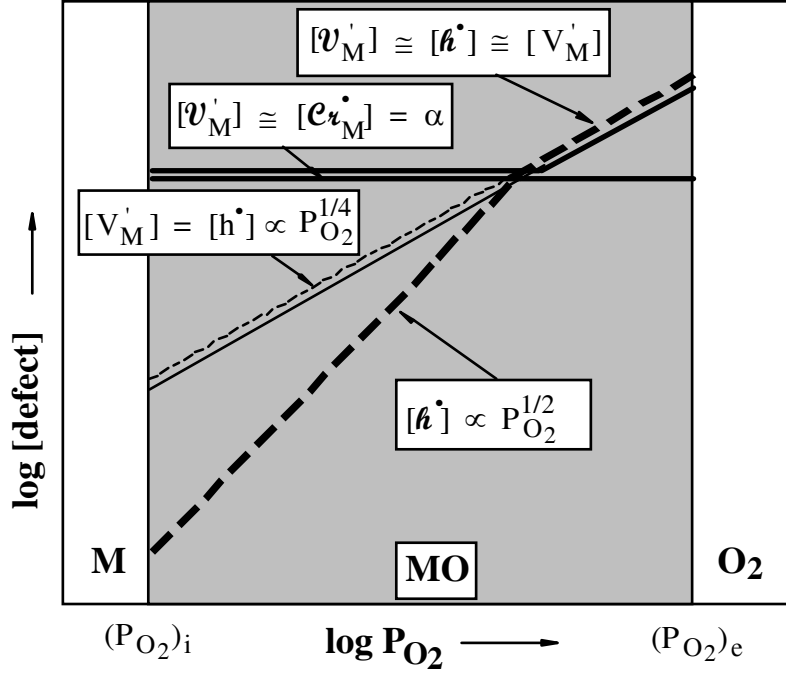


Figure 4.19. Schematic representation of the concentrations of ionic and electronic defects as a function of oxygen pressure P_{O_2} in a metal oxide exhibiting predominantly metal vacancies and doped with a component with higher valency (the case where $z = 1$).

As illustrated in Fig. 4.19, the oxide scale can be considered to consist of two regions depending on the value of α :

1. An outer intrinsic region where α , much smaller than the concentration $[V'_M]$ in the pure oxide, is too small to affect the ionic and electronic defect concentrations. In this region, the conductivity remains essentially electronic.
2. An inner extrinsic region where α , much larger than the concentration $[V'_M]$ in the pure oxide, is large enough to modify the concentrations of the ionic and electronic defects in this region.

For the sake of simplicity, let us consider in the following that α is high enough to modify the concentrations of the ionic and electronic defects throughout **the whole scale** ($\alpha \gg [V'_M]^{eq}_e$). With this assumption, we have: $(h^\bullet) \ll \alpha$ and, by considering that the free electron concentration remains negligible, from relations 4.180 and 4.185:

$$[V'^{z'}_M] \cong \frac{\alpha}{z} \quad (4.190)$$

$$[h^\bullet] = z^{1/z} \left(\frac{K_{V'_M}}{\alpha} \right)^{1/z} \cdot P_{O_2}^{1/2 z} \quad (4.191)$$

The situation in the doped oxide is shown schematically in figure 4.20. In this figure, are superimposed (as thin lines) the ionic and electronic defect concentrations for a non-doped oxide (for the case where $z = 1$).

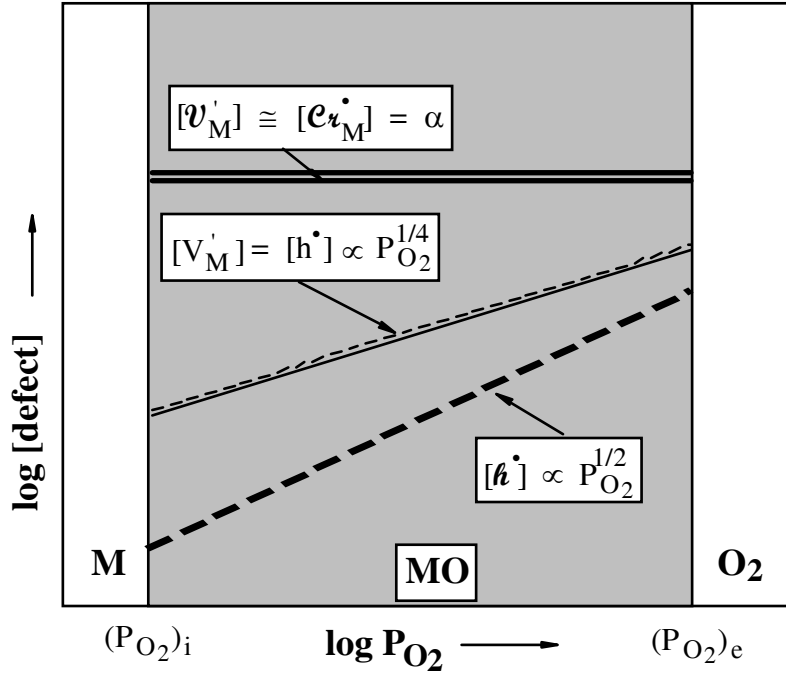


Figure 4.20. The situation across the layer for a highly doped oxide ($\alpha \gg [V_M^{z'}]_e^{\text{eq}}$, $z = 1$).

5.4.3. Calculation of the parabolic rate constant

Starting from the simplified electroneutrality relation 4.190, valid for a highly doped oxide, the differential equation for calculating the flux $\mathcal{J}_{V_M^{z'}}$ may be expressed through the relation 4.183 as:

$$\mathcal{J}_{V_M^{z'}} \left(\frac{1}{\alpha \cdot U_{V_M^{z'}}} + \frac{1}{[h^\bullet] \cdot U_h} \right) = - \frac{1}{\Omega} \frac{R T}{z F} \frac{d \ln [h^\bullet]}{dx} \quad (4.192)$$

Integrating this equation as a function of the only independent variable $[h^\bullet]$ we obtain for the flux $\mathcal{J}_{V_M^{z'}}$ over the whole scale of thickness: y :

$$\mathcal{J}_{V_M^{z'}} = \frac{1}{\Omega} \frac{R T}{z F} \frac{\alpha \cdot U_{V_M^{z'}}}{y} \left[\ln \left(1 + \frac{[h^\bullet] \cdot U_h}{\alpha \cdot U_{V_M^{z'}}} \right) \right]_{[h^\bullet]_i}^{[h^\bullet]_e} \quad (4.193)$$

Integration of the rate equation:

$$\frac{dy}{dt} = \Omega \mathcal{J}_{V_M^{z'}} \quad (4.194)$$

leads to the following expression for the parabolic rate constant k'_p :

$$k'_p = \frac{2RT}{zF} \alpha \cdot U_{V_M^{z'}} \left[\ln \left(1 + \frac{[h^\bullet] \cdot U_h}{\alpha \cdot U_{V_M^{z'}}} \right) \right] \frac{[h^\bullet]_e}{[h^\bullet]_i} \quad (4.195 \text{ a})$$

i.e.

$$k'_p = 2 \alpha \cdot D_{V_M^{z'}} \left[\ln \left(1 + \frac{[h^\bullet] \cdot U_h}{\alpha \cdot U_{V_M^{z'}}} \right) \right] \frac{[h^\bullet]_e}{[h^\bullet]_i} \quad (4.195 \text{ b})$$

These equations show that, in contrast to previously published results¹¹⁻¹⁴, the variation of the parabolic rate constant as a function of the dopant concentration, α , is not monotonic. Consequently, since:

$$[h^\bullet] = z^{1/z} \left(\frac{K_{V_M^{z'}}}{\alpha} \right)^{1/z} \cdot P_{O_2}^{1/2 z} \quad (4.196)$$

the scaling constant k'_p will vary in a complex manner with oxygen pressure, depending on the ratio:

$$\frac{[h^\bullet] \cdot U_h}{\alpha \cdot U_{V_M^{z'}}}.$$

To illustrate this point, let us consider two limiting cases: one where the conductivity is essentially electronic throughout the oxide layer ($[h^\bullet] \cdot U_h \gg \alpha \cdot U_{V_M^{z'}}$) and one where the concentration, α , of the dopant element is sufficiently high that the oxide becomes an ionic conductor ($[h^\bullet] \cdot U_h \ll \alpha \cdot U_{V_M^{z'}}$).

1st case: $[h^\bullet] \cdot U_h \gg \alpha \cdot U_{V_M^{z'}}$

The oxide is an electronic conductor throughout its thickness and the expression for the flux $\mathcal{J}_{V_M^{z'}}$ reduces to:

$$\mathcal{J}_{V_M^{z'}} = \frac{1}{\Omega} \frac{RT}{zF} \frac{\alpha \cdot U_{V_M^{z'}}}{y} \ln \left(\frac{[h^\bullet]_e}{[h^\bullet]_i} \right) \quad (4.197)$$

This expression can be compared with the expression:

$$\mathcal{J}_{V_M^{z'}} = \frac{1}{z\Omega} \frac{\alpha U_{V_M^{z'}}}{y} (\phi_i - \phi_e) \quad (4.198)$$

where Φ_i and Φ_e are the electrical potentials at the inner and outer interfaces, respectively, deduced from integration of the general differential equation:

$$\mathcal{J}_{V_M^{z'}} = -\frac{1}{\Omega} (D_{V_M^{z'}} \frac{d[\mathcal{V}_M^{z'}]}{dx} - [\mathcal{V}_M^{z'}] U_{V_M^{z'}} \frac{d\phi}{dx}) \quad (4.199)$$

when the point defect concentration $[v_M^{z'}]$ is assumed to remain constant over the whole scale and equal to α/z .

Comparison of 4.198 with the expression:

$$j_{V_M^{z'}} = \frac{1}{\Omega} \frac{R T}{z F} \frac{\alpha \cdot U_{V_M^{z'}}}{y} \ln \left(\frac{[h^\bullet]_e}{[h^\bullet]_i} \right) \quad (4.200)$$

shows that:

$$(\phi_i - \phi_e) = \frac{R T}{F} \ln \left(\frac{[h^\bullet]_e}{[h^\bullet]_i} \right) \quad (4.201)$$

Consequently, the parabolic rate constant k'_p may be written:

$$k'_p = \frac{2}{z} \alpha U_{V_M^{z'}} (\phi_i - \phi_e) \quad (4.202)$$

This expression shows that the rate-determining step is point defect diffusion under the influence only of the electrical potential gradient and, as long as the conductivity remains electronic over the whole scale, the parabolic constant k'_p increases with the dopant level α . Moreover, according to equation 4.191:

$$[h^\bullet] = z^{1/z} \left(\frac{K_{V_M^{z'}}}{\alpha} \right)^{1/z} \cdot P_{O_2}^{1/2 z}$$

the constant k'_p depends on the natural logarithm of the oxygen pressure and may be written:

$$k'_p = \frac{R T}{z^2 F} \alpha U_{V_M^{z'}} \left[\ln P_{O_2} \right]_{(P_{O_2})_i}^{(P_{O_2})_e} \quad (4.203 a)$$

or

$$k'_p = \frac{\alpha}{z} D_{V_M^{z'}} \left[\ln P_{O_2} \right]_{(P_{O_2})_i}^{(P_{O_2})_e} \quad (4.203 b)$$

which shows how the dependence of the parabolic rate constant, k'_p , on the ambient oxygen pressure is modified by the presence of impurities in the scale and differs from that for the oxidation of a pure metal.

2nd case: $[h^\bullet] \cdot U_h \ll \alpha \cdot U_{V_M^{z'}}$

In this case, the foreign metal concentration is so high that the oxide becomes an ionic conductor throughout the scale. Expanding equation 4.195 and considering only the first term leads to:

$$k'_p = \frac{2RT}{zF} U_h ([h^\bullet]_e - [h^\bullet]_i) \quad (4.204)$$

It can be seen that the oxidation rate is controlled by the transport of electronic holes across the scale under an electrochemical potential gradient. Using equation 4.199:

$$[h^\bullet] = z^{1/z} \left(\frac{K_{V_M^{z'}}}{\alpha} \right)^{1/z} \cdot P_{O_2}^{1/2 z}$$

we obtain for k'_p :

$$k'_p = \frac{2RT}{zF} U_h z^{1/z} \left(\frac{K_{V_M^{z'}}}{\alpha} \right)^{1/z} ((P_{O_2})_e^{1/2 z} - (P_{O_2})_i^{1/2 z}) \quad (4.205)$$

The scaling constant decreases as α increases but increases with the ambient pressure. The influence of oxygen pressure on k'_p is modified by the presence of a higher-valence impurity and depends on the electrical charge of the defects.

Comment: This pressure law approaches that obtained for oxidation of a pure metal to produce an oxide scale with essentially pure ionic conductivity (expression 4.163).

These results are illustrated in table 4.12.

Table 4.12. Dependence of the parabolic rate constant for oxidation of a metal M to MO on the impurity level α and the ambient oxygen pressure P_{O_2} (MO is assumed to be a metal-deficient oxide with metal-ion charged vacancies as the predominant defect, the trivalent impurity is substitutionally dissolved in the oxide, $\alpha \gg [V_M^{z'}]_e^{eq}$).

PURE METAL	Type of electrical conductivity in the growing scale	Predominantly electronic conductivity	
	Parabolic constant as a function of defect concentrations	$2 (z + 1) D_{V_M^{z'}} ([V_M^{z'}]_e^{\text{eq}} - [V_M^{z'}]_i^{\text{eq}})$	
	Parabolic constant as a function of oxygen pressure	$2 (z + 1) D_{V_M^{z'}} \left(\frac{K_{V_M^{z'}}}{z^z} \right)^{1/(z+1)} \left((P_{O_2})_e^{1/2(z+1)} - (P_{O_2})_i^{1/2(z+1)} \right)$	
METAL WITH A HIGHER-VALENCE IMPURITY	Type of electrical conductivity in the growing scale	When the concentration α of the dopant element is high, the oxide can become an ionic conductor throughout the scale	
	Parabolic constant as functions of impurity level and ionic and electronic defect concentrations	$\frac{2 R T}{z F} \alpha \cdot U_{V_M^{z'}} \left[\ln \left(1 + \frac{[h^\bullet] \cdot U_h}{\alpha \cdot U_{V_M^{z'}}} \right) \right]_{[h^\bullet]_i}^{[h^\bullet]_e} = 2 \alpha \cdot D_{V_M^{z'}} \left[\ln \left(1 + \frac{[h^\bullet] \cdot U_h}{\alpha \cdot U_{V_M^{z'}}} \right) \right]_{[h^\bullet]_i}^{[h^\bullet]_e}$	
	Parabolic constant as functions of impurity level and oxygen pressure	$[h^\bullet] \cdot U_h \gg \alpha \cdot U_{V_M^{z'}}$ Oxide remains an electronic conductor across the whole scale	$[h^\bullet] \cdot U_h \ll \alpha \cdot U_{V_M^{z'}}$ Oxide becomes an ionic conductor across the whole scale
		$\frac{\alpha}{z} D_{V_M^{z'}} \left[\ln P_{O_2} \right]_{(P_{O_2})_i}^{(P_{O_2})_e}$	$\frac{2 R T}{z F} U_h z^{1/z} \left(\frac{K_{V_M^{z'}}}{\alpha} \right)^{1/z} \left[(P_{O_2})_e^{1/2z} - (P_{O_2})_i^{1/2z} \right]$

Such a model can explain the experimental results obtained by Mrowec for the sulphidation of Ni / Cr alloys of low Cr contents (see Fig. 4. 21).

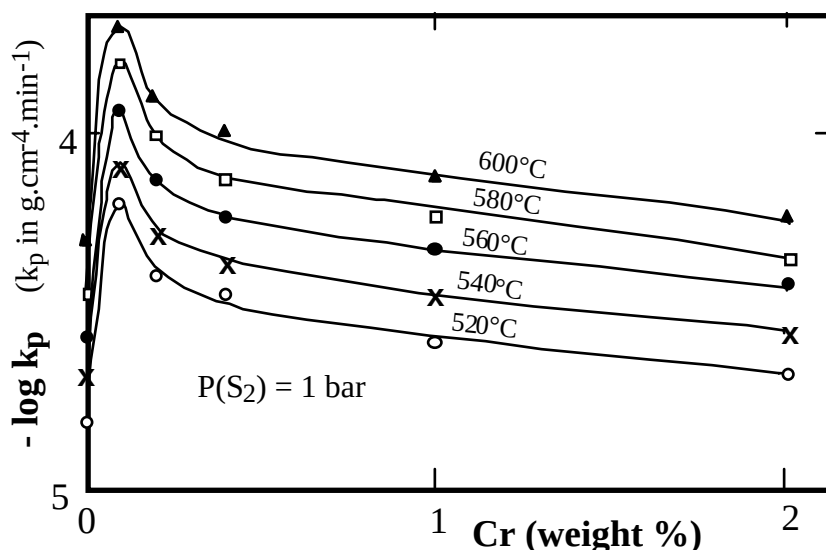


Figure 4.21. Dependence of sulphidation rate on chromium concentration for Ni-Cr alloy containing less than 2 % Cr (from Mrowec et al¹⁶)

Comment: This model might also be valid for oxide scales containing oxygen interstitial defects with $z = 1$ or $z = 2$.

In summary, it has been shown that, as an example, the presence of higher valence impurities may lead to changes in the oxidation rate, assuming that the limiting step is diffusion in the oxide scale. In the same way, the calculation may be developed for the oxidation of a metal M containing an impurity of lower valence. On the same basis, a similar model has been proposed for the oxidation of a metal M leading to an oxygen-deficient oxide MO containing oxygen vacancies or interstitial metal ions as the predominant defect. The effect of higher and lower valence impurities has been studied¹⁷.

6. Calculation of the reaction rate in mixed kinetics

6.1. Definition

All the calculations developed above provide excellent teaching examples for the study of high temperature corrosion. Unfortunately, they are seldom realistic and real corrosion is often more complex, involving not one but several rate-limiting steps in series

¹⁶ S. Mrowec, T. Werber and M. Zastawnik, *Corrosion Science*, **6** (1966) 47.

¹⁷ P. Sarrazin, A. Galerie and M. Caillet, *Oxidation of Metals*, **46** (1996) 1-17.

for the growth of the oxide scale. This results in regimes of mixed kinetics. By “mixed kinetics” we mean any situation where there is more than one rate-limiting step (see section 4.4).

6.2. Principle of the Calculation

For the reaction :



four elementary steps can be defined, as listed below :

- adsorption of oxygen generating the adsorbed species O-s;
- external half-reaction, creating (or consuming) the major point defect^(*);
- diffusion of the defect through the oxide;
- internal half-reaction consuming (or creating) the defect..

In the following, we limit our discussion to the case where two elementary steps only have non-infinite rate constants (i.e. are rate-limiting). We, therefore, have four possible mixed regimes obtained by combining the rate-limiting steps in pairs. The principle of the calculation is described below.

1. Write the differential equation describing the mass balance of the intermediate species exchanged between the two rate-limiting steps.
2. Solve that equation to obtain the expression for the concentration of that species as a function of time.
3. Insert this expression into the rate equations.

In fact, stage 2 is generally critical since the differential equation is rarely integrable. This could be because the order of differentiation is greater than unity for one of the steps involved (the dissociative adsorption of O₂, for example, using two adsorption sites) or to the fact that space and time variables are not separable. The complete calculation is then not possible and only a steady-state approximation can be used. Several of these possibilities are described below.

* For simplification, the predominant point defect involved is considered to be neutral.

6.3. The mixed regime of an external half-reaction and an internal half-reaction: an example of a complete calculation

Let us consider reaction (4.206) described by the following elementary steps**



We assume that the sorption process (4.207) is at thermodynamic equilibrium and that the diffusion coefficient for vacancies is infinite. The two interfacial reactions (4.208 and 4.209) have finite rate constants and are relatively slow.

• Development of the concentration of cation vacancies with time

In the regime being considered, the concentration $[\text{V}_\text{M}]$ of cation vacancies in the oxide is uniform ($[\text{V}_\text{M}]_\text{e} = [\text{V}_\text{M}]_\text{i}$), as shown in Fig. 4.22, and differs from the equilibrium concentrations.

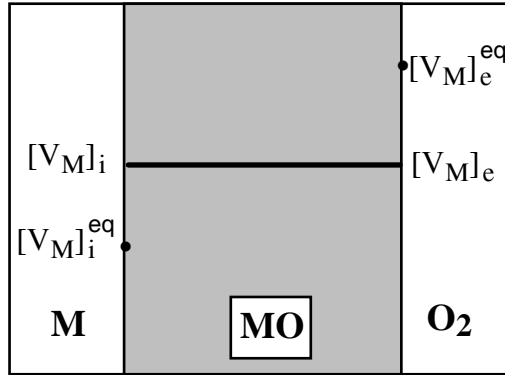


Fig. 4.22. Concentration profile of cation vacancies in the oxide scale growing in a mixed regime of external and internal half-reactions.

The differential equation describing this concentration is (see section 3.1):

$$\frac{d[\text{V}_\text{M}]}{dt} = k'_\text{e} \theta - k''_\text{e} [\text{V}_\text{M}] (1 - \theta) - k'_\text{i} [\text{V}_\text{M}] + k''_\text{i} \quad (4.210)$$

simplified to:

$$\frac{d[\text{V}_\text{M}]}{dt} = \alpha - \beta [\text{V}_\text{M}] \quad (4.211)$$

** The calculation here is for cation vacancies in the oxide but the principles are unchanged for any other predominant defect.

where:

$$\alpha = k'_e \theta + k''_i = k'_e \left(\frac{\sqrt{K_a P_{O_2}}}{1 + \sqrt{K_a P_{O_2}}} + k''_i \right)$$

$$\beta = k''_e (1 - \theta) + k'_i = \frac{k''_e}{1 + \sqrt{K_a P_{O_2}}} + k'_i$$

To integrate this differential equation, the limiting value of $[V_M]$ when $t \rightarrow 0$ must be known; this value is certainly not zero. Indeed, depending on the relative values of the rates of the external and internal half-reactions, it is clear that, at very short times, one of these reactions would determine the initial rate whereas the other would fix a near-equilibrium value for the defect concentration. The two possibilities are, therefore:

- Case 1 : $[V_M]^\circ = [V_M]_i^{eq} = \frac{1}{K_i}$ (4.212)

if the external half-reaction is initially slower than the internal one;

- Case 2 : $[V_M]^\circ = [V_M]_e^{eq} = K_e \sqrt{K_a P_{O_2}}$ (4.213)

for the converse situation that the internal half-reaction is initially slower.

In such conditions, integration of (4.211) leads to:

$$[V_M] = \frac{\alpha}{\beta} - \left[\frac{\alpha - \beta [V_M]^\circ}{\beta} \right] \exp(-\beta t) \quad (4.214)$$

Figure 4.23 is a schematic plot showing the variation with time of the cation vacancy concentration for each of the two cases.

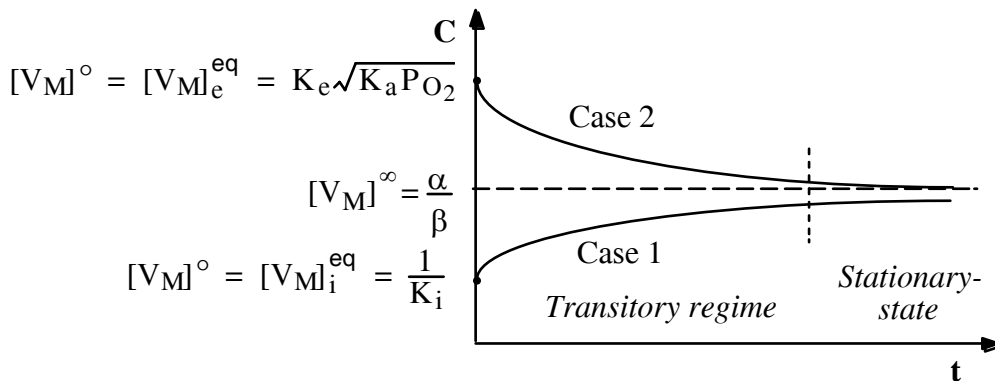


Fig. 4.23. The variation with time of the concentration of cation vacancies in the scale for both of the limiting cases.

For $t \rightarrow 0$, the initial rate of formation of vacancies is:

$$\frac{d[V_M]}{dt} = \alpha - \beta [V_M]^\circ \quad (4.215)$$

For $t \rightarrow \infty$, the rate of formation of vacancies approaches zero and their concentration tends to a steady-state value :

$$[V_M]^\infty = \frac{\alpha}{\beta} = \frac{k'_e \sqrt{K_a P_{O_2}} + k''_i (1 + \sqrt{K_a P_{O_2}})}{k''_e + k'_i (1 + \sqrt{K_a P_{O_2}})} \quad (4.216)$$

Note that this steady-state value is easily verifiable by letting $d[V_M]/dt = 0$ in equation (4.215).

The steady-state is defined as the ideal case where the rates of formation and consumption of the intermediate species are equal. Note that this definition is less restrictive than that proposed above (section 4, Table 4.5) as it does not imply constant interfacial concentrations. Steady-state is never actually achieved in a mixed regime and it is best to think of a *quasi-steady-state* when the rate of change of concentration is small, say, less than an arbitrarily fixed critical value. A *transitory regime* exists before this quasi-steady-state is achieved (see Fig. 4.24).

Expression (4.216) is rather complex but can be simplified into two limiting cases:

• $k'_i \sim k''_i \gg k'_e \sim k''_e$, then

$$[V_M]^\infty = \frac{k''_i}{k'_i} = \frac{1}{K_i} = [V_M]_i^{\text{eq}}$$

which is a pure regime of an external half-reaction (see section 5.1.2)

• $k'_i \sim k''_i \ll k'_e \sim k''_e$, then

$$[V_M]^\infty = \frac{k'_e}{k''_e} \sqrt{K_a P_{O_2}} = K_e \sqrt{K_a P_{O_2}} = [V_M]_e^{\text{eq}}$$

which is a pure regime of an internal half-reaction (see section 5.1.3).

The pure regimes naturally appear as limiting cases of the mixed regimes.

• Oxidation rate

Let us define the rate of oxidation by the rate of mass gain due to the incorporation of oxygen at the external interface:

$$\frac{d\Delta m}{dt} = M_O \frac{dn_O}{dt} = M_O (k'_e \theta - k''_e (1 - \theta) [V_M]) \quad (4.217)$$

with $[V_M]$ given by equation (4.214).

Integrating this equation gives the expression for the extent of reaction as defined by the mass gain:

$$\Delta m = A t - \frac{B}{\beta} \exp (1 - \beta t) \quad (4.218)$$

in which A and B are constants that depend on the elementary rate constants (k'_e , k'_i , k''_e , k''_i) and on K_i or K_a , K_e , P_{O_2} depending on whether Case 1 or 2, as defined above, is followed.

The rate law then exhibits an initial transient stage before a constant rate is achieved and the mass gain increases linearly with time:

$$\Delta m = M_O \left[\frac{k'_e k'_i \sqrt{K_a P_{O_2}} - k''_i k''_e}{k''_e + k'_i (1 + \sqrt{K_a P_{O_2}})} \right] \cdot t \quad (4.219)$$

The two possibilities are shown schematically in Fig. 4.24. If the initial rate-limiting step is internal, then the oxidation rate decreases in the early stages (Case 2). In the other case, that the initial rate-limiting step is external (Case 2), the initial oxidation rate is very low and then increases with time to the steady-state value.

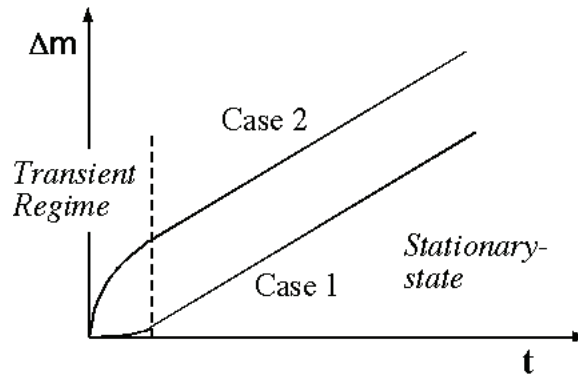


Fig. 4.24. Kinetic curves for two cases of mixed regimes involving external and internal half-reactions.

6.4. Mixed regime of diffusion-internal reaction: oxidation of silicon

The oxidation of silicon is of major technical importance as it generates SiO₂ the dielectric compound of MOS (Metal-Oxide-Semiconductor) electronic devices. The mechanism of this reaction has been described by Deal and Grove¹⁸ who explained the observed linear-parabolic rate law. In fact, the model is more general and had been proposed previously for a number of metals and alloys^{19,20}. In the case of silicon, the following elementary steps are envisaged:

- $O_2 + s \rightleftharpoons O_2-s$ fast chemisorption without dissociation
- $O_2-s \rightleftharpoons (O_2)_i + s$ fast formation of molecular oxygen interstitials at the external interface
- Slow diffusion of molecular interstitials through the SiO₂ scale
- $(O_2)_i + Si \rightarrow SiO_2$ slow internal half-reaction

Thermodynamic equilibrium is assumed to be achieved at the external interface, fixing the concentration $[(O_2)_i]_{ext}^{eq}$ of interstitials. In this section, the subscripts “int” and “ext” are used for “internal” and “external” to avoid confusion with the subscript “i” used for “interstitial”. The diffusion coefficient D of interstitials is not infinite and so the internal half-reaction is not at equilibrium; it will have a rate constant k'_i in the forward direction of finite value and a constant k''_i in the backward direction that is assumed to be zero.

• The concentration of oxygen interstitials at the metal-scale interface

The differential equation governing the concentration of the point defect $[(O_2)_i]_{int}$ at the internal interface can be derived from the above elementary steps:

$$a \frac{d[(O_2)_i]_{int}}{dt} = \frac{D}{y} \{ [(O_2)_i]_{ext}^{eq} - [(O_2)_i]_{int} \} - k'_i [(O_2)_i]_{int} \quad (4.220)$$

The parameter a has the dimension of length and represents, for example, the size of the unit cell of the oxide.

As equation 4.220 contains two time-dependent variables, $[(O_2)_i]_{int}$ and y , complete solution of the equation is not possible. However, a steady-state approximation can be obtained by using one of two procedures: considering the mass balance at the internal interface or using the “slowness rule”.

¹⁸ B.E. Deal et A.S. Grove, *J. Appl. Phys.*, **36** (1965) 3770

¹⁹ U.R. Evans, *Trans. Electrochem. Soc.*, **46** (1924) 247.

²⁰ K. Fischbeck, *Z. Elektrochem.*, **39** (1933) 316.

6.4.1. Mass balance approach

The steady or stationary state is attained when the inward and outward fluxes at the internal interface are equal:

$$D \left(\frac{[(O_2)]_{\text{ext}}^{\text{eq}} - [(O_2)]_{\text{int}}^{\text{stat.}}}{y} \right) = k'_i [(O_2)]_{\text{int}}^{\text{stat}} \quad (4.221)$$

which leads to:

$$[(O_2)]_{\text{int}}^{\text{stat}} = \frac{[(O_2)]_{\text{ext}}^{\text{eq}}}{\left(1 + \frac{k'_i}{D} y\right)} \quad (4.222)$$

with $[(O_2)]_{\text{ext}}^{\text{eq}} = K_e K_a P_{O_2} = \text{constant value}$.

It is therefore observed that, at steady state, the defect concentration at the internal interface is not constant but decreases as scale thickness increases. This example shows clearly that the general definition of the steady state must be expressed in terms of the mass balance and not as a constant interfacial concentration (see section 6.3).

The rate law is given by:

$$\frac{dy}{dt} = \Omega k'_i [(O_2)]_{\text{int}}^{\text{stat}} = \frac{[(O_2)]_{\text{ext}}^{\text{eq}}}{\left[\frac{1}{\Omega k'_i} + \frac{y}{\Omega D}\right]} \quad (4.223)$$

Let us define the linear and parabolic rate constants by:

$$k'_l = k'_i \Omega [(O_2)]_{\text{ext}}^{\text{eq}} \quad (4.224)$$

and

$$k'_p = 2 D \Omega [(O_2)]_{\text{ext}}^{\text{eq}} \quad (4.225)$$

so that equation (4.223) then becomes :

$$\frac{dy}{dt} = \frac{1}{\left[\frac{1}{k'_l} + \frac{2y}{k'_p}\right]} \quad (4.226)$$

or

$$\frac{dy}{k'_l} + 2 \frac{y}{k'_p} dy = dt \quad (4.227)$$

which gives after integration :

$$\frac{y^2}{k'_p} + \frac{y}{k'_l} = t \quad (4.228)$$

Considering that, for $t = 0$, a thin oxide layer of thickness y_0 covers the silicon sample, it follows that:

$$\frac{y^2 - y_0^2}{k'_p} + \frac{y - y_0}{k'_l} = t \quad (4.229)$$

This expression is known as the “Deal and Grove law”. It can also be written as:

$$\frac{y^2}{k'_p} + \frac{y}{k'_l} = t + \tau \quad (4.230)$$

It is easy to verify that:

- for $t \rightarrow 0$, $y \rightarrow k'_l(t + \tau)$ and the rate law is linear
- for $t \rightarrow \infty$, $y^2 = k'_p(t + \tau)$ and the rate law is parabolic.

In this case, steady state kinetics lead to the “linear-parabolic” law, as shown schematically in Fig. 4.25.

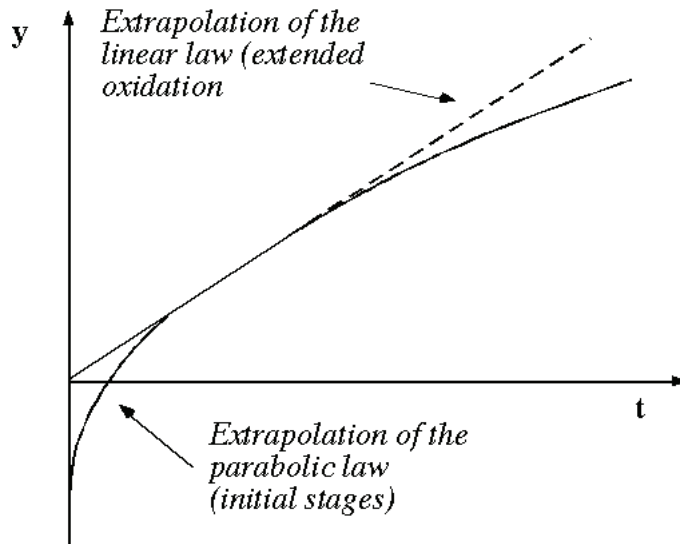


Fig. 4.25. Linear-parabolic rate law as the result of stationary mixed kinetics limited by diffusion and internal half-reaction.

For convenient determination of the constants, two linear transforms are commonly used:

- t/y as a function of y , giving

$$\frac{t}{y} = \frac{y}{k'_p} + \frac{1}{k'_l} \quad \text{valid for } y \gg y_0 \text{ only,}$$
- dt/dy as a function of y , giving

$$\frac{dt}{dy} = \frac{2y}{k'_p} + \frac{1}{k'_l} \quad \text{valid for any } y, \text{ even very small.}$$

These two transforms are shown in Fig. 4.26 together with the appropriate values of the slope and intercept. These constructions are very useful for determining the values of the rate constants.

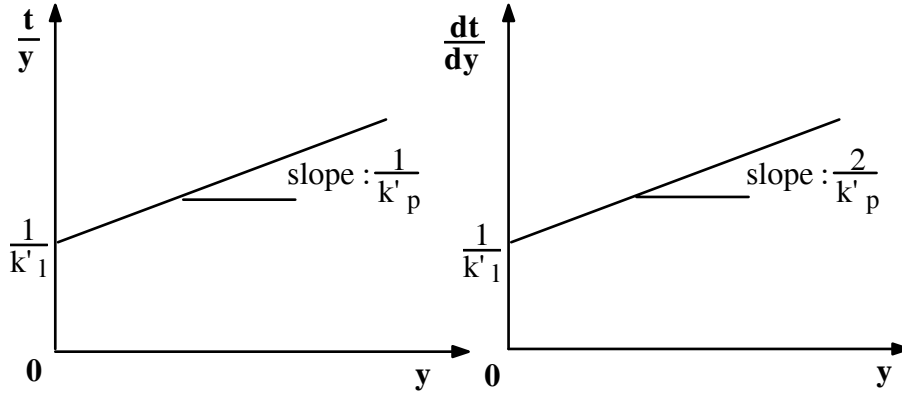


Fig. 4.26. Linear transforms for the linear-parabolic rate law.

6.4.2. Application of the Slowness Rule

“Slowness” is defined as the inverse ($1/R$) of the reaction rate, R . The rule of slowness is as follows:

“In a mixed kinetic regime, the slowness of the overall reaction is the sum of the slowness of each limiting step considered alone”.

In the present case:

$$\frac{1}{R} = \frac{1}{R_{\text{reaction}}} + \frac{1}{R_{\text{diffusion}}} \quad (4.231)$$

or:

$$\Omega \frac{dt}{dy} = \frac{1}{k'_i [(O_2)_{i_{\text{int}}} - k''_i]} + \frac{y}{D [(O_2)_{i_{\text{ext}}} - (O_2)_{i_{\text{int}}}] } \quad (4.232)$$

For the first term of this equation, $[(O_2)_i]_{int} = [(O_2)_i]_{ext}^{eq}$ and is slower than the half-reaction considered alone. The second term represents a diffusion controlled regime for which the internal and external concentrations are at equilibrium:

$$[(O_2)_i]_{int} = [(O_2)_i]_{int}^{eq} = \frac{1}{K_i} \text{ and } [(O_2)_i]_{ext} = [(O_2)_i]_{ext}^{eq} = K_e K_a P_{O_2}.$$

Recalling that $k'_i/k''_i = K_i$, equation (4.232) becomes:

$$\Omega \frac{dt}{dy} = \frac{1}{k'_i \left([(O_2)_i]_{ext}^{eq} - \frac{1}{K_i} \right)} + \frac{y}{D \left([(O_2)_i]_{ext}^{eq} - \frac{1}{K_i} \right)} \quad (4.233)$$

Similar results to those obtained by Deal and Grove can be obtained by defining:

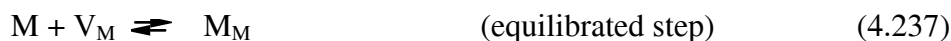
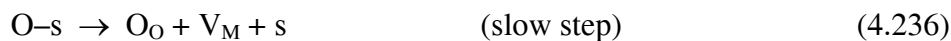
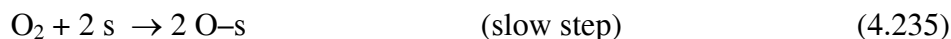
$$k'_p = 2 D \Omega \left\{ [(O_2)_i]_{ext}^{eq} - \frac{1}{K_i} \right\} \text{ and } k'_l = \Omega k'_i \left\{ [(O_2)_i]_{ext}^{eq} - \frac{1}{K_i} \right\} \quad (4.234)$$

The present formalism is more rigorous, however, since it takes the reverse step of the internal half-reaction into account. This was omitted in the mass balance calculation undertaken by Deal and Grove.

The same approach has been used for oxides containing other principal point defects such as cation vacancies²¹.

6.5. Mixed regime of sorption with an external half reaction

As in section 6.3, consider the following three elementary steps :



In the present case, the internal half-reaction is assumed to be at equilibrium and the diffusion coefficient of vacancies in the oxide is considered to be infinite. On the other hand, the sorption and external reactions are assumed to have finite rate constants. The situation is described in Fig. 4.27.

²¹ F.S. Pettit and J.B. Wagner Jr., *Acta Metallurgica*, **12** (1964) 35-40

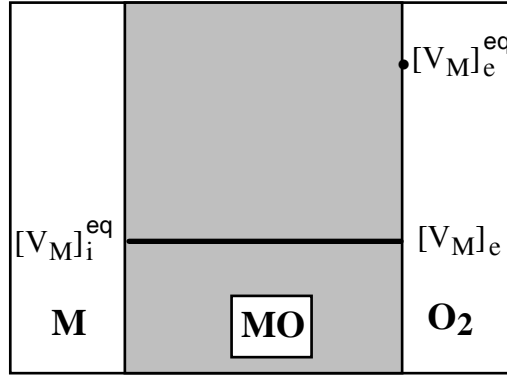


Fig. 4.27. Concentration profile of the cation vacancies in the oxide scale according to a mixed regime of sorption and an external half-reaction.

The differential equation for the mass balance at the external interface is:

$$s_0 \frac{d\theta}{dt} = k'_a P_{O_2} (1 - \theta)^2 - k''_a \theta^2 - k'_e \theta + k''_e (1 - \theta) [V_M]_i^{eq} \quad (4.238)$$

This equation cannot be integrated analytically and numerical methods have to be employed to determine the variation of θ with time, t . However, the steady-state (stationary) solution is easily obtained as:

$$k'_a P_{O_2} (1 - \theta)^2 + k''_e [V_M]_i^{eq} (1 - \theta) = k''_a \theta^2 + k'_e \theta \quad (4.239)$$

leading to:

$\theta_{stat.} =$

$$\frac{2 k'_a P_{O_2} + k'_e + k''_e [V_M]_i^{eq} \pm \sqrt{(2 k'_a P_{O_2} + k'_e + k''_e [V_M]_i^{eq})^2 - 4 (k'_a P_{O_2} - k''_a) (k'_a P_{O_2} + k'_e [V_M]_i^{eq})}}{2 (k'_a P_{O_2} - k''_a)} \quad (4.240)$$

where the smallest root (obtained using the minus sign) has physical meaning (i.e. $\theta \leq 1$).

This expression is complex but numerical values can be readily obtained. It may, however, be simplified by considering only the forward reactions and neglecting those in the backward direction i.e. $k''_a = k''_e = 0$. This leads to :

$$k'_a P_{O_2} (1 - \theta)^2 = k'_e \theta \quad (4.241)$$

from which one obtains :

$$\theta_{\text{stat.}} = \frac{2 k'_a P_{\text{O}_2} + k'_e - \sqrt{4 k'_a k'_e P_{\text{O}_2} + k'^2_e}}{2 k'_a P_{\text{O}_2}} \quad (4.242).$$

The rate law, assuming steady-state conditions from $t = 0$, is therefore* :

$$\Delta m = M_{\text{O}} k'_e \theta_{\text{stat.}} t = M_{\text{O}} k'_e \left[\frac{2 k'_a P_{\text{O}_2} + k'_e - \sqrt{4 k'_a k'_e P_{\text{O}_2} + k'^2_e}}{2 k'_a P_{\text{O}_2}} \right] t \quad (4.243).$$

where M_{O} is the atomic mass of oxygen.

It is interesting to note that the influences of temperature and oxygen pressure on the oxidation rate derived from equations (4.240) is complex but that they simplify when k'_a and k''_a are much larger or much lower than k'_e and k''_e . They then correspond to the expressions (4.46) or (4.54) obtained for the cases of pure sorption or a pure external half-reaction.

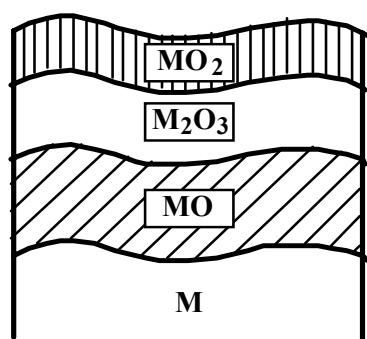
*It has been chosen here to express the extent of oxidation by the amount of oxygen as oxide. Another possible choice is to use the total amount of oxygen in the sample. The difference is the amount of oxygen in the adsorbed phase but this is usually negligible.

Chapter 5

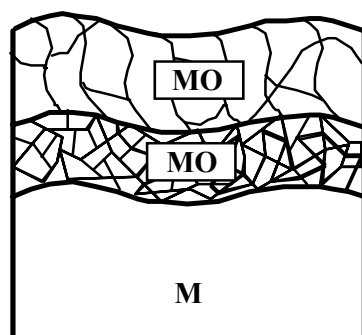
KINETICS ASPECTS OF HIGH TEMPERATURE CORROSION: Formation of multilayered scales

1. INTRODUCTION

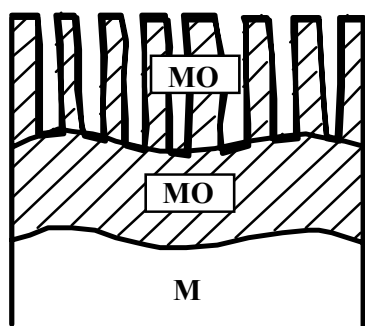
The formation of several corrosion scales on metals or alloys is often observed. These scales may all be compact, exhibiting different morphologies and/or compositions, or one, or several, may be porous. Different possibilities encountered on pure metals are presented in Fig. 5.1.



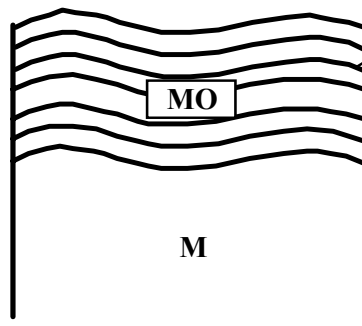
Multilayered compact scales with different compositions



Multilayered compact scales with different morphologies



Formation of compact and porous scales



Laminated scale

Fig. 5.1. Different possible morphologies of oxide scales formed on a pure metal.

In order to understand clearly the growth mechanisms of these scales, it is of major importance to know whether they form concurrently or sequentially. By *sequentially*, we mean that an individual layer or a group of layers forms after the earlier formation of a layer or layers. Two cases are to be considered:

- all subscales are formed in the same sequence : the mechanism necessarily involves a mixed regime;
- several layers are formed in one sequence, several others in another sequence; the mechanism involves “parallel sequences” which may be pure or mixed depending on the number of rate-limiting steps in each sequence (one or several).

