Oxidation of Metals

The General Oxidation Equation

TOR HURLEN

Central Institute for Industrial Research, Blindern-Oslo, Norway

A detailed expression of a general rate equation for metal oxidation processes governed by the transport of material in the oxide film, is derived on the basis of Eyring's theory of absolute reaction rates and on the assumption that the transport is accomplished by defect species, *i. e.* interstitial ions and ion vacancies.

Following previous treatments by Evans and Hoar, the conditions at which this equation may be reduced to the more classical parabolic (Wagner) and inverse logarithmic (Mott-Cabrera) equations are discussed. It is further shown that the general equation under certain conditions may be satisfactorily replaced also by a cubic equation.

All the deductions have been applied to the special case of titanium being oxidized to rutile.

1.0 INTRODUCTION

On the basis of the theory of absolute reaction rates (Eyring [1]), it is possible to derive a general oxidation equation for cases of control by rate of transport of material in the oxide film. In two limiting cases, the general equation may be replaced by simpler forms known as the parabolic and inverse logarithmic equations. Under certain conditions, it may satisfactorily be replaced also by a cubic type of equation.

The general equation and its importance to metal oxidation studies seem first to have been pointed out by Evans [2], who derived a simplified, formal expression for this equation and also showed how it could be reduced to the more conventional oxidation equations. On this basis, Hoar [3] later calculated the limiting conditions of temperature and oxide film thickness under which the general equation for some metals (Fe, Zn, Cu) may be satisfactorily represented either by the inverse logarithmic equation or by the parabolic equation.

Gulbransen [4] seems to have been the first to apply the theory of absolute reaction rates to metal oxidation. He thereby derived an absolute expression for the parabolic rate constant.

To our knowledge, nobody has so far applied the absolute rate theory in deriving the general oxidation equation.

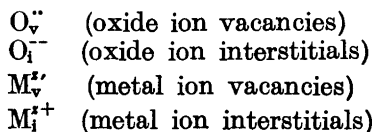## 2.0 DERIVATION OF THE GENERAL EQUATION

From the absolute rate theory, the following expression for the net rate of transport (v) of a species in an ideal solution under the action of chemical and electrical potential fields, may easily be derived (see Ref.[1], pp. 552—555):

$$v = \frac{kT}{h}\,\lambda C\,\exp\left(-\frac{\Delta G_o^{\ddagger}}{RT}\right)\left[\exp\left(-\frac{\alpha\lambda zF}{RT}\,\frac{\mathrm{d}\emptyset}{\mathrm{d}x}\right) - \left(1 + \lambda\,\frac{\mathrm{d}\ln C}{\mathrm{d}x}\right)\right.$$
$$\left.\exp\left(\frac{(1-\alpha)\lambda zF}{RT}\,\frac{\mathrm{d}\emptyset}{\mathrm{d}x}\right)\right] \tag{1}$$

R is the gas constant, k the Boltzmann constant, h the Planck constant, T the Kelvin temperature, F the Faraday, $\Delta G_o^{\ddagger}$ the standard chemical energy of activation, C the concentration of the species, $\emptyset$ the inner potential, x a distance in direction of the transport, z the charge carried by a single migrating entity, λ the distance between equilibrium positions for these entities, and α the so called symmetry factor.

According to the theories of Frenkel [5] and Schottky [6], ionic crystals usually contain reversible defects (ions in interstitial positions and ion vacancies in connection with an equivalent number of quasi-free electrons and electron holes). It seems further well recognized that the transport of material in ionic crystals may be described as a transport of such defects (see *e.g.* Ref.[7]). As a normal crystal with good approximation also may be considered an ideal solution of reversible defects in a perfect crystal, the rate of transport of any one type of such defects in the crystal should be represented by eqn. (1) above.

The thickening of an oxide film on a metal certainly requires transport of material across the film. The defects, which may take part in this transport, generally are:

$O_v^{\cdot\cdot}$ (oxide ion vacancies)
O_i^{--} (oxide ion interstitials)
$M_v^{z'}$ (metal ion vacancies)
M_i^{z+} (metal ion interstitials)

where the symbols $\cdot$ and $\prime$ represent a positive and a negative surplus charge, respectively.

