Application of kinetic methods in studying the defect concentrations and their mobility in transition metal oxides

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A critical discussion of two new methods for investigating the concentration and mobility of point defects in the crystalline lattice of metal oxides is presented. These methods are based on kinetic measurements of metal oxidation in specialized conditions. Using the results obtained on the cobalt-cobaltous oxide-oxygen model system, it has been shown that both these methods lead to correct results being simultaneously more simple and accurate than the classical ones.

1. Introduction

Transition metal oxides have found an increasing application in modern technology, particularly as semiconducting and refractory materials and as catalysts in heavy organic synthesis [1-3]. The semiconducting and catalytic properties, as well as many other valuable properties of these oxides, are due to the occurrence in their crystalline lattice of thermodynamically reversible point defects [1-4]. In contrast to other types of defects in solids, point defects are capable of migration in a crystal by diffusion and their concentration is a function of the temperature and pressure of the surrounding atmosphere.

The defect structure in transition metal oxides is limited in most cases to only one sublattice which results in deviations from stoichiometry of these materials. The two limiting cases of deviations from stoichiometry in transition metal oxides, corresponding to four different types of defect structure in these materials, are shown schematically in Fig. 1.

It follows from this that concentration of point defects predominating under given conditions in the crystal lattice of metal oxides is directly related to deviations from stoichiometry. Hence, by studying the extent of the dependence of these deviations on temperature and equilibrium oxygen pressure, one obtains direct information about concentration, degree of ionization and thermodynamic properties of the defects predominant in crystal lattice.

However, it should be emphasized that

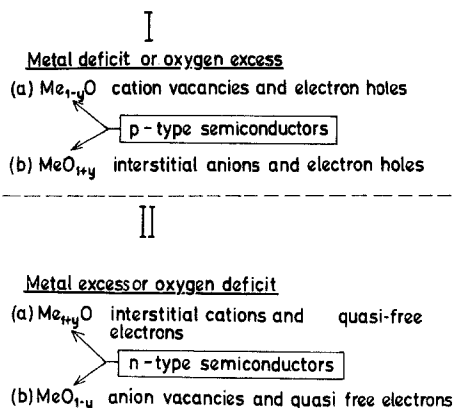DEVIATION FROM STOICHIOMETRY
OF TRANSITION METAL OXIDES

I

Metal deficit or oxygen excess

(a) $Me_{1-y}O$ cation vacancies and electron holes

p - type semiconductors

(b) MeO_{1+y} interstitial anions and electron holes

II

Metal excess or oxygen deficit

(a) $Me_{1+y}O$ interstitial cations and quasi-free electrons

n - type semiconductors

(b) MeO_{1-y} anion vacancies and quasi free electrons

Figure 1 Defect structures in metal oxides.

experimental problems involved in such studies are very difficult as the defect concentration, and thus deviations from stoichiometry in the oxides under consideration, are usually so small that their determination with the required accuracy demands application of very precise experimental methods. Among several methods elaborated for this purpose, the one most widely used is provided by high temperature vacuum microgravimetry in which deviations from stoichiometry are determined by measuring the mass changes occurring on changing the equilibrium oxygen pressure or temperature. Despite the very high accuracy of modern microgravimetric apparatus, the results of these studies are affected

by considerable errors resulting (as already mentioned) from the very small values of the deviations from stoichiometry in metal oxides.

A similar situation exists in studies on the mobility of point defects in the crystalline lattice of metal oxides. This mobility is measured by the self diffusion and chemical diffusion coefficients. The former is a macroscopic measure of the lattice mobility at thermodynamic equilibrium of a crystal with its surrounding atmosphere and the latter is a microscopic measure of the mobility of a particular defect in conditions which are far from equilibrium, i.e. when a gradient of defect concentration is present in the crystal.

The two diffusion coefficients are interrelated by the following Equation [2, 5, 6]:

$$\tilde{D} = (1 + p) D \frac{1}{N_d} \qquad (1)$$

where $\tilde{D}$ is a chemical diffusion coefficient, D a self-diffusion coefficient of a metal or oxygen, depending on the type of the defect structure, N_d is a defect concentration given in mol fractions, and p is the effective charge of a defect with respect to the lattice.

In the present paper a critical discussion of two new methods for investigating the concentration and mobility of point defects in the crystalline lattice of metal oxides is presented. These methods are based on kinetic measurements of metal oxidation in specialized conditions. Using the results obtained in this laboratory on the cobalt-cobaltous oxide-oxygen model system, it has been shown that both these methods lead to correct results which are simultaneously more simple and accurate than the classical ones [7-13].

2. The differential kinetic method

Growth of a mono-phasic, compact single layer scale on a metal surface in isothermal and isobaric conditions follows a parabolic rate law [14, 15]:

$$x^2 = 2k_p't + C \qquad (2)$$

where x is a thickness of a scale at time t, k_p' a parabolic rate constant, C a constant, the value of which is related to deviations from the parabolic course of the reaction in its initial period. The slowest partial process determining the rate of the scale growth is the diffusion of metal or oxygen ions in the oxide phase, occurring through point defects in the crystal

lattice of this phase [15-18]. The parabolic rate constant of the oxidation is then closely related to the self-diffusion coefficient of a metal, D_{Me}, or oxygen, D_0, in the oxide, which forms a scale under given conditions. This relationship was described in 1951 by Wagner [19]. For oxide scales with defects in the cation sublattice ($Me_{1-y} O$ or $Me_{1+y}O$) Wagner's general equation assumes the form:

$$k_p' = \int_{a_0'}^{a_0''} \left(\frac{Z_{Me}}{2}\right) D_{Me} \, d \ln a_0 (D_{Me} \gg D_0) . \quad (3)$$

For the scales with defects in the anion sublattice, MeO_{1-y} or MeO_{1+y} the same equation can be written as:

$$k_p' = \int_{a_0'}^{a_0''} D_0 \, d \ln a_0 (D_0 \gg D_{Me}) \qquad (4)$$

where a_0' and a_0'' are oxygen activities at internal and external surface of the scale respectively. Z_{Me} is the valency of a metal present in the scale.