Several of these case are of technological importance; they are described in the following.

2. FORMATION OF COMPACT LAYERED SCALES

2.1. Several compact layers form in the same sequence

2.1.1. Description of the System

Consider a metal M forming a compact duplex scale containing for example M_2O and MO . Suppose that these oxides are cation vacancy p-type oxides and that, for simplification, the point defects will be considered to be neutral. The defect fluxes leading to scale growth are shown in Fig. 5.2.

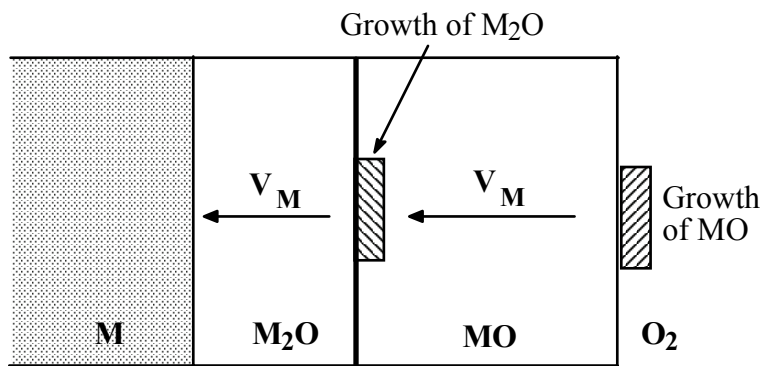
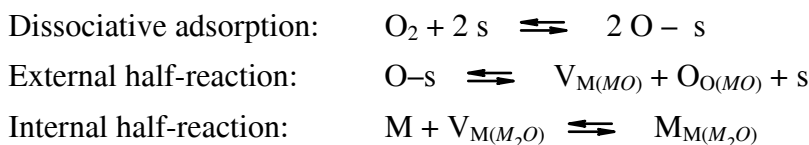


Fig. 5.2. Schematic presentation of the defect fluxes causing the growth of layers of two p-type cation vacancy oxides.

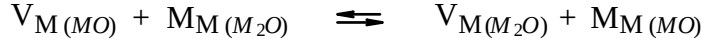
2.1.2. The Nature of the Elementary Reactions

In the present case, there are four discrete interfacial reactions. Three of these are identical to those for the growth of a single –layered scale:

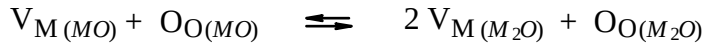


The fourth interfacial reaction is more complex; it is situated at the M_2O - MO interface and consists of two parallel steps :

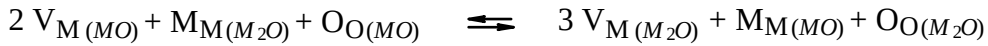
- transfer of cation vacancies from MO to M_2O by a jump of M^+ which oxidises to M^{2+} without any interface displacement :



- reduction of MO to M_2O with a corresponding external displacement of the interface :



A global expression for these interfacial reactions is therefore :



2.1.3. Kinetic aspects

We shall limit ourselves to considering the case where the scale growth occurs through a combination of slow diffusion in both the M_2O and MO layers. In this case, the oxygen chemical potentials reach equilibrium at each interface and, thereby, fix the stoichiometry of these oxides at these interfaces. The situation is described in Fig. 5.3, recalling that the cation vacancies are supposed to be neutral.

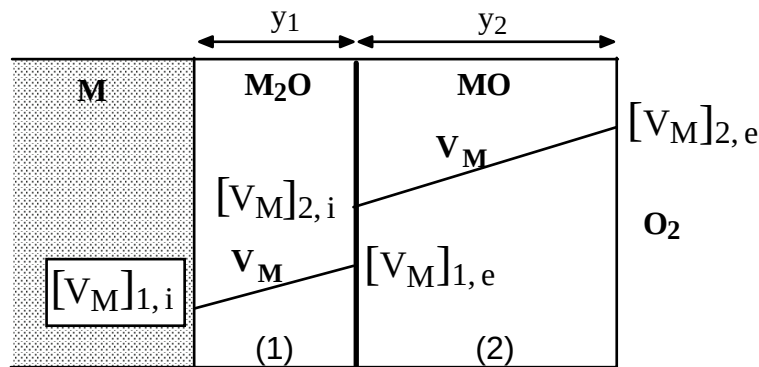


Fig. 5.3. Schematic description of the growth of a duplex scale in a mixed diffusion regime.

Model 1 :

The simplest model envisages that the growth of each layer is independent of the growth of the other :

$$\frac{2}{\Omega_1} \frac{dy_1}{dt} = D_1 \frac{\Delta C_1}{y_1} \quad \text{then: } y_1^2 = k'_{p1} t \quad \text{with } k'_{p1} = \Omega_1 D_1 \Delta C_1 \quad (5.1)$$

$$\frac{1}{\Omega_2} \frac{dy_2}{dt} = D_2 \frac{\Delta C_2}{y_2} \quad \text{then: } y_2^2 = k'_{p2} t \quad \text{with } k'_{p2} = 2 \Omega_2 D_2 \Delta C_2 \quad (5.2)$$

In these equations, the subscripts 1 and 2 refer to the M_2O and MO layers respectively. ΔC is the concentration difference, between the two interfaces of each oxide, of the corresponding point defect ; Ω_1 and Ω_2 are the respective molar volumes.

Defining the total oxide thickness y from Figure 5.3 as $y = y_1 + y_2$, it follows that:

$$y^2 = k'_p t \quad \text{with } k'_p{}^{1/2} = k'_{p1}{}^{1/2} + k'_{p2}{}^{1/2} \quad (5.3)$$

The rate law here is parabolic and the rate constant will show a complex dependence on temperature and pressure. The ratio of the thicknesses of the two layers is exactly equal to the square root of the ratio of their parabolic rate constants :

$$\left(\frac{y_2}{y_1}\right) = \sqrt{\frac{k'_{p2}}{k'_{p1}}} \quad (5.4)$$

Model 2 :

Model 1, presented above, is oversimplified as it does not take into account the displacement of the oxide/oxide interface. It can be developed further by considering the cation flux involved in the growth of each layer .

The cation flux in subscale 1 is

$$J_M = \frac{1}{\Omega_1} \frac{k'_{p1}}{y_1} \quad (5.5)$$

and the amounts, Q , of metal consumed per unit area to form layers 1 and 2 are, respectively

$$Q_1 = \frac{2 y_1}{\Omega_1} \quad \text{and} \quad Q_2 = \frac{y_2}{\Omega_2} \quad (5.6)$$

The fractions of the cation flux involved in the growth of subscales 1 and 2 are, respectively

$$J_{M(M_2O)} = \frac{Q_1}{Q_1 + Q_2} J_M = \frac{2 y_1}{\Omega_1} \frac{1}{\frac{2 y_1}{\Omega_1} + \frac{y_2}{\Omega_2}} \left[\frac{1}{\Omega_1} \frac{k'_{p1}}{y_1} \right] \quad (5.7)$$

$$J_{M(MO)} = \frac{Q_2}{Q_1 + Q_2} J_M = \frac{y_2}{\Omega_2} \frac{1}{\frac{2 y_1}{\Omega_1} + \frac{y_2}{\Omega_2}} \left[\frac{1}{\Omega_1} \frac{k'_{p1}}{y_1} \right] \quad (5.8)$$

with $J_M = J_{M(M_2O)} + J_{M(MO)}$

With this model, it is not possible to express simply the ratio of the thickness of both subscales. However, the ratio of parabolic rate constants can be obtain as:

$$\frac{k'_{p2}}{k'_{p1}} = \left(\frac{y_2}{y_1} \right)^2 \cdot \frac{1 + \frac{\Omega_1 \cdot y_1}{2 \Omega_2 \cdot y_2}}{1 + \frac{2 \Omega_2 \cdot y_2}{\Omega_1 \cdot y_1}} \quad (5.9)$$

When one of the layers is much larger than the other, this expression simplifies to:

$$\text{if } y_2 \gg y_1 \quad \frac{y_2}{y_1} = \frac{k'_{p2}}{k'_{p1}} \cdot \frac{\Omega_1}{2 \Omega_2} \quad (5.10)$$

$$\text{and, if } y_2 \ll y_1 : \quad \frac{y_2}{y_1} = \frac{k'_{p2}}{k'_{p1}} \cdot \frac{\Omega_1}{\Omega_2} \quad (5.11)$$

It appears that this ratio is directly proportional to the ratio of parabolic rate constants for the growth of each layer alone, i.e. roughly proportional to the ratio of the self-diffusion coefficients of the mobile species.

2.1.4. Example of copper oxidation

At temperatures lower than 1000°C and for oxygen pressures around atmospheric, copper has two possible stable oxides : Cu₂O (cuprite) and CuO (tenorite). These oxides form a duplex scale on copper such that Cu₂O is in contact with the metal and CuO is in contact with the gas.

The isothermal gravimetric rate law is parabolic, without any dependence on oxygen pressure, contrary to what is observed when CuO is absent, i.e. at higher temperatures and/or lower O₂ pressures (see section 6, Chapter 7). Such a pressure independence is possibly related to the small thickness of CuO compared with Cu₂O, ensuring that the weight gain is due only to Cu₂O growth under the constant oxygen pressure fixed by the Cu₂O-CuO equilibrium whatever the value of external pressure.

Observation of both layers shows that the relative thickness of CuO reduces when the temperature increases (Fig. 5.4). This is consistent with a lower activation energy for the self diffusion of copper in tenorite than in cuprite.

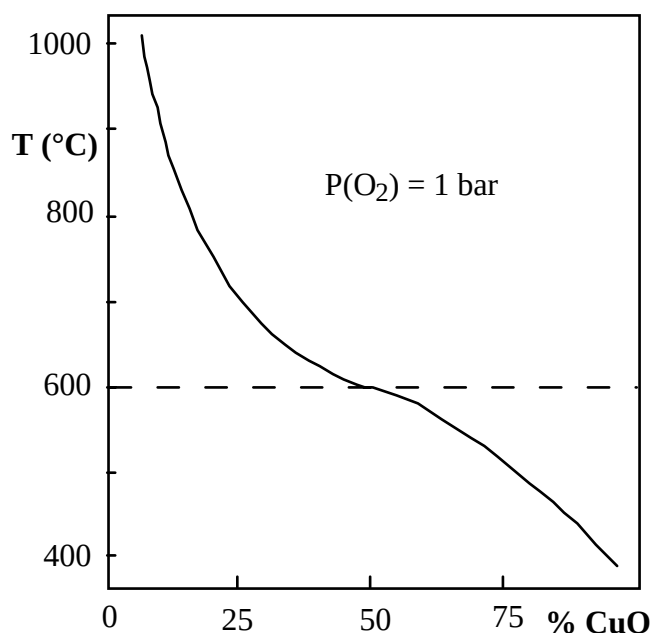


Fig. 5.4. The change with temperature of the fraction of CuO in the Cu₂O-CuO duplex scale grown on copper in oxygen atmosphere.

2.1.5. Example of iron oxidation

In near atmospheric pressure of pure oxygen and temperatures above 600°C, iron oxidises to produce a three-layered oxide scale: an internal subscale or wüstite Fe_{1-x}O, magnetite Fe_{3-x}O₄ and haematite Fe₂O_{3-x}. The relative thicknesses at 1000°C are roughly as follows :

wüstite : 95%
 magnetite : 4%
 haematite 1%.

As the predominant point defects at $T < 1000^\circ\text{C}$ are cation vacancies for the lowest valency p-type oxides and anion vacancies for n-type haematite, it is possible to show schematically the particle fluxes responsible for scale growth as in Fig. 5.5.

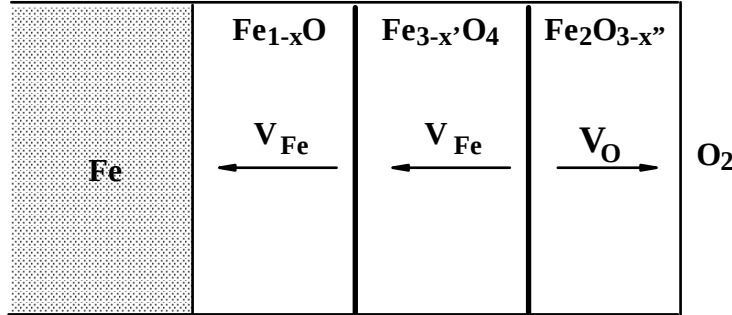
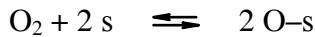


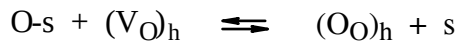
Fig. 5.5. Point defect movements for the growth of the three-layered oxide scale on iron.

Again assuming the point defects to be neutral and designating wüstite by w , magnetite by m and haematite by h , we have the following reactions :

- *Dissociative sorption*

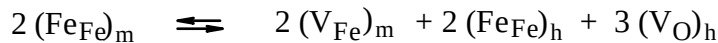


- *External reaction*

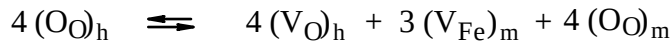


- *Haematite-magnetite interface reactions*

- growth of haematite

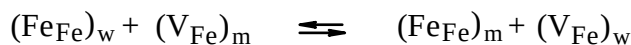


- growth of magnetite

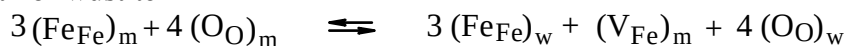


Magnetite-wüstite interface reactions

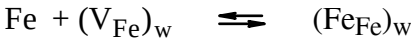
- transfer of cation vacancies



- growth of wüstite



Internal reaction:



From these equations, it can be appreciated that wüstite grows at its interface with the magnetite layer by the reduction of the latter. Magnetite grows at the magnetite-haematite interface where haematite also grows. This interface is therefore immobile due to the opposite directions of defect transport within these two oxides.

The oxidation rate law is parabolic and, as a simplified kinetic model, it may be assumed that all interfacial equilibria are achieved and that diffusion through all three subscales is rate-limiting. The respective thicknesses of the wüstite, magnetite and haematite subscales are in good agreement with the model discussed in section 2.1.3, as they are in the same ranking order as the diffusion coefficients of the major diffusing species within each scale (Figure 5.6).

2.2. Two compact subscales formed by two parallel sequences

Let us consider an oxide in which both cations and anions are mobile and with diffusion coefficients of similar magnitude. This situation may lead to the formation of a duplex scale of the same oxide, i.e. of the same chemical composition, growing in two opposite directions. Oxidising, for example, chromium metal at temperatures near 900°C may generate external columnar and internal equiaxed Cr₂O₃ subscales (Fig. 5.7).

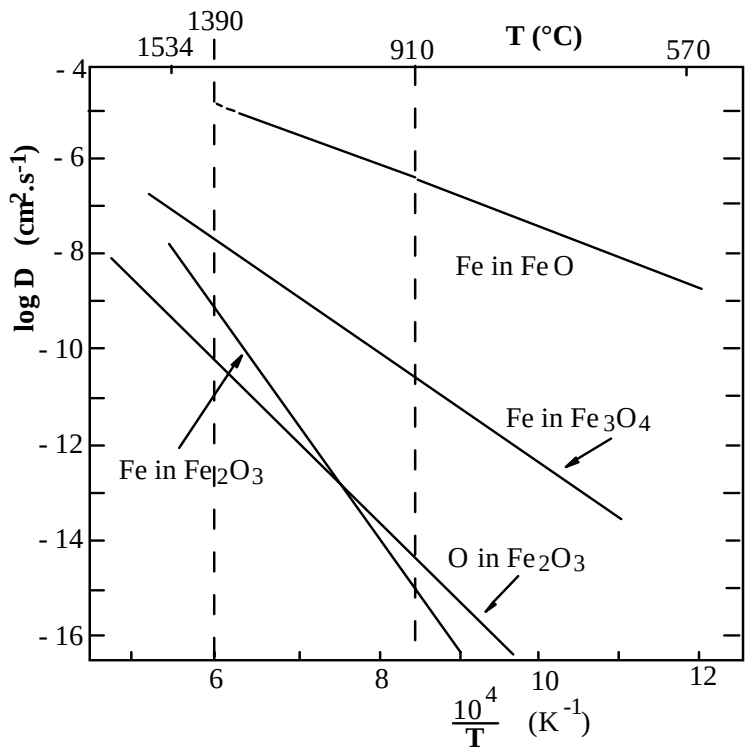


Fig. 5.6. Self-diffusion coefficients of iron and oxygen in iron oxides.

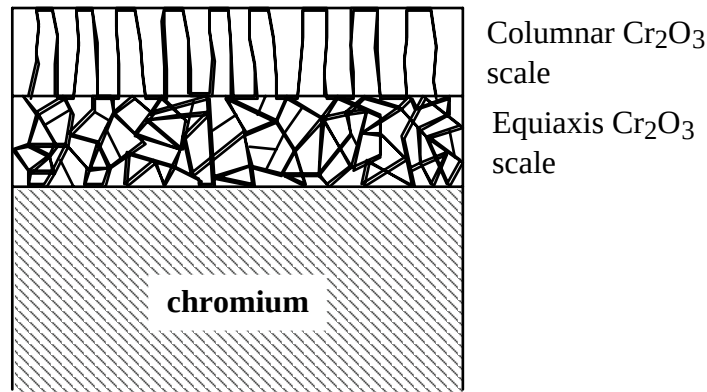


Fig. 5.7. Schematic cross-section of the chromia duplex scale grown on chromium.

Assuming chromium vacancies and oxygen interstitials are mobile in chromia, the respective defect fluxes and the corresponding locations of growth of the subscales are shown in Fig. 5.8.

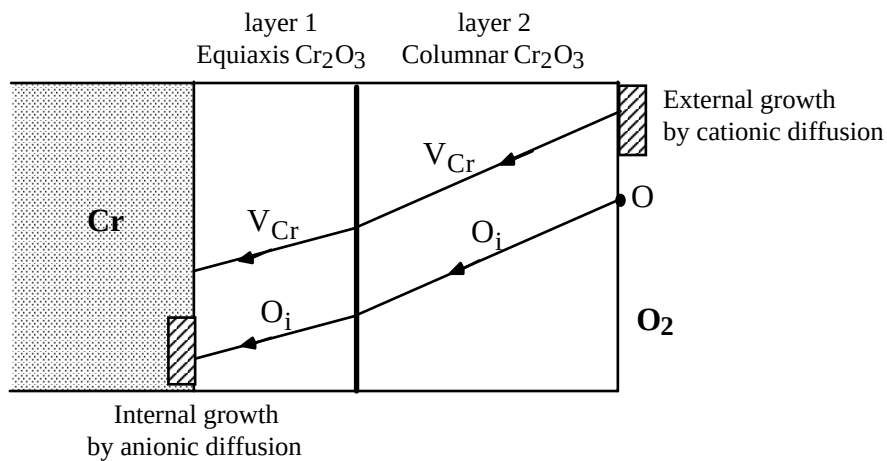


Fig. 5.8. Defect fluxes causing the growth of a chromia duplex scale by opposite mass transport.

A similar case is observed on low-chromium steels, such as Fe-2.25Cr-1Mo or Fe-5Cr, where two subscales of different compositions form (Fig. 5.9). The same scale morphology is also produced on stainless steels when exposed to water vapour.

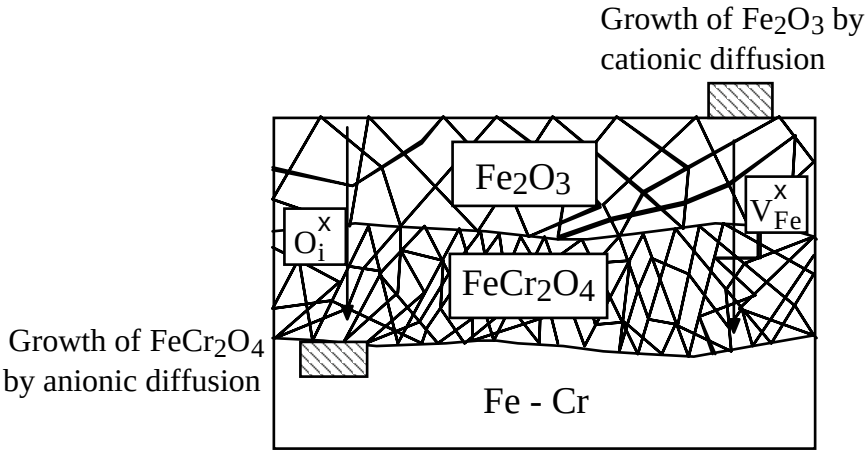


Fig. 5.9. Schematic cross-section of the duplex scale formed on iron-chromium alloys by the opposite transport of oxygen and iron.

Kinetic aspect

For simplification, we limit the analysis to the case where both oxide layers consist of the same oxide, MO , containing metal vacancies and oxygen interstitials as in Fig. 5.7. If diffusion is the controlling process, two cases are to be studied depending on the location of the rate-limiting step, i.e. within the layer grown by the diffusion of a particular ion or in the subscale grown by the other.

1st case : Pure parallel diffusion sequences with the rate control of growth of each located within the respective subscale.

This situation is depicted by Fig. 5.10 for the case of the oxidation of chromium.

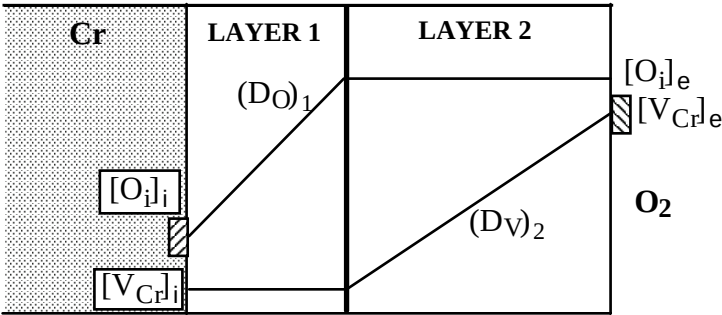


Fig. 5.10. The transport of a given ion through the scale is limited by its diffusion through the subscale for which it is responsible for growth.

In steady-state, neglecting the smallest of the interfacial defect concentrations in each case, the diffusion fluxes can be written as:

$$J_{V_M} = \frac{(D_V)_2 \cdot [V_{Cr}]_e}{y_2} = \frac{1}{\Omega} \frac{dy_2}{dt} \quad (5.12)$$

$$J_{O_i} = \frac{(D_O)_1 \cdot [O_i]_e}{y_1} = \frac{1}{\Omega} \frac{dy_1}{dt} \quad (5.13)$$

leading by integration to:

$$y^2 = k'_p t \text{ with } (k'_p)^{1/2} = (k'_{p1})^{1/2} + (k'_{p2})^{1/2} \quad (5.14)$$

where:

$$k'_{p1} = 2 \Omega (D_O)_1 \cdot [O_i]_e \quad \text{and} \quad k'_{p2} = 2 \Omega (D_V)_2 \cdot [V_{Cr}]_e \quad (5.15)$$

The resulting rate law is parabolic and the influence of oxygen pressure is a complex combination of its influence on both the vacancy and interstitial concentrations at the external interface.

2nd case: Pure parallel diffusion sequences with rate control arising in the subscale grown by the concurrent sequence.

This case is depicted by Fig. 5.11.

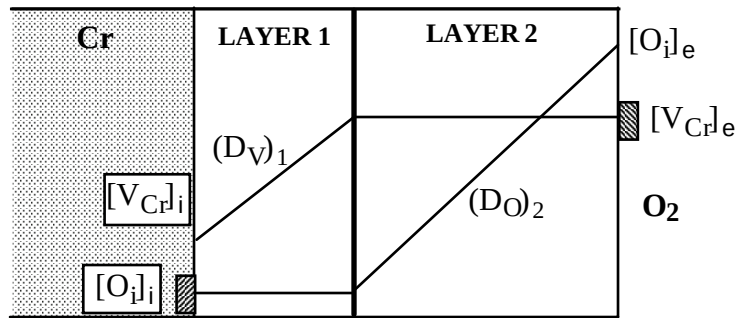


Fig. 5.11. The transport of a given ion through the scale is limited by its diffusion through the layer grown by the other ion.

The defect fluxes are then:

$$J_{V_M} = \frac{(D_V)_1 \cdot [V_{Cr}]_e}{y_1} = \frac{1}{\Omega} \frac{dy_2}{dt} \quad (5.16)$$

$$J_{O_i} = \frac{(D_O)_2 \cdot [O_i]_e}{y_2} = \frac{1}{\Omega} \frac{dy_1}{dt} \quad (5.17)$$

and the differential system is:

$$y_1 \cdot dy_2 = \Omega (D_V)_1 \cdot [V_{Cr}]_e dt \quad (5.18)$$

$$y_2 \cdot dy_1 = \Omega (D_O)_2 \cdot [O_i]_e dt \quad (5.19)$$

By defining: $\alpha = \Omega (D_V)_1 [V_{Cr}]_e$ (5.20)

and $\beta = \Omega (D_O)_2 [O_i]_e$ (5.21)

it follows that:

$$y_1 \frac{dy_2}{dt} = \alpha \quad \text{and} \quad y_2 \frac{dy_1}{dt} = \beta \quad (5.22)$$

Since α and β parameters are constants, we obtain:

$$\frac{d(y_2 y_1)}{dt} = \alpha + \beta \quad (5.23)$$

leading to: $y_1 y_2 = (\alpha + \beta) t$.

By substitution, one obtains : $\frac{dy_2}{y_2} = \frac{\alpha}{\alpha + \beta} \frac{dt}{t}$

so that: $\ln \left(\frac{y_2}{(y_2)_0} \right) = \frac{\alpha}{\alpha + \beta} \ln \frac{t}{t_0}$

with $y_2 = (y_2)_0$ at $t = t_0 \neq 0$.

The thickness of each scale is therefore given by:

$$y_2 = (y_2)_0 \cdot [t_0]^{-(\alpha/(\alpha+\beta))} \cdot [t]^{(\alpha/(\alpha+\beta))} \quad (5.24)$$

$$y_1 = (y_1)_0 \cdot [t_0]^{-(\beta/(\alpha+\beta))} \cdot [t]^{(\beta/(\alpha+\beta))} \quad (5.25)$$

The extent of reaction, defined by the total thickness of the scale $y = y_1 + y_2$ is therefore:

$$y = A \cdot (t^{(\alpha/(\alpha+\beta))} + t^{(\beta/(\alpha+\beta))}) \quad (5.26)$$

It can be appreciated that this rate law is strictly parabolic only when $\alpha = \beta$, that is when the cation and anion self-diffusion coefficients, defined as (see Chapter 3, section 2.1.3):

$$D_M = D_V \cdot [V_M]_e \quad \text{and} \quad D_O = D_{O_i} \cdot [O_i]_e$$

are equal. When they differ, the rate law deviates from parabolic and tends to linear, as observed in Fig. 5.12.

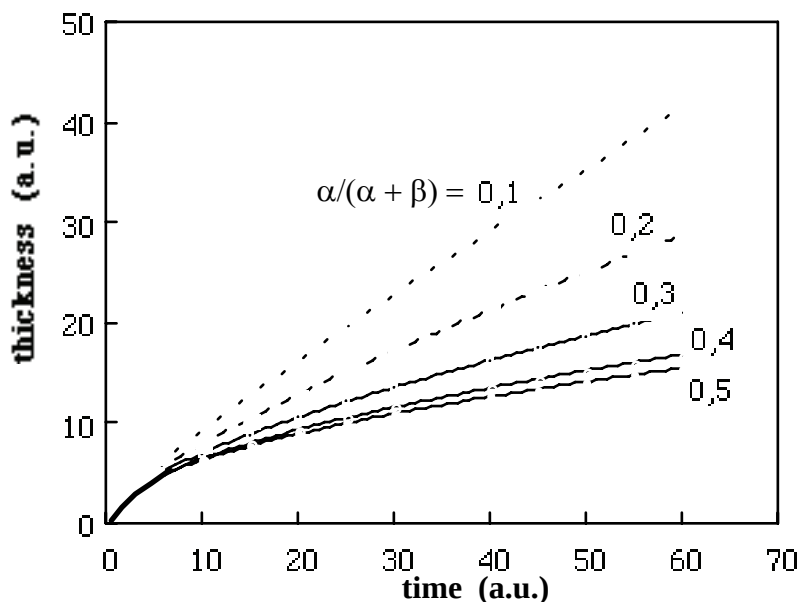


Fig 5.12. Numerical simulation of the growth of a duplex scale according to equation 5.26 showing how increasing the ratio ($\alpha/\alpha + \beta$) changes the rate law from linear to parabolic.

3. FORMATION OF POROUS AND PARTIALLY POROUS SCALES*

3.1. Growth of an external porous oxide layer by oxidation of an inner compact layer (Haycock-Loriers model^{1,2})

Generally, experience shows that the oxidation of a metal is often protective during the early stages but that the protective properties of the scale can be partially or totally lost during later stages. For example, oxidation can lead to the formation of a duplex scale consisting of an inner compact layer adjacent to the metal and an external porous layer formed concurrently by oxidation of the inner compact layer. Such a situation is described in the Haycock-Loriers model.

3.1.1. Quantitative description

According to the Haycock-Loriers model, the oxidation process involves the concurrent growth of an inner compact layer of M_2O_b , controlled by a diffusion mechanism, and its progressive transformation at its outer interface into an external porous layer. The situation is shown schematically in figure 5.13.

* This treatment is also applicable to simultaneous oxidation and evaporation.

¹ J. Loriers, *Comptes Rendus Acad. Sci.*, **231** (1950) 522-524.

² E.W. Haycock, *J. Electrochem. Soc.*, **106** (1959) 771-775.

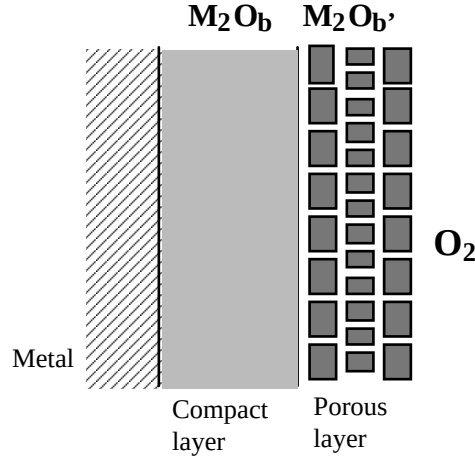


Figure 5.13. The cross-section of the oxide scale consisting of a compact layer of M_2O_b next to the metal and a porous layer of $M_2O_{b'}$ next to the gaseous phase

In the following, Δm_1 and Δm_2 represent the mass of oxygen in the compact and the porous scale, respectively. The rates of growth of the two layers are described by the following expressions:

- the growth of the inner compact layer controlled by diffusional transport:

$$\frac{d(\Delta m_1)}{dt} = \frac{k_p}{2 \Delta m_1} - k_1 \quad (5.27)$$

where k_p is the parabolic rate constant for growth of the layer and k_1 is the rate constant for its transformation;

- rate growth of the outer porous layer controlled by reaction at its interface with the inner compact layer:

$$\frac{d(\Delta m_2)}{dt} = f k_1 \quad (5.28)$$

where $f = \frac{b'}{b}$ is the ratio of the oxygen content in the oxide $M_2O_{b'}$ to that in the oxide M_2O_b .

The equation (5-27) may be rewritten in the form:

$$\frac{\Delta m_1}{1 - 2 \frac{k_1}{k_p} \Delta m_1} \frac{d\Delta m_1}{dt} = \frac{k_p}{2} dt \quad (5.29)$$

Integrating equation (5.29) as a function of the only independent variable Δm_1 , we obtain the expression:

$$\Delta m_1 + \frac{k_p}{2 k_l} \ln \left[1 - 2 \frac{k_l}{k_p} \Delta m_1 \right] + k_l \cdot t = 0 \quad (5.30)$$

Moreover, integration of the differential equation 5.28 gives for Δm_2 :

$$\Delta m_2 = f \cdot k_l \cdot t \quad (5.31)$$

A schematic representation of the partial weight gains Δm_1 and Δm_2 is given in figure 5.14.

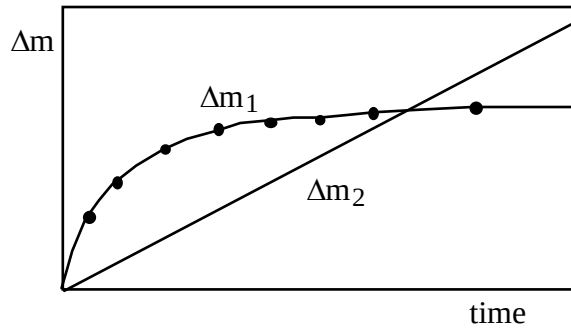


Figure 5.14. Illustration of the respective growth of an inner compact scale, represented by the mass gain, Δm_1 , and an outer porous layer formed from it, represented by the mass gain, Δm_2 .

The total oxidation rate in terms of total mass gain may then be obtained as:

$$\Delta m - k_l (f - 1) t + \frac{k_p}{2 k_l} \ln \left[1 - 2 \frac{k_l}{k_p} (\Delta m - f k_l t) \right] = 0 \quad (5.32)$$

The function $\Delta m = f(t)$ is asymptotic to the straight line given by:

$$\Delta m = f k_l t + \frac{k_p}{2 k_l} \quad (5.33)$$

This equation can be approximated by expansion to its two first terms to give:

$$\Delta m = \sqrt{k_p t} + f k_l t \quad (5.34)$$

This rate equation, illustrated in figure 5.15, describes "paralinear oxidation" for which parabolic kinetics predominate during the early stages of oxidation becoming linear at longer times.

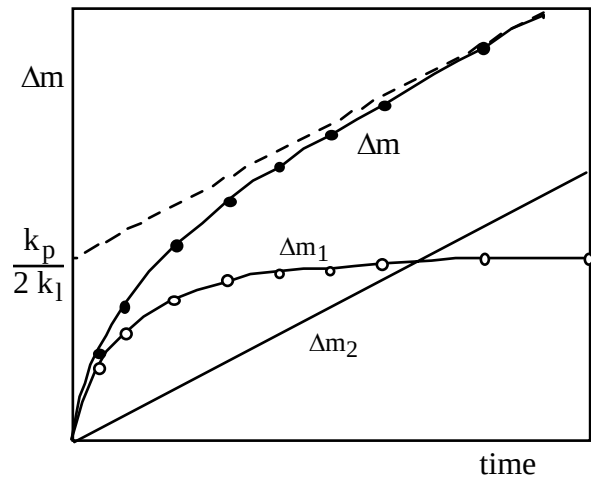


Figure 5.15. Schematic representation of the total weight gain $\Delta m = \Delta m_1 + \Delta m_2$ illustrating the parabolic rate equation.

3.1.2. Particular case of $f = 1$ (Haycock model)

In this case, the scale consists of two layers of the same oxide ($b' = b$). According to Haycock, the outer layer of the scale becomes non protective as a result of crystallization. The situation in the scale is shown schematically in figure 5.16.

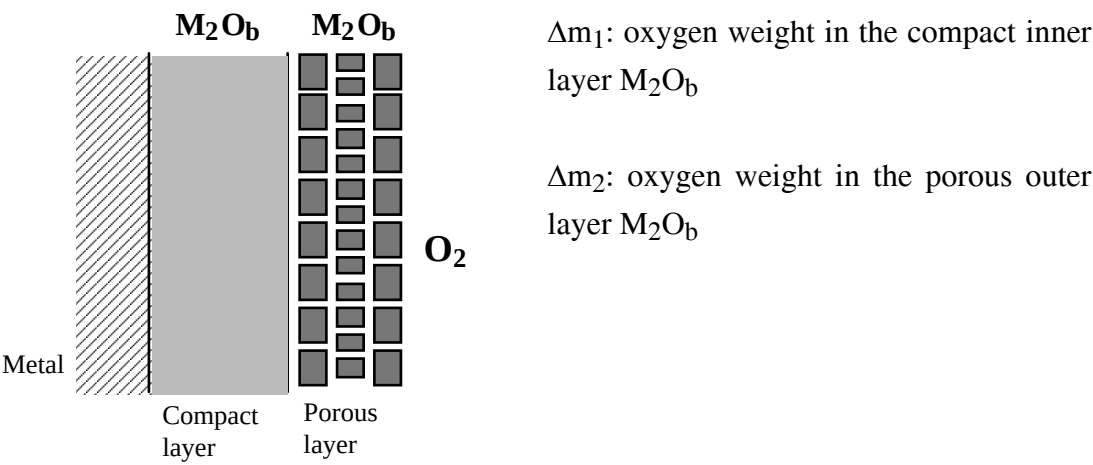


Figure 5.16. Structure of the oxide scale when the two layers are of the same chemical composition.

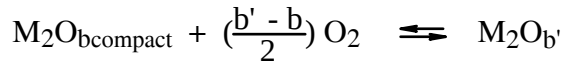
The weight gain Δm is given by the rate equation:

$$\Delta m + \frac{k_p}{2 k_l} \ln \left[1 - \frac{2 k_l}{k_p} (\Delta m - k_l t) \right] = 0 \tag{5.35}$$

where the rate constant k_l is characteristic of a transformation in the solid state.

3.1.3. Oxygen pressure dependence

Under steady state, the reaction rate is controlled by reaction at the oxide/oxide interface:



If $\text{b}' \neq \text{b}$, the rate constant k_1 normally exhibits a large oxygen pressure dependence (see Chapter 4, section 5.12) but if $\text{b}' = \text{b}$, k_1 is characteristic of a solid state transformation and does not depend on the oxygen pressure.

3.1.4. Relevance of paralinear oxidation

Paralinear oxidation is observed during the oxidation of a wide range of metals, especially if mechanical damage occurs to the scale during thermal cycling. This is more likely to be the case if the thermal expansion coefficient of the oxide is much less or greater than unity.

3.2. Formation of stratified scales

3.2.1. Experimental observations

Several metals, particularly in columns IV and V (Ti, Zr, Nb, Ta) of the Periodic Table form stratified scales during their oxidation at high temperatures as a result of periodic cracking of the growing oxide. From a kinetic point of view, such cracking leads to two types of rate laws (Fig. 5.17): the first one is described by successive parabolic or cubic periods (type 1), the second one by an initial parabolic or cubic period followed by a near-linear period.

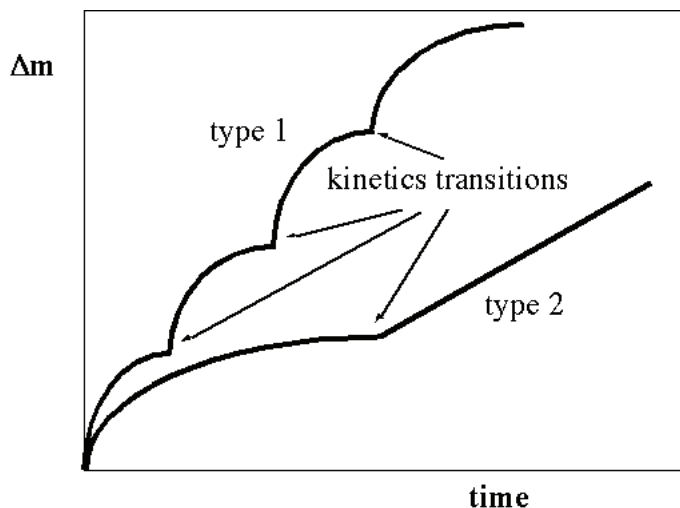


Fig. 5.17. Schematic rate laws associated with the formation of stratified scales.

Both types of curves are characterised by rapid increases in oxidation rate, termed “kinetic transitions”, and it is then of use, particularly for Type 2 curves, to term the period before and after the transition as “pre-transition” and “post-transition”, respectively.

NOTE: care should be taken not to confuse this terminology with the “transitory regime” of mixed kinetics (see Chapter 4, sections 4 and 6.3) since the two phenomena are different.

Examination of the scale formed on such specimens, either on fractured or polished cross sections, shows that for both type 1 or type 2 rate laws :

- a compact and adherent scale is formed before the first transition ;
- after the first transition, a porous scale exists which consists of well-defined layers formed essentially parallel to the metal surface; these may be separated by isolated cracks, also parallel to the metal surface, or by more connected porosity.

3.2.2. *Mechanism of the formation of a stratified scale*

Many authors have discussed the mechanisms of stratification, particularly Stringer³. Their conclusions can be summarised as follows.

3.2.2.1. Diffusional growth of the first layer

In a majority of metal-oxide systems where stratification occurs, mass transport through the oxide occurs by oxygen, mainly by vacancies V_O (diffusing from the internal to the external interface). Since the scale grows in a confined space at the internal interface, the increase in volume on oxide formation, associated with a Pilling-Bedworth ratio greater than unity, may generate large compressive stresses in the oxide (several GPa are currently measured). The metal is concurrently submitted to tensile stresses of smaller magnitude (several ten MPa) due to its larger thickness. The high compressive stresses in the oxide are probably responsible for the often observed tendency for the kinetics to approach cubic due to an associated reduction in the oxygen diffusion flux. In all cases, oxygen pressure has no influence on the rate constants.

3.2.2.2. Metal-oxide decohesion and oxide cracking

As oxide thickness increases, compressive stresses may also increase and result in localised spallation and/or cracking. An example of oxide spallation by a buckling process is shown schematically in Fig. 5.18 (See also Fig. 3.18).

³ J. Stringer, *Acta Metall.* **8** (1960) 758 and 810.

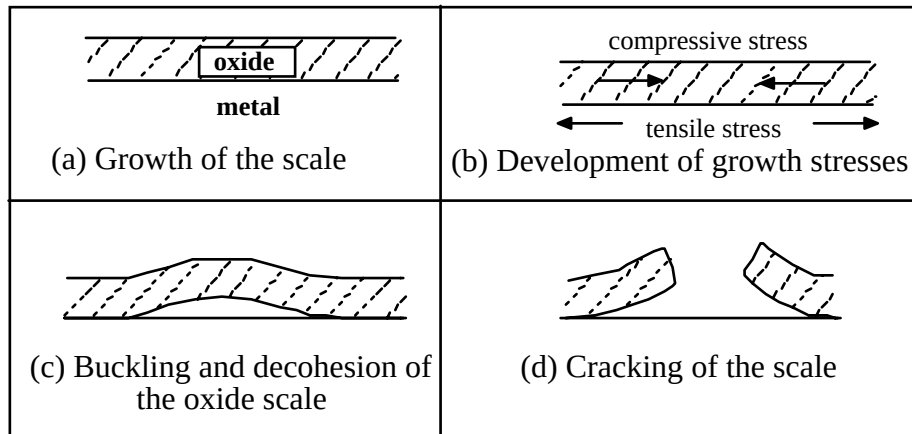


Fig. 5.18. Schematic description of oxide scale buckling and cracking due to compressive stresses.

3.2.2.3. Post-transition oxidation

As a result of oxide cracking or spallation, free access of the gas to a bare metal surface occurs and re-oxidation results. Two cases can be envisaged.

In the first, the bare metal is unchanged compared with that at the beginning of oxidation, in terms of composition, microstructure or mechanical properties. Re-oxidation occurs exactly as in the initial period and the rate law is the exact repetition of the first pre-transition curve. Kinetics of type 1 (Fig. 5.17) are then observed with a succession of parabolic-type periods.

In the second example, the bare metal differs from the initial state, for example, dissolution of oxygen may have occurred, leading to increased hardness and lower creep relaxation rates. The second oxide layer that forms does not then reach the thickness of the first since stress increases at a higher rate and early separation occurs from the metal. In the case of TiO_2 growth on titanium at 850°C , for example, the second and all subsequent layers have a thickness of $1 - 2 \mu\text{m}$, whereas the first attains $10 - 15 \mu\text{m}$ ⁴. The spallation or cracking of these scales does not occur at the same time for all locations on the specimen surface and the resulting rate law is approximately linear with an increased rate compared to that in the pre-transition period. The system can be described as a metal covered by an oxide of statistically constant thickness.

3.2.3. Industrial aspects

In industrial applications, the formation of layered scales and the associated enhanced rate of oxidation is clearly undesirable. This sort of stratification has been found in titanium and zirconium alloy high temperature components and can be understood and possibly

⁴ A. Galerie, M.R. De Nicola, J.P. Petit, Microscopy of Oxidation 2, S.B. Newcomb and M.J. Bennett Eds., The Institute of Materials, London, 1993, pp. 338-346.

combated in the light of the above mechanisms.

One possible approach may be to modify the nature of the oxide layer through the use of alloying additions. It will be seen in Chapter 6 that appropriate alloying elements may have a higher affinity for oxygen than the base metal but this is difficult in the case of Ti and Zr.

A second approach is to increase the plasticity of the metal so that it can relax oxide stress levels by deformation. Unfortunately, this is often contrary to the industrial need for strong metal parts with a good resistance to high temperature creep.

A third approach would be to increase oxide plasticity, possibly by reducing its grain size or by using solid solution doping to increase its deviation from stoichiometry (see Chap. 4, section 5.4) or by incorporating mobile extrinsic defects as substitutional or interstitial hydroxide ions (oxidation in presence of water vapour, for example).

These last two approaches generally decrease the tendency to stratification but concurrently increase the reaction rate. A compromise is therefore necessary.

Chapter 6

CORROSION PROTECTION

Three methods are available to protect metals and alloys from high temperature corrosion :

- Control of the atmosphere
- Alloying addition of species more easily oxidised than the base metal (chromium, aluminium) and which form a protective scale during oxidation
- Use of protective coatings deposited by various methods (cementation, plasma spraying, ion beam bombardment, etc.)