During oxidation, oxide ion vacancies and metal ion interstitials will move *outwards* and oxide ion interstitials and metal ion vacancies *inwards* through the film. If we now choose the outward direction (from the metal to the gas) as our single reference direction or x-direction (instead of having to consider two transport directions), the total net rate of transport of defects through a plane at a distance x from the metal/oxide interface is given by:

$$v_x(\text{total}) = \sum_i \pm v_{i,x} \tag{2}$$

$v_{i,x}$ means here the rate of transport of the defect species i in the x direction and is given by (1) when $(\mathrm{d}\emptyset/\mathrm{d}x)$ and $(\mathrm{d}C/\mathrm{d}x)$ are considered gradients also in this direction (not in the actual transport directions). The signs $+$ and

— apply to positively and negatively charged species, respectively. In this way, all the rate terms in (2) become positive.

When $+$ and $-$ are put together as in the above equation, it will in this paper always mean that the upper sign applies to positive species and the lower to negative ones.

As both the concentration and the concentration gradient of a defect species as well as the electric potential gradient at any given time may vary from point to point within the film, it is obvious that v_x(total) also may vary. It is a question, therefore, how the momentary rate of oxidation is connected to the various momentary rates of transport in the oxide film.

What is actually measured however by gravimetric and volumetric methods of investigation of oxidation of metals, is the rate of entrance of oxygen from the gas phase into the oxide phase. The other rate processes in the system (such as the transfer of metal ions from the metal phase into the oxide phase and the migration of ions in the oxide phase) are not directly susceptible to measurements of this kind, and information on these processes must be obtained either by theoretical deductions from the oxidation measurements or by other types of measurements.

The measured oxidation rate can be assumed to be equal to the rate of entrance of oxygen into the oxide, provided the concentration of chemisorbed oxygen on the oxide surface does not change during oxidation. On this basis, the oxidation rate, v(ox), may be represented by the following formula:

$$v(\text{ox}) = \lim_{x \to y} v_x(\text{total}) \tag{3}$$

where y is the oxide film thickness, and where the various rates must be expressed in equivalent units (number of equivalents per unit area per unite time).

Eqn. (3) combined with (1) and (2) may thus be regarded as a general oxidation equation for cases of control by rate of transport of material in the oxide film. In practice, one also has to add the requirement that the area undergoing oxidation must be constant with time as experimental oxidation rates usually are determined on the basis of the apparent surface area of the specimens at the start of the experiment.

The general equation will be somewhat easier to handle if we introduce the following approximations:

$$v(\text{ox}) = \frac{1}{V}\,(\mathrm{d}y/\mathrm{d}t) \tag{4a}$$

$$\mathrm{d}\varnothing/\mathrm{d}x = \Delta\varnothing/y \tag{4b}$$

$$\mathrm{d}C/\mathrm{d}x = \Delta C/y \tag{4c}$$

$$F\Delta\varnothing = \Delta G \tag{4d}$$

$$\alpha = \tfrac{1}{2} \tag{4e}$$

and the following substitute:

$$V\lambda(kT/h)\,\exp(-\Delta G_0^{\ddagger}/RT) = K \tag{5}$$

V is the equivalent volume of the oxide, $\Delta\varnothing$ the total potential increase in the film from metal to gas, ΔC the total concentration increase (for species

i) in the film from metal to gas, and ΔG the energy of formation of one gram-equivalent oxide at the actual oxidation conditions.

On this basis (eqns (1) to (5) above), the general oxidation equation may be written:

$$\frac{dy}{dt} = \sum_i \pm K_i C_{i,y} \left[\exp\left(-\frac{\lambda_i\, z_i\, \Delta G}{2\ RT\ y}\right) - \left(1 + \frac{\lambda_i \Delta C_i}{y\ C_{i,y}}\right) \exp\left(\frac{\lambda_i\ z_i\ \Delta G}{2\ RT\ y}\right)\right] \quad (6)$$

where $C_{i,y}$ means the limiting value of C_i for $x = y$ (i.e. when approaching the oxide/gas interface).

3.0 DEDUCTIONS FROM THE GENERAL EQUATION

The general oxidation equation (6) is rather clumsy. Under special conditions, however, it may be replaced by equations of simpler forms. This greatly increases its applicability and facilitates the testing of its validity.

Following previous treatments by Evans [2] and Hoar [3], we shall in the following discuss how the more classical parabolic (Wagner [8]) and inverse logarithmic (Mott-Cabrera [9]) equations may be regarded as limiting cases of the general oxidation equation. It shall also be shown how the general equation under certain conditions may be approximately, though satisfactorily, replaced even by a cubic type of equation.