1. ATMOSPHERE CONTROL

Industrial processes such as heat treatment are carried out under controlled gaseous atmospheres. The chemical reactivity of the gases depends on their nature, their partial pressures, the nature and composition of the alloy and on temperature (see table 6.1). Oxygen, carbon dioxide and water vapour are oxidising and decarburising (via the Boudouard reaction); hydrogen is reducing; carbon monoxide and hydrocarbons (e.g., methane, propane, natural gas) are reducing and carburising; ammonia is nitriding; nitrogen is generally considered to be inert but may be nitriding at high temperatures; rare gases are, of course, inert. Anhydrous ammonia dissociated by catalytic cracking is used for the atmospheric protection of alloys that are very sensitive to high temperature corrosion. It should also be noted that the reactivity of a gas depends significantly on its water vapour content.

Table 6.1. Main chemical reactions between a gas and a metal or an alloy (from Kostelitz¹). Atmospheres referred to as "incompatible" yield unacceptable chemical reactions.

¹ M. Kostelitz, in: *Techniques de l'Ingénieur*, Traitements Thermiques, M1 220, Paris.

Metals	Gas								
	O ₂	CO	CO ₂	H ₂	[H ₂ O]	hydro-carbons	NH ₃	N ₂	Ar, He
Carbon steels	Oxid. and decarb.	Red. and carbur.	Oxid. and decarb.	Red.	Oxid. and decarb.	Carbur.	Nitrid.	Neutral	Inert
Stainless steels	Oxid.	Red. and carbur.	Oxid. and decarb.	Red.	Oxid.	Carbur.	Nitrid.	Neutral	Inert
Cast irons	Oxid. and decarb.	Red.	Oxid. and decarb.	Red.	Oxid. and decarb.	Carbur.	Nitrid.	Neutral	Inert
Al and alloys	Oxid.	Neutral	Oxid.	incompa tible	Oxid.	incompa tible	incompa tible	Neutral	Inert
Cu and alloys	Oxid.	Red.	Oxid.	Red.	Neutral	incompa tible	incompa tible	Neutral	Inert
Ti and alloys	Oxid.	incompa tible	Oxid.	incompa tible	Oxid.	incompa tible	Nitrid. (T>1000°C)	Nitrid.	Inert

Thermal treatments under vacuum permit high temperature operations, even up to 2000°C in cold-walled furnaces. However, such treatments may lead to modification of the surface composition of the alloy by sublimation, e.g. chromium loss in the case of stainless steels or loss of zinc in the case of brass. Treatments under high vacuum are generally carried out only as part of laboratory experiments.

In most industrial treatments, the gaseous atmospheres are generally obtained from partial oxidation of by-products of oil or natural gas. Atmospheres are referred to as "*exothermic*" (obtained by burning the fuel with controlled amounts of air) or "*endothermic*" (produced by heating a mixture of fuel and air over a catalyst to provide a gas of the following composition: nitrogen (ca 40 %), hydrogen (ca 40 %) and carbon monoxide (ca 20 %)).

Protective atmospheres are used to avoid or minimise oxidation and/or superficial decarburisation or carburisation of steels during heat treatments. The thermodynamic calculations presented in Chapter 1 allow us to determine the composition of the gas mixtures which are inert to the alloy at the treatment temperature. Darken diagrams can be used to identify, at a given temperature and as functions of the oxygen and carbon mole fractions, the different zones, i.e., in which oxidation, reduction, carburisation or

decarburisation will occur. As an example, figure 6.1 shows the "bright annealing" zone for iron in a complex gas mixture of H_2 - H_2O - CH_4 - CO - CO_2 .

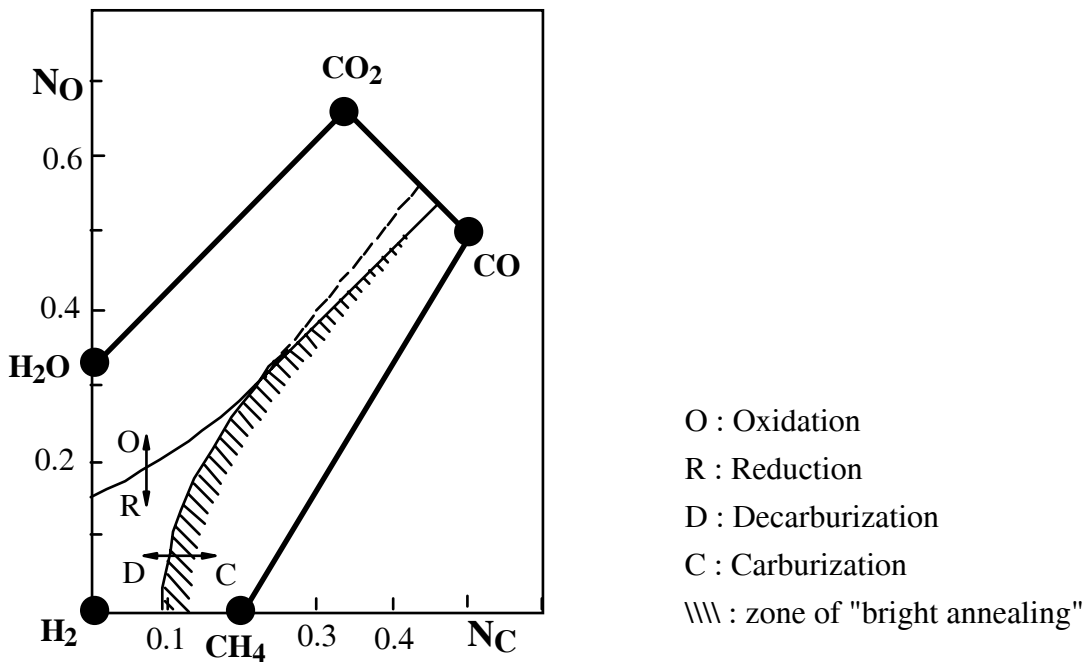


Figure 6.1. Darken diagram showing the bright annealing zone for pure iron at 650°C.

2. USE OF ALLOYS

2.1. Introduction

Alloys are used for improving:

- mechanical properties of metallic materials at extreme temperatures, e.g. in creep-resistant or refractory alloys, in steels used for cryogenic purposes;
- quenchability;
- formability;
- resistance to wet and/or hot corrosion (stainless steels, for example).

The oxidation of alloys is a complex process consisting of a large number of phenomena which may, themselves, be dependent on alloy composition and environment, i.e. temperature, mechanical stress, gas composition, etc. To obtain effective protection of a metallic material, the oxide formed must lead to a continuous scale (this process is termed "**external oxidation**") and not to precipitates within the alloy (this process is known as "**internal oxidation**").

Comment: The terms "internal oxidation" and "external oxidation" must not be confused with the concepts developed in Chapter 4 where the elementary steps referred to as « external » and « internal » processes describe, in the case of formation of a continuous scale, the exchanges of matter between gas phase and oxide and between metal and oxide, respectively.

Although numerous works have been devoted to corrosion of alloys, the oxidation mechanisms are often still not fully understood. In fact, the models have usually been developed for the oxidation of the relatively simple example of pure metals and are inadequate to describe alloy corrosion. In order to do this, additional factors have to be taken into account, e.g. the different affinity for oxygen of each of the alloy's constituents, dissolution of oxygen into the alloy, solid solubility between the oxides formed, formation of complex oxides, different mobilities of the various metal ions in the oxide phases, etc. Moreover, alloy oxidation involves complex processes for which the equilibrium state is reached very slowly or even never reached.

It is unrealistic to try to classify all the various types of alloy oxidation using simple criteria. However, a classification system has been proposed by Bénard² to account for the diverse morphologies of oxidation scales. We will use here a system proposed by Gesmundo³ which allows us to account for the oxidation mechanisms in binary alloys. It uses thermodynamic diagrams based on the combination of the phase diagram of the alloy and of the corresponding stability diagram of the condensed phases.

First, we will consider a binary alloy AB, based on metal A, which is less reactive than the alloying element B. The oxides formed will be referred to as AO_a and BO_b , respectively. We will consider the complex case of multi-components alloys but, for simplicity, examine only the role of the alloying elements in improving the oxidation resistance.

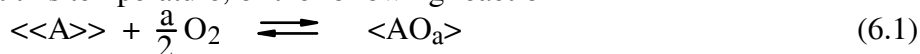
The main factors responsible for the scale morphology derive from both thermodynamic and kinetic considerations. Obviously, other factors could be taken into account, such as structural, morphological or mechanical features but, again for simplicity, they will not be considered here.

² J. Bénard, *Oxydation des métaux*, Vol. 1 and 2, Gauthier Villard et cie, Paris, 1962-1964.

³ F. Gesmundo, private communication.

2.2. Thermodynamic approach

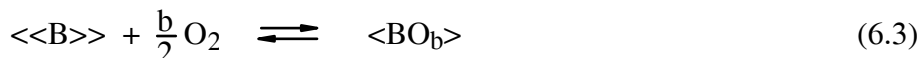
Let $\langle\langle A, B \rangle\rangle$ be an alloy for which, at temperature T , A and B form an ideal solid solution but two immiscible oxides, $\langle AO_a \rangle$ and $\langle BO_b \rangle$. Let $\Delta_r G_1^\circ$ be the standard Gibbs free energy, at this temperature, of the following reaction:



For a binary alloy $\langle\langle A, B \rangle\rangle$, in which N_B is the mole fraction of the solute B , the equilibrium oxygen pressure obeys the following relationship:

$$\log P_{O_2} = -\frac{2}{a} \log (1 - N_B) + \frac{2 \Delta_r G_1^\circ}{a R T \ln 10} \quad (6.2)$$

The variation of the oxygen pressure as a function of the alloy composition, at a given temperature, is plotted in figure 6.2 (curve (1))⁴. Likewise, the variation of the oxygen pressure of the following equilibrium ($\Delta_r G_2^\circ$ is the standard Gibbs free energy of the reaction):



obeys the equation:

$$\log P_{O_2} = -\frac{2}{b} \log N_B + \frac{2 \Delta_r G_2^\circ}{b R T \ln 10} \quad (6.4)$$

The corresponding variation of the oxygen pressure with the alloy composition is also drawn in figure 6.2 (curve (2)).

In $\log P_{O_2}$ vs N_B space, three domains can be identified corresponding to the diagram of condensed phases described in Chapter 1. The point of intersection between curves (1) and (2) (point E in figure 6.2) corresponds to equilibrium between both the oxides $\langle AO_a \rangle$, $\langle BO_b \rangle$ and the alloy (at an equilibrium pressure termed P_l). The mole fraction N_B^0 of component B , corresponding to point E, depends on the standard Gibbs free energy of reactions (6.1) and (6.3), according to:

$$\log \frac{(N_B^0)^{1/b}}{(1 - N_B^0)^{1/a}} = \frac{a \Delta_r G_2^\circ - b \Delta_r G_1^\circ}{a b R T \ln 10} \quad (6.5)$$

Figure 6.2 was drawn, assuming that the solute B is much more reactive with oxygen than the base component A . In that case, $\Delta_r G_2^\circ \ll \Delta_r G_1^\circ$ and the mole fraction N_B^0 corresponding to point E is very much less than 0.5.

⁴ F. Gesmundo and Y. Niu, *Oxidation of Metals*, **50** (1998) 1-26.

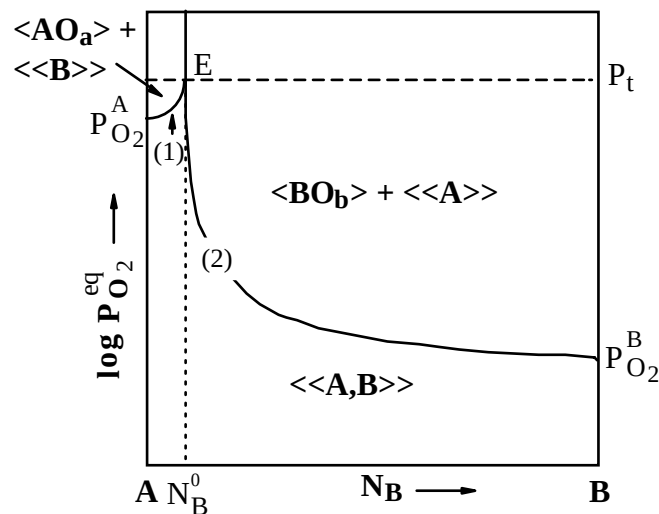


Figure 6.2. Diagram of condensed phases in the case of the oxidation of a binary alloy for which solute B is much more reactive with oxygen than component A, i.e., $P_{O_2}^B \ll P_{O_2}^A$.

It is necessary to plot the diagrams of condensed phases to check the compatibility of the proposed models with the experimental results.

2.3. The different types of binary-alloy oxidation

Two cases may be considered, depending on whether the oxygen pressure P_{O_2} is higher or lower than the equilibrium pressure $P_{O_2}^A$ for the oxidation of the base constituent A. The main oxidation modes, depending on the alloy composition, are given in Table 6.2.

Table 6.2. Different modes of alloys oxidation.

$P_{O_2} < P_{O_2}^A$	$P_{O_2} > P_{O_2}^A$
Internal oxidation of solute B (dilute alloys)	External oxidation of A and internal oxidation of B (dilute alloys)
External oxidation of solute B (alloys richer in B)	External oxidation of B (alloys richer in B)
	Formation of an oxide mixture ($AO_a + BO_b$) (at intermediate concentrations of B)

2.3.1. Oxygen pressure less than $P_{O_2}^A$

2.3.1.1. Internal oxidation ($P_{O_2} < P_{O_2}^A$ and dilute alloys)

For the case of a dilute alloy, oxygen atoms diffuse into the alloy and react with the solute B to form particles of the oxide BO_b dispersed within the metal matrix A in a sub-surface zone of thickness δ . If the diffusion coefficient of solute B is sufficiently high, it will diffuse outwards during this process of internal oxidation so as to increase the concentration of constituent B, as BO_b , within the zone of internal oxidation. It follows that a region depleted in B and of thickness δ' forms beneath the oxidised zone. The concentration profiles of atomic oxygen and B in solution are shown schematically in figure 6.3.

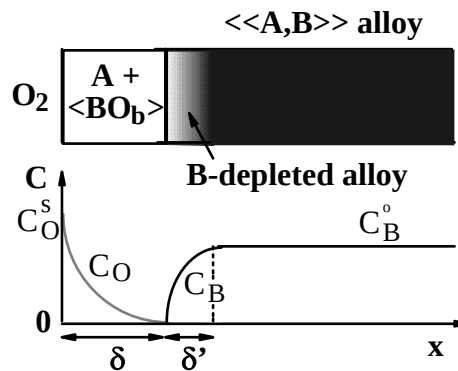


Figure 6.3. Concentration profiles of atomic oxygen (C_O) in solution and of element B (C_B) in solution in the sub-surface oxidation zone.

Figure 6.4 shows the thermodynamic stability diagram and the composition of the scale formed during the internal oxidation of the alloy.

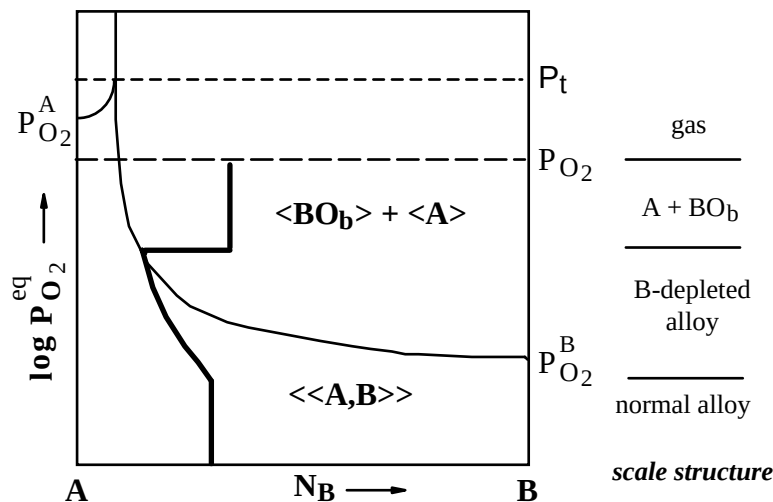


Figure 6.4. Diagram of condensed phases and scale composition during the internal oxidation of a binary alloy.

The system may be described by the two equations:

$$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} \quad \text{and} \quad \frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} \quad (6.6)$$

with the following boundary conditions:

$$\begin{aligned} \text{at } t = 0 \quad & C_O = C_O^s \quad \text{and } C_B = 0 \quad \text{for } x < 0 \\ \text{at } t = 0 \quad & C_O = 0 \text{ for } x > 0 \text{ and } C_B = C_B^0 \quad \text{for } x \geq 0 \\ \text{and whatever } t \quad & C_O = C_O^s \text{ for } x = 0 \quad \text{and } C_B = C_B^0 \text{ for } x \rightarrow \infty \end{aligned}$$

where C_O^s is the oxygen concentration (moles/unit volume) at the alloy surface in equilibrium with the gaseous atmosphere. This treatment is more general than that originally developed by Wagner⁵ and follows that published by various authors^{6,7,8}.

If the oxygen diffusion rate is much higher than that of the solute B, a simplified solution can be obtained by assuming that the oxygen concentration varies linearly within the internal oxidation zone, δ in thickness, and that the concentrations C_O and C_B are zero at the δ/δ' interface, as shown schematically in figure 6.5. The oxygen flux J_O obeys Fick's first law:

$$J_O = D_O \frac{C_O^s}{\delta} \quad (6.7)$$

where D_O is the oxygen diffusion coefficient.

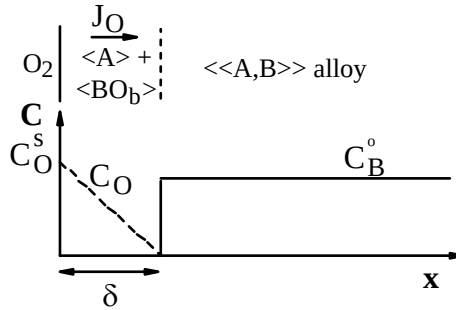


Figure 6.5. Simplified treatment of the concentration profiles of atomic oxygen (C_O) and element B (C_B) in solution within the sub-surface oxidation zone.

In this model and under steady-state conditions, the element B is oxidised within the zone of depth δ . If the oxide formed, BO_b , is very stable, the number of moles of element B that react under unit area of the specimen surface are equal to the number of moles of diffusing oxygen:

$$b C_B^0 d\delta = D_O \frac{C_O^s}{\delta} dt \quad (6.8)$$

⁵C. Wagner, *Z. Elektrochem.*, **63** (1959) 772.

⁶N. Birks and G.H. Meier, *Introduction to High Temperature Oxidation of Metals*, Edward Arnold, 1982.

⁷G. Böhm and M. Kahlweit, *Acta Metall.*, **12** (1964) 641.

⁸D. Landolt, *Traité des matériaux*, n° 12, Corrosion et chimie de surface des métaux, Presses polytechniques et universitaires romandes, 1993.

By integration, a parabolic law for the depth, δ , of oxidation is obtained:

$$\delta^2 = 2 D_O \frac{C_O^s}{b C_B^0} \cdot t \quad (6.9)$$

Comments:

- The depth of the oxidation zone at a given time is inversely proportional to the square root of the concentration of element B in the alloy.
- Measurement of the depth, δ , for an alloy with a known concentration of element B permits us to estimate the product $C_O^s D_O$ which is the oxygen permeability within the alloy.

2.3.1.2. External oxidation ($P_{O_2} < P_{O_2}^A$ and concentrated alloys)

If the concentration of B is high and the oxygen solubility in the alloy is low, the oxidation takes place at the alloy surface. A dense oxide layer can be formed and *selective external oxidation* is observed.

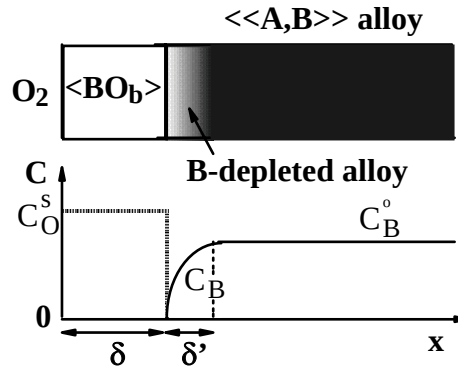


Figure 6.6. Concentration profiles of dissolved oxygen, C_O , and of the alloying element, C_B , within the alloy sub-surface.

The thermodynamic phase-stability diagram and the composition of the scale formed for the case of external oxidation of an alloy are given in figure 6.7.

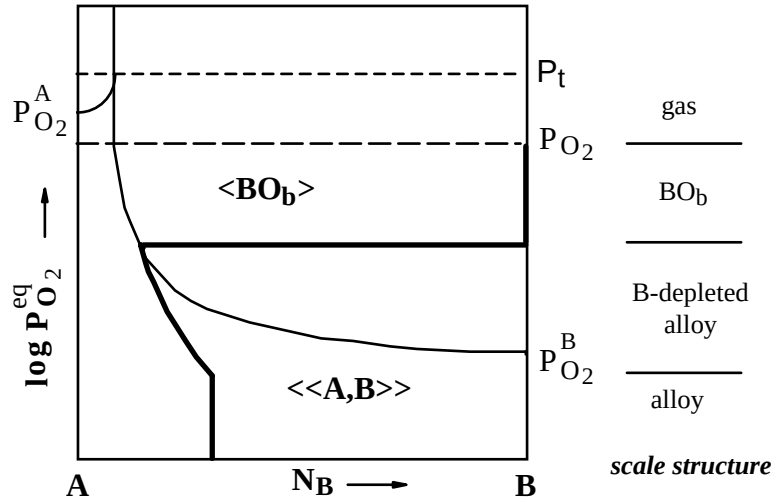


Figure 6.7. Diagram of condensed phases and scale composition for the case of external oxidation of a binary alloy.

For the case of diffusion controlled oxidation, the situation may be simplified, as in the case of internal oxidation, by assuming that the concentration of the component B is virtually zero at the alloy-oxide interface and that the concentration profile is linear within the B-depleted zone of thickness δ' , as shown schematically in figure 6.8.

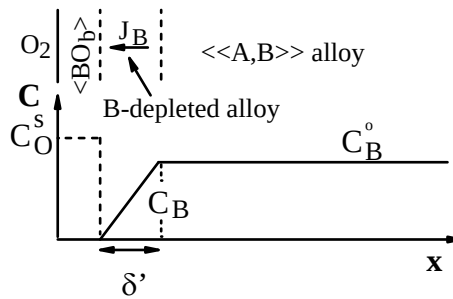


Figure 6.8. Concentration profiles of dissolved oxygen, C_O , and of the alloying element, C_B , within the alloy sub-surface for the case of diffusion controlled oxidation.

In this approximation, one may write:

$$J_B = D_B \frac{C_B^0}{\delta'} \quad (6.10)$$

where D_B is the diffusion coefficient of element B. A steady state is attained at the oxide-alloy interface if the oxygen atoms are fully consumed by the flux, J_B , of B to produce the oxide, BO_b . The number of moles consumed of component B is then strictly equal to the number of moles of oxide formed. Hence, the rate of the oxidation reaction can be expressed by the following equation:

$$\frac{d n_{BO_b}}{dt} = J_B = D_B \frac{C_B^0}{\delta'} \quad (6.11)$$

Since there is a linear variation in the concentration of B within the depleted zone, the consumption rate of B is equal to:

$$\frac{d n_B}{dt} = \frac{1}{2} C_B^0 \frac{d\delta'}{dt} = \frac{d n_{BO_b}}{dt} \quad (6.12)$$

Then:

$$\frac{1}{2} C_B^0 \frac{d\delta'}{dt} = D_B \frac{C_B^0}{\delta'} \quad (6.13)$$

Integration of equation 6-13 leads to a parabolic time dependence for the thickness of the zone depleted in B:

$$\delta'^2 = 4 D_B \cdot t \quad (6.14)$$

2.3.1.3. Transition from internal oxidation to external oxidation

In the case of internal oxidation, the penetration rate of the oxidation zone is of the form (see equation 6.8):

$$\frac{d\delta}{dt} = D_O \frac{C_O^s}{b C_B^0 \delta} \quad (6.15)$$

This rate decreases with increasing concentration of element B and decreasing oxygen concentration, C_O^s , at the alloy surface produced, for example, by a decrease in the oxygen partial pressure of the oxidising gas. It can be appreciated that there is a limiting concentration of component B above which a continuous blocking oxide scale is formed. This corresponds to the transition from internal to external oxidation and a consequent decrease in the oxidation rate.

The conditions determining whether internal or an external oxidation occurs are summarised in Table 6.3.

Table 6.3. Main conditions that favour either internal or external oxidation.

INTERNAL OXIDATION	EXTERNAL OXIDATION
The alloying element is less noble than the base alloy.	The mole fraction of alloying component B is sufficiently high and/or the diffusion coefficient D_B is high
Oxygen permeability within the base alloy is sufficiently high.	Oxygen permeability within the base alloy is low
Oxygen dissolution within the alloy is not inhibited by a surface layer of oxide.	
The mole fraction of alloying element B is sufficiently low	

Comment: Wagner⁹ has proposed a criterion based on the comparison of both the diffusion coefficients and the equilibrium concentrations of B and O in the alloy. For an oxide BO_b, this criterion is expressed, in a simplified form, as the ratio between the depths of the B-depleted zone (external oxidation) and the internally oxidized zone:

$$\gamma = \frac{\delta'}{\delta} = \left(2b \frac{D_B}{D_O} \cdot \frac{C_B^0}{C_O^s} \right)^{1/2} \quad (6.16)$$

$\gamma > 1$ leads to external oxidation whereas internal oxidation occurs when $\gamma < 1$.

This transition is the basis for the design of alloys based on iron, nickel and cobalt and containing elements such as Cr, Al and Si, which give highly stable oxides, e.g., Cr₂O₃, Al₂O₃, and SiO₂ (see section 2.4.1 and 2.4.2). With a sufficiently high content of alloying component, a complete external scale of oxide is formed which protects the alloy from further oxidation. It should be pointed out that with alloying concentrations around the critical value, mechanical damage of the protective scale may result in transient non-protective oxidation of the solute-depleted zone.

2.3.2. Oxygen pressure greater than $P_{O_2}^A$

Under these conditions, both the base metal A and the alloying addition B may be oxidised and three situations may be identified:

- external oxidation of A and internal oxidation of B (for dilute alloys)
- selective external oxidation of B
- external oxidation of both A and B.

Figures 6.9 to 6.11 show the composition of the scale formed and the corresponding thermodynamic phase-stability diagrams.

For the case of a dilute alloy, the oxidation mechanism involves external oxidation of A and internal oxidation of B, as schematized in Fig. 6.9. The internal oxidation of B forms BO_b particles within a matrix of almost pure A covered by an outer scale of AO_a. This case is often encountered with steel, owing to the high rates of growth of iron oxides.

⁹ C. Wagner, *Z. Elektrochem.*, **63** (1959) 772.

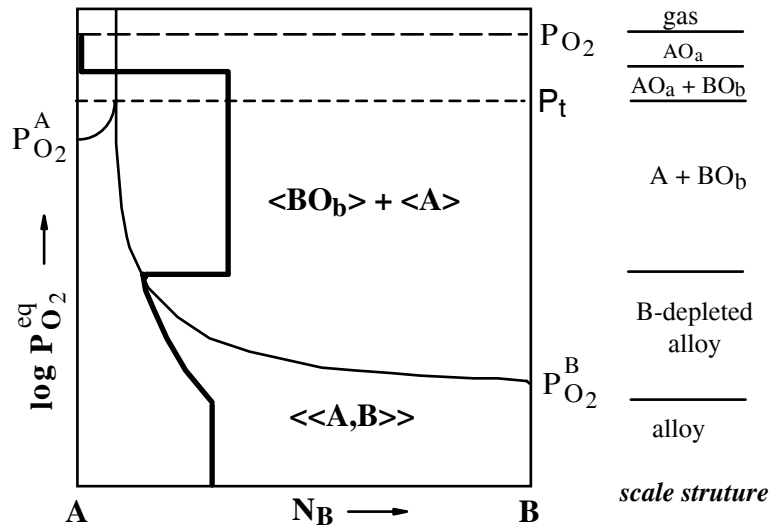


Figure 6.9. Diagram of condensed phases and scale composition for the case of external oxidation of A and internal oxidation of B.

If the component B exhibits an affinity for oxygen significantly higher than that of the matrix, then selective oxidation of B can occur to form an external scale if the initial solute concentration exceeded a critical value. The oxidation mechanism is similar to that described in section 2.3.1.2. (see Figure 6.10 a).

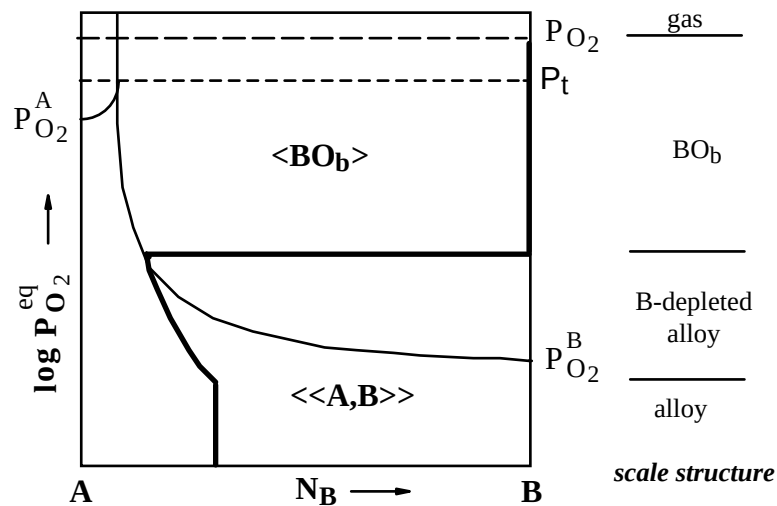


Figure 6.10 a. Diagram of condensed phases and scale composition for the case of selective oxidation of B (slow diffusion of B).

In the case of rapid diffusion of the alloying component, the B-depleted zone, underlying the oxide scale is no longer localised but extends into the specimen. Concentration gradients are then shallow as shown schematically in Fig. 6.10 b.

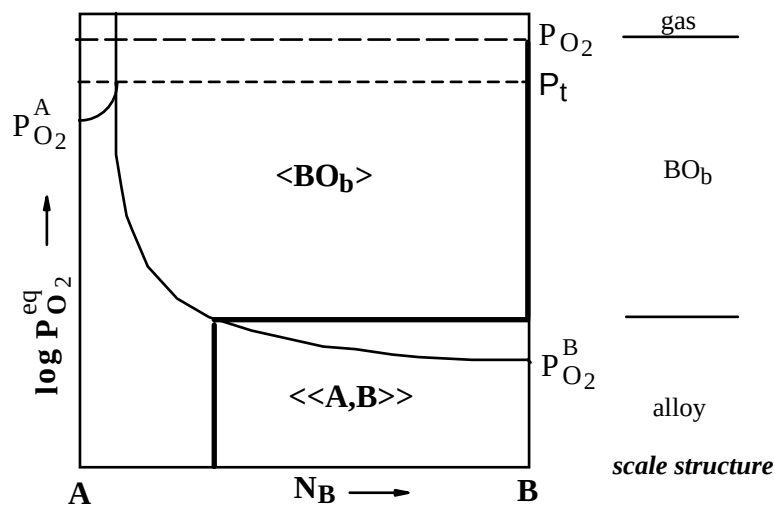


Figure 6.10 b. Diagram of condensed phases and scale composition for the case of selective oxidation of B (very fast diffusion of B).

The corrosion protection of stainless steels at high temperatures is based on the addition of aluminium or chromium which, on selective oxidation, form a protective scale of aluminum or chromium oxide, respectively.

In many industrial alloys, the scale formed is, generally, complex due to the mutual miscibility of both oxides or even the formation of a compound with a spinel structure, such as $NiCr_2O_4$. For the simple notional binary alloy, the mutual miscibility of both oxides, i.e., AO_a and BO_b , may lead to an eutectic composition with a low melting point, inducing "catastrophic oxidation". This is the case of some Fe-Si alloys which can form a mixed oxide, $FeO-FeSiO_4$, with a melting temperature of $1170^\circ C$.

Figure 6.11 shows the case where oxides AO_a and BO_b are not miscible.

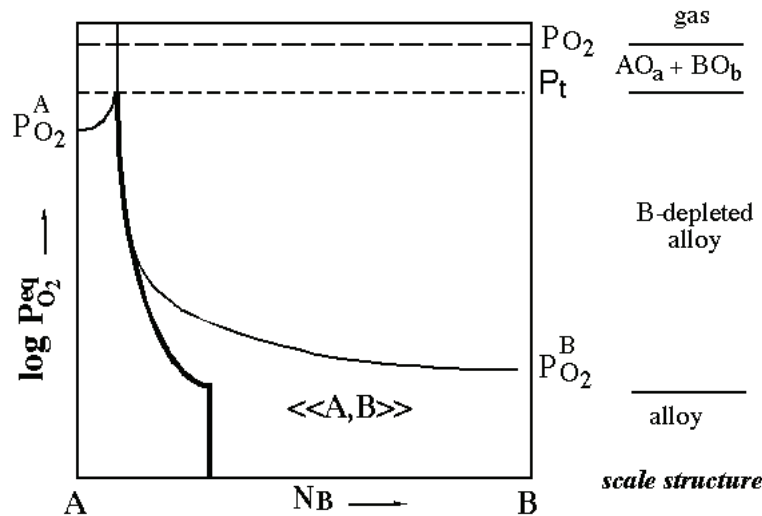


Figure 6.11. Diagram of condensed phases and scale composition in the case of the formation of both oxides, i.e., AO_a and BO_b .

2.4. Use of multi-component alloys

The choice of a high temperature alloy is guided not only by the conditions of use but also by secondary factors such as its ease of fabrication, the temperature of thermal treatments, its mechanical properties, such as rupture life and creep resistance, and its availability and cost. High temperature alloys exhibiting good corrosion properties belong to one of the two families:

- chromium-forming alloys which are protected by a Cr_2O_3 layer;
- aluminium-containing alloys which are protected by an Al_2O_3 layer.

To obtain good protection at high temperature it is necessary that no volatile oxides are formed under the surface conditions. Table 6.4 shows that, under some conditions, it is possible for chromia-forming alloys to suffer from such volatilisation.

Table 6.4. Equilibrium pressures with solid Al_2O_3 or Cr_2O_3 and 1 bar oxygen of different gaseous species (calculated using thermochemical data from Barin¹⁰)

T (K)	AlO_2 (bar)	CrO_3 (bar)
1 000	5.10^{-26}	7.10^{-12}
1 500	8.10^{-15}	3.10^{-7}
2 000	3.10^{-9}	5.10^{-5}

It is usually assumed that significant volatilisation will occur for oxide partial pressures greater than 1 nanobar (10^{-4} Pa). The volatilisation rate is then calculable from the Hertz-Langmuir equation:

$$V = \frac{\alpha P}{(2 \pi M R T)^{1/2}} \quad (6.17)$$

where P and M are the partial pressure and the molar mass of the volatile oxide, respectively, T the absolute temperature, R the ideal gas constant and α the volatilisation coefficient. For CrO_3 volatilisation from Cr_2O_3 at 1200 K using $\alpha = 1$, this relation gives:

$$V \approx 150 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$$

which is not negligible. It should be noted, though, that the volatile oxide species is not the same as the solid oxide and the volatilisation factor α should probably have a substantially lower value, $\alpha \ll 1$. This reflects the fact that the volatilisation kinetics are likely to be limited by the rate of surface oxidation of chromia to chromium trioxide. As a simple rule of

¹⁰ I. Barin, Thermochemical data of pure substances, VCH, Weinheim, 1989.

thumb, it is considered that chromia-forming alloys will suffer significant volatilisation in high oxygen environments at temperatures of 1000°C and above.

2.4.1. Chromia-forming alloys

Iron-chromium alloys

The minimum chromium concentration for iron-chromium alloys to be protected by an external compact and adherent chromia scale is approximately 13 wt.%. For lower chromium contents, the oxide layer consists of two distinct subscales:

- an internal spinel-type magnetite subscale where ferric sites are partially occupied by Cr^{3+} ions, therefore leading to a formula lying between Fe_3O_4 and FeCr_2O_4 ;
- an external subscale consisting of haematite (Fe_2O_3).

Such behaviour is observed for low chromium alloys ranging from Fe-2.25Cr-1Mo to Fe-9Cr-1Mo which are used for good creep resistance up to 500°C. At higher chromium contents, the rate of oxidation is much lower but good long-term behaviour is obtained only with chromium contents of at least 17%.

It should be noted that Fe-Cr alloys should not be used at temperatures exceeding the $\alpha \rightarrow \beta$ transformation. This transformation induces changes in the molar volume and in the Cr diffusion coefficient which lead to large changes in oxidation kinetics and/or loss of scale adhesion on cooling. Industrial grades of these steels often use α -stabilisers like Ti at concentrations between 0.1 and 0.5 wt.%.

Nickel-chromium alloys

Nickel-chromium alloys are more susceptible to internal oxidation than the corresponding iron-chromium alloys, particularly at low Cr contents. For Cr > 10%, protective chromia forms after an initial period where NiCr_2O_4 is observed. The most common grade of alloy is Ni-20Cr (wt. %).

Iron-nickel-chromium alloys

Fe-Ni-Cr alloys are mostly austenitic due to the strong γ stabilisation by Ni. They exhibit therefore a high thermal expansion coefficient, leading to large compressive stresses in the oxide during cooling. They have also a low diffusivity for chromium resulting from their compact structure and are susceptible to localised surface depletion of chromium as described above (§ 2.3.1.2 and Fig. 6.6). They can suffer from severe spallation and are used only with high chromium contents (~20 – 35%) in industrial situations where thermal cycling is not excessive or as thick-sectioned components if frequent spallation is likely.

Influence of minor alloying additions

Silicon, as a minor alloying addition at 0.2 to 2 wt.% to chromia-forming alloys segregates during high temperature oxidation to form a more or less continuous SiO_2 sublayer at the alloy-scale interface. Its formation leads to a decrease in the parabolic rate-constant due to a reduction in the flux of chromium to the external surface. This improvement in behaviour is particularly noticeable for extended oxidation exposures.

Yttrium, rare earth elements (Ce, Nd, etc.) and several other very reducing elements (Th, Zr, Hf, etc.) are known to be very beneficial when added in very low concentrations to chromia-forming alloys. This benefit, which is not dependent on the method of addition nor on the valency state (i.e. whether added in the elemental or oxidised state), is called the *reactive element effect* (REE). The mechanisms responsible for the improvement in oxidation behaviour have been extensively studied but are still under debate. It seems likely that the benefit is associated with the high affinity of the reactive elements for oxygen and sulphur and on their low solubility in the metal and in the oxide. One of these mechanisms is of particular importance and postulates that chromium diffusion through Cr_2O_3 becomes blocked as a result of the addition and that scale growth subsequently takes place by inward oxygen diffusion only. Marker experiments confirm this inversion of the growth direction (Fig. 6.12). Alloys containing reactive elements in oxide form are known as ODS alloys ("Oxide Dispersion Strengthened") and exhibit high creep strength as a consequence of the dispersion.

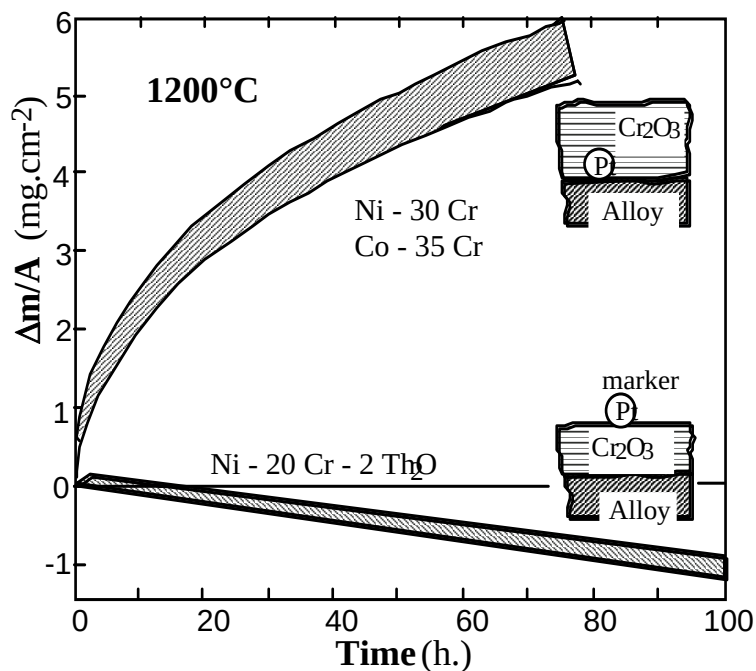


Fig. 6.12. Comparison of the oxidation kinetics of several chromia-forming alloys with or without a thoria dispersion and the corresponding results of marker experiments¹¹.

¹¹ P. Kofstad, High Temperature Corrosion, Elsevier Applied Science, London, 1988, p. 403.

The suppression of chromium transport reduces the number of interfacial voids resulting from the metal-oxide interfacial reaction, thus promoting scale adherence. The behaviour of such alloys containing reactive elements is then significantly improved particularly during thermal cycling (Fig. 6.13).

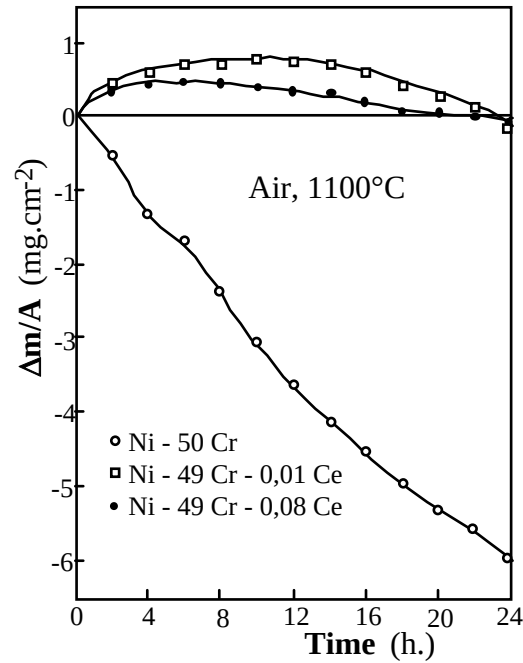


Fig. 6.13. Influence of cerium addition on the cyclic oxidation behaviour of a nickel-chromium alloy¹².

It is interesting to note in Figs. 6.12 and 6.13 a slight decrease of the weight gain in situations where no spallation occurs. This is probably due to CrO_3 volatilisation as described above.

2.4.2 Alumina-forming alloys

Alumina Al_2O_3 exhibits a very low deviation from stoichiometry, much lower than chromia, and therefore ensuring more protective behaviour (Table 6.5).

¹² N. Birks and G.H. Meier, Introduction to high temperature oxidation of metals, Edward Arnold, London, 1993, p. 123.

Table 6.5. A comparison of the deviation from stoichiometry, self-diffusion coefficients and parabolic rate constants for the growth of alumina and chromia scales.

	Al ₂ O ₃	Cr ₂ O ₃
Deviation from stoichiometry	10 ⁻⁴ (at 1000°C)	10 ⁻³ (at 600°C)
Cation self-diffusion coefficient in oxide at 1000°C (cm ² .s ⁻¹)	10 ⁻¹⁵	10 ⁻¹²
Parabolic rate constant at 1000°C (on Fe-25Cr-5Al for Al ₂ O ₃ , on Fe-20Cr for Cr ₂ O ₃) (g ² .cm ⁻⁴ .s ⁻¹)	2.7 × 10 ⁻¹³	2.0 × 10 ⁻¹¹

Iron-aluminium alloys

The minimum concentration of aluminium in iron required to form a protective alumina layer is around 12 wt.%. However, at such Al concentrations, Fe-Al alloys are very brittle and cannot be used commercially.

Iron-chromium-aluminium alloys

Chromium additions to Fe-Al alloys reduces the minimum Al concentration needed to form a protective alumina scale. For example, an alloy of composition Fe-20Cr-5Al (wt.%) combines excellent long-term high temperature oxidation properties and sufficient ductility to be used for making coiled heating resistors.

MCrAlY alloys

MCrAlY alloys are superalloys, used as bulk components or coatings, with M = Ni and/or Co and/or Fe. The alloys most frequently used are Ni-based, with a γ (NiAl) / γ' (Ni₃Al) microstructure exhibiting strong orientation relationships. Such a structure produces high mechanical strength even at high temperatures and superalloys are used in hot parts of combustion systems, e.g. as blades and vanes for aeronautic, marine or land-based turbines, at temperatures of 1000°C or above. High temperature protection in service is obtained through the formation of a compact alumina scale having improved properties due to the presence of yttrium. These improvements are similar to those described in the case of chromia-forming alloys that contain yttrium.

Future developments of turbines will lead to temperature increases that cannot readily be attained by the use of metallic materials but possible proposed solutions highlight the multidisciplinary of modern technology. These could involve:

- development of oriented or monocrystalline parts with improved mechanical properties;
- the use of hollow parts that are internally air-cooled;
- deposition of ceramic coatings, mainly zirconia, by plasma spraying or PVD (see section 3.2.2) which act as thermal barriers; such a barrier, several hundreds of microns thick, could reduce the surface temperature of the metal by a few hundred degrees.

As an example of the cost of such improvements, a hollow monocrystalline turbine blade for jet engines, with dimensions 70 cm long and 50 cm wide, covered by a thermal barrier coating, would cost ~ 4000 €.

2.4.3. Industrial alloys

The composition of several commonly used high temperature steels and related alloys are given in Table 6.6 together with the corresponding maximum temperature of operation in oxidising atmospheres.