The parabolic equation. At sufficiently high temperatures and large film thicknesses, the general equation (6) may be reduced to the simpler form:

$$\frac{dy}{dt} = \frac{1}{y} \sum_i \mp K_i \lambda_i C_{i,y} \left(\frac{z_i \Delta G}{RT} + \frac{\Delta C_i}{C_{i,y}}\right) \quad (7)$$

which is the parabolic oxidation equation ($y^2 = k_p t$) in its differential form.

This simplification is easily performed by extending the exponential functions in (6) and omitting the higher powers of the exponents. This is very nearly the same as omitting p^2 in the expression $6 + p^2$, where p in our case is given by:

$$p = \mp \lambda z \Delta G / 2RTy \quad (8)$$

The parabolic equation should thus be expected to represent the oxidation rate within about 10 % accuracy when $p^2 < 6/10$, which means:

$$y > \mp 0.65\ \lambda\ z\Delta G/RT \quad (9)$$

A similar requirement has previously been pointed out by Hoar [3].

The inverse logarithmic equation. At sufficiently low temperatures and small film thicknesses, one of the exponential terms in (6) vanishes as compared to the other one, and it is easily seen that the general equation under these conditions may be reduced to:

$$\frac{dy}{dt} = \sum_i K_i C_{i,y} \exp\left(\mp \frac{\lambda_i z_i \Delta G}{2RTy}\right) \quad (10)$$

Through integration and some simplification we obtain:

$$\frac{1}{y} = \sum_i \pm 2.303 \frac{2RT}{\lambda_i z_i \Delta G} \left[\log\left(\frac{K_i C_{i,y}}{y}\right) + \log t\right] \tag{11}$$

assuming $y = 0$ when $t = 0$.

For small values of y, $\log 1/y$ may be considered a constant as compared to $1/y$, whereby (11) represents a so called inverse logarithmic oxidation equation ($1/y = A - B \log t$). It also gives an interpretation of the constants (A and B) in this equation.

In integrating (10) to obtain (11), one has to make the requirement that $\exp(\pm \lambda z \Delta G/2RTy) \ll 1$, and in reducing (6) to obtain (10), the necessary requirement is that $\exp(\pm \lambda z \Delta G/2RTy) \ll \exp(\mp \lambda z \Delta G/2RTy)$. Of these requirements, the former seems to be strongest. As this is the most difficult one to evaluate, however, we shall here assume that the other requirement is sufficient.

The inverse logarithmic equation should thus represent the general equation within about 10 % accuracy when

$$y < \mp \lambda z \Delta G/2.32 \ RT \tag{12}$$

Also this requirement has previously been pointed out by Hoar [3].

The cubic equation. Under conditions at which $\exp(p) - \exp(-p)$ with sufficient accuracy might be replaced by ap^2, where a is a constant and p as given by eqn. (8), the general equation reduces to:

$$\frac{dy}{dt} = \frac{a}{y^2} \sum_i K_i C_{i,y} \left(\frac{\lambda_i z_i \Delta G}{2RT}\right)^2 \tag{13}$$

when $\Delta C/C_y$ is negligible compared to 1.

This is the cubic oxidation equation ($y^3 = k_c t + \text{const.}$) in its differential form, and it gives an interpretation of the cubic rate constant (k_c).

In Fig. 1, a graphical test is made on the validity of the approximation on which the reduction of the general equation to the cubic type of equation is based. As may be seen from this test, the approximation may be considered valid with reasonable accuracy through at least a part of the film-thickness region between those covered by the inverse logarithmic equation and the parabolic equation, respectively.

In accordance with the requirements suggested there (Fig. 1), the following film-thickness limits may be given for the validity of the cubic approximation:

$$\mp \lambda z \Delta G/1.72 \ RT > y > \mp \lambda z \Delta G/2.32 \ RT \tag{14}$$