Table 6.6. Examples of high temperature steels and related alloys (wt.%)

	DIN number	UNS number	Current designation	Composition	Maximum use temperature (°C)
Ferritic alloys	1.4016	S43000	430	18Cr, bal. Fe	750
	1.4512	S40900	409	12Cr, 0.2Ti, bal. Fe	800
	1.4510	S43036	430Ti	17Cr, 0.4Ti, bal. Fe	815
	1.4509	S44100	441	18Cr, 0.4Ti, 0.2Nb, bal. Fe	950
	1.4763	S44600	446	25Cr, bal. Fe	1150
	1.4767	K92400	Aluchrom I	20Cr, 5Al, 0.005 Y, bal. Fe	1300
Austenitic steels	1.4301	S30400	304	10Ni, 18Cr, bal. Fe	850
	1.4833	S30908	309S	14Ni, 24Cr, bal. Fe	1000
	1.4854	S35315	353MA	35Ni, 25Cr, 0.05Ce, bal. Fe	1170
Ni-base alloys			242	8Cr, 25Mo, 14W, 0.005Y, 0.03Zr, bal. Ni	815
	2.4816	N06600	600	10Fe, 17Cr, 0.5Ti, bal.Ni	1150
ODS alloy		S67956	MA956	20Cr, 4.5Al, 0.5Ti, 0.5Y ₂ O ₃ , bal.Ni	1300

3. PROTECTION BY COATINGS

The protection of high-temperature alloys by means of a surface coating becomes necessary when the alloy's rate of reaction with the environment becomes excessive. In many cases, this protection then permits the alloy's mechanical properties to be utilised to their full potential. The protective coating is usually produced by one of two processes:

- enrichment of the external part of the metal with elements designed to produce a ***new surface alloy***; this new alloy will also contain some of the elements of the base metal and will form a more or less diffuse interface with it;
- application of a discrete, physically well-defined coating layer which separates the metal from the gas; this coating is often chemically very different from the base metal, as for example with the application of ceramic coatings.

3.1. Surface alloys

Surface alloys are of different types and may be produced by chemical methods, such as *pack cementation*, by physical methods, such as *ion implantation*, or by processes involving both chemical and physical phenomena, such as in *laser surface alloying*.

3.1.1. Pack cementation

The pack cementation process is depicted in Fig. 6.14. Here, the substrate to be treated is immersed in a powdered mixture (the pack) contained in a partially-gas-tight box. The system is generally placed under an inert (argon) or a reducing (H_2) gas, and maintained at high temperature (800-1100°C) for a few hours. In such conditions, the pack generates active gases which transport the chosen element(s) from the pack to the substrate into which it or they dissolve to form the surface alloy. Three different types of packs are mainly used depending on the species to be added to the metal surface: aluminising, chromising or siliconising.

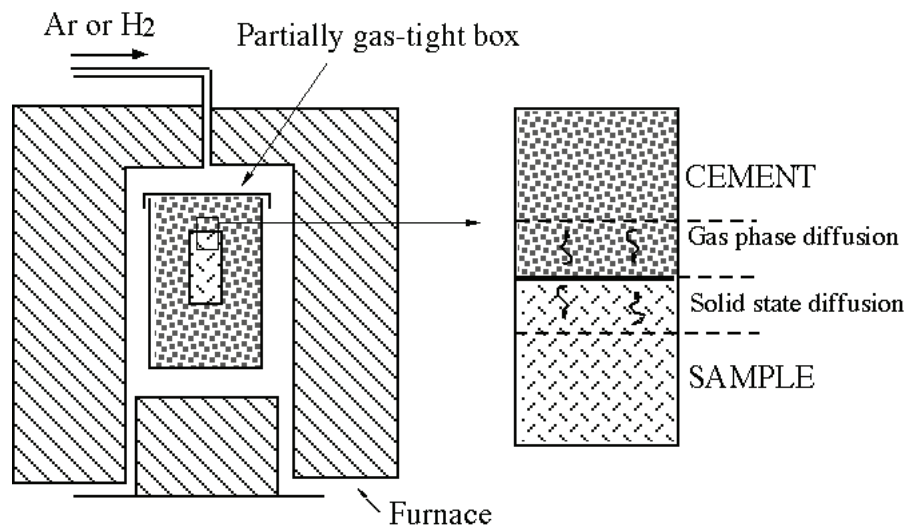


Fig. 6.14. Schematic depiction of a pack cementation system and illustration of the diffusion processes in the pack and in the substrate.

3.1.1.1. Chemistry of the pack

A typical pack consists of three main components:

- *the donor*, which is the source of the element to be added to the alloy, may be an elementary species (Al, Cr, Si), a definite compound (NiAl, FeSi₂) or a solid solution (Fe-Cr, Fe-Si);
- *the activator*, which permits the donor element to be converted into a volatile species, is currently a halide (e.g. NaF, NaCl, NH₄F, NH₄Cl, CrF₂);
- *the dilutant* is a stable oxide such as Al₂O₃ or Cr₂O₃.

The proportions of these three components are in the range: donor 20-40 wt.%, activator ~ 5 wt.%, dilutant 55-75 wt.%.

It is usually considered that chemical equilibrium between the various species (with the exception of the substrate to be treated) is achieved within the pack, which then allows the respective partial pressures to be calculated of all the volatile species formed. Consider, for example, the aluminising pack of composition (wt.%):



Such a system contains 5 independent constituents (5 elements) and 4 phases (3 solids, 1 gas); its variance is therefore:

$$V = 5 + 2 - 4 = 3.$$

At a given imposed temperature and pressure, each pack composition (Al_{metal}/F ratio) defines the composition of the gas phase, particularly the partial pressure P_c of all aluminium fluorides. This can be readily calculated and some results obtained by Gibbs enthalpy minimisation for the above pack are shown in Fig. 6.15. It can be seen that such a mixture

generates a variety of aluminium fluorides but with a marked predominance for AlF which can be considered as the main vector for aluminium transport.

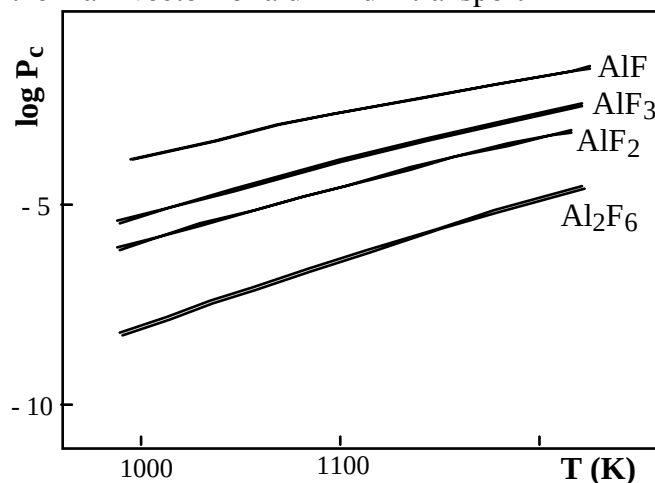


Fig. 6.15. Dependence on temperature of the partial pressure P_c (bar) of aluminium fluorides generated from an aluminising pack consisting of Al: 40 wt.%, CrF_2 : 5 wt.%, Al_2O_3 : 55 wt.%, He: 1 bar.

Such a pack, where the donor (Al in the present case) is present as an elementary species with a thermodynamic activity equal to unity, is called a *High Activity Pack*. By contrast, a pack where the donor is a compound, or where a *moderator* (Fe, Ni, Ti) is added to react with the donor, is called a *Low Activity Pack*. In low activity packs, the value of the donor activity is an important parameter.

3.1.1.2. The gas-substrate reaction.

Let us now suppose that the metallic substrate to be treated, and buried in the pack, behaves as if it were exposed to the gaseous species, whose partial pressures were calculated in 3.1.1.1, in a closed vessel. For the aluminising of iron, for example, the system to be considered is now:



with a variance of:

$$V = 4 + 2 - 2 = 4.$$

Such a system is therefore completely determined for a given temperature, pressure and initial number of moles of aluminium fluorides provided that the number of moles of reacting iron is also fixed. It is usual to take this quantity equal to that observed experimentally, corresponding to an aluminised thickness of several hundred microns. Under these conditions, it is then possible to calculate the partial pressures P_s of the various aluminium

fluorides in equilibrium with the substrate and to compare them with the values in equilibrium with the pack as calculated in 3.1.1.1. It can be seen from Fig. 6.16 that AlF has a much higher pressure in contact with the pack than with the substrate whereas the converse holds for AlF₃ and Al₂F₆. The aluminising reaction, therefore, occurs principally by the disproportionation of the monofluoride according to:

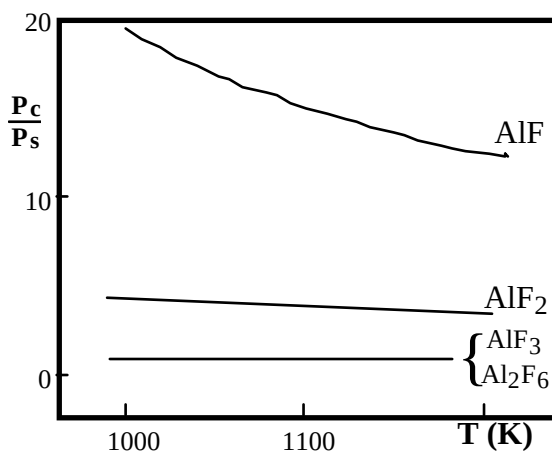
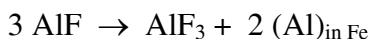


Fig. 6.16. The variation with temperature of the ratio P_c/P_s , the equilibrium pressures of aluminium fluorides in contact with the pack (P_c) and substrate (P_s).

3.1.1.3. Mass transport in the pack

As a simple model, it is assumed that gaseous species are transported in the pack across a boundary zone around the substrate. The thickness y of this zone can be defined according to two assumptions:

- in the “boundary layer” model, y is fixed by temperature only and does not vary with time; this model is used in packs with a high concentration of donor;
- in the “increasing layer” model, y corresponds to the thickness near the substrate where the concentration of the donor is zero; this thickness increases with consumption of the donor; such a model is physically realistic in packs with a low amount of donor.

Supposing that the kinetics of cementation are limited by gas diffusion in the pack (pure diffusion kinetics), the molar flux of donor is then given by:

$$J = \frac{D\Phi}{\tau} \frac{(P_c - P_s)}{yRT} \quad (6.18)$$

where D is the diffusion coefficient of the active gaseous species in the inert shield gas, Φ the pack porosity and τ is the tortuosity of the pack.

It follows that the rate law depends on the model chosen for the thickness y of the boundary layer:

- for the “boundary layer” model, the rate law is linear;
- in the “thickening layer” model, the rate law is parabolic.

Considering that diffusion coefficients in the gas phase depend only weakly on temperature, e.g. as $T^{3/2}$, the apparent activation energy for the rate of cementation is of the order of the enthalpy of formation of the gaseous active species from the solid constituents of the pack. It is often the case that this value is small, making the pack cementation rate nearly independent of temperature.

3.1.1.4. Composition and morphology of diffusion layers

The nature of the diffusion layer depends on the substrate-donor phase diagram, which may exhibit well-defined intermetallic compounds or only solid solutions. Another important factor is the ratio of the diffusion fluxes in the gas and in the substrate. In fact, the regime of pure diffusion discussed above is oversimplified and the overall process is always a mixed one, where solid state diffusion takes place in series with gas diffusion. The surface concentration of donor is therefore fixed by steady-state kinetics, but may vary with time as at least one parabolic diffusion step is involved. The dependence on temperature is much more marked for solid-state diffusion compared with gas diffusion, making the surface alloy zone more diluted but thicker when temperature increases.

The morphology of diffusion layers mainly depends on their growth direction. For all solid solutions (Fe-Cr, Fe-Si, Ni-Cr, etc.), growth is inwards. In the particular case of nickel aluminisation, which is of much technological importance, the growth direction is directly related to the Ni/Al ratio in the NiAl layer that is formed. This value is fixed by the Al activity in the pack. High activity packs generate NiAl_{1+x} layers which grow inwards and eventually incorporate precipitates from the substrate. Low activity packs, on the other hand, form NiAl_{1-x} layers which grow outwards and may incorporate solid particles from the pack. These features are summarised in Fig. 6.17.

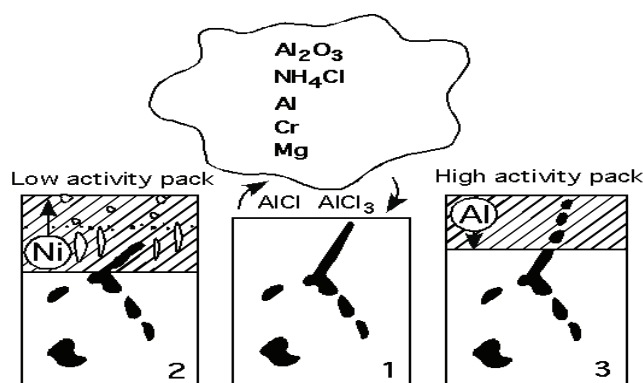


Fig. 6.17. Growth direction of the diffusion layer in the case of aluminisation of nickel as a function of pack Al activity (from Duret and Pichoir¹³).

¹³ C. Duret and R. Pichoir, in *Coatings for High Temperature Applications*, E. Lang Ed., Appl. Sci. Pub., 1983, pp. 33-78.

3.1.1.5. Industrial applications

Protection of vanes and blades for high temperature turbines is the main application for the aluminisation of Ni-based superalloys. This process currently competes with MCrAlY plasma sprayed coatings (see section 3.2.2.). In the petrochemical industry, internal chromisation or aluminisation of refractory steel tubes is used in order to form a protective oxide film to resist carbon deposition (coking) from gases of high carbon activity.

3.1.2. Ion implantation

3.1.2.1. Description of the technique

Ion implantation consists in enriching the near-surface of solids with a chosen species by bombarding them with an energetic ion beam. This technique requires the use of a high voltage accelerator working under vacuum (0.1 mPa). The energy range generally used is 50-400 keV and, depending on their mass, the implanted ions penetrate into the substrate to a mean depth of 20 to 100 nm with a near-Gaussian distribution (Fig. 6.18). The maximum concentration achieved (the maximum of the distribution curve) is limited to 5 - 30 at. % for fluences of $10^{16} - 10^{17}$ ions.cm⁻² due to sputtering effects.

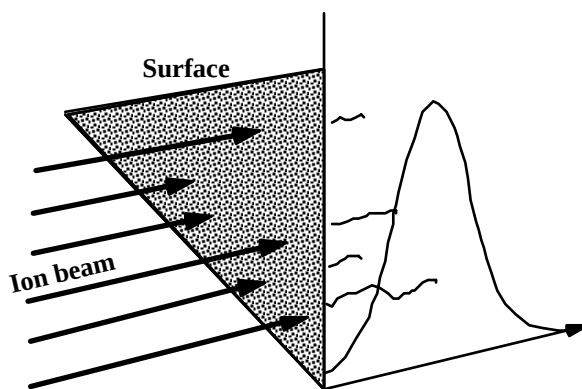


Fig. 6.18. Schematic distribution of implanted species in a solid.

3.1.2.2. Characteristics of the technique

Ion implantation is characterised by:

- the possibility of forming surface alloys that are not in thermodynamic equilibrium;
- the shallow depth of alloy affected by doping compared with thermal diffusion techniques;
- the small amount of dopant involved;
- the difficulty of treating large parts.

Applications of ion implantation are, therefore, restricted to small parts as the final stage of their fabrication. The advantage is that it is easy to dope with elements difficult to introduce by conventional chemical methods, for example, elements with a very low

solubility in the matrix-alloy. The effects of ion implanted species is magnified if they have a localised action on the corrosion mechanism, as described in the two following examples.

Segregation of ion-implanted species at the oxide grain boundaries and blocking of intergranular transport

In the Arrhenius plot of Fig. 6.19 is shown the variation with temperature of the parabolic rate constant of oxidation of iron implanted with bismuth, an element with virtually zero solid solubility.

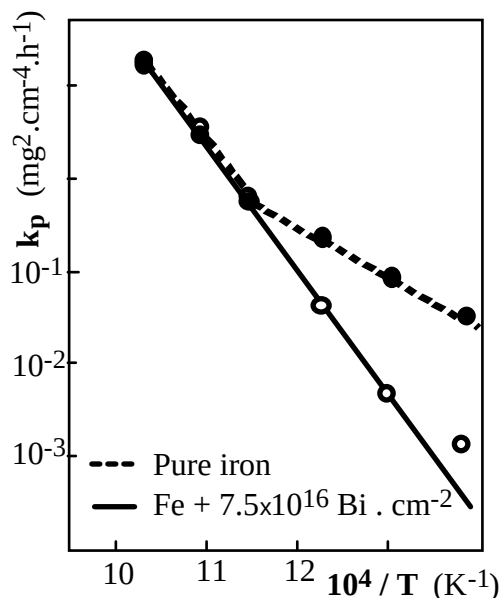


Figure 6.19. Arrhenius plot of the parabolic constant for the oxidation, under 133 mbar of oxygen, of pure iron and of iron implanted with bismuth (from Pons et al.¹⁴).

The comparison with the curve for non-implanted iron shows that:

- the Arrhenius plot for the oxidation of pure iron shows the classical dependence on temperature in that grain boundary transport in the oxide dominates at lower temperatures and lattice diffusion at higher temperatures;
- the Arrhenius plot for the Bi-implanted iron consists of one straight line only, with a slope corresponding to the lattice diffusion of iron, so showing that grain boundary transport is inhibited by the implantation; this effect is due to the blocking action of a mixed oxide, $\text{Fe}_2\text{B}_4\text{O}_9$ ¹⁴ which decorates the oxide grain boundaries.

Segregation of ion-implanted species at the metal-oxide interface and blocking of the interfacial half-reaction

The model proposed by Pieraggi and Rapp¹⁵ of interfacial reaction blocking by pinning interfacial dislocations is well suited to discuss the observed effects of ion

¹⁴ M. Pons, A. Galerie and M. Caillet, *Corrosion Science*, **23** (1983) 1181-1189.

¹⁵ B. Pieraggi and R.A. Rapp, *J. Electrochem. Soc.*, **140** (1993) 2844-2850.

implantation. Implanted elements rapidly segregate to that interface and block interface movements. They may also form an oxide diffusion barrier due to their substantial enrichment during the external growth of p-type cation-deficient oxides. Such effects are clearly shown by the kinetic curves of iron oxidation after aluminium or boron implantation.

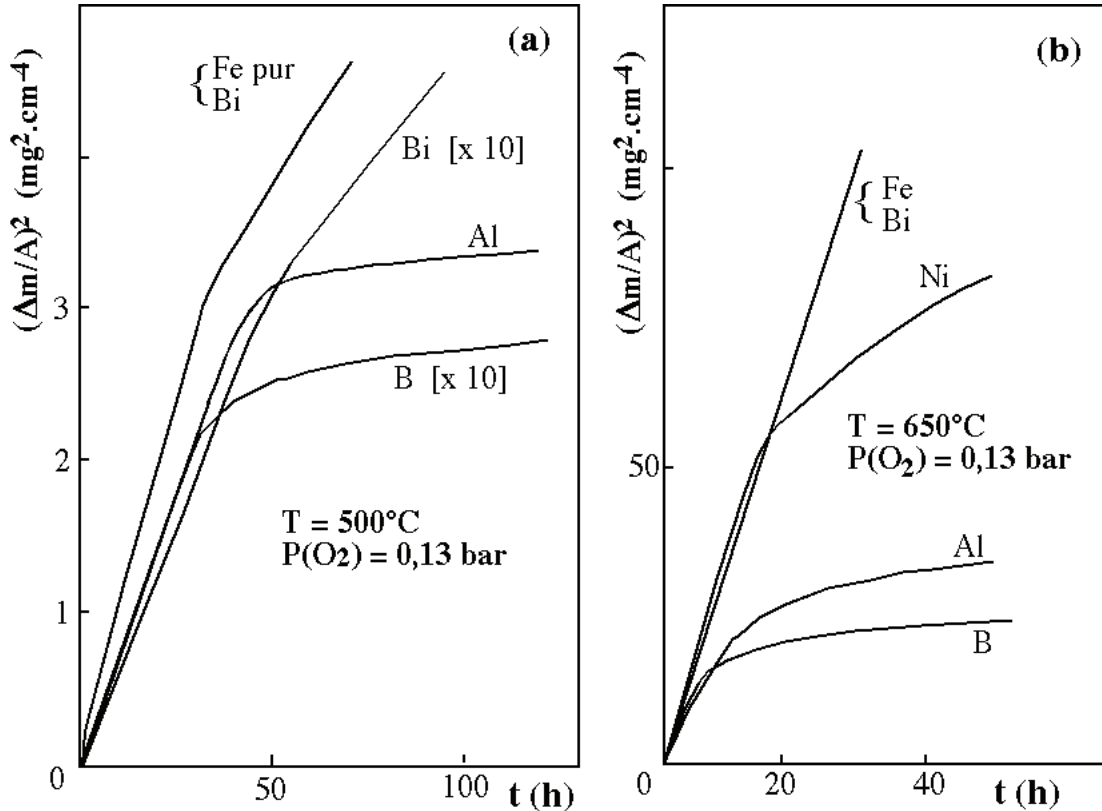


Fig. 6.20. The blocking of iron oxidation by aluminium or boron implantation (from Pons et al.¹⁶)

3.1.2.3. Industrial applications

Although it has substantial potential, ion implantation is seldom used in the field of high temperature corrosion although it is a very interesting tool for research purposes. However, the technique will probably gain more attention with the development of large scale plasma immersion ion implantation where large parts of complex shapes can be easily treated.

3.1.3. Laser surface alloying (LSA)

3.1.3.1. Principle of the technique

Surface alloys can be manufactured by surface melting with concurrent matter addition in the liquid state. For such purpose one needs a convenient surface melting device, able to create a solid liquid interface that can propagate rapidly into the metallic material to

¹⁶ M. Pons, A. Galerie and M. Caillet, *Defect and Diffusion Forum*, **57-58** (1988) 189-206.

be treated to a depth of a fraction of millimetre; this is the melting phase of the process. It is then necessary for the melting device to return to the surface at the end of the heating period; this is the solidification phase of the process. The total duration of the process is between 1 ms and 1 s. Electron bombardment may be used to effect melting but laser irradiation is preferred, either with pulsed or continuous sources.

In addition, there needs to be a system of matter distribution so allowing the introduction of chosen elements or compounds into the melted pool. Rapid convection within the pool leads to liquid homogeneity. The added matter may be deposited before melting, as a coating or paint, but is preferably blown onto the melted zone. A schematic description of the Laser Surface Alloying technique is given in Fig. 6.21 for the case of a pre-deposited coating.

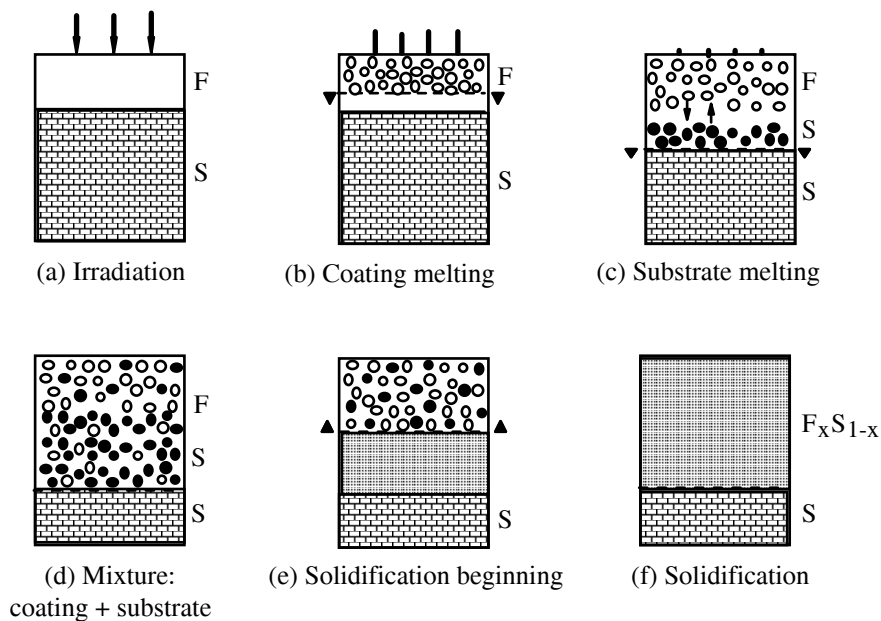


Fig. 6.21. Successive steps of surface alloy formation by LSA from a deposited film (F) on a metallic substrate (S) leading to the alloy $F_xS_{(1-x)}$.

3.1.3.2. Potential applications

Due to their large thickness, laser surface alloys behave as bulk alloys and have similar properties to these. Interest in the technique lies in the possibility of separately optimising the bulk and surface properties. It is, for example, possible to generate thin Fe-Al surface alloys up to 25 at.% Al although bulk materials of this composition are definitely too brittle to be prepared or used. Such surface alloys behave very well in sulphur-containing atmospheres due to the selective oxidation of aluminium to Al_2O_3 even at very low oxygen partial pressures (Fig. 6.22). It is also possible to produce two-phase surface alloys on steels, with the ferritic or austenitic matrix being enriched with a soluble element, affording good

corrosion properties, and a second phase, of low solubility (Fe_2B , FeB , Cr_7C_3 , TiC , SiC , etc.), to provide wear resistance or a reservoir effect..

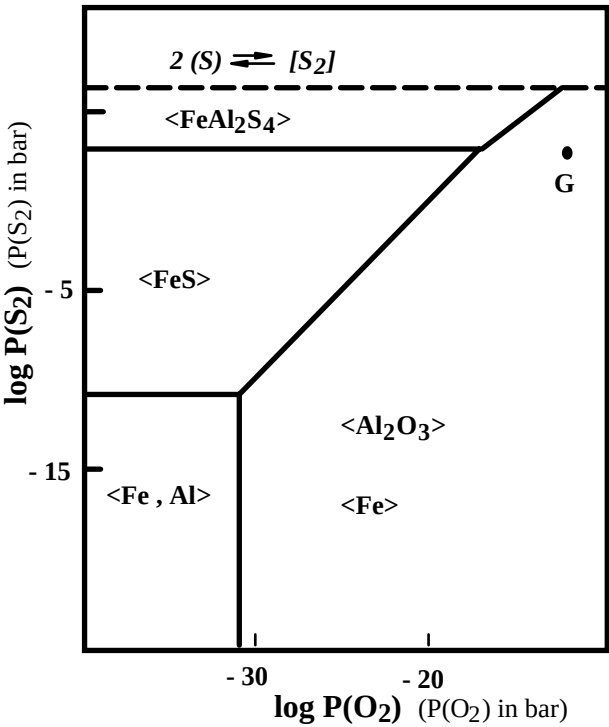


Fig. 6.22. Phase stability diagram used for discussing oxidation of iron-aluminium surface alloys in industrial gas mixtures containing sulphur and oxygen (G is an example of conditions in a coal gasification atmosphere).

The use of laser-modified surface alloys is today dependent on the technical development of high-power lasers, particularly with regard to power stability, reliability and cost.

3.2. Coatings

Surface coatings may be applied by various physical and/or chemical techniques but only vapour deposition and plasma spraying will be described in this Chapter. These techniques are those with potential industrial applications in the field of high temperature corrosion protection.

3.2.1. Chemical Vapour Deposition (CVD)

3.2.1.1. Principle of the technique

CVD is a thermochemical treatment where the coating grows by reaction with species from the gas phase, as shown in Fig. 6.23.

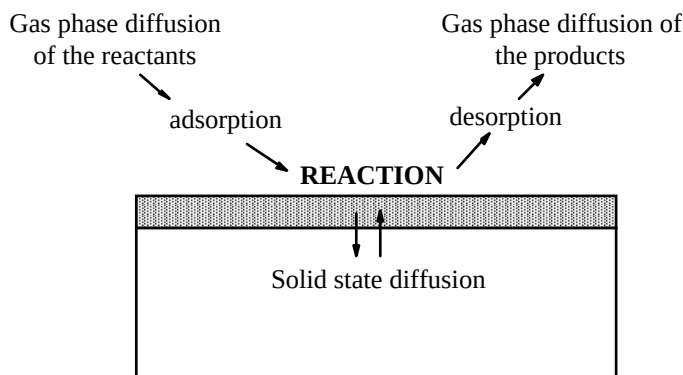


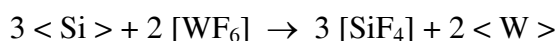
Fig. 6.23. A schematic description of the CVD technique.

3.2.1.2. Precursors

CVD coatings generally contain a metallic element (or sometimes a near-metallic element, such as Si or B), associated with a non metallic one such as C, O or N. The metallic element is mainly transported by a volatile halide (TiCl_4 , WF_6 , AlBr_3 , etc.), generated from a gasifier which evaporates the solid product or through reaction of the metal with the halogen. Silicon and boron may be transported in the form of the hydrides SiH_4 and B_2H_6 which are gaseous at room temperature. Organometallic compounds (aluminium tri-isobutyl) or oxygen-containing metallates (alcooates, acetylacetonates) are used increasingly. The second (non-metallic) element is mostly used in its simplest form (O_2 , N_2) but also as a compound such as H_2O , CO_2 , NH_3 or CH_4 . Dilution by a carrier gas is necessary to control the partial pressures; argon is commonly used or hydrogen if reducing conditions are needed.

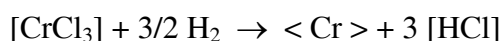
3.2.1.3. Examples of CVD reactions

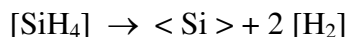
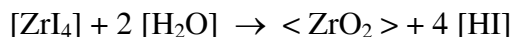
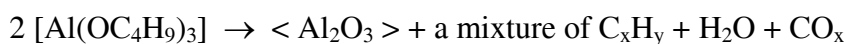
Reduction by the substrate



This is called a “displacement” reaction and occurs only in the early stages of coating formation. Its interesting feature is the possibility of selective deposition of tungsten on bare areas of the substrate.

Reduction on inert substrates



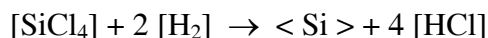
Internal redox reaction**Intermolecular acid-base reaction****Intramolecular acid-base reaction**

It should be noted that, for metallic substrates treated at high temperatures, it can be difficult to differentiate between CVD coatings and surface alloys. This is because solid state diffusion occurring during the CVD process may lead to surface alloys where the surface material is never the pure deposited element or compound. The term *gas phase cementation* describes the technique used, for example, to aluminise superalloys or refractory alloys without using a powder pack.

3.2.1.4. Thermodynamic aspects

CVD reactions at high temperature (500 – 1000°C) may rapidly achieve thermodynamic equilibrium. Predictions of stable phases are therefore often realistic and can be done by considering the system to be either open or closed.

- Calculations in an open system suppose that all intensive parameters are fixed and, so, may be done “by hand”, using combinations of equilibrium constants corresponding to clearly identified reactions, for example



The variance of this reaction is 3 and the equilibrium condition can be plotted on a $P(\text{SiCl}_4)$ / temperature diagram, provided that the H_2 and HCl pressures are fixed (Fig. 6.24).

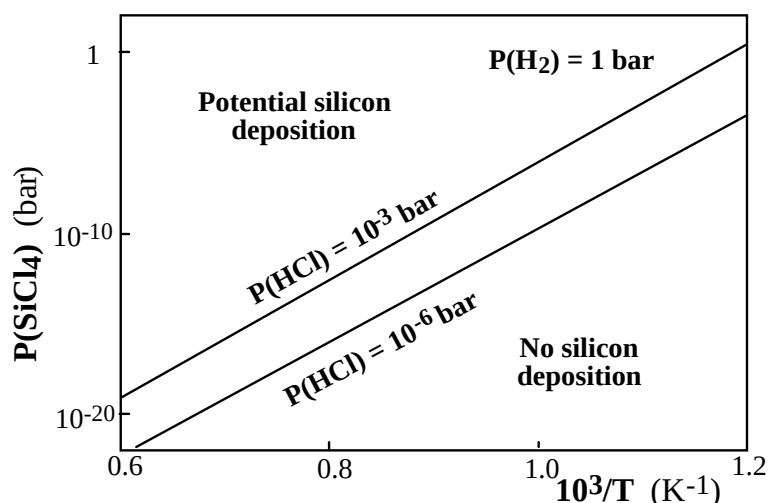


Fig. 6.24. Condition for the formation of silicon deposits as a function of temperature and partial pressures of the reactant and product gases.

- Calculations in closed system assume the amount of matter in the CVD reactor is fixed. Gibbs enthalpy minimisation can be numerically calculated without stipulating the reactions that take place. The results of such calculations for the Ti-Si-H-Cl system are shown in Fig. 6.25. Beside its power and rapidity, an advantage of this method is that direct connections can be made not only with thermodynamic but also with kinetic and hydrodynamic databases. These can provide information on the nature and amount of the CVD coating as a function of temperature, pressure, time, flow-rates and reactor geometry.

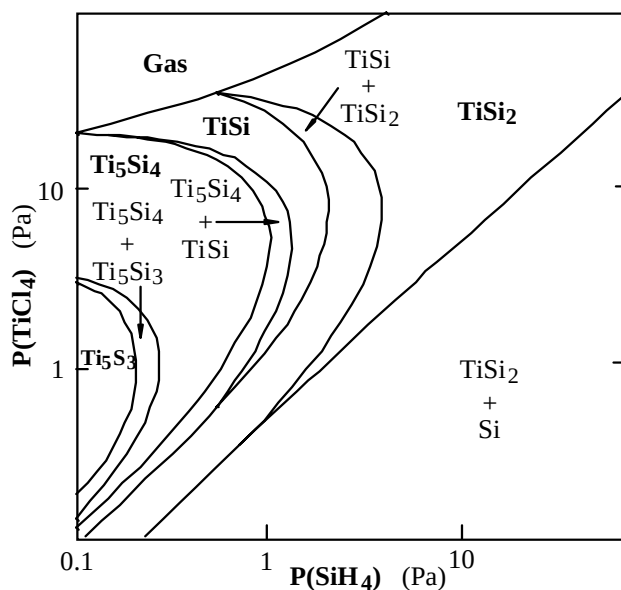


Fig. 6.25. Phases formed at equilibrium in the system $\text{SiH}_4 - \text{TiCl}_4 - \text{Ar}$ at a total pressure of 330 Pa and temperature of 1073 K as a function of the partial pressures of the reacting species (from Pons et al.¹⁷).

¹⁷ M. Pons, J.N. Barbier, C. Bernard and R. Madar, *Applied Surface Science*, **73** (1993) 71-81.

Kinetic aspects

A simplified kinetic model of a CVD reaction is to consider it as a series of two elementary steps:

- diffusion of the reacting gas with a diffusion coefficient D from the gas source (at partial pressure P) to the solid surface through the boundary diffusion layer of constant thickness δ where the major constituent is the inert diluting gas,
- reaction at the surface of the growing solid product, supposed far from equilibrium, with a rate proportional to the pressure P_s of the reacting species at the substrate surface.

Assuming steady-state conditions, the two steps will have equal rates:

$$J = D \frac{P - P_s}{\delta} = kP_s \quad (6.19)$$

It follows that the reactant pressure in contact with the substrate is then:

$$P_s = \frac{DP}{D + k\delta} \quad (6.20)$$

The reaction rate is therefore:

$$r = \frac{kDP}{D + k\delta} \quad (6.21)$$

which is generally used in the following form:

$$r = \frac{kP}{\left(1 + k \frac{\delta}{D}\right)} \quad (6.22)$$

In Eq. 6.22, the dimensionless number $k\delta/D$ is called the *CVD number*. For extreme values of this number, two limiting cases can be defined:

- $k\delta/D \ll 1$ leads to $r = kP$ and the CVD process occurs in a pure reaction regime.
- $k\delta/D \gg 1$ leads to $r = DP/\delta$ and the limiting step is then gas phase diffusion.

Noting that temperature has a very much smaller influence on the diffusion coefficient D in the gas phase than on the reaction rate constant k , the Arrhenius plots of CVD rates have the trends shown in Fig. 6.26. It can be seen that at low temperatures a significant temperature dependence exists whereas virtually no temperature effect is observed at high

temperatures. One important fact also is that limitation by the reaction step becomes more important at low pressures, encouraging CVD production processes towards low pressures to obtain very uniform films. In this regime, the influence of δ , the boundary diffusion layer thickness, is minimised. This parameter is indeed difficult to control experimentally.

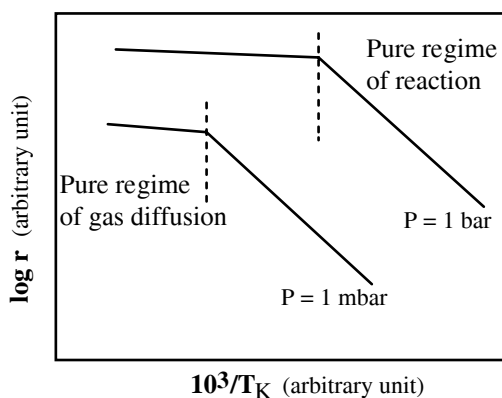


Fig. 6.26. Schematic Arrhenius plot of CVD reactions at different reactant pressures.

3.2.1.5. Industrial developments

CVD processes are mostly used in the electronic industry but have also a large market in metallurgy when wear has to be prevented for which TiC, TiN or CrN coatings may be used. In high temperature applications, mixed coatings may be used, consisting of TiN associated with aluminium, forming $\text{Ti}_{1-x}\text{Al}_x\text{N}$, which are good candidates for high temperature wear resistance through the formation of a thin alumina surface film. For turbine applications, the use of aluminium diffusion from the gas phase to replace pack cementation techniques is rapidly becoming more widespread.

3.2.2. Plasma spraying

Thermal spraying consists in the use of a flame to melt and transport materials, originally in the form of powders, onto the substrate to be coated. Thermal flames, used in the past, have now been replaced by plasmas in which temperatures lie in the range 10000 – 30000 K and have velocities as high as several 100 m.s^{-1} (Fig. 6.27). Particles injected into the plasma are therefore rapidly melted even for very short residence times and splat onto the cool substrate, forming the coating by rapid solidification. All materials can be sprayed by this technique, even refractory alloys or ceramics. For high temperature applications, Ni-based superalloys and zirconia thermal barriers are the most common materials used.

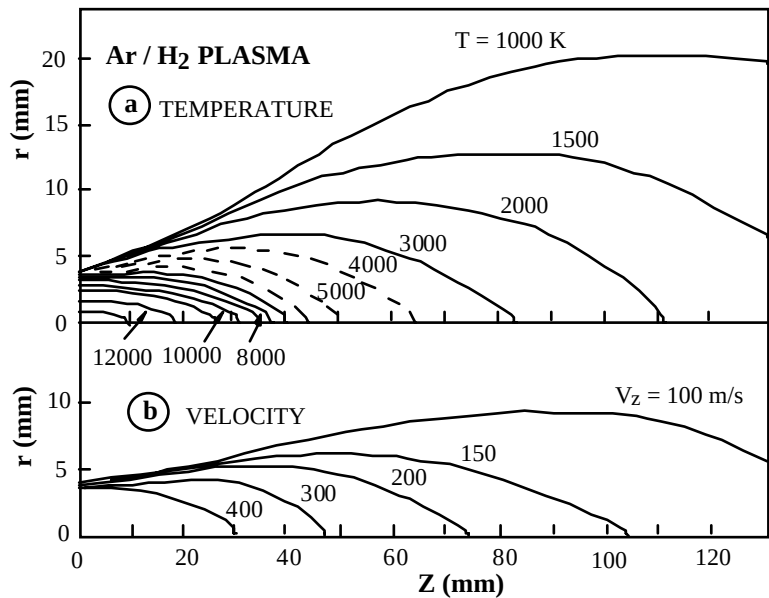


Fig. 6.27. Temperature and gas velocity in a 29 kW Ar-H₂ plasma flame at different places in the flame (Z: distance from the nozzle, r: distance from the flame axis).

3.2.2.1. Superalloy coatings

MCrAlY-type superalloy coatings, with M = Ni, Co, Fe, exhibit two interesting properties:

- they can be adjusted to have compositions near that of the substrate, avoiding differential strain problems and possible loss of adhesion;
- they provide high resistance to oxidation due to the combined effects of Al and Y (see section 2.4.2).

3.2.2.2. Thermal barrier coatings (TBCs)

A thermal barrier is defined as a coating with a thermal conductivity much lower than that of the substrate. Provided that the substrate is internally cooled, it generates a thermal gradient lowering the surface temperature of the substrate. As a result, the operating temperature of the system can be increased by the same amount without degrading the base alloy excessively. The most commonly used material for this purpose is zirconia, ZrO₂, due to its excellent thermal properties as shown in Table 6.7.

Table 6.7. Comparison of thermal conductivities of zirconia and two metallic materials.

MATERIAL	Zirconia	Stainless steels	Superalloys
Thermal conductivity (W.m ⁻¹ .K ⁻¹)	0.5 – 2.0 (depending on density)	approx. 300	approx. 12

For reliable use, zirconia must be stabilised by small additions of yttria, Y₂O₃, producing a cubic fluorite-type structure at all temperatures. This inhibits the possible monoclinic-tetragonal transformation which produces cracking due to volume changes (Table 6.8).

Table 6.8. Comparison of the molar volumes of monoclinic and tetragonal zirconia.

	Monoclinic	Tetragonal
Stability range	T < 1 300 K	T > 1 300 K
Molar volume (cm ³ .mol ⁻¹)	21.9	20.2

Plasma spraying produces zirconia with a high porosity (5 – 10 %) which increases the thermal insulation due to the presence of the small gas inclusions and may also relax high thermal stresses by grain boundary sliding. If low porosity is needed, spraying must be performed under reduced pressure.

Chapter 7

CASE STUDIES and WORKED EXAMPLES

1. Stoichiometry and electrical conductivity of NiO

N.B. In this example, the defect concentrations in the NiO lattice will be expressed in number of moles per mole of NiO.

We have: $Ni = 58.7 \text{ g.mol}^{-1}$ $O = 16 \text{ g.mol}^{-1}$.

Let Ω be the volume of one mole of oxide.

In the temperature range 1173 K - 1373 K, nickel monoxide NiO is a non-stoichiometric, metal-deficient compound, so that:

$$\frac{\text{number of moles of Ni}}{\text{number of moles of O}} < 1$$

In the following, the oxide will be referred as $Ni_{1-x}O$.

1.1. Section 1

1.1.1. The Arrhenius plots of the self-diffusion coefficients of nickel D_{Ni} and of oxygen D_O in nickel monoxide are given in Fig. 7.1 (oxygen pressure, $P = 1$ bar).

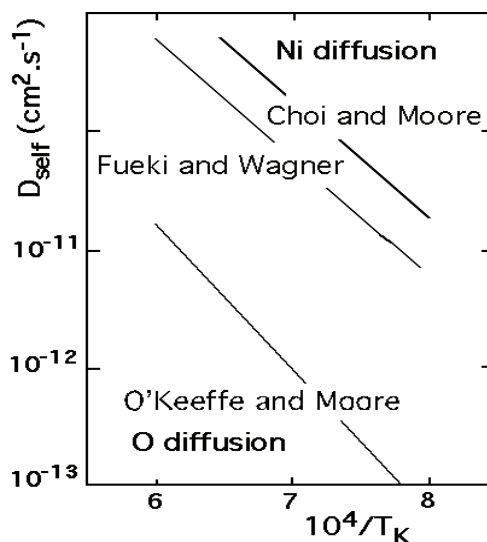


Figure 7.1. Arrhenius plot of the self-diffusion coefficients of nickel D_{Ni} and of oxygen D_O ¹.

¹ P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*, J. Wiley, New York, 1972, p. 259.

Deduce the nature of the predominant defects in the NiO lattice between 1173 K and 1373 K.

1.1.2. Write the external equilibria assuming that neutral, singly and doubly ionised defects coexist in the NiO lattice.

1.1.3. List the system of equations needed to calculate the deviation from stoichiometry x and the electrical conductivity σ as a function of the oxygen pressure P .

The thermodynamic equilibrium constants of the previous reactions leading to defect formation and referred to one mole of defects will be designated K_0 , K_1 and K_2 , respectively; d_0 , d_1 and d_2 will be the ionic defect concentrations (the subscripts correspond to their degree of ionisation); u_1 and u_2 will be their electrical mobilities; h , the electronic defect concentration and u_h , the electronic mobility.

1.1.4. Deduce from the previous system the expression for x and σ as a function of P assuming that only one type of defect is predominant (degree of ionisation of 0, 1 or 2). The results should be presented in the form of a table.

What limit does the deviation, x , from stoichiometry tend towards when the oxygen pressure becomes very low?

1.2. Section 2

At 1373 K, a sample of nickel monoxide, 6.683 g in weight, previously maintained for several hours under very low oxygen pressure ($P = 10^{-8}$ bar), is submitted to increasing pressures of this gas. The weight change Δm of this sample as a function of the oxygen pressure is given in the following table.

P bar	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
Δm μg	6	11	20	35	66	107	201

1.2.1. Let m_0 be the weight of the stoichiometric sample of nickel monoxide and m the weight of the non-stoichiometric sample, respectively. Give the expression for x as functions of m and m_0 and deduce from the previous table the variation of x as a function of P .

1.2.2. Plot x as a function of P using appropriate axes for the graph.

1.2.3. What is the nature of the predominant defect at 1373 K? Is it possible to calculate K_0 , K_1 and K_2 ?

1.2.4. From the results of Choi and Moore, calculate the diffusion coefficient D_d of this defect at 1373 K (correlation factor $f = 0.78$). Deduce the expression for the nickel self-diffusion coefficient D_{Ni} as a function of the oxygen pressure at 1373 K.