To our knowledge, this is the first explanation of the cubic oxidation equation not implying any assumptions as to the semiconductor properties of the oxide. The cubic equation derived by Cabrera and Mott [9] and the one derived by Engell, Hauffe, and Ilschner [10] are only valid for p-type conducting oxides. Rutile, for instance, which we are going to discuss below, is an n-conductor [11-13].
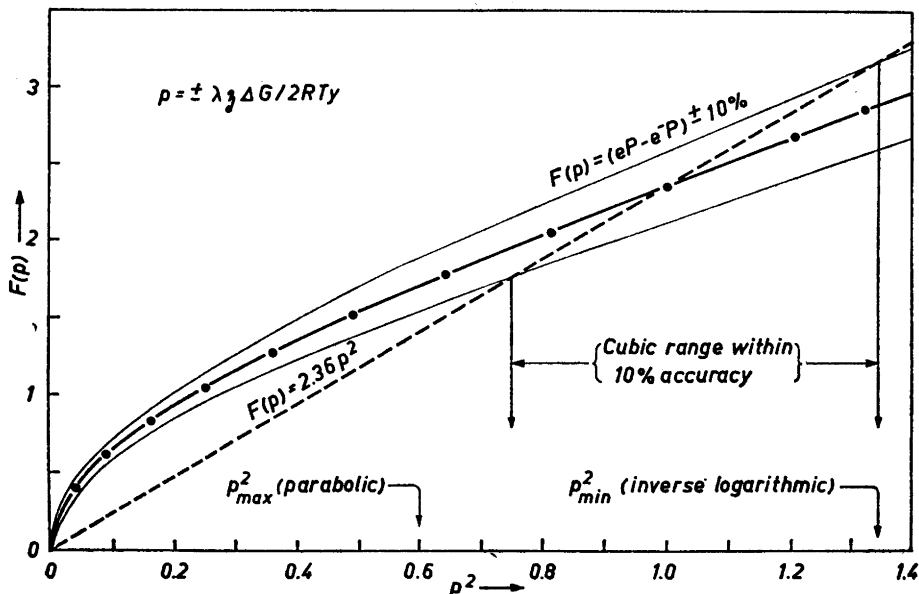
Fig. 1. Test on the validity of the "cubic" approximation (see eqn. 13).

By comparing the expressions for the parabolic (7) and the cubic (13) equations it is seen that one should expect to find the same Arrhenius energy of activation for the cubic as for the parabolic oxidation of a metal, provided the variation with temperature of the pre-exponential factors might be neglected. This could possibly be used as a basis for testing if an observed cubic and parabolic oxidation of a metal should have a common root in the general equation, or if the cubic oxidation should have another origin.

4.0 APPLICATION OF THE DEDUCTIONS

As an example, we shall here apply the above deductions to the special case of titanium being oxidized to rutile.

To simplify the discussion, we shall at first assume that it is mainly a titanium transport in rutile ($z = \pm 4$), that $\lambda = 3$ Å (which is close to the shortest Ti—Ti distance in rutile [15,16]), and that the oxidation takes place at an oxygen pressure of one atmosphere. On this basis, and using the ΔG-values given by Mah, Kelley, Gellert, King, and O'Brien [22] for rutile (see Table 1), one may from (9), (12), and (14) calculate the limiting film-thickness values for the validity of the parabolic (7), the cubic (13), and the inverse logarithmic (11) equations.

Table 1. Energy of formation of one gram-equivalent rutile at an oxygen pressure of one atmosphere (Ref.[22])

T (°K)	600	700	800	900	1 000
$- \Delta G$ (Kcal)	49.75	48.75	47.75	46.75	45.50

The results of some calculations of this kind are graphically presented in Fig. 2, where the various validity regions and their temperature dependence are clearly shown. The weight increase (w) connected to the film thickening (y), is also indicated. The following formula have been used in relating w to y:

$$w = \frac{32}{47.9 + 32} \ 4.2 \ y$$

The shortest distance between interstitial positions for titanium ions in rutile has been shown [16] to be the half only of the shortest Ti—Ti distance in an ideal rutile lattice. If this should be determining for the elementary diffusion step, one should have to lower the film-thickness values in Fig. 2 by a factor of two in case the interstitial transport mechanism predominates over the vacancy mechanism. This is easily seen from (9), (12), and (14).

If it should be mainly an oxygen transport in rutile ($z = \pm 2$), and if a λ-value of 3 Å should apply also to this transport, the limiting film-thickness values should also in this case be the half only of those calculated on the assumption of a titanium vacancy transport (Fig. 2).
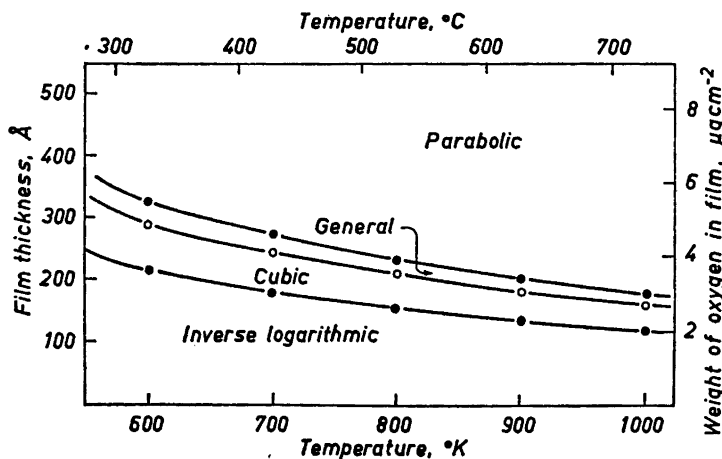

Fig. 2. Calculated regions for the validity of the varius rate equations in the case of titanium being oxidized to rutile (see text for underlying assumptions).
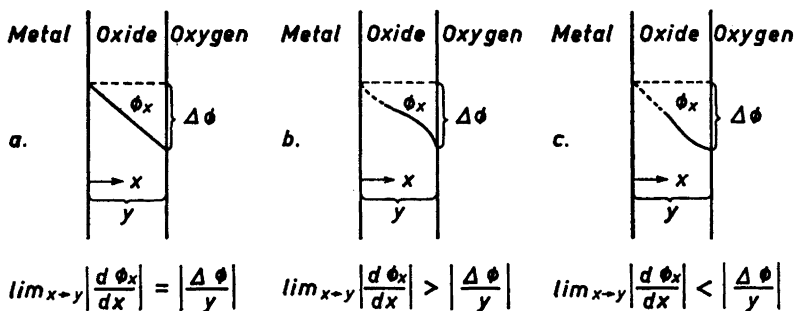
$$\lim_{x \to y}\left|\frac{d\,\phi_x}{dx}\right| = \left|\frac{\Delta\,\phi}{y}\right| \qquad \lim_{x \to y}\left|\frac{d\,\phi_x}{dx}\right| > \left|\frac{\Delta\,\phi}{y}\right| \qquad \lim_{x \to y}\left|\frac{d\,\phi_x}{dx}\right| < \left|\frac{\Delta\,\phi}{y}\right|$$

Fig. 3. Hypothetical variations of electric potential within oxide films.

If the oxidation should be governed by grain boundary diffusion instead of volume diffusion, the calculations should mainly be affected by a possible difference in the λ-values for these two types of diffusion. It seems likely, however, that this difference should be rather small, whereby a possible grain boundary diffusion should not be expected to alter the above picture very much. Another point is that a grain boundary diffusion — because of a lower energy of activation — may increase the oxidation rate and thereby decrease *the duration* of the inverse logarithmic and cubic types of oxidation at a given temperature. It is here important clearly to distinguish between time periods and film-thickness regions.

The correctness of calculations of this kind depends on the validity of the approximations (4). Of these, assumption (4b), which implies

$$\lim_{x \to y} (\mathrm{d}\varnothing/\mathrm{d}x) = \Delta\varnothing/y$$

probably is the most questionable one. The physical significance of this assumption is somewhat illustrated by the sketches in Fig. 3. From the general knowledge of space charge phenomena in phase boundary layers [7,17], the situation sketched in Fig. 3b seems the most probable one. This means that the limiting film-thickness values calculated from (9), (12), and (14) would be too low. It seems very difficult at present to estimate the actual electric potential gradient at the oxide/oxygen interface, to which gradient the limiting film-thicknesses should be proportional.

5.0 SUMMARY AND CONCLUSION

It has been shown how a general oxidation equation under certain conditions may be derived from the theory of absolute reaction rates, chapter 2.0, and how this equation may be represented by an inverse logarithmic, a cubic, and a parabolic type of equation at low, medium, and high values, respectively, of the oxide film thickness (chapter 3.0). These derivations do not involve any assumptions as to the semi-conductor properties of the oxide, and should apply just as well to metals forming p-type oxides as to those forming n-type oxides.

The general equation — and all the deductions made from this equation — are only valid for cases in which the oxidation is controlled by the rate of transport of material (not electrons) in the oxide film, and in which the area undergoing oxidation is constant with time. When these conditions are sufficiently satisfied, one should thus expect to observe oxidation/time curves running smoothly from an initial period of inverse logarithmic oxidation, through a medium period of cubic oxidation and general oxidation, into a final period of parabolic oxidation.