1.3. Section 3

The previously published variation of the electrical conductivity of NiO as a function of the oxygen pressure, at the same temperature, is given in the following table:

P bar	1	1.94×10^{-1}	5.75×10^{-2}	1.58×10^{-2}	3.98×10^{-3}
σ_t $\Omega^{-1} \cdot \text{cm}^{-1}$	3.98×10^{-1}	2.63×10^{-1}	1.86×10^{-1}	1.45×10^{-1}	1.05×10^{-1}

P bar	1.45×10^{-3}	2.51×10^{-4}	7.94×10^{-5}	1.26×10^{-5}	2.51×10^{-6}
σ_t $\Omega^{-1} \cdot \text{cm}^{-1}$	7.50×10^{-2}	5.24×10^{-2}	4.46×10^{-2}	4.16×10^{-2}	3.99×10^{-2}

Show that these results are not in agreement with the previous ones (see section 1.2) in the low oxygen pressure range.

1.4. Section 4

To explain this difference, it has been assumed that the NiO samples used by these last authors would contain monovalent metallic impurities (such as Li), that would occupy normal cationic sites in the lattice.

1.4.1. For such conditions, list the system of equations needed to calculate the concentrations of vacancies and electron holes (referred to as $\bar{x}$ and $\bar{h}$, respectively), as a function of the oxygen pressure **P**. The concentration of the monovalent impurity will be referred to as α .

1.4.2. Deduce the relationship $\bar{h} = f(P)$.

1.4.3. Show that the shape of the experimental conductivity curve agrees with this equation.

1.4.4. Calculate the order of magnitude of the concentration of the monovalent impurity in the oxide.

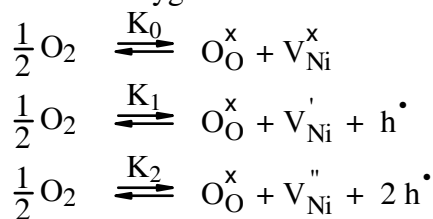
1.4.5. From the K_1 value, calculated in 1.2.3, plot $\bar{x}$ as a function of P for the doped NiO sample (referred to as $\text{Ni}_{1-\bar{x}-\alpha}\text{Li}_\alpha\text{O}$). Compare with the results obtained in 1.2.2.

Answers

1.1.1. The nickel self-diffusion coefficient is significantly greater than that of oxygen. Thus it is likely that the predominant defects are located in the cationic sub-lattice.

Moreover, since $\frac{\text{Ni number of moles}}{\text{O number of moles}} < 1$, the predominant defects are: V_{Ni}^x , V_{Ni}' and V_{Ni}'' .

1.1.2. Equilibria at the oxygen/oxide interface:



1.1.3. System of equations:

$$\begin{aligned}[V_{\text{Ni}}^x] &= d_0 = K_0 P^{1/2} \\ [V_{\text{Ni}}'] \cdot [h^\bullet] &= d_1 \cdot h = K_1 P^{1/2} \\ [V_{\text{Ni}}''] \cdot [h^\bullet]^2 &= d_2 \cdot h^2 = K_2 P^{1/2} \\ x &= [V_{\text{Ni}}^x] + [V_{\text{Ni}}'] + [V_{\text{Ni}}''] \quad \text{or, } x = d_0 + d_1 + d_2 \\ [h^\bullet] &= [V_{\text{Ni}}'] + 2 [V_{\text{Ni}}''] \quad \text{or, } h = d_1 + 2 d_2 \quad (\text{electroneutrality}) \\ \sigma &= \frac{F}{\Omega} (u_1 \cdot d_1 + 2 u_2 \cdot d_2 + h \cdot u_h).\end{aligned}$$

The mobility of the electronic defects is much higher than that of the ionic defects, (i.e., $u_h \gg u_1$ and u_2). This then leads to:

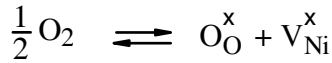
$$\sigma = \frac{F}{\Omega} (h \cdot u_h) = \frac{F}{\Omega} (d_1 + 2 d_2) \cdot u_h$$

1.1.4. Expressions for x and σ as a function of P .

Predominant defects	$[V_{\text{Ni}}^x]$	$[V_{\text{Ni}}'] = h$	$[V_{\text{Ni}}''] = \frac{h}{2}$
x	$K_0 P^{1/2}$	$K_1^{1/2} P^{1/4}$	$\left(\frac{K_2}{4}\right)^{1/3} P^{1/6}$
σ	depends on the nature of the "predominant" ionic defect	$\frac{F \cdot u_h}{\Omega} K_1^{1/2} P^{1/4}$	$\frac{2 F \cdot u_h}{\Omega} \left(\frac{K_2}{4}\right)^{1/3} P^{1/6}$

The deviation from stoichiometry x tends towards zero when the oxygen pressure becomes very low.

1.2.1. When the pressure P is increased, oxygen is transferred from the gas into the NiO lattice according to:



The total vacancy concentration, x , may be calculated as a function of the initial weight m_0 and of the weight m under the pressure P :

$$x = \frac{\frac{m - m_0}{16}}{\frac{m_0}{16 + 58.7}} = 0.699 \Delta m, \text{ with } \Delta m \text{ expressed in g}$$

Or: $x = 0.699 \times 10^{-6} \Delta m$, with Δm expressed in μg .

$$x = A \cdot P^{1/n}$$

1.2.2. Plot of x versus P .

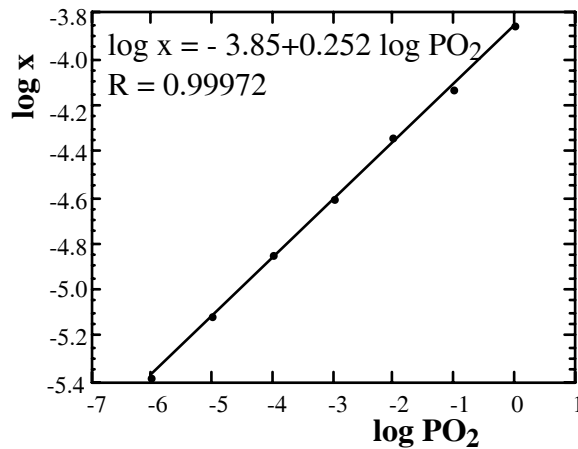


Figure 7.2. Non-stoichiometry in NiO (x in Ni_{1-x}O) as a function of the partial pressure of oxygen.

Thus, we obtain: $x = 1.41 \times 10^{-4} P^{1/4}$

(in fact, $x = 1.41 \times 10^{-4} \left[\frac{P}{P^\circ} \right]^{1/4}$ with $P^\circ = 1 \text{ bar}$)

1.2.3. It may be concluded that the predominant defects are the singly charged nickel vacancies, $\text{V}_{\text{Ni}}^{\cdot}$.

From the x expression (see question 1.1.4), K_1 may be calculated. Substitution yields:

$$K_1 = 2 \times 10^{-8}.$$

K_0 and K_2 cannot be calculated.

1.2.4. At 1373 K, D_{Ni} lies around $1 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ (Fig. 7.1) and $x = 1.41 \times 10^{-4}$ (Fig. 7.2).

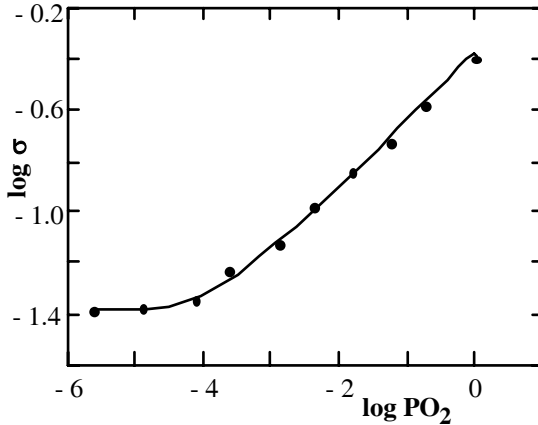
$$D_{Ni} = \frac{C_d}{C_{Ni}} D_d = x \cdot D_d$$

$$D_d = 7.09 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$$

$$D_{Ni} = 10^{-10} \cdot P^{1/4}$$

The nickel self-diffusion coefficient depends on P but D_d does not and is independent of the oxygen pressure.

1.3.



For $P > 10^{-3}$ bar, σ is proportional to $P^{1/4}$ (as is x):

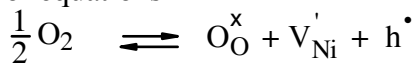
$$\sigma = 0.39 P^{1/4} = \sigma_0 \cdot P^{1/4}$$

For $P < 10^{-5}$ bar, σ is virtually constant.

Figure 7.3. The conductivity of NiO as a function of the oxygen pressure.

1.4. Influence of the metallic impurity: Li'_{Ni}

1.4.1. System of equations.



$$[V'_{Ni}] \cdot [h^\bullet] = \bar{d}_1 \cdot \bar{h} = K_1 P^{1/2}$$

$$\bar{h} = \bar{d}_1 + \alpha \quad (\text{electroneutrality})$$

Thus: $(\bar{h} - \alpha) \cdot \bar{h} = K_1 P^{1/2}$

1.4.2. $\bar{h}^2 - \bar{h} \cdot \alpha - K_1 P^{1/2} = 0$

$$\bar{h} = \frac{\alpha + \sqrt{\alpha^2 + 4 K_1 P^{1/2}}}{2}$$

1.4.3. Under high oxygen pressure P :

$$\bar{h} = K_1^{1/2} P^{1/4}$$

Under very low oxygen pressure:

$$\bar{h} = \alpha = \text{cst}$$

1.4.4. Order of magnitude of the concentration of the monovalent impurity.

$$\sigma = a \cdot h$$

$$\frac{\sigma_{\text{high } P}}{\sigma_{\text{low } P}} = \frac{x}{\alpha}$$

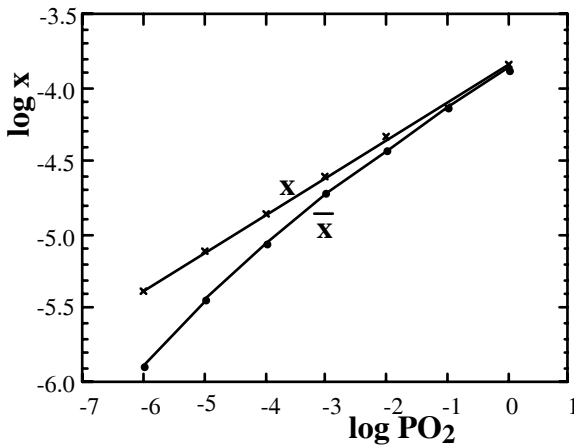
$$\alpha = 0.1 x_{\text{high } P}$$

$$\alpha = 1.4 \times 10^{-5}$$

1.4.5. Variation of $\bar{x}$ with P .

$$\bar{h} = \frac{\alpha + \sqrt{\alpha^2 + 4 K_1 P^{1/2}}}{2}$$

$$\bar{x} = \bar{h} - \alpha = \frac{-\alpha + \sqrt{\alpha^2 + 4 K_1 P^{1/2}}}{2}$$



The curves compare the variations of x and of $\bar{x}$ as a function of P .

$$\text{Under high } P: \bar{x} = K_1^{1/2} P^{1/4}$$

$$\text{Under low } P: \bar{x} = \frac{K_1 P^{1/2}}{\alpha}$$

Figure 7.4. Comparison of the dependences of x and $\bar{x}$ on the oxygen partial pressure.

$$\bar{h}^2 - \bar{h} \cdot \alpha - K_1 P^{1/2} = 0 \text{ and } \sigma = a \cdot h$$

Or:
$$\frac{P^{1/2}}{\sigma} = \frac{\sigma}{K_1 a^2} - \frac{\alpha}{a K_1}$$

If the proposed model is valid, the $\frac{P^{1/2}}{\sigma}$ ratio has to be proportional to the electrical conductivity σ .

It may be noticed that the linear relationship is not followed over the whole oxygen pressure range.

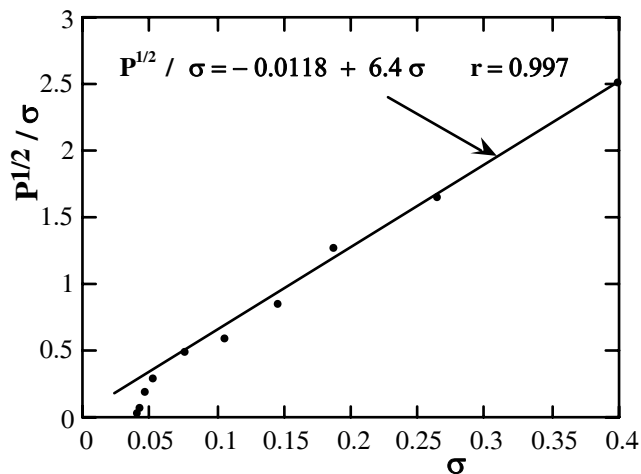


Figure 7.5. Verification of the proposed model.

2. Stoichiometry of Nb_2O_5

N.B. All the defect concentrations will be expressed in number of moles per mole of oxide.

The electron concentration will be referred to as n .

The thermodynamic constants of the equilibria (written in the direction of defect formation) will be referred to one mole of defects.

Over the temperature range 1173 K - 1473 K, Nb_2O_5 is a nonstoichiometric, oxygen-deficient compound so that ($\frac{\text{O number of mole}}{\text{Nb number of mole}} < \frac{5}{2}$). In the following, the oxide will be referred to as $\text{Nb}_2\text{O}_{5-x}$.

2.1. Section 1

2.1.1 What are the types of defects (vacancies or interstitials) that can be present in the lattice? Give all the expected electrical charges for each type of defect considered.

2.1.2. Under the assumption that the predominant defects in the lattice would be doubly ionised oxygen vacancies, with concentration v_2 :

2.1.2.1. Express the equilibrium of the crystal under the oxygen pressure P (equilibrium constant K_{v_2}).

2.1.2.2. Express the relationship between x and the vacancy concentration v_2 .

2.1.2.3. List the system of equations that permits the relationship between x and P to be determined.

2.1.2.4. Solve the system of equations. Deduce the relationship between x and P .

2.1.3. Under the assumption that the predominant defects would be doubly charged metal interstitials, with concentration i_2 :

2.1.3.1. Express the equilibrium of the crystal under the oxygen pressure P (equilibrium constant K_{i_2}).

2.1.3.2. Express the relationship between x and the interstitial concentration i_2 .

2.1.3.3. List the system of equations needed to determine the relationship between x and P .

2.1.3.4. Solve the system of equations. Deduce the relationship between x and P .

2.2. Section 2

Over the temperature range 1173 - 1473 K, the deviation from stoichiometry x (x in $\text{Nb}_2\text{O}_{5-x}$) found experimentally as a function of the oxygen pressure P is given in figure 7.6.

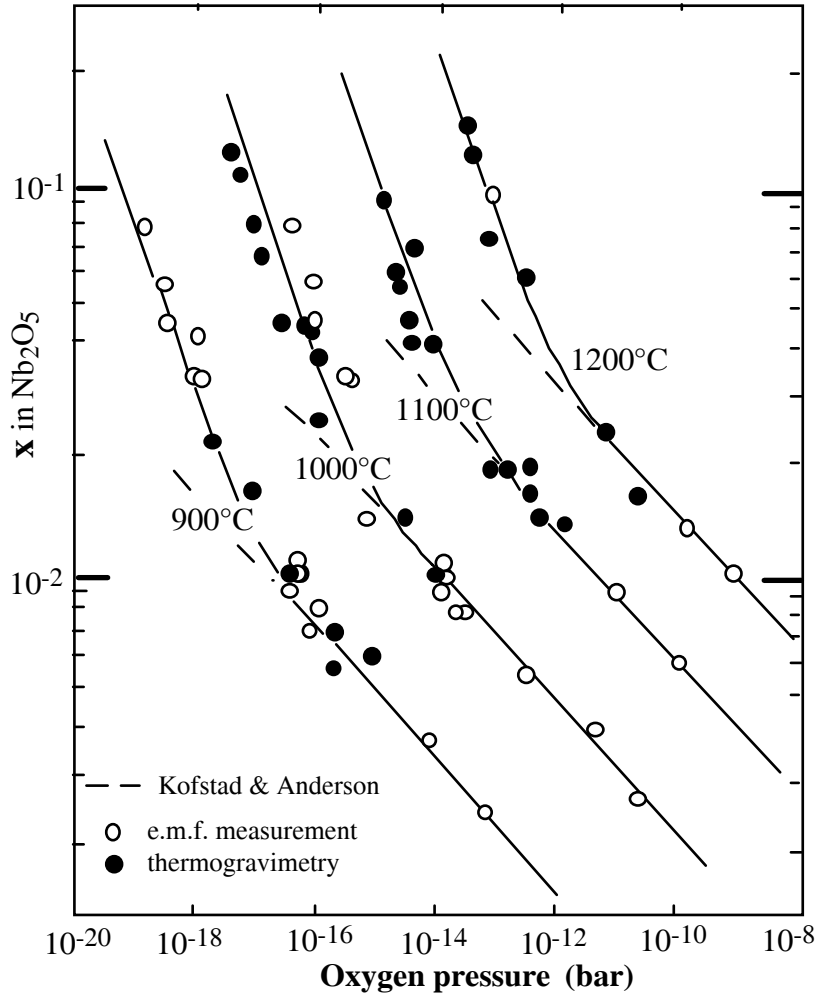


Figure 7.6. The deviation from stoichiometry in Nb_2O_5 (x in $\text{Nb}_2\text{O}_{5-x}$) as a function of the oxygen partial pressure from 1173 K to 1473 K².

Several authors have interpreted these results on the assumption that two types of point defects co-exist within the lattice.

2.2.1. On this hypothesis, what are the point defects and the effective charge? In answering this question, plot in figure 7.6 straight lines with slopes of $-\frac{1}{6}$ and $-\frac{5}{12}$.

2.2.2. On this hypothesis, express the relationship between x and the point defect concentrations.

² P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*, J. Wiley, New York, 1972, p. 186.

2.2.3. List the system of equations needed to determine the relationship between x and P .

2.2.4. Show that under an oxygen pressure P_c both types of defects have the same concentration. Determine the value of P_c .

2.2.5. Solve the system of equations. Deduce the relationship between x and P .

2.3. Section 3

2.3.1. Show that the preceding model allows the shape of the experimental curves at 1173, 1273, 1373 and 1473 K to be explained. Hint: study the limit of $x = f(P)$ for low and high values of P , respectively.

2.3.2. Determine the K_{v_2} and K_{i_2} values at 1173, 1273, 1373 and 1473 K.

2.3.3. Plot K_{v_2} and K_{i_2} as a function of the temperature according to an Arrhenius representation. Deduce the free energy of formation of the vacancies and of the interstitials.

Answers

2.1.1. Possible defects are:

- oxygen vacancies: V_O^x , $V_O^\bullet$, $V_O^{\bullet\bullet}$

- niobium interstitials: Nb_i^x , $Nb_i^\bullet$, $Nb_i^{\bullet\bullet}$, $Nb_i^{3\bullet}$, $Nb_i^{4\bullet}$ and $Nb_i^{5\bullet}$

2.1.2. The predominant defects in the Nb_2O_5 lattice is: $V_O^{\bullet\bullet}$ (with concentration v_2).



2.1.2.2. Structural formula of the oxide: $Nb_2O_{5-v_2}$

where $x = v_2$

$$2.1.2.3. \quad v_2 n^2 P^{1/2} = K_{v_2}$$

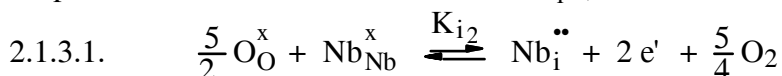
$$2 v_2 = n$$

$$x = v_2$$

2.1.2.4. Solving this system of equations leads to:

$$x = \left(\frac{K_{v_2}}{4}\right)^{1/3} P^{-1/6}$$

2.1.3. The predominant defect in the lattice is: $Nb_i^{\bullet\bullet}$ (with concentration i_2).



2.1.3.2. The structural formula of the oxide is $Nb_{2+i_2}O_5$

Comparison of this formula with $\text{Nb}_2\text{O}_{5-x}$, associated with the definition of x , leads to:

$$\frac{5-x}{5} = \frac{2}{2+i_2}$$

and thus: $x = \frac{5 i_2}{2+i_2}$

since $i_2 \ll 2$, we obtain: $x = \frac{5}{2} i_2$

$$2.1.3.3. \quad i_2 n^2 P^{5/4} = K_{i_2}$$

$$2 i_2 = n$$

$$x = \frac{5}{2} i_2$$

$$2.1.3.4. \text{ Solving this system of equations leads to: } x = \frac{5}{2} \left(\frac{K_{i_2}}{4} \right)^{1/3} P^{-5/12}$$

2.2.1. Point defects: $\text{Nb}_i^{\bullet\bullet}$ and $\text{V}_\text{O}^{\bullet\bullet}$

2.2.2. The structural formula of the oxide is $\text{Nb}_{2+i_2}\text{O}_{5-v_2}$

Comparison with the formula $\text{Nb}_2\text{O}_{5-x}$, leads to:

$$\frac{5-x}{5-v_2} = \frac{2}{2+i_2}$$

and thus: $x = \frac{5 i_2 + 2 v_2}{2+i_2}$

since $i_2 \ll 2$, we obtain : $x = \frac{5}{2} i_2 + v_2$

$$2.2.3. \quad v_2 n^2 P^{1/2} = K_{v_2} \quad (1)$$

$$i_2 n^2 P^{5/4} = K_{i_2} \quad (2)$$

$$2 (i_2 + v_2) = n \quad (3)$$

$$x = \frac{5}{2} i_2 + v_2 \quad (4)$$

$$2.2.4. \text{ From the equality } i_2 = v_2, \text{ we obtain: } P_c = \left(\frac{K_{i_2}}{K_{v_2}} \right)^{4/3}$$

2.2.5. Equations (1), (2) and (3), lead to:

$$n^2 (i_2 + v_2) = K_{v_2} P^{-1/2} + K_{i_2} P^{-5/4}$$

$$n^3 = 2 [K_{v_2} P^{-1/2} + K_{i_2} P^{-5/4}]$$

$$n = (2 [K_{v_2} P^{-1/2} + K_{i_2} P^{-5/4}])^{1/3}$$

$$v_2 = \frac{K_{v_2} P^{-1/2}}{(2 [K_{v_2} P^{-1/2} + K_{i_2} P^{-5/4}])^{2/3}}$$

$$i_2 = \frac{K_{i_2} P^{-5/4}}{(2 [K_{v_2} P^{-1/2} + K_{i_2} P^{-5/4}])^{2/3}}$$

$$x = \frac{\frac{5}{2} K_{i_2} P^{-5/4} + K_{v_2} P^{-1/2}}{(2 [K_{v_2} P^{-1/2} + K_{i_2} P^{-5/4}])^{2/3}}$$

2.3.1. If $K_{v_2} P^{-1/2} \gg K_{i_2} P^{-5/4}$ i.e. $P \gg \left(\frac{K_{i_2}}{K_{v_2}}\right)^{4/3}$ then $P \gg P_c$

$$x = \frac{K_{v_2} P^{-1/2}}{(2 K_{v_2} P^{-1/2})^{2/3}} = \frac{1}{2^{2/3}} (K_{v_2} P^{-1/2})^{1/3}$$

$$x = \left(\frac{K_{v_2}}{4}\right)^{1/3} P^{-1/6}$$

This result may be compared with that obtained in 2.1.2.4 for the case that doubly ionised vacancies predominate.

If $K_{v_2} P^{-1/2} \ll K_{i_2} P^{-5/4}$ i.e. $P \ll \left(\frac{K_{i_2}}{K_{v_2}}\right)^{4/3}$ then $P \ll P_c$

$$x = \frac{5}{2} \frac{K_{i_2} P^{-5/4}}{2^{2/3} (K_{i_2} P^{-5/4})^{2/3}} = \frac{5}{2} \frac{1}{2^{2/3}} (K_{i_2} P^{-5/4})^{1/3}$$

$$x = \frac{5}{2} \left(\frac{K_{i_2}}{4}\right)^{1/3} P^{-5/12}$$

This result may be compared with that obtained in 2.1.3.4 for the case that doubly ionised niobium interstitials predominate.

2.3.2. Determination of K_{v_2} and K_{i_2} .

T	1173 K	1273 K	1373 K	1473 K
K_{i_2}	2.4×10^{-28}	1.7×10^{-25}	2.3×10^{-23}	10^{-20}
K_{v_2}	1.5×10^{-14}	5.3×10^{-13}	9.5×10^{-12}	1.3×10^{-10}

2.3.3. Enthalpies of formation of vacancies and interstitials

$$\text{As } K = \exp\left(-\frac{\Delta_f G^\circ}{RT}\right) = \exp\left(-\frac{\Delta_f H^\circ}{RT}\right) \exp\left(\frac{\Delta_f S^\circ}{R}\right), \quad \frac{d \ln K}{d(1/T)} = -\frac{\Delta_f H^\circ}{R},$$

$$\text{or } \frac{d \log K}{d(1/T)} = -2.303 \times \frac{\Delta_f H^\circ}{R}$$

Enthalpies of defect formation are easily deductible from the slopes of the curves in an Arrhenius-type diagram (Fig. 7.7).

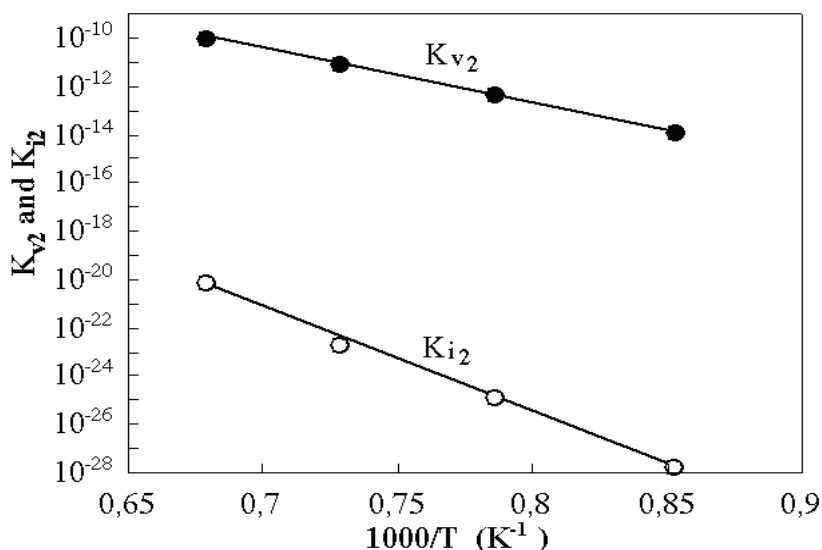


Figure 7.7. Arrhenius plot of the constants K_{i2} and K_{v2} .

$$\Delta H(K_{i2}) = 2.3 \times 8.32 \times 43.1 = 826 \text{ kJ.mol}^{-1} = 8.5 \text{ eV}$$

$$\Delta H(K_{v2}) = 2.3 \times 8.32 \times 22.6 = 433 \text{ kJ.mol}^{-1} = 4.5 \text{ eV}$$

3. Phase equilibria in the system Ni - S - O at 900K

3.1. Stability of nickel oxide in an oxygen atmosphere

3.1.1. What is the equilibrium oxygen pressure of the system Ni - NiO - O₂, at 900K ?

3.1.2. Plot, as a function of the oxygen pressure, the respective stability ranges of Ni and NiO.

3.2 Stability of nickel sulphide in a sulphur atmosphere.

Answer the same questions as above but for the Ni - S system and the following sulphides: Ni₃S₂, NiS and NiS₂.

3.3. The relative stability of nickel oxides and sulphides in mixed sulphur-oxygen atmospheres.

3.3.1. Plot the phase stability diagram for the Ni-O-S system, at 900 K (using $\log P(S_2) / \log P(O_2)$ axes) indicating the stability ranges of the different solid phases, i.e., metal oxide and sulphides.

3.3.2. What part of this diagram has no physical meaning ?

3.3.3. How many degrees of freedom are there at the three triple points ? How many degrees of freedom are there along the straight lines of the diagram ? What can you say regarding the straight lines parallel to the axes?

3.4. Stability domain of nickel sulfate

3.4.1. Indicate the stability domain of NiSO_4 in the diagram plotted in question 3.3.

3.4.2. What is the compound that would be formed starting with nickel, its oxide or one of its sulphides, in an excess of equimolar mixture of O_2 and S_2 under atmospheric pressure at 900 K ? The formation of other sulphur-bearing gaseous species can be neglected.

3.4.3. What is the compound that would be formed in the following mixture: O_2 ($P(\text{O}_2) = 1$ bar) + S_2 ($P(\text{S}_2) = 10^{-10}$ bar) ? Comment.

3.5. Phase equilibria under SO_2

In this section, it will be assumed that SO_2 is the only sulphur and oxygen compound formed.

3.5.1. Plot in the diagram the straight line corresponding to thermal decomposition of SO_2 ($P(\text{SO}_2) = 1$ bar) according to the thermodynamic equilibrium of the reaction:



3.5.2. What is the compound formed in contact with the gaseous phase ($P(\text{SO}_2) = 1$ bar) in the following cases:

- the sulphur dioxide is supposed to be initially pure; when answering this question, plot in the $\log P(\text{S}_2) / \log P(\text{O}_2)$ diagram the line corresponding to the relation between $P(\text{S}_2)$ and $P(\text{O}_2)$.

- the sulphur dioxide, of commercial purity, contains 100 ppm of oxygen.

3.5.3. What is the most probable case, when either a closed or an open reaction vessel is used?

3.6. Phase equilibrium in the presence of SO_2 and SO_3

At low temperatures, the existence of sulphur trioxide SO_3 has to be taken into account.

3.6.1. List the system of equations needed to determine the partial pressure of each gaseous component in an open reaction vessel:

- it will be assumed that the sulphur dioxide is initially pure (in these conditions, the ratio of the number of oxygen atoms to the number of sulphur atom is 2),

- the total pressure will be taken as equal to 1 bar.

3.6.2. The system of equations may be solved numerically or by means of a simple graphical method, proposed by Sarrazin et al.³. Assuming that $X = P(\text{S}_2)^{1/2}$ and $Y = P(\text{O}_2)^{1/2}$, show that the system of equations may be reduced to two quadratic equations in X.

3.6.3. Solve both equations for three values of Y ($\log Y = -6.5$; -7 and -7.5) at 900 K.

3.6.4. Using a $\log P(\text{S}_2) = f(\log P(\text{O}_2))$ diagram, determine the partial pressures of all the gaseous species.

3.7. Comparison with experimental observations

In the temperature range 773 - 1073 K and for a total pressure of 1 bar, nickel oxidation under the atmosphere generated by pure sulphur dioxide leads to the formation of a duplex scale (see chapter 5) as shown schematically in figure 7.8.

³ P. Sarrazin and A. Skalli, *Oxidation of Metals* **30** (1988) 107.

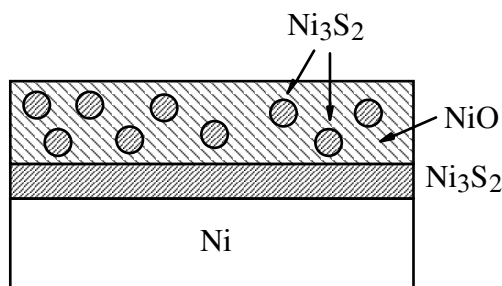


Figure 7.8. Schematic illustration of the scale formed on nickel at 900 K under the atmosphere generated by pure sulphur dioxide.

Can the corrosion products formed be explained from the results obtained in sections 3.4 and 3.5 ? Show that the experimental results could be interpreted taking into account SO_3 in the gas phase.

Data: Gibbs free energy of formation at 900 K (from⁴)

$$\Delta_r G^\circ(\text{NiO}) = -157\,828 \text{ J.mol}^{-1}$$

$$\Delta_r G^\circ(\text{Ni}_3\text{S}_2) = -187\,191 \text{ J.mol}^{-1}$$

$$\Delta_r G^\circ(\text{NiS}) = -74\,601 \text{ J.mol}^{-1}$$

$$\Delta_r G^\circ(\text{NiS}_2) = -96\,380 \text{ J.mol}^{-1}$$

$$\Delta_r G^\circ(\text{NiSO}_4) = -535\,491 \text{ J.mol}^{-1}$$

$$\Delta_r G^\circ(\text{SO}_2) = -295\,973 \text{ J.mol}^{-1}$$

$$\Delta_r G^\circ(\text{SO}_3) = -310\,198 \text{ J.mol}^{-1}$$

$$\text{Boiling of sulphur: } 2 (\text{S})_{\text{liq.}} \rightleftharpoons [\text{S}_2]_{\text{gaz}} \quad \Delta_r G^\circ = -2\,336 \text{ J.mol}[\text{S}_2]^{-1}$$

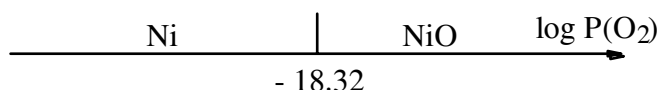
Answers

3.1. Nickel oxide stability in an oxygen atmosphere

$$3.1.1. \text{Ni} + 1/2 \text{O}_2 \rightleftharpoons \text{NiO} \quad \Delta_r G^\circ = -157\,828 \text{ J.mol}^{-1}$$

$$\log P(\text{O}_2) = \frac{2 \Delta_r G^\circ}{2.3 RT} = -18.32$$

3.1.2.



3.2. Nickel sulphide stability in a sulphur atmosphere.

$$3 \text{Ni} + \text{S}_2 \rightleftharpoons \text{Ni}_3\text{S}_2 \quad \Delta_r G^\circ = -187\,191 \text{ J.mol}^{-1}$$

$$\log P(\text{S}_2) = \frac{\Delta_r G^\circ}{2.3 RT} = -10.87$$

$$\begin{aligned} \text{Ni}_3\text{S}_2 + 1/2 \text{S}_2 &\rightleftharpoons 3 \text{NiS} & \Delta_r G^\circ &= 3(-74\,601) + 187\,191 \\ & & &= 36\,612 \text{ J.mol}^{-1} \end{aligned}$$

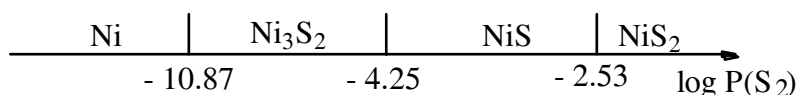
⁴ I. Barin, *Thermochemical Data of Pure Substances*, VCH - Weinheim, 1989.

$$\log P(S_2) = \frac{2 \Delta_r G^\circ}{2.3 RT} = -4.25$$

$$NiS + 1/2 S_2 \rightleftharpoons NiS_2 \quad \Delta_r G^\circ = -96\,380 + 74\,601$$

$$= -21\,779 \text{ J.mol}^{-1}$$

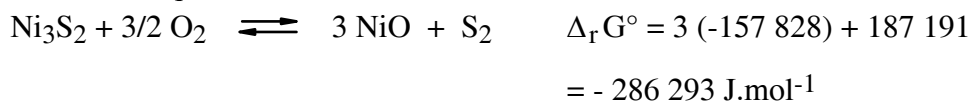
$$\log P(S_2) = \frac{2 \Delta_r G^\circ}{2.3 RT} = -2.53$$



It should be pointed out that the equilibrium pressures increase monotonically as a function of the nickel valence. Thus, each phase has a stability domain. If this were not the case, one (or several) phase(s) would be missing due to their disproportionation.

3.3. Relative stability of oxides and sulphides in sulphur-oxygen mixed atmospheres

3.3.1. Ni_3S_2 / NiO equilibrium



$$\log \left[\frac{P(S_2)}{P(O_2)^{3/2}} \right] = -\frac{\Delta_r G^\circ}{2.3 RT} = 16.620 \quad \log P(S_2) = 16.620 + \frac{3}{2} \log P(O_2)$$

NiS / NiO equilibrium

In the same way:

$$\log P(S_2) = 9.663 + \log P(O_2)$$

NiS_2 / NiO equilibrium

In the same way:

$$\log P(S_2) = 3.567 + \frac{1}{2} \log P(O_2)$$

Figure 7.9 shows the corresponding stability diagram.

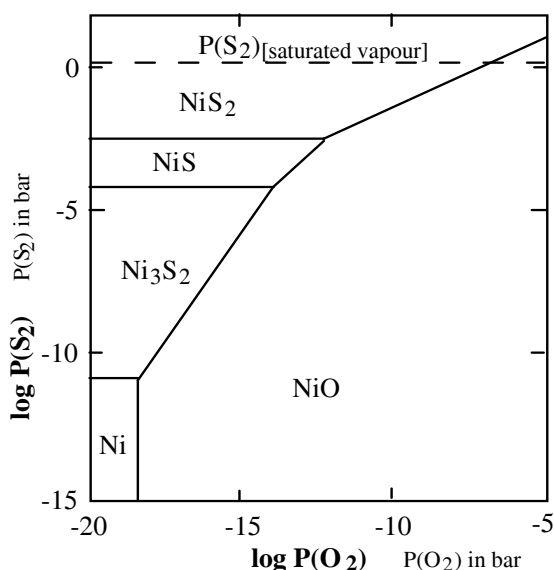
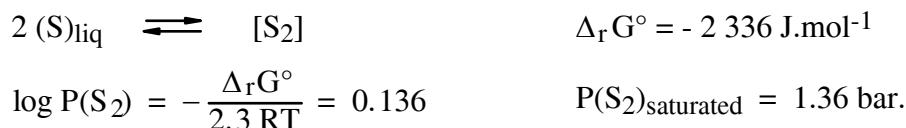


Figure 7.9. Phase stability diagram for the Ni-S-O system, at 900 K, in terms of the activities of O_2 and S_2 .

3.3.2. The equilibrium of sulphur condensation does not permit the S_2 saturated vapour pressure at 900 K to be exceeded:



The corresponding horizontal line has been plotted in figure 7.9. Higher partial pressures of sulphur cannot be reached experimentally.

3.3.3. Expression for the variance: $v = C + 2 - \phi$

The three points with zero degree of freedom correspond to the equilibria between three solid phases and the gas phase ($\phi = 4$). The number of independent components is 3 (Ni, S and O) and, so, $v = 3 + 2 - 4 = 1$.

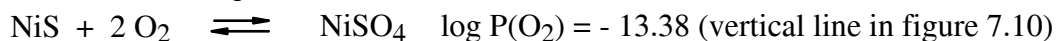
By mixing the phases existing at each triple point, at a given temperature, all the thermodynamic quantities of the system are determined (in particular, $P(S_2)$ and $P(O_2)$ are fixed). If, in addition a partial pressure is fixed at an arbitrary value, the equilibrium is destroyed and it will result in the destruction of one of the solid components. Then the composition of the system follows one of the straight lines in the diagram where the variance is equal to 2. The particular case of the straight lines parallel to the axes may be treated in two different ways:

- all the components are taken into account, hence $v = 2$, but one of the species has no influence on the equilibrium; the system may then be considered as univariant.

- the component (S or O) that is not involved in the reaction is omitted from the list of the independent species; the calculation then gives $v = 1$; the first solution has to be preferred.

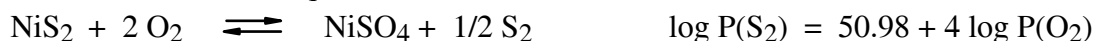
3.4. Stability domain of nickel sulfate

3.4.1 NiS / NiSO₄ equilibrium



Effectively, this calculated NiS/NiSO₄ limit bounds the NiS stability domain determined in question 3.3.1. The limits of the NiSO₄ stability domain may be calculated from the following equilibria:

NiS₂ / NiSO₄ equilibrium



NiO / NiSO₄ equilibrium



The final diagram is shown in figure 7.10.

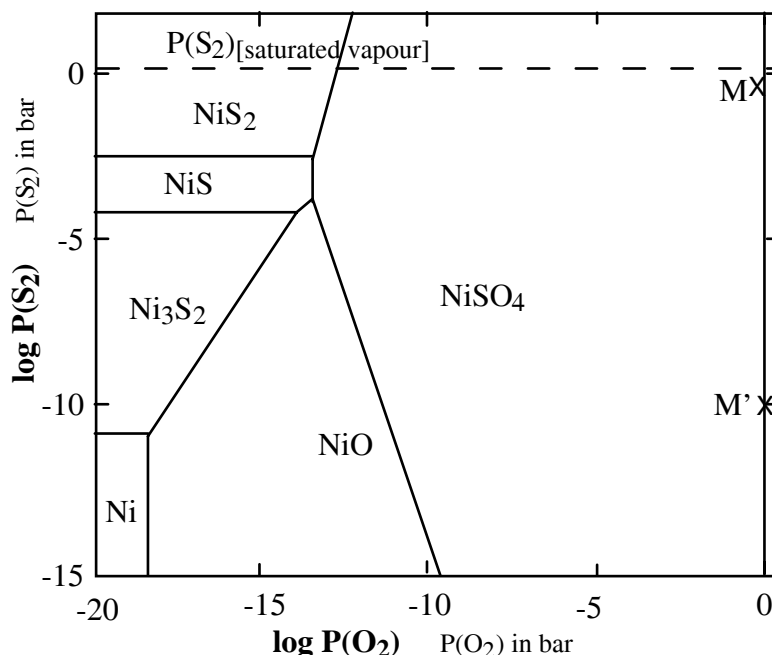


Figure 7.10. Phase stability diagram for the Ni-S-O system at 900 K, taking into account the NiSO₄ stability range.

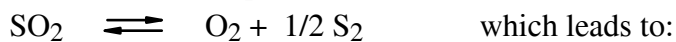
3.4.2. For an O₂ / S₂ equimolar mixture under atmospheric pressure: $P(S_2) = P(O_2) = 0.5$ bar and this is shown as point M in figure 7.10. This point is in the NiSO₄ stability domain and, so, this compound is the equilibrium product whatever the compound submitted initially to this gaseous atmosphere.

3.4.3. The mixture being considered here corresponds to the point M' in the diagram. Again, nickel sulfate, NiSO₄, is theoretically stable.

Comment: In practice, the sulphur pressure is so small that the rate of sulphidation is very low and only NiO is formed.

3.5. Phase equilibria in the presence of SO₂

3.5.1. The thermal decomposition of SO₂ may be written:



$$-\log K_1 = \log \left(\frac{P(O_2) (P(S_2))^{1/2}}{P(SO_2)} \right) = \frac{\Delta_r G^\circ_{SO_2}}{2.3 RT} = -17.18$$

Hence: $\log P(S_2) = -34.36 + 2 \log P(SO_2) - 2 \log P(O_2)$

The graphical representation of this equation leads to a set of isobaric straight lines in $P(SO_2)$. The isobaric straight line for $P(SO_2) = 1$ bar is plotted in figure 7.11.

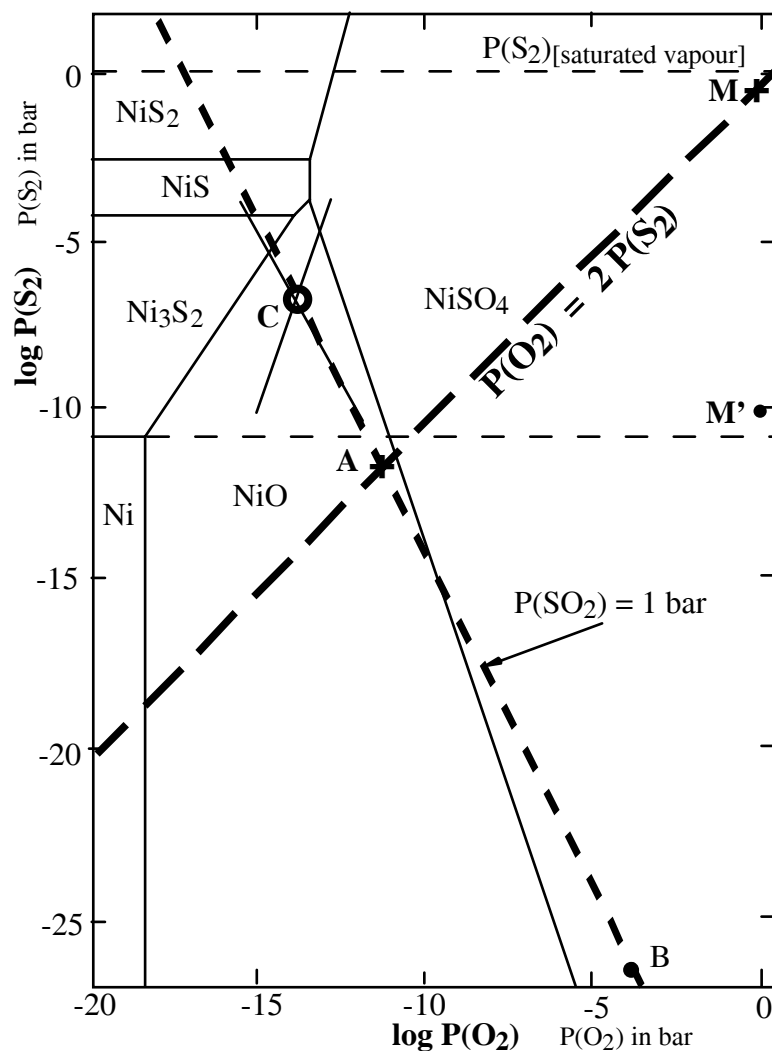


Figure 7.11. Phase stability diagram for the Ni-S-O system, at 900 K, in terms of the activities of O_2 and S_2 .

3.5.2. Compound in equilibrium with the gas phase ($P(SO_2) = 1$ bar).

1st case: SO_2 is perfectly pure

$$P(O_2) = 2 P(S_2)$$

Hence: $\log P(O_2) = \log P(S_2) + \log 2$

$$\log P(S_2) = -34.36 + 2 \log P(SO_2) - 2 \log P(O_2)$$

$$\log P(S_2) = -34.36 - 2 \log P(S_2) - 2 \log 2$$

$$3 \log P(S_2) = -34.96$$

$$\log P(S_2) = -11.65 \quad \log P(O_2) = -11.35 \quad \text{Point A in the diagram} \quad (\text{NiO stable})$$

2nd case: $P(O_2) = 10^{-4}$ bar

$$\log P(S_2) = -26.36$$

Point B in the diagram

($NiSO_4$ stable).

3.5.3. The first case is appropriate to a closed reaction vessel where the gas impurities are rapidly consumed and are not renewed. The second case is typical of an open reaction vessel with gas flow.

3.6. Phase equilibria in the presence of SO₂ and SO₃

3.6.1. System of equations:

$$\text{O}_2 + \frac{1}{2} \text{S}_2 \rightleftharpoons \text{SO}_2 \qquad K_1 = \frac{P(\text{SO}_2)}{P(\text{O}_2) [P(\text{S}_2)]^{1/2}} \qquad (1)$$

$$\frac{1}{2} \text{S}_2 + \frac{3}{2} \text{O}_2 \rightleftharpoons \text{SO}_3 \qquad K_2 = \frac{P(\text{SO}_3)}{P(\text{O}_2)^{3/2} [P(\text{S}_2)]^{1/2}} \qquad (2)$$

$$P(\text{O}_2) + P(\text{S}_2) + P(\text{SO}_2) + P(\text{SO}_3) = P_t \qquad (3)$$

$$2 P(\text{O}_2) + 2 P(\text{SO}_2) + 3 P(\text{SO}_3) = 2 (2 P(\text{S}_2) + P(\text{SO}_2) + P(\text{SO}_3)) \qquad (4)$$

3.6.2. From equations (1) to (4), we obtain, assuming $X = P(\text{S}_2)^{1/2}$ and $Y = P(\text{O}_2)^{1/2}$:

$$X^2 + X (K_1 Y^2 + K_2 Y^3) + Y^2 - 1 = 0 \qquad (5)$$

$$- 4 X^2 + X K_2 Y^3 + 2 Y^2 = 0 \qquad (6)$$

3.6.3. Solving equations (5) and (6) for three Y values

	log Y = - 6.5 P(O ₂) = 10 ⁻¹³ bar	log Y = - 7 P(O ₂) = 10 ⁻¹⁴ bar	log Y = - 7.5 P(O ₂) = 10 ⁻¹⁵ bar
log P(S ₂) (equation (5))	- 4.15	- 7.15	- 10.15
log P(S ₂) (equation (6))	- 8.39	- 6.39	- 4.39

3.6.4. Graphical determination of the equilibrium pressures P(O₂) and P(S₂) at 900 K.

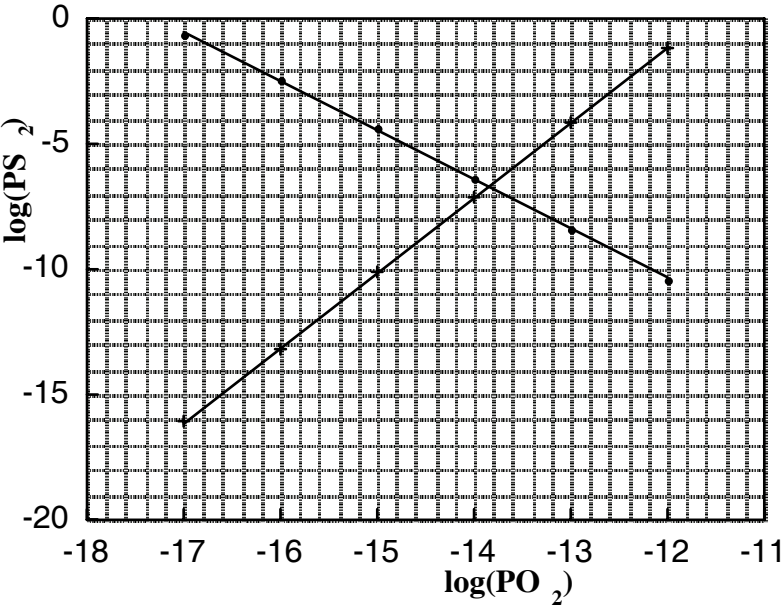


Figure 7.12. Graphical determination of the oxygen and sulphur pressures taking into account the presence of SO₂ and SO₃ (P_t = 1 bar).

This plot is shown as the thin lines intersecting at point C in figure 7.11.

Partial pressures of the different compounds are:

$$P(\text{O}_2) = 1.6 \times 10^{-14} \text{ bar}$$

$$P(\text{S}_2) = 1.6 \times 10^{-7} \text{ bar}$$

$$P(\text{SO}_2) = 0.99 \text{ bar}$$

$$P(\text{SO}_3) = 8.3 \times 10^{-7} \text{ bar}$$

This composition corresponds to point C in figure 7.11.

3.7. Comparison with experimental observations

Neglecting the presence of SO_3 (point A in figure 7.11), NiO is the stable species in equilibrium with the gas phase. The sulphur partial pressure is insufficient to form Ni_3S_2 . On the other hand, in the presence of SO_3 , the sulphur pressure ($P(\text{S}_2) = 1.6 \times 10^{-7} \text{ bar}$, point C in figure 7.11) is higher than that required for nickel sulphidation (i.e., the horizontal line at $\log P(\text{S}_2) = -10.87$).

Comment: In the publication quoted as reference³, the problem is solved more completely, by taking into account all the species likely to be in equilibrium in the gas phase.

4. Manganese sulphide (MnS) properties - Manganese sulphidation

N.B. All the defect concentrations will be expressed in number of moles per mole of sulphide. The thermodynamic constants of the equilibria (written in the direction of defect formation) will be referred to one mole of defects with a subscript indicating the degree of ionisation of the defect.

4.1. Section 1

Between 600°C and 1000°C and in sulphur partial pressures ranging from 10^{-10} bar to 1 bar , the manganese(II) sulphide MnS is a non-stoichiometric compound (see Figure 7.13).

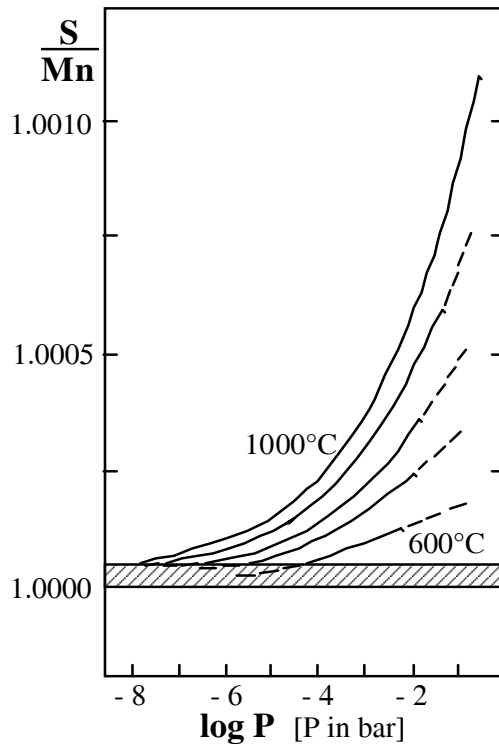


Figure 7.13. The S/Mn ratio as a function of the sulphur partial pressure: the dashed zone indicates the experimental uncertainty⁵.

4.1.1. Is the ratio

$$\frac{\text{number of S atoms}}{\text{number of Mn atoms}}$$

greater or less than one? Deduce the nature of the point defects likely to be present in the sulphide lattice in these experimental conditions.

4.1.2. The manganese sulphide will be referred to as Mn_{1-x}S . What are the highest and lowest values of the deviation, x , from stoichiometry? Can the existence of complex defects be ruled out *a priori* ?

4.1.3. In these experimental conditions, only defects involving the cation sub-lattice have to be considered. Determine the predominant point defects and indicate every possible degree of ionisation.

4.1.4. Assuming a predominant degree of ionisation, z :

4.1.4.1. Write the equilibrium reaction for the crystal in a gaseous sulphur atmosphere S_2 , at a pressure P ;

4.1.4.2. list the system of equations needed for the calculation of the ionic and electronic defect concentrations, the deviation x , from stoichiometry and the electrical conductivity σ as a function of the sulphur pressure P . U_z will be the electrical mobility of an ionic defect with a degree, z , of ionisation, U_e is the mobility of the electronic defects, F the charge on one mole of electrons and Ω the volume of one mole of manganese sulphide.

⁵ H. Le Brusq and J.P. Delmaire, *Rev. Int. Htes Temp. Réfract.*, **11** (1974) 193.

4.1.5. Deduce from the system of equations, as a function of P:

- 4.1.5.1. the concentrations of the ionic defects with a degree, z , of ionisation;
- 4.1.5.2. the deviation, x , from stoichiometry;
- 4.1.5.3. the electrical conductivity σ .

4.1.6. Make a summary table of the results obtained according to each degree, z , of ionisation.

4.2. Section 2

Between 873 K and 1273 K and in the pressure range 10^{-10} bar - 1 bar, studies of the deviation, x , from stoichiometry with the sulphur pressure gave the results presented in figure 7.14.

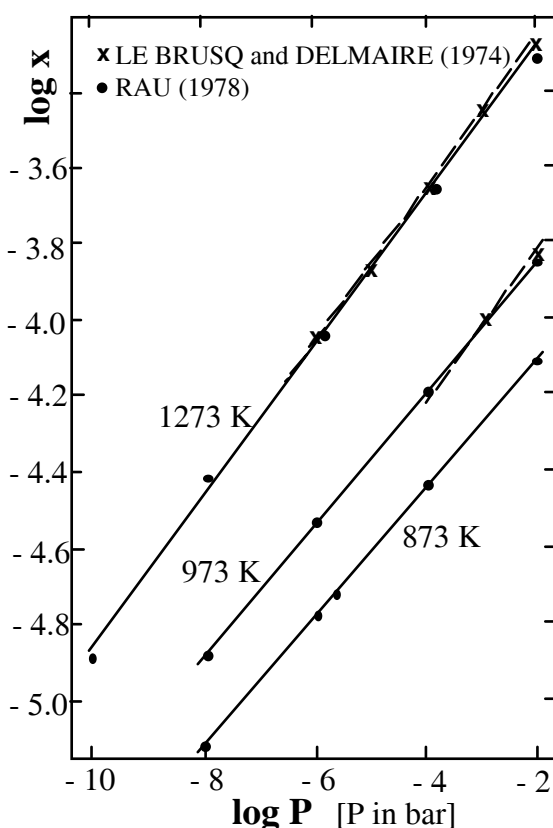


Figure 7.14. The deviation from stoichiometry of MnS (x in Mn_{1-x}S) as a function of the sulphur pressure from 873 K to 1273 K⁶.

4.2.1. Determine, in this pressure range, the experimental relationships between x and P at the following temperatures: 873 K, 973 K and 1273 K.

4.2.2. Do these results confirm the hypothesis formulated in section 4.1.3 ? Then what would be the degree, z , of ionisation of the point defects ?

⁶ S. Mrowec and K. Przybylski, *Oxidation of Metals*, **23** (1985) 107.

4.3. Section 3

Between 700 and 1000°C and in sulphur partial pressures ranging from 10⁻¹⁰ bar to 1 bar, the study of the variation of the sulphide total electrical conductivity σ as a function of P gave the results presented in figure 7.15.

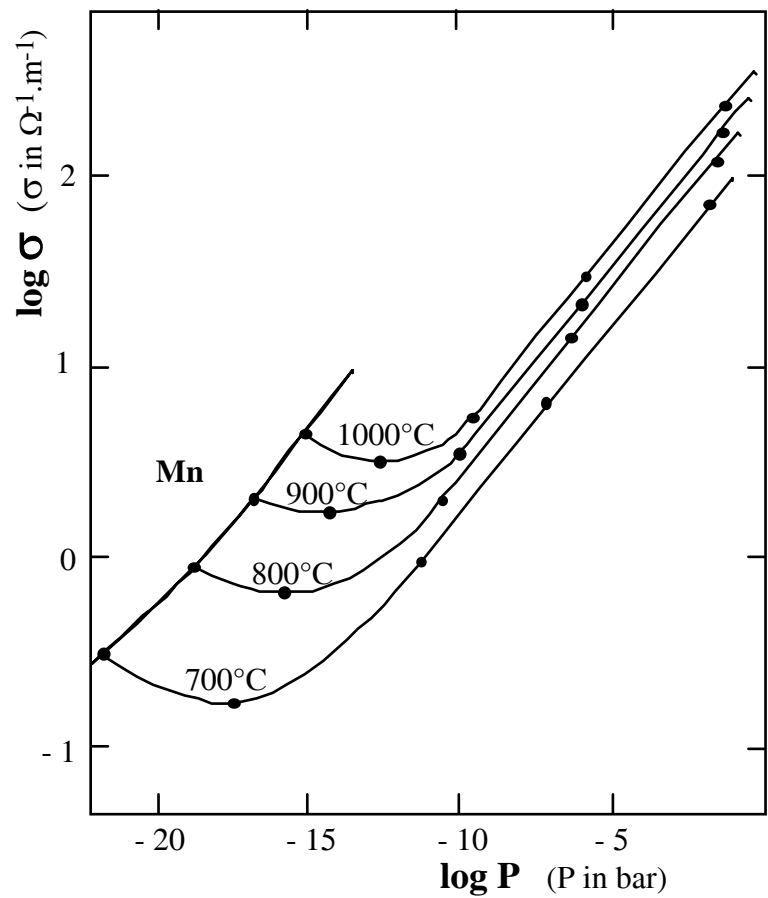


Figure 7.15. Isothermal variation of the MnS electrical conductivity as a function of the sulphur partial pressure from 700 to 1000°C⁷.

4.3.1. Draw on this figure a straight line with a slope of 1/5. Deduce the relationships between σ and P between 700 and 900°C in the 10⁻¹⁰ - 1 bar pressure range.

What can you hypothesise about the degree of ionisation of the point defects present in the sulphide lattice ?

4.3.2. Propose an interpretation for the conductivity minimum observed at pressures less than 10⁻¹⁰ bar ?

4.3.3. Why is this domain limited to the very low pressure range ? Determine graphically the sulphur pressure limits. What are their significance ?

⁷ J. Rasneur and N. Dherbomez, *C.R. Acad. Sc. Paris*, **t. 292** (1981) 593-596.

4.4. Section 4

In the temperature domain 1073 - 1273 K and under a S_2 pressure ranging from 10^{-8} bar to 1 bar, manganese sulphidation obeys a parabolic law. The reaction leads to the formation of a dense scale of manganese (II) sulphide.

4.4.1. In figure 7.16, is shown the position of a platinum wire initially deposited onto the surface of the manganese sample used in the sulphidation experiment.

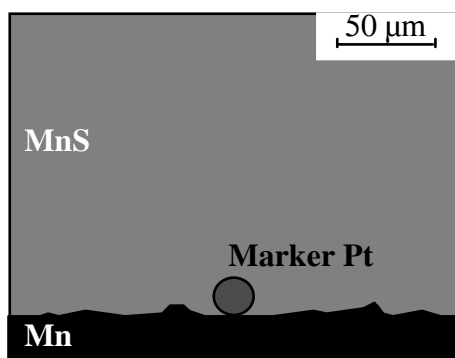


Figure 7.16. Cross-section of the sulphide scale formed, at 1225 K, under a sulphur pressure of 10^{-2} bar.

Which previously-formulated hypothesis can be confirmed from these results ?

4.4.2. What is the rate controlling process?

4.5. Section 5

In the following, it will be assumed that the predominant defects are metal vacancies with a degree, z , of ionisation.

4.5.1. Give the theoretical expression for the parabolic constant k'_p ($y^2 = k'_p t$, where y is the scale thickness) as a function of the metal vacancy concentration, i.e., $[V_{Mn}^{z'}]_e^{eq}$ and $[V_{Mn}^{z'}]_i^{eq}$, in equilibrium at the external and internal interfaces, respectively. The vacancy diffusion coefficient will be referred to as D_V .

4.5.2. Deduce the expression for this constant k'_p as a function of the sulphur pressures P_e and P_i at the external and internal interfaces, respectively. K_z is the equilibrium constant of the following reaction:



4.5.3. Deduce from the previous expression the theoretical relationship between the parabolic constant k_p ($(\frac{\Delta m}{A})^2 = k_p \cdot t$) and the sulphur pressures, P_e and P_i .

4.6. Section 6

Studies of the variation of the parabolic constant k_p with the sulphur vapour pressure P led to the results shown in figure 7.17.

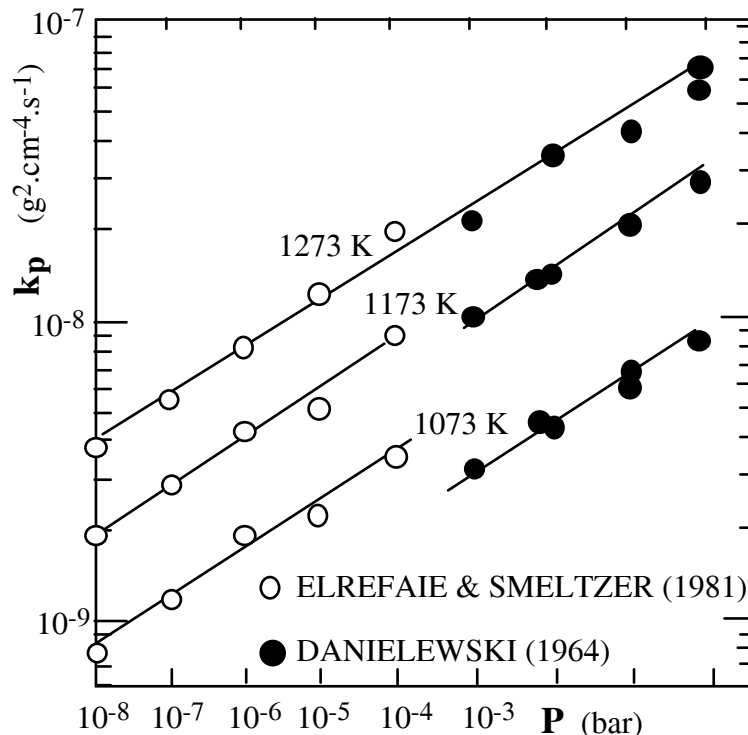


Figure 7.17. The parabolic constant for manganese sulphidation, as a function of the oxygen partial pressure, from 1073 K to 1273 K⁸.

4.6.1. Determine, for 1073 K, 1173 K and 1273 K, the experimental relationship between k_p and P . Hint: draw a straight line in figure 7.17 with a slope of 1/6.

4.6.2. The experimental results may be explained using a simplified equation starting from the theoretical one obtained in section 4.5.3.

4.6.2.1. Give the simplified equation and state the assumptions made.

4.6.2.2. What type of point defect model in the manganese sulphide lattice leads then to the interpretation of the experimental results ?

4.6.3. At 1273 K, is the simplified formula used for the interpretation of the experimental results still valid if $P = 10^{-8}$ bar ?

4.6.4. Can the conductivity measurements carried out on manganese sulphide be used to validate the oxidation mechanism ?

⁸ *Defects and Properties of Sulfides and Sulfidation of Metals*, S. Mrowec and K. Przybylski, *High Temperature Materials and Processes*, Sci. Publ. Div., vol. 6, 1984, p. 60.

4.7. Section 7

Using the results obtained in section 4.6, the self-diffusion coefficient of manganese in the sulphide lattice will be determined.

4.7.1. Give the theoretical relationship between D_{Mn} and k_p .

4.7.2. Hence, deduce the expression for D_{Mn} as a function of P at 1073 K, 1173 K and 1273 K.

Data: $\Omega = 21.7 \text{ cm}^3 \cdot (\text{mol MnS})^{-1}$ $S = 32 \text{ g} \cdot \text{mol}^{-1}$

Answers

$$4.1.1. \quad 1 < \frac{\text{number of S atoms}}{\text{number of Mn atoms}} < 1.0010$$

hence, the point defects likely to be present in the sulphide lattice are:
 S_i^x , S_i' , S_i'' , V_{Mn}^x , V_{Mn}' and V_{Mn}''

4.1.2. If the manganese sulphide is referred to as Mn_{1-x}S , the deviation, x , from stoichiometry may be defined as:

$$\frac{\text{number of S atoms}}{\text{number of Mn atoms}} = \frac{1}{1-x}$$

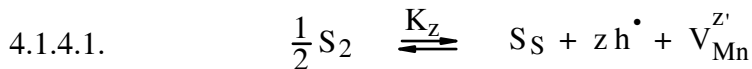
and, since $1 < \frac{1}{1-x} < 1.0010$, then $0 < x < 10^{-3}$

The existence of complex defects can be, *a priori*, ruled out since $x < 10^{-2}$.

4.1.3. The defects within the metal sublattice are then necessarily metal vacancies:

V_{Mn}^x and/or V_{Mn}' and/or V_{Mn}'' .

4.1.4. Assuming that the predominant defect is $V_{\text{Mn}}^{z'}$ with a degree, z , of ionisation ($0 \leq z \leq 2$):



$$4.1.4.2. \quad [V_{\text{Mn}}^{z'}] \cdot [\text{h}^\bullet]^z = K_z \cdot P^{1/2}$$

$$z [V_{\text{Mn}}^{z'}] = [\text{h}^\bullet]$$

$$x = [V_{\text{Mn}}^{z'}]$$

$$\sigma = \frac{zF}{\Omega} [V_{\text{Mn}}^{z'}] \cdot (U_z + U_\epsilon) \text{ if } z \neq 0$$

4.1.5. If $z \neq 0$, $z [V_{\text{Mn}}^{z'}] = [\text{h}^\bullet]$

$$[V_{Mn}^{z'}] = (\frac{K_z}{z^z})^{1/(z+1)} \cdot P^{1/2(z+1)}$$

hence, $x = (\frac{K_z}{z^z})^{1/(z+1)} \cdot P^{1/2(z+1)}$

$$\sigma = \frac{zF}{\Omega} \cdot U_{\varepsilon} \cdot (\frac{K_z}{z^z})^{1/(z+1)} \cdot P^{1/2(z+1)}$$

If $z = 0 \qquad x = [V_{Mn}^x] = K_0 \cdot P^{1/2}$

then, σ depends on the nature of the predominant ionised defect.

4.1.6. Expressions for the deviation from stoichiometry and for the electrical conductivity vs. sulphur pressure according to the degree of ionisation of the predominant point defect are given in the table below.

z	0	1	2
x	$K_0 \cdot P^{1/2}$	$K_1^{1/2} \cdot P^{1/4}$	$(\frac{K_2}{4})^{1/3} \cdot P^{1/6}$
σ	?	$\frac{F}{\Omega} \cdot U_{\varepsilon} \cdot K_1^{1/2} \cdot P^{1/4}$	$\frac{2F}{\Omega} \cdot U_{\varepsilon} \cdot (\frac{K_2}{4})^{1/3} \cdot P^{1/6}$

4.2.1. The relationship between x and P at three temperatures is given in the table below.

T (K)	873	973	1273
x	$1.71 \times 10^{-4} \cdot P^{1/6}$	$3.16 \times 10^{-4} \cdot P^{1/5.71}$	$1.21 \times 10^{-3} \cdot P^{1/5.21}$

4.2.2. These results are in agreement with the hypothesis formulated in section 4.1.3 that leads to a variation of x of $P^{1/n}$ ($2 \leq n \leq 6$). It may be expected that both simply and doubly ionised defects are present but with a predominance of V_{Mn}'' .

4.3.1. The variation of the electrical conductivity with P at various temperatures is:

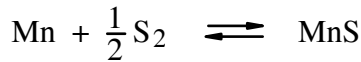
T (°C)	700	800	900	1000
σ	$171 P^{1/5}$	$251 P^{1/5}$	$331 P^{1/5}$	$436 P^{1/5}$

One may deduce, as previously, the presence of the metal vacancies, V_{Mn}' and V_{Mn}'' , but with a predominance of the doubly ionised defect, V_{Mn}'' .

4.3.2. The minimum in the electrical conductivity vs. P curve may be explained:

- either by the stoichiometric composition of the manganese sulphide, corresponding to a Frenkel disorder ($V_{Mn}'' + Mn_i^{\bullet\bullet}$) or a Schottky disorder ($V_{Mn}'' + V_S^{\bullet\bullet}$).
- or by the presence of impurities in the sulphide lattice (see case 1 for NiO).

4.3.3. On the very low pressure side, the limit to the chemical stability of the sulphide is obtained according to:



The limiting values of the pressure P corresponding to the decomposition of the sulphide as a function of temperature are given in the following table:

T (°C)	700	800	900	1000
P (bar)	1.8×10^{-22}	1.8×10^{-19}	1×10^{-17}	1×10^{-15}

4.4.1. The platinum wire is initially located on the metal surface. As shown in figure 7.16, after sulphidation, the marker is found within the scale. Hence, the sulphide scale grows by outward manganese diffusion either by an interstitial mechanism (requiring $Mn_i^{z'}$ defects) or by a vacancy mechanism (requiring $V_{Mn}^{z'}$ defects). These results confirm the hypothesis formulated in section 4.1.3.

4.4.2. Since the sulphidation of manganese follows a parabolic law, the limiting step is manganese diffusion.

$$4.5.1. \quad J = -\frac{1}{\Omega} (z+1) D_V \frac{d[V_{Mn}^{z'}]}{dx} = \frac{1}{\Omega} (z+1) D_V \left(\frac{[V_{Mn}^{z'}]_e^{eq} - [V_{Mn}^{z'}]_i^{eq}}{y} \right)$$

$$\text{or} \quad \frac{dy}{dt} = \Omega \cdot J$$

$$y^2 = 2 (z+1) D_V ([V_{Mn}^{z'}]_e^{eq} - [V_{Mn}^{z'}]_i^{eq}) \cdot t$$

$$\text{with} \quad k'_p = 2 (z+1) D_V ([V_{Mn}^{z'}]_e - [V_{Mn}^{z'}]_i)$$

$$[V_{Mn}^{z'}]_e^{eq} = \left(\frac{K_z}{z^z}\right)^{1/(z+1)} \cdot P_e^{1/2(z+1)}$$

$$[V_{Mn}^{z'}]_i^{eq} = \left(\frac{K_z}{z^z}\right)^{1/(z+1)} \cdot P_i^{1/2(z+1)}$$

$$k'_p = 2(z+1) D_V \left(\frac{K_z}{z^z}\right)^{1/(z+1)} (P_e^{1/2(z+1)} - P_i^{1/2(z+1)})$$

4.5.3. Assuming that: $\frac{\Delta m}{A} = 32 \frac{y}{\Omega}$

$$\frac{k_p}{k'_p} = \left(\frac{32}{\Omega}\right)^2$$

hence, $k_p = 2(z+1) D_V \left(\frac{32}{\Omega}\right)^2 \left(\frac{K_z}{z^z}\right)^{1/(z+1)} (P_e^{1/2(z+1)} - P_i^{1/2(z+1)})$

4.6.1. The relationships between k_p and P at three temperatures are given below:

T (K)	1073	1173	1273
k_p (g ² cm ⁻⁴ s ⁻¹)	$P > 10^{-3}$ bar $1 \times 10^{-8} P^{1/6}$	$P > 10^{-3}$ bar $3 \times 10^{-8} P^{1/6}$	$7 \times 10^{-8} P^{1/6}$
	$P < 10^{-3}$ bar $1.8 \times 10^{-8} P^{1/6}$	$P < 10^{-3}$ bar $4 \times 10^{-8} P^{1/6}$	

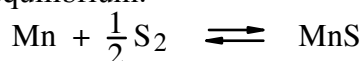
4.6.2.1. A simplified expression for the parabolic rate constant is:

$$k_p = 2(z+1) D_V \left(\frac{32}{\Omega}\right)^2 \left(\frac{K_z}{z^z}\right)^{1/(z+1)} P_e^{1/2(z+1)}$$

assuming that $\left(\frac{P_i}{P_e}\right)^{1/2(z+1)} \ll 1$

4.6.2.2. Comparing the experimental results with the simplified formula for k_p , we obtain $z = 2$. This means that the predominant point defects in manganese sulphide are doubly ionised manganese vacancies.

4.6.3. At 1273 K, the sulphur pressure, P_i , at the internal interface is the pressure corresponding to the following equilibrium:



i.e., $P_i = 10^{-15}$ bar.

Hence: $\left(\frac{P_i}{P_e}\right)^{1/6} \geq \left(\frac{10^{-15}}{10^{-8}}\right)^{1/6}$ i.e., $\left(\frac{P_i}{P_e}\right)^{1/6} \geq 7 \times 10^{-2}$ and this is the

limiting value for the application of the simplified formula for k_p .

4.6.4. The conductivity measurements, to a first approximation, permit us to account for the proposed oxidation mechanism (i.e. $\sigma \propto P^{1/5}$ and $k_p \propto P^{1/6}$).

$$4.7.1. \quad k'_p = 2(z+1) D_V [V_{Mn}']_{eq}$$

which can be written:

$$k'_p = 2(z+1) D_{Mn} = \left(\frac{\Omega}{32}\right)^2 k_p$$

where D_{Mn} is the self-diffusion coefficient of Mn in the manganese sulphide, then:

$$D_{Mn} = \frac{1}{2(z+1)} \left(\frac{\Omega}{32}\right)^2 k_p$$

4.7.2. Numerical application for $z = 2$.

$$D_{Mn} = 7.66 \times 10^{-2} k_p$$

T (K)	1073	1173	1273
D_{Mn} (cm ² s ⁻¹)	$P > 10^{-3} \text{ bar}$ $1.4 \times 10^{-9} P^{1/6}$	$P > 10^{-3} \text{ bar}$ $2.3 \times 10^{-9} P^{1/6}$	$5.36 \times 10^{-9} P^{1/6}$
	$P < 10^{-3} \text{ bar}$ $7.7 \times 10^{-10} P^{1/6}$	$P < 10^{-3} \text{ bar}$ $3.1 \times 10^{-9} P^{1/6}$	

5. Cobalt (II) oxide (CoO) properties - Oxidation of cobalt

N.B. All the defect concentrations will be expressed in number of moles per mole of oxide. The thermodynamic constants of the equilibria (written in the direction of defect formation) will be referred to one mole of defects with a subscript indicating the degree of ionisation of the defect.

5.1. Section 1

At high temperatures, cobalt monoxide, CoO , is a non-stoichiometric compound. Initially, we shall assume that, under oxygen pressures higher than 10^{-3} bar, simply ionised metal vacancies are the predominant point defects in the oxide lattice.

5.1.1. Write the equilibrium reaction between the oxide crystal and the oxygen atmosphere.

5.1.2. List the system of equations needed to calculate the ionic defect concentrations, the electrical conductivity σ , and the self-diffusion coefficient D_{Co} as a function of the oxygen pressure P . U_1 and U_e will denote the mobility of the ionic and electronic defects, respectively, D_V the metal vacancy diffusion coefficient, F the Faraday constant and Ω the volume of one mole of oxide.

5.1.3. Deduce from the previous system of equations the expressions, as a function of P :

5.1.3.1. of the ionic defect concentrations,

5.1.3.2. of the electrical conductivity σ ,

5.1.3.3. of the self-diffusion coefficient D_{Co} .

5.1.4. Let m_0 be the weight of a stoichiometric CoO sample and m the weight of the corresponding non-stoichiometric sample under a pressure P .

5.1.4.1. Give the relationship linking the metal vacancy concentration $[V'_{\text{Co}}]$ to m and m_0 .

5.1.4.2. Deduce the theoretical expression for m as a function of m_0 and of the metal vacancy concentration.

5.2. Section 2

In the 10^{-2} bar - 1 bar oxygen pressure range and at temperatures in the range 1000°C to 1200°C , the weight variation of a cobalt monoxide sample as a function of the oxygen pressure P is given in figure 7.18.

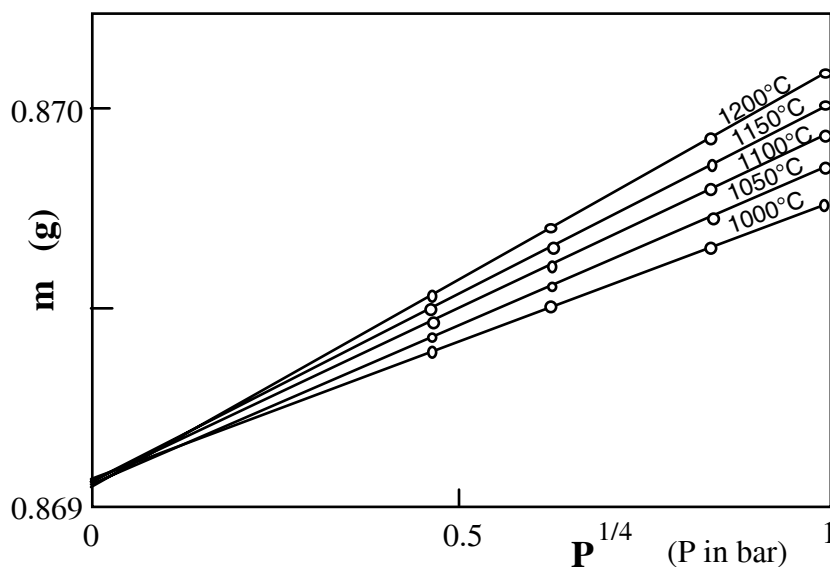


Figure 7.18. The weight variation of a cobalt monoxide sample as a function of the oxygen pressure from 1000°C to 1200°C⁹.

5.2.1. Does figure 7.18 confirm the validity of the model proposed in section 5.1 for the 10^{-2} - 1 bar oxygen pressure domain ?

5.2.2. Does this representation allow the determination of:

5.2.2.1. the weight m_0 of the stoichiometric sample and the metal vacancy concentration in the stoichiometric compound ?

5.2.2.2. the value of the constant K_1 at the following temperatures: 1000°C, 1050°C, 1100°C, 1150°C and 1200°C ? If so, calculate the constant K_1 at 1000°C and 1150°C.

5.3. Section 3

In the 10^{-12} - 1 bar oxygen pressure range and between 986°C and 1191°C, the variation of the total conductance with oxygen pressure is shown in figure 7.19.

⁹ N.G. Eror and J.B. Wagner Jr., *J. Phys. Chem. Solids*, **29** (1968) 1597.

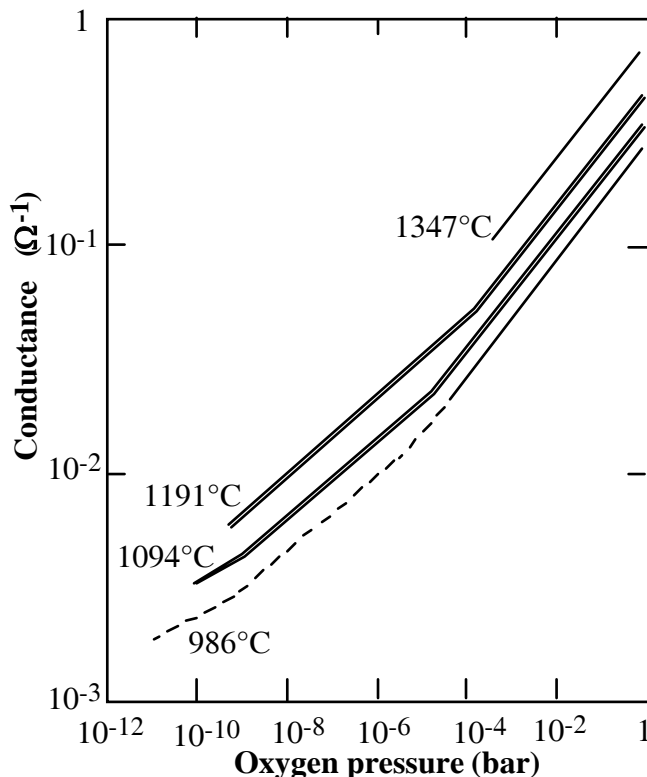


Figure 7.19. The electrical conductance of cobalt monoxide CoO as a function of the oxygen partial pressure¹⁰.

5.3.1. What do you notice ? To answer this question, you may draw in figure 7.19 two straight lines with slopes of $\frac{1}{4}$ and $\frac{1}{6}$, respectively.

5.3.2. Are these results in agreement with those obtained in section 5.2 ?

5.3.3. Could you justify the results obtained for oxygen pressures less than 10^{-4} bar ?

5.3.4. Assuming the presence of both V_{Co}' and V_{Co}'' vacancies, give the relationship between the electron hole concentration and the pressure P for both high and low values of $[h^{\bullet}]$. Are these results in agreement with the observations made in section 5.3.1 ?

5.4. Section 4

Between 1000°C and 1150°C and in the 10^{-3} - 1 bar oxygen pressure range, cobalt oxidation in an oxygen atmosphere obeys a parabolic law. Only the non-stoichiometric oxide CoO is assumed to be formed. In the following, it will be assumed that the predominant defects are metal vacancies with a degree, z , of ionisation.

¹⁰ P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*, J. Wiley, New York, 1972, p. 240.

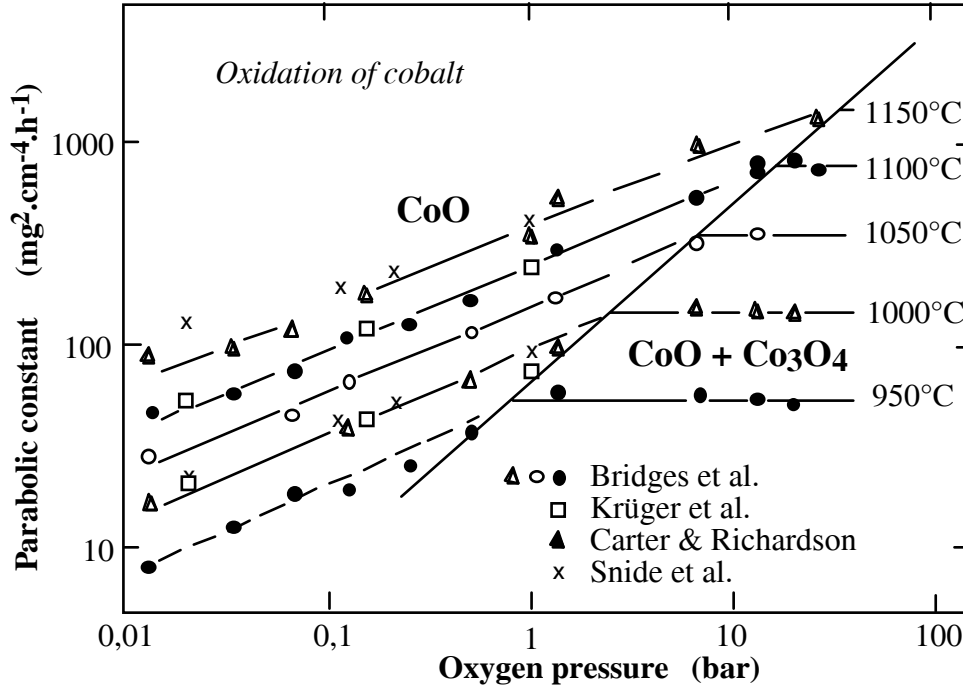


Figure 7.20. The parabolic rate constant for the oxidation of cobalt as a function of the oxygen partial pressure¹¹.

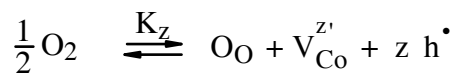
5.4.1. What is the limiting step ?

5.4.2. Recall the theoretical expression for the parabolic rate constant k'_p ($y^2 = k'_p t$, y being the scale thickness) as a function of the metal vacancy concentrations at the external and internal interfaces, respectively.

5.4.3. Deduce the theoretical expression for the constant k_p ($(\frac{\Delta m}{A})^2 = k_p t$).

5.4.4. Let P be the oxygen pressure in the gas phase and P_i the equilibrium oxygen pressure at the internal interface.

Give the expression for k_p as a function of P and P_i . K_z will denote the equilibrium constant of the following reaction:



¹¹ P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science, London, 1988, p. 186.

5.4.5. Show that, for the required experimental conditions (temperature: 1000°C - 1150°C, oxygen pressure between 10⁻³ bar and 1 bar), we can write, for whatever value of z:

$$\left(\frac{P_i}{P}\right)^{1/2(z+1)} \ll 1.$$

5.4.6. Hence, deduce the simplified expression for k_p as a function of the metal vacancy concentration at the external interface.

5.5. Section 5

At 1000°C and 1150°C and in the 10⁻³ - 1 bar oxygen pressure range, a comparative study of the variation with the oxygen pressure of the parabolic rate constant k_p and of the diffusion coefficient D^{*}_{Co} of the Co radioactive tracer gave the results reported in figure 7.21 (correlation factor: f = 0.78).

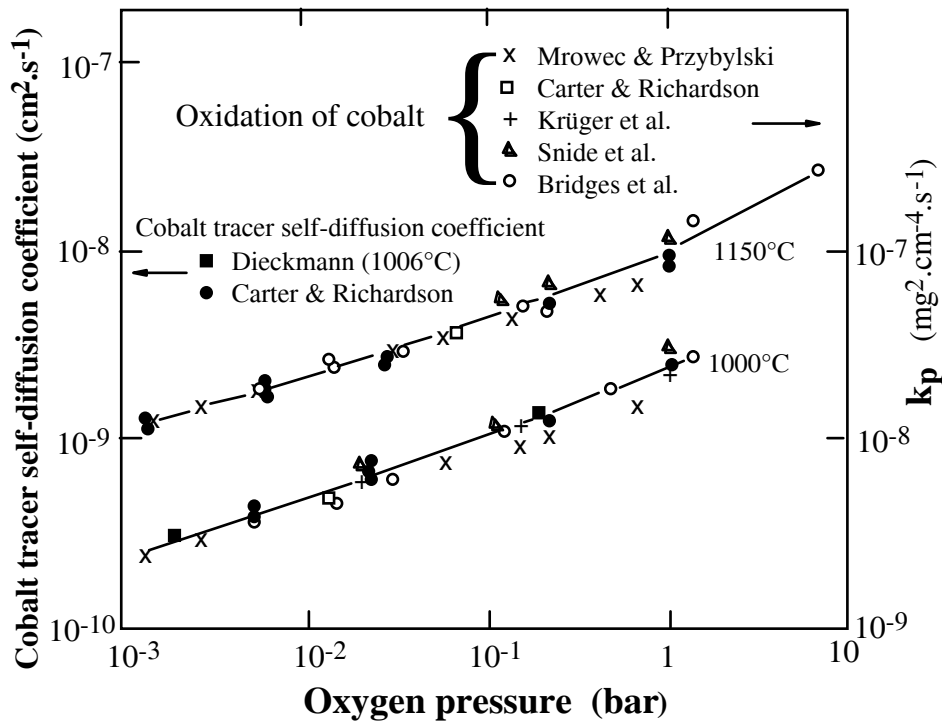


Figure 7.21. Comparison of the dependences on the oxygen pressure of the cobalt tracer self-diffusion coefficient D^{*}_{Co} in CoO and the parabolic rate constant k_p for cobalt oxidation¹².

5.5.1. Determine the experimental relationship between k_p and D^{*}_{Co} with oxygen pressure at both temperatures, i.e., 1000°C and 1150°C. Could these results confirm the defect model proposed in section 5.1 for cobalt oxide CoO ?

¹² P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science, London, 1988, p. 183.

5.5.2. Give the theoretical expression for the ratio: $\frac{k_p}{D_{Co}^*}$.

5.5.3. Determine the experimental values of this ratio at 1000°C and 1150°C in the 10^{-3} - 1 bar oxygen pressure range.

5.5.4. Hence, deduce the degree of vacancy ionisation.

5.5.5. Are these results in agreement with the previous ones ?

5.6. Section 6

In the same temperature domain (1000 - 1150°C) and under oxygen pressures greater than 1 bar, cobalt oxidation leads to the formation of a two-layered scale, i.e., a layer of cobalt monoxide CoO next to the metal, and a very thin layer of Co₃O₄ in contact with the gas phase.

Assuming that the limiting step remains the same as previously, could you explain why the parabolic constant k_p , then becomes independent of the oxygen pressure (see figure 7.20) ?

Data:

O : 16 g.mol⁻¹

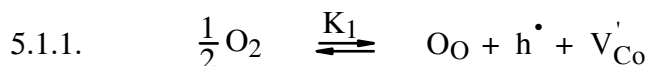
Co : 58.93 g.mol⁻¹

$\Omega = 11.6 \text{ cm}^3.\text{mol}^{-1}$

$R = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$.

Gibbs free energy of formation of one mole of CoO : $\Delta_f G^\circ = -232.872 + 0.06933 T \quad (\text{kJ})$

Answers



5.1.2. $[\text{V}'_{\text{Co}}] \cdot [\text{h}^\bullet] = K_1 \cdot P^{1/2}$

$[\text{V}'_{\text{Co}}] = [\text{h}^\bullet]$

$D_{\text{Co}} = [\text{V}'_{\text{Co}}] \cdot D_V$

$$\sigma = \frac{F}{\Omega} ([\text{V}'_{\text{Co}}] \cdot U_1 + [\text{h}^\bullet] \cdot U_\varepsilon) - \frac{F}{\Omega} \cdot [\text{h}^\bullet] \cdot U_\varepsilon$$

5.1.3. $[\text{V}'_{\text{Co}}] = K_1^{1/2} \cdot P^{1/4}$

$[\text{h}^\bullet] = K_1^{1/2} \cdot P^{1/4}$

$$\sigma = \frac{F}{\Omega} \cdot U_{\varepsilon} \cdot K_1^{1/2} \cdot P^{1/4}$$

$$D_{Co} = D_V \cdot K_1^{1/2} \cdot P^{1/4}$$

5.1.4. During the formation of one oxygen lattice site, O_O , a cobalt vacancy V'_{Co} is formed (ratio of regular lattice sites rule).

$$5.1.4.1. \quad [V'_{Co}] = \frac{\frac{m - m_0}{16}}{\frac{m}{M_{CoO}}}$$

$$5.1.4.2. \quad m = \frac{m_0}{1 - \frac{16}{M_{CoO}} [V'_{Co}]}$$

$$m - m_0 (1 + \frac{16}{M_{CoO}} [V'_{Co}])$$

5.2.1. Using the previous defect model, one obtains the relationship between m and P :

$$m = m_0 + \frac{16}{M_{CoO}} m_0 K_1^{1/2} P^{1/4}$$

This equation gives a straight line between m and $P^{1/4}$ with a slope of $\frac{16}{M_{CoO}} m_0 K_1^{1/2}$ and an intercept of m_0 .