The "transitions" between the oxidation equations ought not occur at too low values of the film thickness if these values are to be measured with reasonable accuracy. From (9), (12), and (14) it is seen that metals with a high free energy of oxidation are to be expected the most suitable in this respect. Most of these unnoble metals, however, either do not fulfill the condtions on which the theory is based, or they have unsuitably high oxidation rates. All considerations of this kind taken into account, it seems that titanium might be one of the most suitable metals for testing the above theory.

Some approximate calculations have been made, therefore, of the film-thickness regions in which one should expect the inverse logarithmic, the cubic, and the parabolic equations to be satisfactory substitutes for the genral equation in the case of titanium being oxidized to rutile (chapter 4.0).

From previous work on the oxidation of titanium [17],[18] is known, however, that titanium at low oxide film-thickness and low temperatures usually is not oxidized according to an inverse logarithmic equation, but rather according to a direct logarithmic one, and that this logarithmic film growth probably is best explained by the theory of Evans [19] based on the assumption of the formation of cavities at the metal/oxide interface. This assumption implies that the effective area undergoing oxidation is not constant, whereby one of the conditions for the validity of the general equation is not satisfied.

As generally discussed by Birchenall [20] and quite recently shown by Engell and Wever [21] in the case of iron, there seems to be an inherent tendency of the oxide film to try to follow the retreating metal interface by a plastic flow mechanism, thereby counteracting the cavity formation. It seems quite reasonable to assume that this effect also is present in the case of titanium, and probably also that it increases in importance both with increasing film thickness and with increasing temperature, whereby the basic conditions for the validity of the general oxidation equation subsequently may be reached.

A further discussion of this matter will be given in a separate paper on the oxidation mechanism of titanium.

REFERENCES

1. Glasstone, S., Laidler, K. J. and Eyring, H. *Theory of Rate Processes*, Mc Graw-Hill, New York 1941.
2. Evans, U.R. *Revs. Pure and Appl. Chem. Australia* **5** (1955) 1.
3. Hoar, T. P. *J. Chim. Phys.* **53** (1956) 826.
4. Gulbransen, E. A. *Ann. N. Y. Acad. Sci.* **58** (1954) 830.
5. Frenkel, J. *Z. Physik.* **35** (1926) 652.
6. Schottky, W. *Z. physik. Chem.* **(B) 11** (1930) 163.
7. Hauffe, K. *Reaktionen in und an festen Stoffen*, Springer Verlag, Berlin 1955.
8. Wagner, C. *Z. physik. Chem.* **(B) 21** (1933) 25.
9. Cabrera, N. and Mott, N. F. *Repts. Progr. in Phys.* **12** (1949) 163.
10. Engell, H. J., Hauffe, K. and Ilschner, B. *Z. Elektrochem.* **58** (1954) 478.
11. Breckenridge, R. G. and Hosler, W. R. *Phys. Rev.* **83** (1951) 227.
12. Hauffe, K., Grunewald, H. and Tränckler-Greese, R. *Z. Elektrochem.* **56** (1952) 937.
13. Cronemeyer, D. C. *Electrical and Optical Properties of Rutile Single Crystals.* Technical Report 46, Laboratory for Insulation Research, M.I.T., August 1951.
14. Kofstad, P., Hauffe, K. and Kjøllesdal, H. *Acta Chem. Scand.* **12** (1958) 239.
15. Anderson, S., Collén, B., Kuylenstierna, U. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1641.
16. Hurlen, T. *Acta Chem. Scand.* **13** (1959) 365.
17. Hauffe, K. *Oxydation von Metallen und Metallegierungen*, Springer Verlag, Berlin 1956.
18. Kofstad, P. and Hauffe, K. *Werkstoffe u. Korrosion* **7** (1956) 642.
19. See Ref.[2], pp. 5—6.
20. Birchenall, C. E. *J. Electrochem. Soc.* **103** (1956) 619.
21. Engell, H. J. and Wever, F. *Acta Met.* **5** (1957) 695.
22. Mah, A. D., Kelley, K. H., Gellert, N. L., King, E. G. and O'Brien, C. J. *Thermodynamic Properties of Titanium-Oxygen Solutions and Compounds*, Bureau of Mines, U.S.A., Report of Investigations 5316, March 1957.