Figure 7.18 permits validation of the defect model only in the following domain:

$$0.5 < P^{1/4} < 1 \quad \text{i.e.,} \quad 6.25 \times 10^{-2} \text{ bar} < P < 1 \text{ bar.}$$

5.2.2.1. Figure 7.18 cannot be used for the determination of the weight of the stoichiometric sample m_0 because the proposed defect model is not valid near the stoichiometric composition due to the existence of two types of point defects.

5.2.2.2. On the other hand, Figure 7.18 allows the determination of the value of the constant K_1 , as :

$$\frac{\text{slope}}{\text{ordinate at zero point}} = \frac{16}{M_{CoO}} K_1^{1/2}$$

Hence:

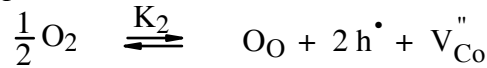
T (°C)	Straight line equations	K ₁
1000	m = 0.869045 + 7.149 x 10 ⁻⁴ P ^{1/4}	1.5 x 10 ⁻⁵
1150	m = 0.869045 + 9.697 x 10 ⁻⁴ P ^{1/4}	2.7 x 10 ⁻⁵

5.3.1. The conductance vs. P graph (logarithmic scales) may be indentified with two straight lines:

- for P > 10⁻⁴ bar, the conductance is proportional to P^{1/4}
- for P < 10⁻⁶ bar, the conductance is proportional to P^{1/6}.

5.3.2. These results confirm the model proposed in section 5.1 for oxygen pressures greater than 10⁻⁴ bar (in agreement with the thermogravimetric study, see section 5.2).

5.3.3. Under oxygen pressures less than 10⁻⁶ bar, the following equilibrium is predominant:



5.3.4. Assuming that both metal vacancies are present in the oxide lattice, i.e., V_{Co}' and V_{Co}'', one may write:

$$[\text{h}^\bullet] = [\text{V}_{\text{Co}}'] + 2 [\text{V}_{\text{Co}}'']$$

$$[\text{V}_{\text{Co}}'] \cdot [\text{h}^\bullet] = K_1 \cdot P^{1/2}$$

$$[\text{V}_{\text{Co}}''] \cdot [\text{h}^\bullet]^2 = K_2 \cdot P^{1/2}$$

Hence: $[\text{h}^\bullet]^3 = (K_1 [\text{h}^\bullet] + 2 K_2) P^{1/2}$

if $K_1 [\text{h}^\bullet] \gg 2 K_2$ then: $[\text{h}^\bullet] = K_1^{1/2} P^{1/4}$

if $K_1 [\text{h}^\bullet] \ll 2 K_2$ then: $[\text{h}^\bullet] = (2 K_2)^{1/3} P^{1/6}$

These results show that the variation with oxygen pressure of [h[•]], and hence of σ, depends on the oxygen pressure domain. Since σ is a monotonic function of P, then:

- under low oxygen pressures: $\sigma \propto P^{1/6}$
- under high oxygen pressures: $\sigma \propto P^{1/4}$.

5.4.1. The limiting step is diffusion of the metal vacancies V_{Co}^{Z'}.

5.4.2. $\frac{1}{\Omega} \frac{dy}{dt} = J_z$ where J_z is the flux of cobalt vacancies with a degree, z , of ionisation.

$$J_z = \frac{1}{\Omega} (z + 1) D_V \frac{\partial [V_{Co}^{z'}]}{\partial x}$$

Integrating this vacancy flux leads to:

$$J_z = \frac{1}{\Omega} (z + 1) D_V \left(\frac{[V_{Co}^{z'}]_{eq}^e - [V_{Co}^{z'}]_{eq}^i}{y} \right)$$

Hence: $y^2 = 2 (z + 1) D_V ([V_{Co}^{z'}]_{eq}^e - [V_{Co}^{z'}]_{eq}^i) \cdot t = k'_p \cdot t$

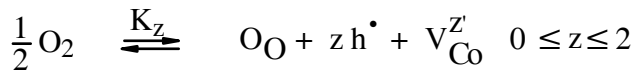
with : $k'_p = 2 (z + 1) D_V ([V_{Co}^{z'}]_{eq}^e - [V_{Co}^{z'}]_{eq}^i)$

in which $[V_{Co}^{z'}]_{eq}^e$ and $[V_{Co}^{z'}]_{eq}^i$ are the equilibrium metal vacancy concentrations at the external and internal interfaces, respectively.

5.4.3. Combining previous equations: $\left(\frac{\Delta m}{A \cdot y} \right)^2 = \frac{k_p}{k'_p} = \left(\frac{16}{\Omega} \right)^2$

one obtains: $k_p = 2 (z + 1) \left(\frac{16}{\Omega} \right)^2 D_V ([V_{Co}^{z'}]_{eq}^e - [V_{Co}^{z'}]_{eq}^i)$

5.4.4. At every point of the experimental curve, the following equilibrium is obeyed:



Using the equilibrium constant K_z , one may write:

$$k_p = 2 (z + 1) D_V \left(\frac{16}{\Omega} \right)^2 \left(\frac{K_z}{z^z} \right)^{1/(z+1)} (P^{1/2(z+1)} - P_i^{1/2(z+1)})$$

which may be rewritten as:

$$k_p = 2 (z + 1) D_V \left(\frac{16}{\Omega} \right)^2 \left(\frac{K_z}{z^z} \right)^{1/(z+1)} P^{1/2(z+1)} \left[1 - \left(\frac{P_i}{P} \right)^{1/2(z+1)} \right]$$

5.4.5. The equilibrium oxygen pressure P_i at the internal interface may be calculated using the Gibbs free energy of formation of one mole of CoO.



T (°C)	P _i (bar)	$\left(\frac{P_i}{P}\right)_{\max}$ for P = 10 ⁻³ bar	$\left(\frac{P_i}{P}\right)_{\max}^{1/2}$ for P = 10 ⁻³ bar and z = 0	$\left(\frac{P_i}{P}\right)_{\max}^{1/6}$ for P = 10 ⁻³ bar and z = 2
1000	1.35 x 10 ⁻¹²	1.35 x 10 ⁻⁹	3.69 x 10 ⁻⁵	3.32 x 10 ⁻²
1150	1.40 x 10 ⁻¹⁰	1.40 x 10 ⁻⁷	3.74 x 10 ⁻⁴	7.22 x 10 ⁻²

5.4.6. A simplified expression for k_p:

$$k_p = 2(z+1) D_V \left(\frac{16}{\Omega}\right)^2 \left(\frac{K_z}{z^z}\right)^{1/(z+1)} P^{1/2(z+1)}$$

$$k_p = 2(z+1) \left(\frac{16}{\Omega}\right)^2 D_V [V_{Co}^{z'}]_e^{eq}$$

5.5.1. The experimental variation with P of k_p and D_{Co}^{*} :

T (°C)	k _p	D _{Co} [*]
1000	2.24 x 10 ⁻⁸ P ^{1/2.85}	2.24 x 10 ⁻⁹ P ^{1/2.85}
1150	10 ⁻⁷ P ^{1/3}	10 ⁻⁸ P ^{1/3}

These results do not fully confirm the model proposed in section 5.2. In the present case, the oxygen pressure dependence suggests the co-existence of both defects, i.e., V_{Co}^x and V_{Co}['].

5.5.2. The following equation:

$$k_p = 2(z+1) \left(\frac{16}{\Omega}\right)^2 D_V [V_{Co}^{z'}]_e^{eq}$$

may also be written as:

$$k_p = 2(z+1) \left(\frac{16}{\Omega}\right)^2 D_{Co}$$

$$k_p = 2(z+1) \left(\frac{16}{\Omega}\right)^2 \frac{D_{Co}^*}{f}$$

Hence:

$$\frac{k_p}{D_{Co}^*} = \frac{2}{f} (z+1) \left(\frac{16}{\Omega}\right)^2$$

5.5.3. Values of the ratio $\frac{k_p}{D_{Co}^*}$ at 1000°C and 1150°C : $\frac{k_p}{D_{Co}^*} = 10$

5.5.4. From the data, i.e., $\Omega = 11.6 \text{ cm}^3$ and $f = 0.78$, one may deduce that $z = 1.05$.

5.5.5. These results are not fully in agreement with the previous but they do confirm the model proposed in section 5.2.

6. Properties of copper(I) oxide Cu_2O and copper oxidation

N.B. All the defect concentrations will be expressed in number of moles per mole of oxide. The thermodynamic constants K_z of the equilibria (written in the direction of defect formation) will be referred to one mole of defects with a subscript indicating the degree of ionisation of the defect.

Data: $\text{Cu} = 63.5 \text{ g.mol}^{-1}$ $\text{O} = 16 \text{ g.mol}^{-1}$

6.1. Stoichiometry and electrical conductivity of Cu_2O

6.1.1. At temperatures higher than 700°C and in the 10^{-5} - 1 bar oxygen pressure range, Cu_2O is a non-stoichiometric compound such that:

$$\frac{\text{number of moles of O}}{\text{number of moles of Cu}} > \frac{1}{2}$$

The oxide formula will be written as: $\text{Cu}_2\text{O}_{1+x}$.

6.1.1.1. What are the types of defects (vacancies or interstitials) that can be present in the lattice ? Give all the expected charges for each type of the defects considered.

6.1.1.2. In the following, it will be assumed that ionic defects having all the possible degrees of ionisation co-exist.

Assuming that the ionic defects affect only the cationic sub-lattice:

- express the equilibria of the crystal under the oxygen pressure P ;
- express the deviation, x , from stoichiometry as a function of the point defect concentrations;
- tabulate the system of equations needed to express, as a function of P , the ionic and electronic defect concentrations, as well as the deviation, x , from stoichiometry;
- show that the system of equations may be solved analytically; hence, deduce the expressions for x and h as a function of P .

6.1.2. In the 700°C - 1000°C temperature domain, the total electrical conductivity σ_t vs. P is plotted in figure 7.22.

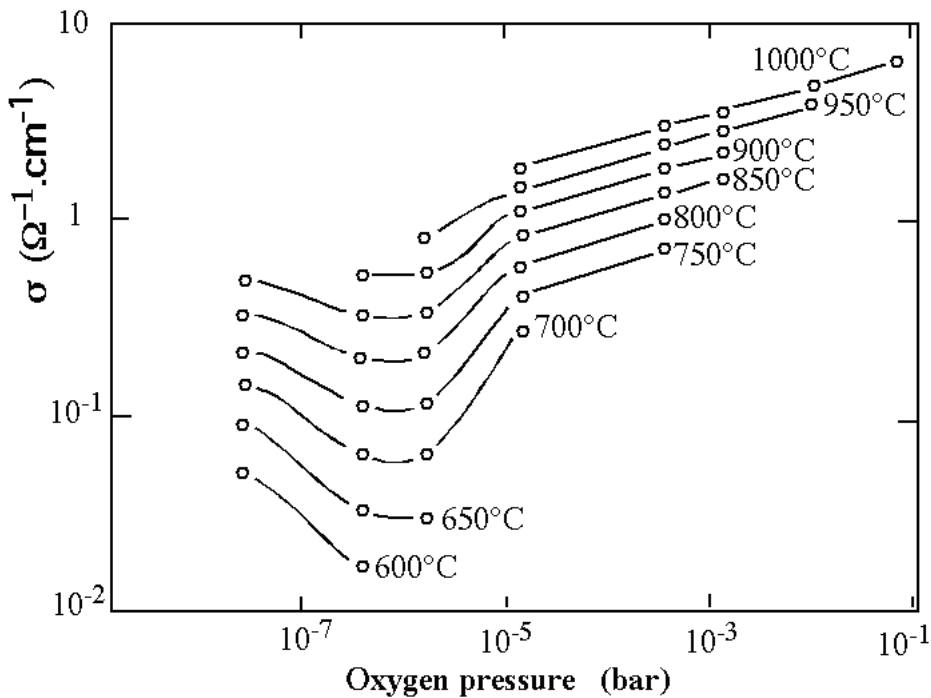


Figure 7.22. The electrical conductivity of Cu_2O as a function of the oxygen partial pressure¹³.

6.1.2.1. Draw on the graph a straight line with a slope of $\frac{1}{7}$.

6.1.2.2. Hence deduce, for the 10^{-5} - 10^{-1} bar oxygen pressure range, the relationship between σ and P .

6.1.2.3. Do these results permit the nature of the predominant point defects at 1000°C and for oxygen pressures greater than 10^{-5} bar to be identified?

6.1.2.4. Explain why the conductivity curve exhibits a minimum at temperatures less than 900°C.

6.1.3. The Arrhenius plots of the oxygen and copper self-diffusion coefficients in Cu_2O , determined using radio-tracers, are given in figure 7.23.

- What hypothesis do these results confirm ?
- Determine the activation energy of the copper self-diffusion coefficient.

¹³ P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*, J. Wiley, New York, 1972, p. 330.

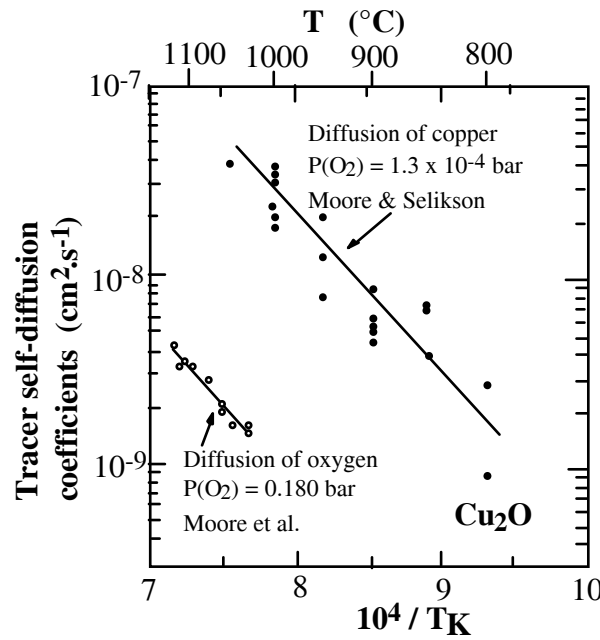


Figure 7.23. Arrhenius plots of the oxygen and copper self-diffusion coefficients in Cu_2O ¹⁴.

6.1.4. The experimental results showing the deviation from stoichiometry (x in $\text{Cu}_2\text{O}_{1+x}$) vs. oxygen pressure, between 970°C and 1026°C are given in figure 7.24 (oxygen pressure range: 7×10^{-4} - 10^{-1} bar).

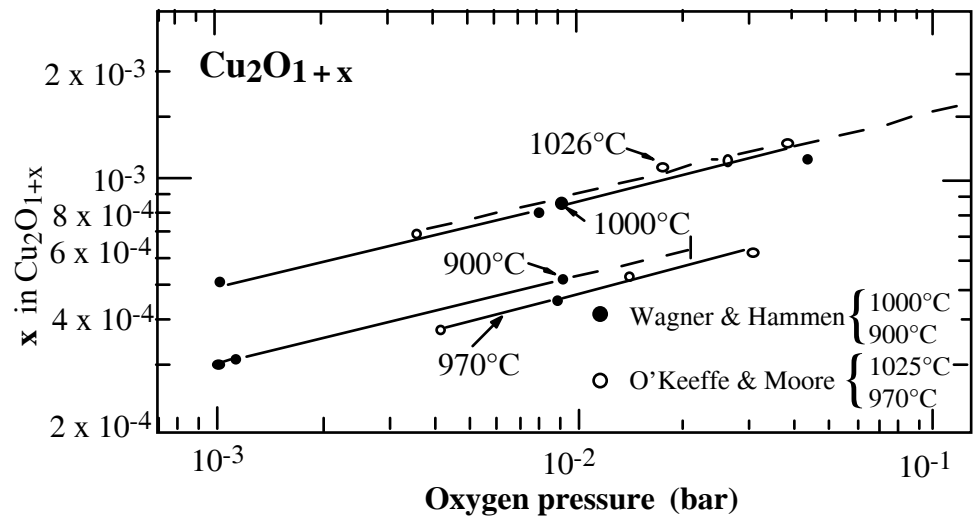


Figure 7.24. The deviation from stoichiometry in $\text{Cu}_2\text{O}_{1+x}$ as a function of the oxygen partial pressure¹⁵.

¹⁴ P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*, J. Wiley, New York, 1972, p. 330.

¹⁵ P. Kofstad, *ibid.*, p. 329.

6.1.4.1. Draw on the graph a straight line with a slope of $\frac{1}{4}$. What conclusion can you draw?

6.1.4.2. To what extent does the model proposed in section 6.1.1.2 account quantitatively for the variation of x with P ? Determine the values of K_0 at 900°C and 1000°C .

6.1.4.3. Does the model proposed in section 6.1.1.2 account quantitatively for the variation of σ with P ?

6.2. Copper oxidation

In the 900°C - 1050°C temperature range and oxygen pressures between 10^{-4} bar and 1 bar, copper oxidation obeys a parabolic law. It will be assumed that a single-phase layer of Cu_2O is formed, in which the predominant defects are neutral copper vacancies.

6.2.1. Write the elementary steps of the oxidation reaction assuming a dissociative adsorption of oxygen.

6.2.2. Give the theoretical relationship for the parabolic rate constant k_p ($(\frac{\Delta m}{A})^2 = k_p t$) as functions of the vacancy concentration at the external interface and of the vacancy diffusion coefficient $D_{V_{\text{Cu}}}$. The vacancy concentration at the internal interface will be considered as negligible.

6.2.3. The variation of the parabolic rate constant with oxygen pressure at 900, 950, 1000 and 1050°C are given in figure 7.25. Draw on the graph a straight line with a slope of $\frac{1}{4}$. Hence, deduce the pressure law.

Show that these results confirm the hypothesis of the nature of the predominant point defects.

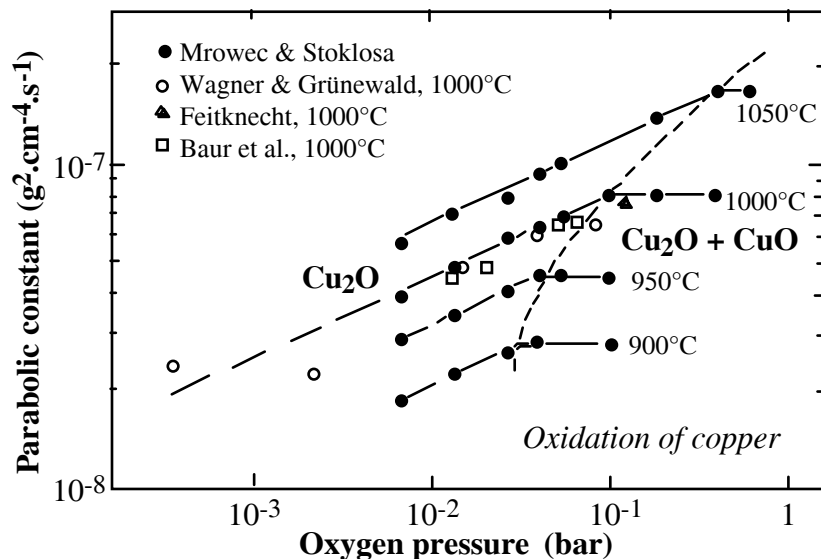


Figure 7.25. The parabolic rate constant for oxidation of copper as a function of the oxygen pressure from 900 to 1050°C¹⁶.

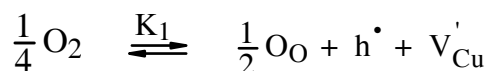
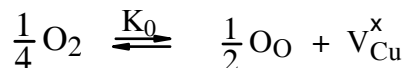
Answers

6.1.1.1. Two types of defects are possible:

- Oxygen interstitials: O_i^x , O_i' and O_i''
- Copper vacancies: V_{Cu}^x , V_{Cu}'

6.1.1.2. Assuming that defects exist only on the cation sub-lattice, the ionic defects are: V_{Cu}^x , V_{Cu}'

a) *Equilibrium under oxygen pressure P*



b) *In an oxide with the formula Cu_2O_{1+x} , from the definition of x :*

$$\frac{\text{number of moles of oxygen}}{\text{number of moles of copper}} = \frac{1}{2 - ([V_{Cu}^x] + [V_{Cu}'])} = \frac{1+x}{2}$$

¹⁶ P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science, London, 1988, p. 188.

Insofar as $x \ll 1$ (see Figure 7.24):

$$x = \frac{1}{2} ([V_{Cu}^x] + [V_{Cu}'])$$

c) System of equations:

$$[V_{Cu}^x] = K_0 \cdot P^{1/4}$$

$$[V_{Cu}'] = [h^\bullet]$$

$$[V_{Cu}'] [h^\bullet] = K_1 \cdot P^{1/4}$$

$$x = \frac{1}{2} ([V_{Cu}^x] + [V_{Cu}'])$$

d) Solving this system of equations leads to:

$$x = \frac{K_0 \cdot P^{1/4} + K_1^{1/2} \cdot P^{1/8}}{2}$$

$$[h^\bullet] = K_1^{1/2} \cdot P^{1/8}$$

6.1.2.2. In the 10^{-5} - 10^{-1} bar oxygen pressure range, the electrical conductivity is proportional to $P^{1/7}$.

6.1.2.3. The conductivity can give information only on the nature of the predominant ionised defect ($[V_{Cu}'] = [h^\bullet]$). In the present case this conductivity curve confirms the presence of the ionised defect $[V_{Cu}']$. This curve does not give information on the relative concentrations of neutral (i.e., $[V_{Cu}^x]$) and ionised (i.e., $[V_{Cu}']$) point defects.

6.1.2.4. The conductivity minimum could be interpreted by the existence of the stoichiometric composition.

6.1.3.

a) Experimentally, $\frac{D_{Cu}}{D_O} > 10$. This result is not inconsistent with the hypothesis of defects in the cationic sub-lattice.

b) The activation energy of the copper self-diffusion coefficient is:

$$E_a = 159 \text{ kJ.mol}^{-1} = 1.65 \text{ eV}.$$

6.1.4. Variation of the deviation from stoichiometry with oxygen pressure.

6.1.4.1. Experimentally, one finds that $x \propto P^{1/4}$.

6.1.4.2. The model developed in section 6.1.1.2 does account for the variation of $x = f(P)$ if it is assumed that $[V_{Cu}^x] \ll [V_{Cu}']$.

$$x = \frac{1}{2} (K_0 \cdot P^{1/4} + K_1^{1/2} \cdot P^{1/8}) \text{ in which } K_1^{1/2} \cdot P^{1/8} \text{ is negligible.}$$

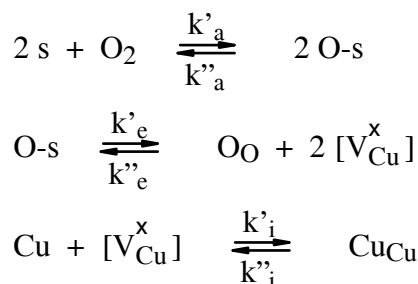
K_1 cannot be determined. However, K_0 may be calculated from the x vs. P curves by fitting with the following equation: $x = \frac{K_0}{2} \cdot P^{1/4}$.

T (°C)	P (bar)	x	$\frac{K_0}{2}$	K_0
900	8×10^{-3}	3×10^{-4}	1.00×10^{-3}	2.00×10^{-3}
1000	8×10^{-3}	3×10^{-4}	1.67×10^{-3}	3.34×10^{-3}

6.1.4.3. According to the model, the total conductivity, proportional to the electronic defect concentration ($[V_{Cu}'] = [h^\bullet]$) could vary as $P^{1/8}$. In practice, one finds experimentally that $\sigma \propto P^{1/7}$. It may be assumed that the observed difference is of the order of magnitude of the experimental uncertainty and, hence, one may consider that the model accounts for the electrical properties of the oxide.

6.2. Copper oxidation

6.2.1. Elementary steps of the oxidation reaction:



6.2.2. If y is the scale thickness:

$$y^2 = k'_p t$$

and if Δm is the mass of reacted oxygen:

$$\left(\frac{\Delta m}{A}\right)^2 = k_p t$$

$$k_p = k'_p \cdot \left(\frac{M_O}{\Omega}\right)^2$$

in which M_O is the mass of one mole of oxygen and Ω the volume of one mole of oxide.

6.2.3. In the case of a diffusion limiting step (neutral defects):

$$J_{V_{Cu}} = \frac{1}{\Omega} D_{V_{Cu}} \left(\frac{[V_{Cu}^x]_e^{eq} - [V_{Cu}^x]_i^{eq}}{y} \right) \quad (\text{stationary state})$$

Since: $2 Cu + 1/2 O_2 = Cu_2O$ then: $\frac{1}{2} \frac{dn_{Cu}}{dt} = \frac{J_{V_{Cu}}}{2} = \frac{dn_{Cu_2O}}{dt}$

hence: $\frac{1}{\Omega} \frac{dy}{dt} = \frac{1}{2} J_{V_{Cu}}$

$$\frac{dy}{dt} = \frac{1}{2} D_{V_{Cu}} \left(\frac{[V_{Cu}^x]_e^{eq} - [V_{Cu}^x]_i^{eq}}{y} \right)$$

$$y^2 = D_{V_{Cu}} ([V_{Cu}^x]_e^{eq} - [V_{Cu}^x]_i^{eq}) \cdot t$$

This may be simplified to:

$$y^2 = D_{V_{Cu}} [V_{Cu}^x]_e^{eq} \cdot t$$

i.e.: $k'_p = D_{V_{Cu}} [V_{Cu}^x]_e^{eq}$ and $k_p = \left(\frac{M_O}{\Omega} \right)^2 D_{V_{Cu}} [V_{Cu}^x]_e^{eq}$

Experimentally, we obtain:

T (°C)	900	950	1000	1050
k_p	$6.3 \times 10^{-8} P^{1/4}$	$1.0 \times 10^{-7} P^{1/3.8}$	$1.51 \times 10^{-7} P^{1/3.8}$	$2.3 \times 10^{-7} P^{1/3.8}$

The constant k_p , within experimental errors, varies with oxygen pressure according to $P^{1/4}$. These results confirm the hypothesis of a predominance of neutral vacancies within the Cu_2O scale.

7. Niobium oxidation in oxygen and water vapour

The oxidation of niobium leads to the formation of three oxides, i.e., NbO , NbO_2 and Nb_2O_5 , which are solid in typical experimental temperature ranges.

7.1. Stability of the different phases

7.1.1. Calculate, at 800 and 1400 K, the equilibrium oxygen pressures of the following systems: NbO/Nb , NbO_2/NbO , Nb_2O_5/NbO_2 .

Table 7.1. Gibbs free energy of formation of the compounds ($\text{kJ}\cdot\text{mol}^{-1}$), from Barin¹⁷.

	T = 800 K	T = 1400 K
NbO	- 346.330	- 294.084
NbO ₂	- 647.837	- 547.112
Nb ₂ O ₅	- 1546.491	- 1296.802
H ₂ O	- 205.595	- 170.260

7.1.2. Draw the phase stability diagram for the system Nb - O as a function of temperature, using $\log P(\text{O}_2) - 10^3/T(\text{K})$ co-ordinate axes. The Ellingham approximation will be considered valid.

7.1.3. Oxidation in oxygen atmosphere

What is the stable oxide in contact with pure oxygen ($P(\text{O}_2) = 1 \text{ bar}$) in the above temperature range? Draw a schematic diagram of the multi-layered corrosion scale, assuming that all the interfacial equilibria are reached.

7.1.4. Oxidation in water vapour

7.1.4.1. Calculate, at 800 and 1400 K and for vapour pressures of 1 bar and 1 mbar, the equilibrium oxygen pressure resulting from water vapour decomposition in H_2 and O_2 . What is the stable oxide in contact with the resulting gaseous atmosphere?

7.1.4.2. Answer the same question but for a mixture of H_2O (10 mbar) / H_2 (1 bar). Determine graphically the temperature above which Nb_2O_5 is no longer stable.

7.1.5. Experiment reveals that, in the 800-1000°C temperature range, pure water vapour ($P(\text{H}_2\text{O}) = 20 \text{ mbar}$), carefully de-aerated, reacts with niobium to form a NbO_2 scale. Is this observation in agreement with thermodynamic calculations ? What do you infer about the thermodynamical equilibrium at the gas-oxide interface ?

7.2. Oxidation kinetics in water vapour

The results of thermodynamic measurements, between 800 and 1000°C, and under various water vapour pressures between 2.6 and 65.8 mbar show that the oxidation kinetics may conform to a linear rate equation (after an initial short period with decreasing rate that will be neglected). The rate constants k_1 are given in table 7.2 as functions of T and $P(\text{H}_2\text{O})$.

Table 7.2. Logarithm of the linear rate constants of oxidation k_1 ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) of niobium by water vapour.

¹⁷ I. Barin, *Thermochemical Data of Pure Substances*, VCH - Weinheim, 1989.

	T (°C)	800	900	1000
P(H ₂ O) (mbar)				
2.60		- 1.00	- 0.921	- 0.699
6.60		- 0.824	- 0.638	- 0.495
13.16		- 0.721	- 0.420	- 0.276
26.30		- 0.658	- 0.268	- 0.071
39.50		- 0.620	- 0.194	0.029
65.80		- 0.585	- 0.155	0.124

7.2.1. Determine, at every pressure, the apparent activation energy. Is this value of activation energy constant ?

7.2.2. Plot, for the three temperatures, k_1 as a function of $P(\text{H}_2\text{O})$. What does the form of the curve suggest of the nature of the rate limiting step ?

7.2.3. Oxidation rate calculation

7.2.3.1. *Sorption*: H_2O sorption on NbO_2 will be considered on the basis of thermodynamic equilibrium. This process may be totally dissociative, partially dissociative or non-dissociative. Express, in each case, the fractional surface coverage of adsorbed species, i.e., θ_{O} , θ_{OH} or $\theta_{\text{H}_2\text{O}}$. K_{O} , K_{OH} and $K_{\text{H}_2\text{O}}$ will be the equilibrium constants for the corresponding sorption reactions. It will be assumed that the adsorption of one water molecule removes only one surface site, whatever its dissociation level. Which of these three factors expressing coverage does not depend on $P(\text{H}_2)$?

7.2.3.2. *External elementary step*: The external elementary process is assumed to be rate limiting.

(a) Write, for each of the three cases considered in section 7.2.3.1, the balance equation depicting the external elementary step. It will be assumed that niobium oxide NbO_2 is a n-type semi-conductor with neutral oxygen vacancies.

(b) Express the reaction rate, for each of the three cases. The reaction order with regards to the fractional surface coverage of adsorbed species will be taken equal to one and the reactions are assumed to be far from equilibrium (the reverse reactions will be neglected). The reaction rate will be expressed as functions of the equilibrium constants K_{O} (K_{OH} , $K_{\text{H}_2\text{O}}$), of the rate constants of the external processes k'_{O} (k'_{OH} , $k'_{\text{H}_2\text{O}}$), of the equilibrium concentration $[\text{VO}]_i^{\text{eq}}$, of the water vapour pressure $P(\text{H}_2\text{O})$ and, if necessary, of the hydrogen pressure $P(\text{H}_2)$.

(c) *Influence of temperature*

Temperature has little influence on the equilibrium concentration $[V_O]_i$ but explain why the apparent activation energy depends on $P(H_2O)$. Hence, deduce the true activation energy for k'_e and a value for the sorption enthalpy ΔH°_s .

(d) *Influence of water vapour pressure*

Using an appropriate linear transform, show that the rate equations found in question 7.2.3.2.b account for the experimental results. Show that this transform does not depend on the type of sorption process for H_2O .

(e) *Influence of hydrogen pressure*

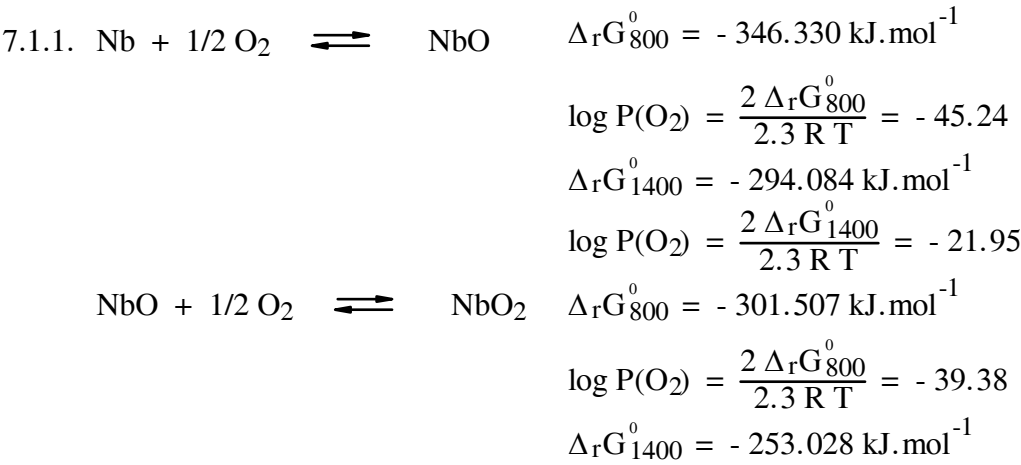
It has been shown experimentally that the reaction rate depends on the hydrogen pressure. At 1000°C , it was observed that the reaction rate slows down when $P(H_2)$ is increased, as shown in table 7.3.

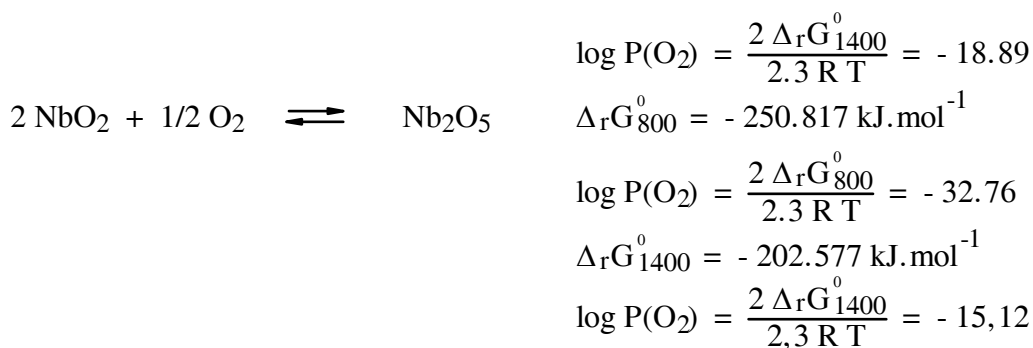
Table 7.3. Influence of hydrogen pressure on the niobium oxidation rate ($T = 1000^\circ\text{C}$, $P(H_2O) = 26.6 \text{ mbar}$).

$P(H_2) \text{ (mbar)}$	$k_l \text{ (mg.cm}^{-2}\text{.h}^{-1}\text{)}$
0	0.920
53	0.606
134	0.370
334	0.086

Draw an appropriate linear transform and show that the best fit is obtained by assuming a totally dissociative chemisorption.

Answers





Comment: The equilibrium oxygen pressures increase with the niobium valency at both temperatures and, hence, each oxide has a well-defined domain of stability.

7.1.2. Plotting the points obtained at 7.1.1 on a $\log P(\text{O}_2) = f(1/T)$ diagram and drawing the corresponding straight lines (Ellingham approximation), one obtains the phase stability diagram for the system Nb - O as a function of temperature, as shown in figure 7.26.

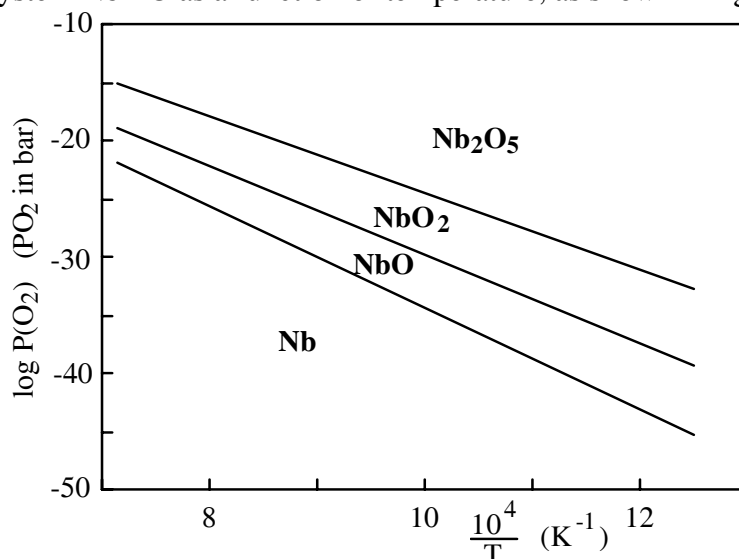


Figure 7.26. Phase stability diagram for the system Nb - O as a function of temperature.

7.1.3. In the temperature range being considered, the horizontal line at $P(\text{O}_2) = 1$ bar ($\log P(\text{O}_2) = 0$) is totally within the stability domain of Nb_2O_5 . Therefore, this oxide is the stable compound in contact with a pure oxygen atmosphere. The corrosion scale is shown schematically in figure 7.27.

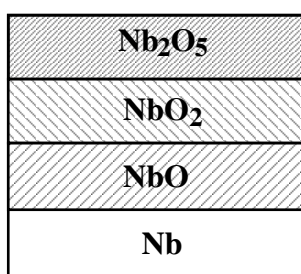
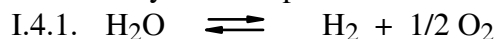


Figure 7.27. Schematic diagram of the corrosion scale formed on niobium.

7.1.4. Oxidation by water vapour



$$\boxed{T = 800 \text{ K}}$$

$$\Delta_r G_{800}^0 = + 205.595 \text{ kJ.mol}^{-1}$$

$$\log \frac{P(\text{H}_2) \sqrt{P(\text{O}_2)}}{P(\text{H}_2\text{O})} = - \frac{\Delta_r G_{800}^0}{2.3 R T} = -13.43$$

$$\boxed{P(\text{H}_2\text{O}) = 1 \text{ bar}}$$

$$\log P(\text{H}_2) + 1/2 \log P(\text{O}_2) = -13.43 \text{ and } P(\text{H}_2) = 2 P(\text{O}_2)$$

$$3/2 \log P(\text{O}_2) = -13.43 - \log 2 \quad \log P(\text{O}_2) = -9.5$$

$$\boxed{P(\text{H}_2\text{O}) = 1 \text{ mbar}}$$

$$\log P(\text{O}_2) = -11.15$$

$$\boxed{T = 1400 \text{ K}}$$

$$\Delta_r G_{1400}^0 = + 170.26 \text{ kJ.mol}^{-1}$$

$$\boxed{P(\text{H}_2\text{O}) = 1 \text{ bar}}$$

$$\log P(\text{H}_2) + 1/2 \log P(\text{O}_2) = -6.35 \quad \text{and} \quad P(\text{H}_2) = 2 P(\text{O}_2)$$

$$3/2 \log P(\text{O}_2) = -6.35 - \log 2 \quad \log P(\text{O}_2) = -4.44$$

$$\boxed{P(\text{H}_2\text{O}) = 1 \text{ mbar}}$$

$$\log P(\text{O}_2) = -6.44$$

The stable oxide is Nb_2O_5 whatever the experimental conditions.

$$7.1.4.2. \quad P(\text{H}_2\text{O}) = 10 \text{ mbar and } P(\text{H}_2) = 1 \text{ bar}$$

$$\boxed{T = 800 \text{ K}}$$

$$\log \frac{P(\text{H}_2) \sqrt{P(\text{O}_2)}}{P(\text{H}_2\text{O})} = -13.43 \quad \log P(\text{O}_2) = -30.85$$

$$\boxed{T = 1400 \text{ K}}$$

$$\log \frac{P(\text{H}_2) \sqrt{P(\text{O}_2)}}{P(\text{H}_2\text{O})} = -6.35 \quad \log P(\text{O}_2) = -16.71$$

Stable oxide at 800 K : $\log P(\text{O}_2) (\text{H}_2\text{O}/\text{H}_2) > \log P(\text{O}_2) (\text{Nb}_2\text{O}_5/\text{NbO}_2)$
and, so Nb_2O_5 is stable.

Stable oxide at 1400 K : $\log P(\text{O}_2) (\text{H}_2\text{O}/\text{H}_2) < \log P(\text{O}_2) (\text{Nb}_2\text{O}_5/\text{NbO}_2)$
and, so NbO_2 is stable.

By drawing on figure 7.26 the straight line joining the oxygen equilibrium pressures calculated at both temperatures, it can be seen that it cuts that corresponding to the $\text{Nb}_2\text{O}_5/\text{NbO}_2$ equilibrium at 1044 K ($1/T = 0.000958 \text{ K}^{-1}$). Below this temperature, Nb_2O_5 is stable in contact with the gas but above this transition temperature, NbO_2 is stable.

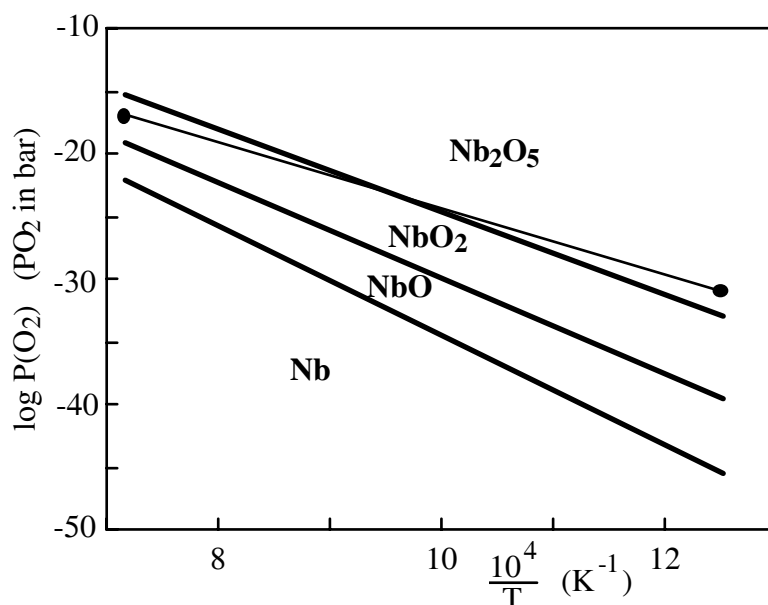


Figure 7.28. Determination of the stability domain of Nb_2O_5 .

7.1.5. According to question 7.1.4.1, Nb_2O_5 should be formed. The fact that it does not is not in agreement with the thermodynamical predictions. Hence, one of the external equilibria (sorption or external elementary step) has not been attained.

7.2. Kinetics of niobium oxidation by water vapour

7.2.1. The rate constants k_1 are plotted on the Arrhenius diagram of figure 7.29. It can be seen that the activation energies are not constant but increase with $P(\text{H}_2\text{O})$. The two extreme values are:

- $P(\text{H}_2\text{O}) = 2.6 \text{ mbar}$ $E_A = 38.7 \text{ kJ.mol}^{-1}$
- $P(\text{H}_2\text{O}) = 65.8 \text{ mbar}$ $E_A = 93.0 \text{ kJ.mol}^{-1}$

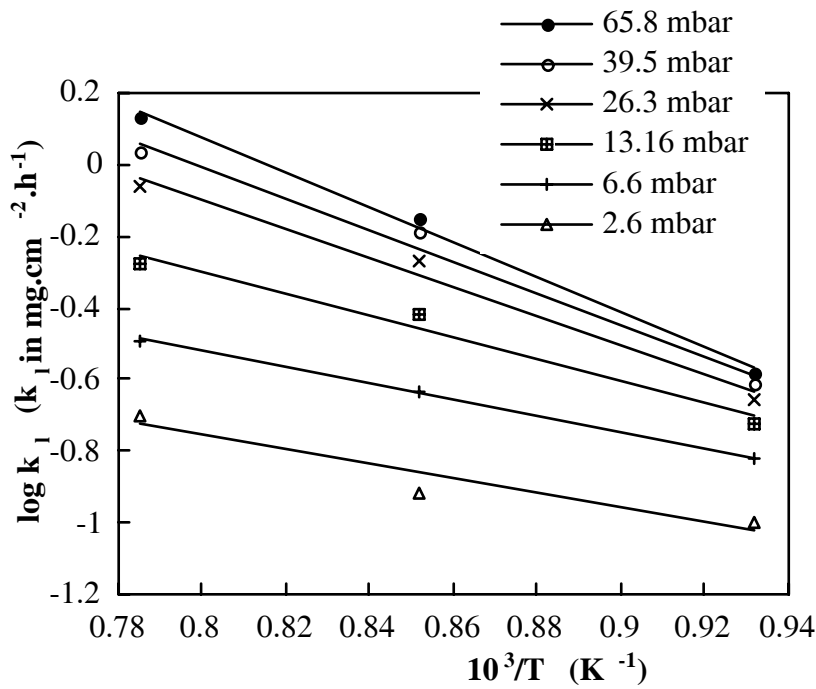


Figure 7.29. Arrhenius plot of the linear rate constants.

7.2.2. The linear constants k_l are plotted as a function of $P(\text{H}_2\text{O})$ in figure 7.30. The curves exhibit a hyperbolic behaviour that suggests an external interfacial reaction limiting step.

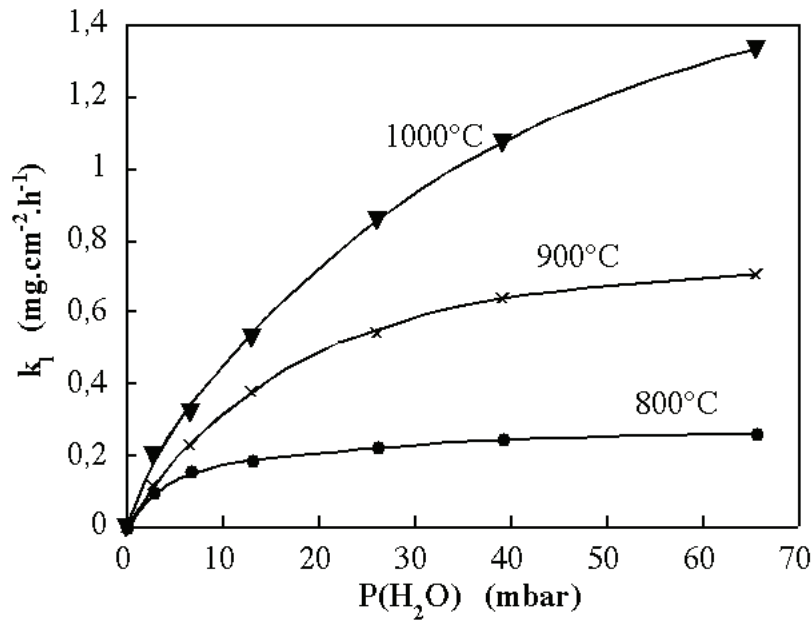


Figure 7.30. Variation of the linear rate constant as a function of the water vapour pressure.

7.2.3. Oxidation rate calculation

7.2.3.1.

- Totally dissociative sorption $\text{H}_2\text{O} + \text{s} \rightleftharpoons \text{O-s} + \text{H}_2$
- Partially dissociative sorption $\text{H}_2\text{O} + \text{s} \rightleftharpoons \text{OH-s} + 1/2 \text{H}_2$
- Non dissociative sorption $\text{H}_2\text{O} + \text{s} \rightleftharpoons \text{H}_2\text{O-s}$

$$\theta_{\text{O}} = \frac{K_{\text{O}} \frac{P(\text{H}_2\text{O})}{P(\text{H}_2)}}{1 + K_{\text{O}} \frac{P(\text{H}_2\text{O})}{P(\text{H}_2)}} \quad \theta_{\text{OH}} = \frac{K_{\text{OH}} \frac{P(\text{H}_2\text{O})}{\sqrt{P(\text{H}_2)}}}{1 + K_{\text{OH}} \frac{P(\text{H}_2\text{O})}{\sqrt{P(\text{H}_2)}}} \quad \theta_{\text{H}_2\text{O}} = \frac{K_{\text{H}_2\text{O}} P(\text{H}_2\text{O})}{1 + K_{\text{H}_2\text{O}} P(\text{H}_2\text{O})}$$

Only $\theta_{\text{H}_2\text{O}}$ is independent of $P(\text{H}_2)$.

7.2.3.2.

- (a) $\text{O-s} + \text{V}_{\text{O}} \rightarrow \text{O}_{\text{O}} + \text{s}$
 $\text{HO-s} + \text{V}_{\text{O}} \rightarrow \text{O}_{\text{O}} + 1/2 \text{H}_2 + \text{s}$
 $\text{H}_2\text{O-s} + \text{V}_{\text{O}} \rightarrow \text{O}_{\text{O}} + \text{H}_2 + \text{s}$
- (b) $v_{\text{O}} = k'_{\text{O}} \theta_{\text{O}} [\text{V}_{\text{O}}]_{\text{i}}^{\text{eq}}$
 $v_{\text{OH}} = k'_{\text{OH}} \theta_{\text{OH}} [\text{V}_{\text{O}}]_{\text{i}}^{\text{eq}}$
 $v_{\text{H}_2\text{O}} = k'_{\text{H}_2\text{O}} \theta_{\text{H}_2\text{O}} [\text{V}_{\text{O}}]_{\text{i}}^{\text{eq}}$

hence:

$$v_{\text{O}} = k'_{\text{O}} [\text{V}_{\text{O}}]_{\text{i}}^{\text{eq}} \frac{K_{\text{O}} \frac{P(\text{H}_2\text{O})}{P(\text{H}_2)}}{1 + K_{\text{O}} \frac{P(\text{H}_2\text{O})}{P(\text{H}_2)}}$$

$$v_{\text{OH}} = k'_{\text{OH}} [\text{V}_{\text{O}}]_{\text{i}}^{\text{eq}} \frac{K_{\text{OH}} \frac{P(\text{H}_2\text{O})}{\sqrt{P(\text{H}_2)}}}{1 + K_{\text{OH}} \frac{P(\text{H}_2\text{O})}{\sqrt{P(\text{H}_2)}}}$$

$$v_{\text{H}_2\text{O}} = k'_{\text{H}_2\text{O}} [\text{V}_{\text{O}}]_{\text{i}}^{\text{eq}} \frac{K_{\text{H}_2\text{O}} P(\text{H}_2\text{O})}{1 + K_{\text{H}_2\text{O}} P(\text{H}_2\text{O})}$$

- (c) Whatever the adsorbed species, the reaction rate obeys the equation:

$$v = k' [\text{V}_{\text{O}}]_{\text{i}}^{\text{eq}} \frac{K P}{1 + K P}$$

with: $k' = k'_0 \exp(-\frac{E_{\text{A}}}{R T})$ et $K = \exp(-\frac{\Delta H^{\circ}_{\text{s}}}{R T})$

E_{A} is the activation energy of the external interfacial reaction and $\Delta H^{\circ}_{\text{s}}$, the standard enthalpy of sorption.

Hence, the apparent activation energy E is:

$$E \approx E_{\text{A}} + \Delta H^{\circ}_{\text{s}} \quad \text{when } K P \ll 1$$

$$E \approx E_{\text{A}} \quad \text{when } K P \gg 1$$

Thus:

$$E_{\text{A}} = 93.0 \text{ kJ.mol}^{-1}$$

$$\Delta H^\circ_s = -54.3 \text{ kJ.mol}^{-1} \quad (\text{exothermal chemisorption})$$

(d) The linear transform of a hyperbolic function obeys the following equation:

$$\frac{1}{v} = \frac{A}{P} + B$$

$$\frac{1}{v_O} = \frac{P(H_2)}{k'_O K_O [V_O]_i^{eq}} \frac{1}{P(H_2O)} + \frac{1}{k'_O [V_O]_i^{eq}}$$

$$\frac{1}{v_{OH}} = \frac{\sqrt{P(H_2)}}{k'_{OH} K_{OH} [V_O]_i^{eq}} \frac{1}{P(H_2O)} + \frac{1}{k'_{OH} [V_O]_i^{eq}}$$

$$\frac{1}{v_{H_2O}} = \frac{1}{k'_{H_2O} K_{H_2O} [V_O]_i^{eq}} \frac{1}{P(H_2O)} + \frac{1}{k'_{H_2O} [V_O]_i^{eq}}$$

This transform then linearises the three previous equations. Only the values of A and B are different.

(e) The reaction rate depends on the hydrogen pressure which is inconsistent with a mechanism of non dissociative sorption. For the other two mechanisms, the following linear transforms $v = f[P(H_2)]$ have to be considered:

- complete dissociation: $\frac{1}{v_O} = A_O P(H_2) + B_O$

- partial dissociation: $\frac{1}{v_{OH}} = A_{OH} \sqrt{P(H_2)} + B_{OH}$

These transforms are plotted in figures 7.31 and 7.32.

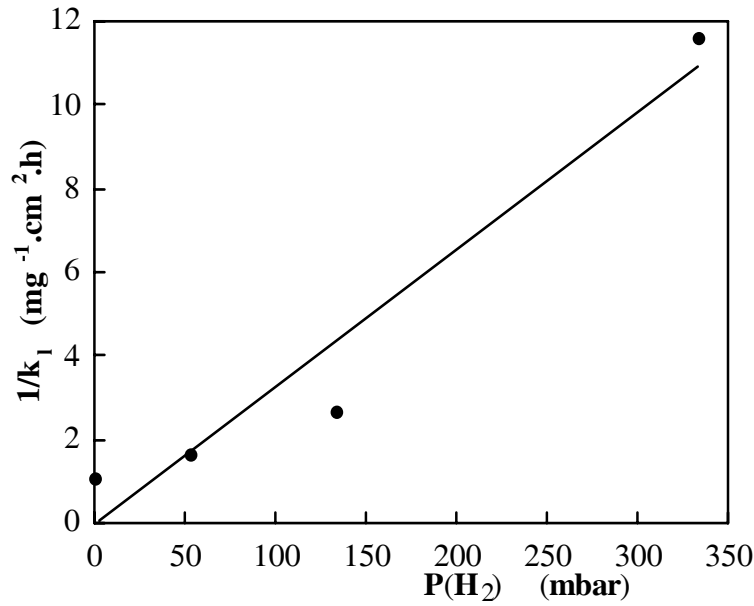


Figure 7.31. Linear transform $v = f[P(H_2)]$ for the case of complete dissociation ($T = 1000^\circ\text{C}$).

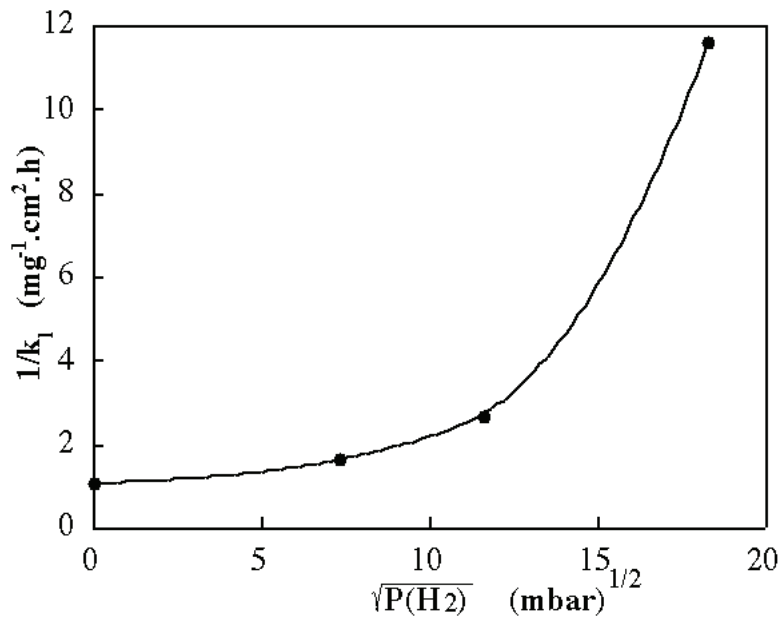


Figure 7.32. Linear transform $v = f[P(H_2)]$ for the case of partial dissociation ($T = 1000^\circ\text{C}$).

It can be seen that a mechanism involving a complete dissociation (Fig. 7.31) shows the best agreement with the experimental results.

8. Lead chlorination

8.1. Section 1

Lead chloride PbCl_2 is a gaseous species at 300°C . A thermogravimetric study of its sublimation at this temperature under a chlorine stream gave the following results. Δm_s denotes the evaporated mass at time t .

t (hours)	0	10	20	30	40	50	60	70	80
$\Delta m_s \times 10^5$ (g.cm^{-2})	0	18	32	50	68	83	100	119	133

What is the rate equation for the process of PbCl_2 sublimation?

Calculate the corresponding rate constant k_s .

8.2. Section 2

At 300°C and under a continuous chlorine stream, lead reacts with the gas and PbCl_2 is formed. The kinetic study shows that, in these experimental conditions, a dense chloride scale is formed with concurrent PbCl_2 sublimation.

It will be assumed that the kinetics of scale growth is controlled by a diffusion process. k_p denotes the rate constant for the limiting process and Δm_p the weight of chlorine uptake by the compact scale.

8.2.1. Express the scale growth rate $\frac{d(\Delta m_p)}{dt}$ as functions of k_p , k_s , Δm_p and of the molar weight ratio β of PbCl_2 and Cl_2 ($\beta = 3.91$). Hence, deduce the rate equation: $\Delta m_p = f(t)$. Show that the scale reaches a limiting thickness $(\Delta m_p)_{\text{max}}$ that can be expressed as a function of both of the constants k_p and k_s .

8.2.2. The weight change recorded during a chlorination experiment will be referred to as Δm (g.cm^{-2}).

8.2.2.1. Write the relationship between Δm , Δm_p , Δm_s and β . Hence, deduce the equation for the chlorination rate measured with the microbalance $\frac{d(\Delta m)}{dt}$, as a function of Δm_p .

8.2.2.2. Calculate the value of $(\Delta m_p)_0$ at which the chlorination rate is zero. Hence deduce that the curve $\Delta m = f(t)$ exhibits a maximum and express the co-ordinates $(\Delta m_0, t_0)$ of this maximum as a function of k_p and k_s .

8.2.2.3. Give the relationship between Δm and t . Draw qualitative sketch graphs of the curves $\Delta m(t) = 0$ and $\Delta m_p(t) = 0$.

8.3. Section 3: Numerical application.

The thermogravimetric study of lead chlorination in the experimental conditions previously described gave the following results (from¹⁸):

t (hours)	0	10	20	30	40	50	60	70
$\Delta m \times 10^6$ (g.cm ⁻²)	0	185	540	645	700	720	720	710

t (hours)	80	90	100	110	120	130	140	150
$\Delta m \times 10^6$ (g.cm ⁻²)	695	670	650	620	590	550	510	470

8.3.1. Draw the curve $\Delta m = f(t)$ and estimate the co-ordinates of its maximum.

8.3.2. Assuming that the kinetic model proposed in section 8.2 applies, calculate the constants k_p and k_s .

8.3.3. Compare the value of k_s determined in question 8.3.2 to that obtained directly in section 8.1. What conclusion do you draw regarding the validity of the proposed model ?

¹⁸ D. Vajszel, *J. Electrochem. Soc.*, **110** (1963) 504-507.

Answers

8.1. Section 1

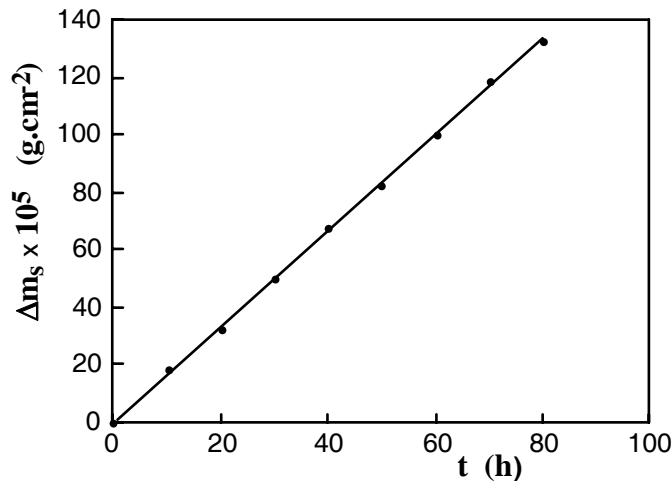


Figure 7.33. PbCl₂ weight loss due to its sublimation at 300°C in a chlorine atmosphere.

PbCl₂ sublimation obeys the following linear rate equation:

$$k_s = 1.67 \times 10^{-5} \text{ g.cm}^{-2}.\text{h}^{-1} = 4.65 \times 10^{-9} \text{ g.cm}^{-2}.\text{s}^{-1}$$

8.2. Section 2

8.2.1. Scale growth rate:

$$\frac{d(\Delta m_p)}{dt} = \frac{k_p}{2 \Delta m_p} - \frac{k_s}{\beta}$$

The integration of this differential equation yields:

$$\Delta m_p + \beta \frac{k_p}{2 k_s} \ln \left(1 - \frac{2 k_s}{\beta k_p} \Delta m_p \right) + \frac{k_s}{\beta} \cdot t = 0$$

The curve of Δm_p is asymptotic to an horizontal line of the form:

$$(\Delta m_p)_{\max} = \beta \frac{k_p}{2 k_s}$$

8.2.2. Let Δm be the weight change recorded during a thermogravimetric study of lead chlorination.

8.2.2.1. Relationship between Δm, Δm_p, Δm_s and β:

$$\Delta m = \Delta m_p + \frac{\Delta m_s}{\beta} - \Delta m_s$$

$\swarrow$ uptake $\nwarrow$ lost by sublimation $\nwarrow$ PbCl_2 lost by sublimation
 Balance of chlorine having reacted

This may also be written as:

$$\Delta m = \Delta m_p - \left(\frac{\beta - 1}{\beta}\right) \cdot \Delta m_s$$

Hence:
$$\frac{d\Delta m}{dt} = \frac{d\Delta m_p}{dt} - \left(\frac{\beta - 1}{\beta}\right) \cdot \frac{d\Delta m_s}{dt}$$

$$\frac{d\Delta m}{dt} = \frac{k_p}{2 \Delta m_p} - \frac{k_s}{\beta} - (\beta - 1) \cdot \frac{k_s}{\beta}$$

$$\frac{d\Delta m}{dt} = \frac{k_p}{2 \Delta m_p} - k_s$$

8.2.2.2. The necessary condition for the chlorination curve to exhibit a maximum is that:

$$\frac{d\Delta m}{dt} = 0.$$

Then, Δm_p has the following value: $(\Delta m_p)_0 = \frac{k_p}{2 k_s} < (\Delta m_p)_{\max}$.

Calculation of the co-ordinates $(t_0, \Delta m_0)$ of the maximum:

- *calculation of t_0*

Replacing $(\Delta m_p)_0$ in the expression for $\Delta m_p(t) = 0$, yields:

$$t_0 = \frac{\beta^2 k_p}{2 k_s^2} \left[\ln \frac{\beta}{\beta - 1} - \frac{1}{\beta} \right]$$

- *calculation of Δm_0 :*

$$\Delta m_0 = (\Delta m_p)_0 - \left(\frac{\beta - 1}{\beta}\right) \cdot k_p \cdot t_0$$

$$\Delta m_0 = \frac{\beta k_p}{2 k_s} \cdot \left[1 - (\beta - 1) \ln \left(\frac{\beta}{\beta - 1} \right) \right]$$

8.2.2.3. Relationship between Δm and t

$$\Delta m = \Delta m_p - \left(\frac{\beta - 1}{\beta} \right) \cdot \Delta m_s$$

then:

$$\Delta m_p = \Delta m + \left(\frac{\beta - 1}{\beta} \right) \cdot k_s \cdot t$$

Inserting this in the expression for $\Delta m_p(t) = 0$ (see section 8.2.1), yields:

$$\Delta m + \beta \frac{k_p}{2 k_s} \ln \left[1 - \frac{2 k_s}{\beta k_p} \left(\Delta m + \left(\frac{\beta - 1}{\beta} \right) \cdot k_s \cdot t \right) \right] + k_s \cdot t = 0$$

This curve is asymptotic to the straight line equation:

$$\Delta m = \beta \frac{k_p}{2 k_s} - \left(\frac{\beta - 1}{\beta} \right) \cdot k_s \cdot t$$

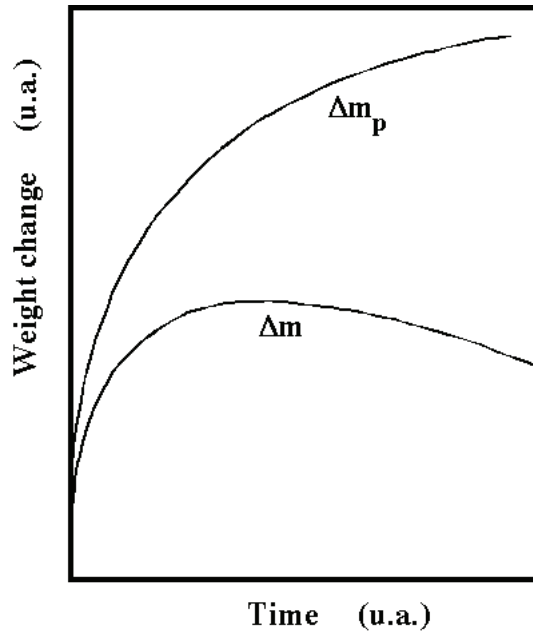


Figure 7.34. Sketch graphs of the weight variation during lead chlorination.

8.3. Section 3

8.3.1. Plot of the curve $\Delta m = f(t)$

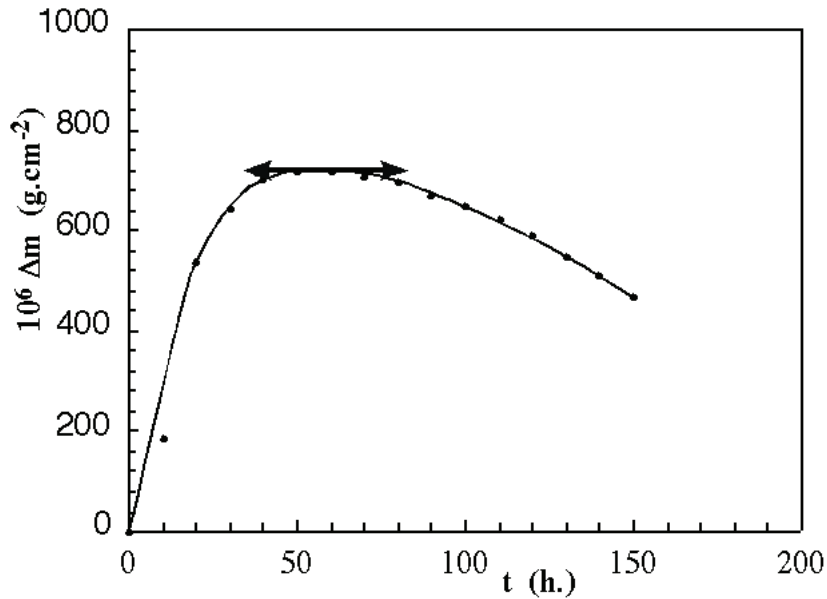


Figure 7.35. Rate curve for chlorination of lead at 300°C under a chlorine stream.

Co-ordinates of the maximum of the rate curve are:

$$t_0 = 55 \text{ hours} = 2 \times 10^5 \text{ s} \quad \Delta m_0 = 7.2 \times 10^{-4} \text{ g.cm}^{-2}$$

8.3.2. Define:

$$A = 1 - (\beta - 1) \ln \left(\frac{\beta}{\beta - 1} \right)$$

$$B = \ln \left(\frac{\beta}{\beta - 1} \right) - \frac{1}{\beta}$$

Combining the expressions for t_0 and Δm_0 , yields:

$$k_s = \beta \frac{B}{A} \cdot \frac{\Delta m_0}{t_0} \quad \text{and} \quad k_p = \frac{2B}{A^2} \cdot \frac{(\Delta m_0)^2}{t_0}$$

Numerical application:

$$A = 1.30 \times 10^{-1} \quad B = 4.40 \times 10^{-2}$$

$$k_s = 4.81 \times 10^{-9} \text{ g.cm}^{-2}.\text{s}^{-1} \quad k_p = 1.36 \times 10^{-11} \text{ g}^2.\text{cm}^{-4}.\text{s}^{-1}$$

8.3.3. The result obtained is close (within 5 %) to that obtained directly in section 8.1 and this justifies the model.

9. Zircaloy-4 oxidation

9.1. Introduction

Zircaloy-4 is used principally as fuel cladding in pressurised water nuclear reactors (PWRs). Its mean composition is:

$$\text{Zr} - 1.5 \% \text{ Sn} - 0.2 \% \text{ Fe} - 0.1 \% \text{ Cr}.$$

In the primary circuit, liquid water exists under 100 bar pressure at 315°C and alloy oxidation leads to the almost exclusive formation of zirconia, ZrO₂. In order to simulate this behaviour out of reactor, oxidation in autoclaves is carried out under pressurised water vapour or even in oxygen under atmospheric pressure. The kinetic curves obtained in the latter case, at 415 and 470°C, respectively, are given in figures 7.36 and 7.37. It will be assumed in the following that only ZrO₂ is formed during zircaloy oxidation.

Table 7.4. Zircaloy-4 oxidation at two temperatures in pure oxygen under atmospheric pressure.

T = 415°C		T = 470°C	
t (h.)	Δm (mg.cm ⁻²)	t (ks)	ZrO ₂ thickness(μm)
0	0	0	0
50	0.085	10	0.50
100	0.117	25	0.70
150	0.144	50	0.97
200	0.165	100	1.30
300	0.200	150	1.55
400	0.228	200	1.72
500	0.250	250	1.89
600	0.267	300	2.00
700	0.279	350	2.30
800	0.333	400	2.,60
900	0.417	500	3.20
100	0.492	600	3.80
1100	0.583	700	4.45
1200	0.658	800	5.10

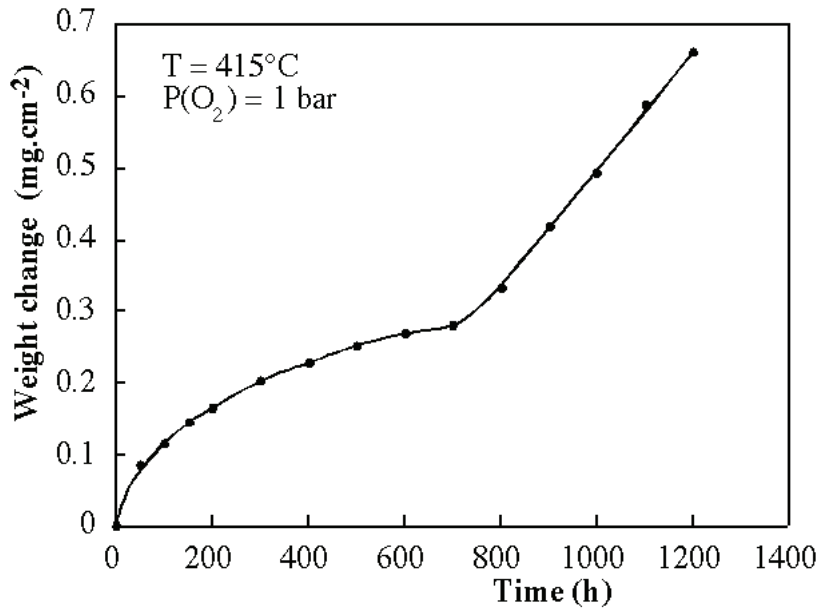


Figure 7.36. Oxidation of zircaloy-4 at 415°C in 1 bar O₂.

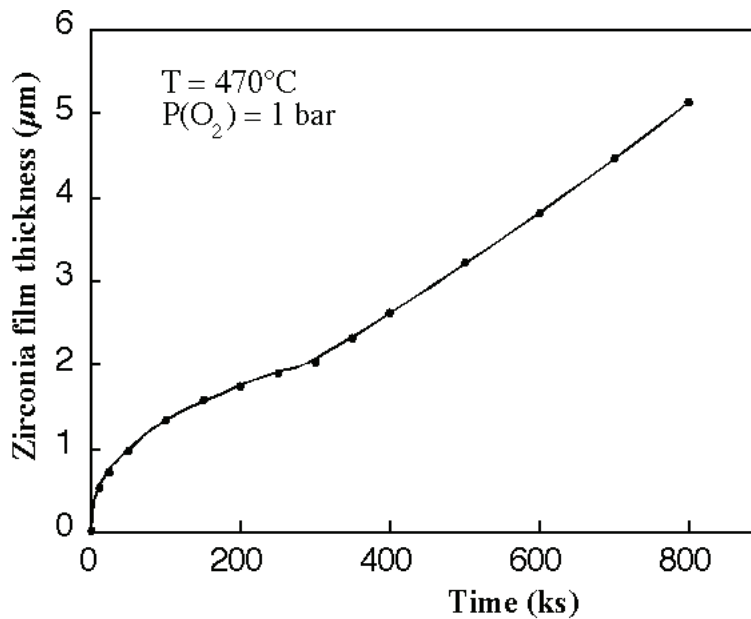


Figure 7.37. Oxidation of zircaloy-4 at 470°C in 1 bar O₂.

9.1. Describe the kinetic curves as a series of three stages.

9.2. Identify the zirconia thickness at which the kinetic transition takes place and verify that this thickness is the same for both temperatures.

9.2. Pre-transition oxidation

9.2.1. Can the pre-transition oxidation of Zircaloy-4 be considered to be parabolic ?

9.2.2. If this is not the case, then the oxidation kinetics may be described by the general rate equation: $(\Delta m)^n = k t$. Determine the value of n . Is this value the same at both temperatures ?

9.2.3. Indicate the rate limiting step. What type of further phenomenon may lead to the same exponent " n " ? (hint: calculate the Pilling and Bedworth ratio and recall that zirconia is a n -type semiconductor with oxygen vacancies as predominant ionic defects).

9.2.4. Is it reasonable to determine the apparent activation energy of the constant k in the rate equation: $(\Delta m)^n = k t$?

9.3. Time and nature of the transition

In order to determine the transition using a mathematical method, plot the transforms:
 $y = f\left(\frac{t}{y}\right)$.

9.3.1. Under what conditions are these transforms straight lines ? What does one observe if the rate equation is linear ?

9.3.2. What are the transition times determined using this method ?

9.3.3. Explain the origin of this transition.

9.4. Post-transition oxidation

9.4.1. Determine, at 415 and 470°C, the linear rate constants k_l expressed in terms of the thickness of corroded metal (assumed to be pure zirconium) per unit of time.

9.4.2. The life time of PWR fuel rods is defined as the time necessary to corrode 10 % of the zircaloy clad thickness, originally 570 μm thick at start of life. What is the lifetime deduced from figures 7.36 and 7.37, assuming, as a simplification, that the rate equation is linear from time zero ?

9.4.3. What is the apparent activation energy of k_l ?

9.4.4. What is the life time at 315°C, which is the operating temperature of the fuel rods ?

Data:Zr: 91.2 g.mol⁻¹O: 16.0 g.mol⁻¹ $\rho(\text{Zr}) = 6.49 \text{ g.cm}^{-3}$ $\rho(\text{ZrO}_2) = 5.60 \text{ g.cm}^{-3}$ **Answers**

9.1.1. The rate curves of figures 7.36 and 7.37 show three stages:

- a pre-transition stage with a parabolic-type form in the sense that the rate continuously decreases;
- a transition period where the rate suddenly increases;
- a post-transition stage with constant rate (linear kinetic law).

9.1.2. Calculation of the equivalence between mass increase and zirconia thickness, y :

$$y = \frac{\Delta m M(\text{ZrO}_2)}{2 M_{\text{O}} \rho(\text{ZrO}_2)}$$

where 1 μm ZrO_2 corresponds to 0.1455 mg.cm⁻² of mass increase

1 mg.cm⁻² of mass increase corresponds to 6.87 μm of zirconia thickness.

Zirconia thickness at transition:

- 415°C: ~ 0.29 mg.cm⁻², equivalent to 2 μm thickness
- 470°C: 2 μm thickness.

This thickness is the same at both temperatures.

9.2.1. The transforms $\Delta m^2 = f(t)$ or $y^2 = f(t)$ are not exactly straight lines but show a concavity with lower values of Δm or y . Hence, the kinetic law is a power law with an exponent higher than 2.

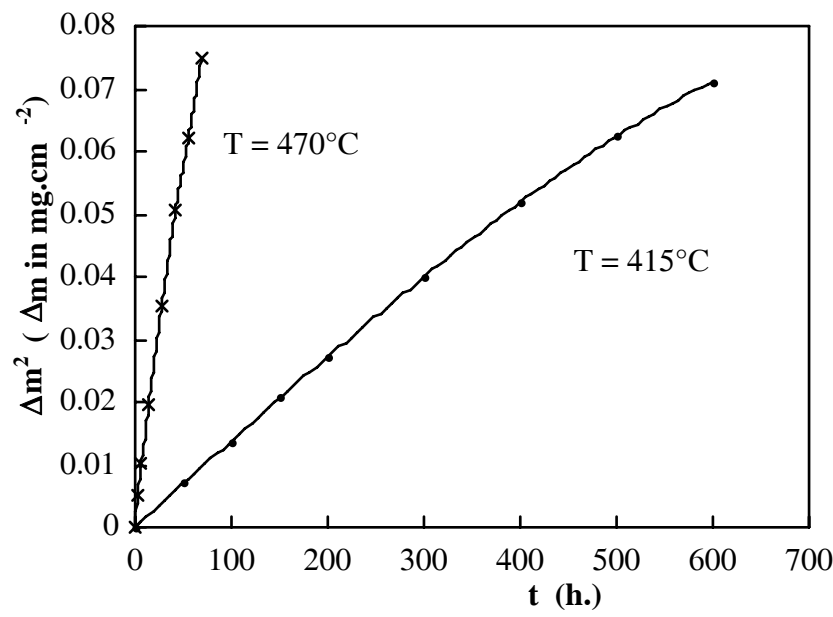


Fig. 7.38. Parabolic plot of weight gain versus time for the oxidation of Zircaloy-4 at 415°C and 470°C.

9.2.2. In double-logarithmic plots (see Figures 7.39 and 7.40), the value of n in the rate equation $\Delta m^n = k t$ may be found from the slopes of the straight lines obtained:

$$\Delta m^n = k t \qquad \log \Delta m = \frac{1}{n} \log t + \text{cste}$$

At $T = 415^\circ\text{C}$: $n = 2.14$

$T = 470^\circ\text{C}$: $n = 2.40$

The exponent increases with temperature.

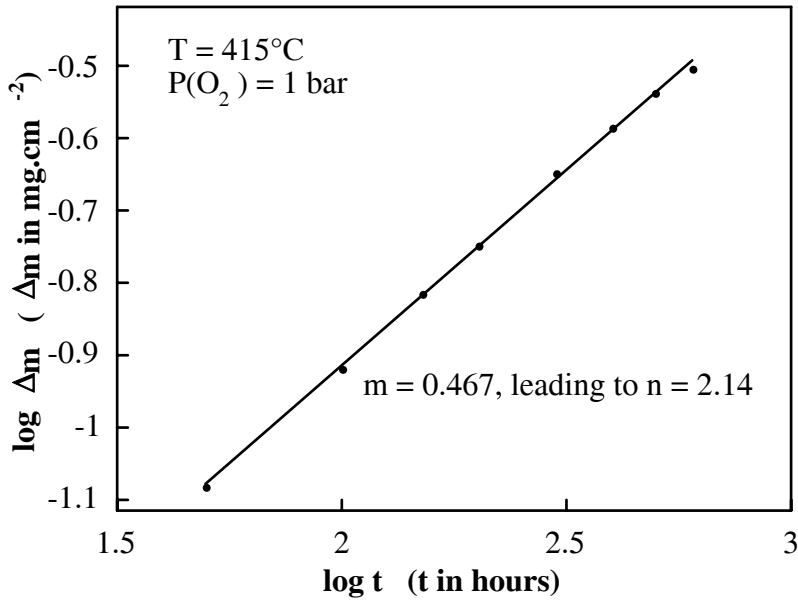


Figure 7.39. Double-logarithmic plot of weight gain versus time for the oxidation of Zircaloy-4 in oxygen, at 415°C.

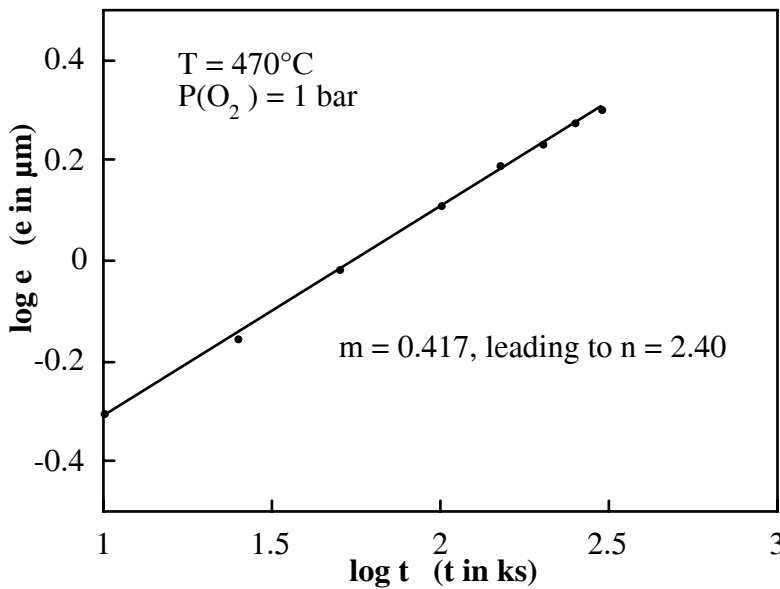


Figure 7.40. Double-logarithmic plot of the film thickness versus time for the oxidation of Zircaloy-4 in oxygen, at 470°C.

9.2.3. Parabolic kinetics is characteristic of a reaction controlled by the diffusion of oxygen vacancies through the compact ZrO_2 scale. An exponent $n > 2$ suggests that the vacancy diffusion coefficient decreases as scale thickness increases due to the compressive growth stress generated during oxidation.

The Pilling and Bedworth ratio (PBR) is

$$\text{PBR} = \frac{M(\text{ZrO}_2)}{M(\text{Zr})} \frac{\rho(\text{Zr})}{\rho(\text{ZrO}_2)} = 1.57$$

Since the oxide is growing at the scale-metal interface by inward migration of oxygen ions, the compressive stresses, produced by the volume expansion, increase continuously during scale growth.

9.2.4. Both parameters of the power law: $\Delta m^n = k t$, i.e., n and k , depend on temperature. Hence, studying the temperature influence on only one of these two parameters is not sensible.

9.3.1. A strictly parabolic law: $y^2 = k_p t$ leads to a transform $y = k_p \frac{t}{y}$ which is a straight line with a slope of k_p .

A $y^n = k t$ law leads to a transform $y = \frac{k}{y^{(n-2)}} \left(\frac{t}{y}\right)$, with a slope equal to: $\frac{k}{y^{(n-2)}}$.

If $n = 1$, this slope is equal to $k y$ and tends to infinity when y becomes very large.

9.3.2. The transforms are given in figures 7.41 and 7.42. The times of transition can be estimated from the change in slope of the kinetic curve:

at $T = 415^\circ\text{C}$ $t = 700 \text{ h}$
 at $T = 470^\circ\text{C}$ $t = 300 \text{ ks} \approx 83 \text{ h}$.

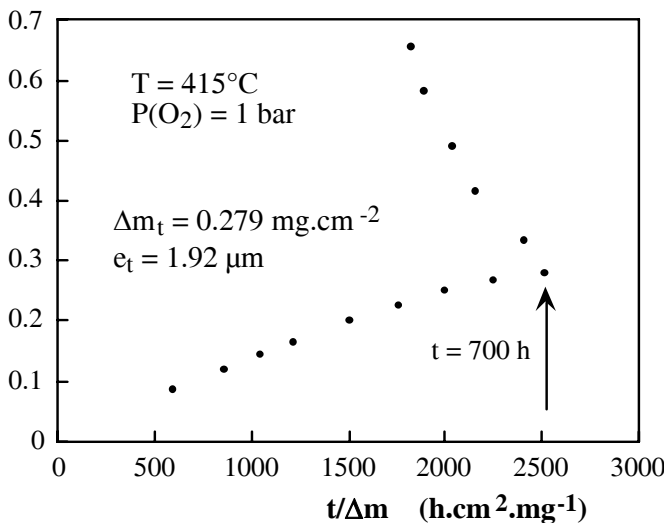


Figure 7.41. The transform $\Delta m = f\left(\frac{t}{\Delta m}\right)$ at 415°C .

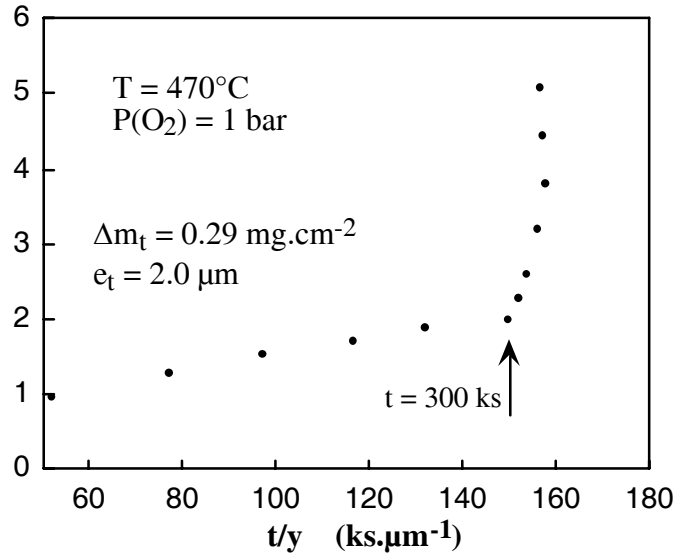


Figure 7.42. The transform $y = f\left(\frac{t}{y}\right)$ at 470°C.

9.3.3. It may be expected that the transition, occurring at the same zirconia thickness rather than at a given time, results from mechanical effects. The compressive stresses accumulated in the zirconia layer during scale growth cause, at this thickness, the spalling of the oxide from the alloy substrate. The oxide layer is then no longer protective and an increase of the corrosion rate ensues.

9.4.1. Linear constants:

$$T = 415^{\circ}\text{C} \quad k_1 = 8 \times 10^{-4} \text{ mg.cm}^{-2}.\text{h}^{-1}$$

$$T = 470^{\circ}\text{C} \quad k_1 = 6.2 \times 10^{-2} \text{ } \mu\text{m ZrO}_2.\text{ks}^{-1}.$$

If the oxidation rate is expressed in thickness, e , of corroded metal per unit time, i.e.:

$$e = y \left(\frac{M(\text{Zr}) \rho(\text{ZrO}_2)}{M(\text{ZrO}_2) \rho(\text{Zr})} \right) = 0.64 y$$

these linear constants become:

$$T = 415^{\circ}\text{C} \quad k'_1 = 3.5 \times 10^{-3} \text{ } \mu\text{m Zr.h}^{-1}$$

$$T = 470^{\circ}\text{C} \quad k'_1 = 0.143 \text{ } \mu\text{m Zr.h}^{-1}.$$

9.4.2. The maximum thickness of alloy permitted to be consumed by corrosion is 57 μm and so the corresponding lifetimes are:

$$T = 415^{\circ}\text{C} \quad 16286 \text{ h}$$

$$T = 470^{\circ}\text{C} \quad 398 \text{ h.}$$

9.4.3. The apparent activation energy, E_A , of the linear rate constant is first obtained from the experimental data at 470°C and 415°C and then an extrapolation from 470°C to 315°C is carried out.

$$\log \left(\frac{k_I(470)}{k_I(415)} \right) = - \frac{E_A}{2.303 R} \left[\frac{1}{(470 + 273)} - \frac{1}{(415 + 273)} \right]$$

$$E_A \sim 106 \text{ kJ.mol}^{-1}.$$

$$\log \left(\frac{k_I(470)}{k_I(315)} \right) = - \frac{1.06 \times 10^5}{2.303 R} \left[\frac{1}{(470 + 273)} - \frac{1}{(315 + 273)} \right]$$

$$\frac{k_I(470)}{k_I(315)} = 1.965$$

i.e., $k_I(315) = 1.5 \times 10^{-3} \text{ } \mu\text{m.h}^{-1}$.

Hence, the anticipated lifetime at 315°C is 4.3 years (38 000 hours).

9.4.4. The lifetime may equally well be estimated by graphical extrapolation of an Arrhenius plot that expresses lifetime as the reciprocal of the linear rate constant, as shown in figure 7.43. The temperature dependence of this expression has the same absolute value as the activation energy of the corrosion process.

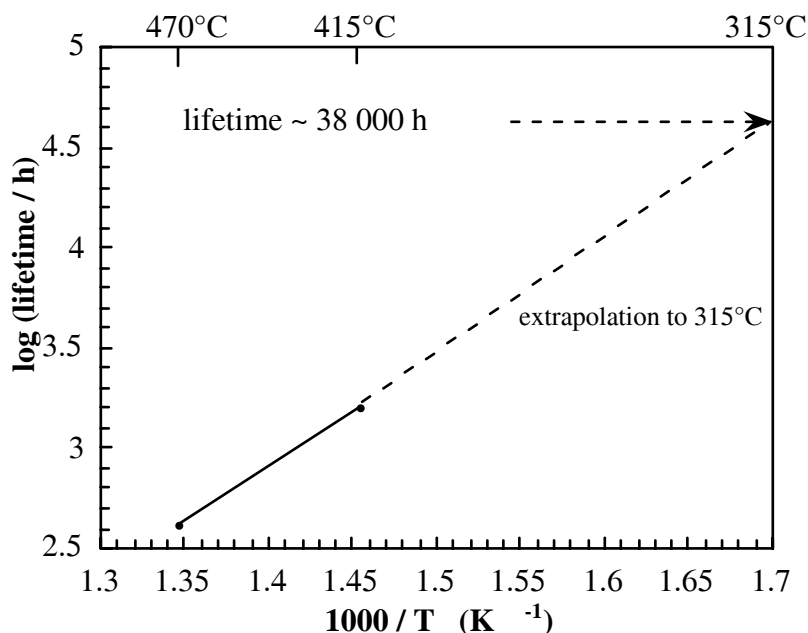


Figure 7.43. Determination of the lifetime by extrapolation to 315°C.

It should be pointed out that in industrial reactors, three additional phenomena are observed but these have not been discussed here:

- hydridation of the alloy,
- thermal flux through the cladding and the oxide scale,
- massive neutron irradiation.

These phenomena shorten the effective fuel lifetime that is nowadays below than three years.

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