To calculate coefficients D_{Me} or D_0 one has to integrate Equation 3 or 4. These coefficients depend, however, on defect concentration and hence on the oxygen activity (pressure); for the integration it is necessary, therefore, to know the dependence of D_{Me} or D_0 on a_0 or p_{O_2}. The character of these dependencies cannot be estimated *a priori* and therefore Equations 3 and 4 have not been used for calculation of the diffusion coefficients for many years. In 1965 Fueki and Wagner [20] showed that the solution of this problem for oxides of the $Me_{1-y}O$ or MeO_{1+y} type is possible by differentiating Equation 3 or 4.

These authors have drawn attention to the fact that the equations under discussion are composed of two terms, one of which is a function of a_0'' whereas the other depends on a_0'. At constant temperature the activity of oxygen at the scale/metal interphase (a_0') is constant independent of the external pressure of oxygen since, in agreement with experimentally confirmed assumptions of the Wagner theory [12, 21-25], a state of local thermodynamic equilibrium is achieved at this phase boundary. Equations 3 and 4 can be then differentiated with respect to a_0'':

$$\left(\frac{dk_p'}{d\ln a''_0}\right) = \frac{Z_{Me}}{2} D_{Me} \qquad (5)$$

$$\left(\frac{dk_{\mathrm{p}}'}{d\ln a_0''}\right)_{a_0'} = D_0 . \qquad (6)$$

The activity of oxygen can then be replaced by its pressure:

$$d\ln a_0 = \tfrac{1}{2}d\ln p_{O_2} \qquad (7)$$

which leads to the following dependencies:

$$\left(\frac{dk_{\mathrm{p}}'}{d\ln p_{O_2}''}\right)_{pO_2'} = \frac{Z_{\mathrm{Me}}}{4} D_{\mathrm{Me}} \qquad (8)$$

and

$$\left(\frac{dk_{\mathrm{p}}'}{d\ln p_{O_2}''}\right)_{pO_2'} = \tfrac{1}{2} D_0 . \qquad (9)$$

It follows from these equations that a self-diffusion coefficient of a metal or oxygen in an oxide, which forms a scale on the metal at a given temperature, can be determined as being dependent on the oxygen pressure by measurement of the parabolic rate constant of metal oxidation, performed at different oxygen pressures (different values of p_{O_2}''). By plotting k_{p}' versus $\ln p_{O_2}''$ the value of the ratio $dk_{\mathrm{p}}'/d\ln p_{O_2}''$ directly for any value of oxygen pressure in the studied range and thus the respective values of D_{Me} or D_0. It should be noted that the values of the diffusion coefficients obtained in this way correspond to equilibrium of the studied oxide with oxygen at the experimental pressure.

To ensure success in these studies, it is important that over the whole period during which the kinetic curve is registered, the scale formed is compact, composed of one layer and adheres closely to the metallic core. Only then does the metal-oxide-oxygen system fulfil all assumptions of the Wagner theory which underly Equations 8 and 9. Mrowec and co-workers [26-29] have shown that by appropriate selection of shape and size of the metal samples which are oxidized, this is possible. In particular, it has been demonstrated that the most favourable conditions for plastic flow of the scale, and hence for preservation of its full contact with the surface of the metallic core, exist when samples which have the form of flat discs are oxidized [12, 28-30]. The ratio of the disc thickness to radius should be small and selected for each case of a given system and reaction conditions.

Experimental determination of the parabolic rate constant, k_{p}', by direct measurement is inconvenient and produces inaccurate results. In order to calculate k_{p}', it is necessary to determine the thickness of the scale after various periods of metal oxidation. This requires the performance of many experiments in which different metal samples are oxidized for different periods of time. To avoid such time-consuming procedures the parabolic Tammann's constant, k_{p}', is calculated from the results of experiments in which the gains in weight of the oxidized sample are registered continuously during the reaction. In such experiments the course of the parabolic reaction is described by the familiar Pilling-Bedworth equation [31]:

$$\left(\frac{\Delta m}{q}\right)^2 = k_{\mathrm{p}}''t + C \qquad (10)$$

where Δm is the gain in weight after time, t, q is the surface area of the metal, k_{p}'' is a Pilling-Bedworth parabolic rate constant of oxidation and C is a constant.

At the present state of microgravimetry, which allows the determination of the increases in weight with an accuracy of the order of 10^{-6} to 10^{-7} g, the parabolic rate constant, k_{p}'', can be determined with very high accuracy. It should be noted, however, that in calculations of the unit weight gain ($\Delta m/q$) one should take into account the changes in the surface area of the metallic core which occur as the oxidation process proceeds. If these changes are ignored, application to Equation 10 of an unchanged surface area of the metallic core, equal to the initial surface area ($q = q_0 = $ constant) gives rise, on the one hand, to apparent deviations from the parabolic reaction course and, on the other, to values of k_{p}'' lower than normal [12, 28-30]. Mrowec and Stokłosa [29, 30] have shown that the above error may be eliminated by introducing into Equation 10 a correction factor, which consists in replacing of the unchanged metal surface area by a hypothetical surface, q^x. The latter can be calculated for a given increase in mass by the method described by these authors [29, 30].

Knowing k_{p}'', the Tammann's constant may be calculated with the aid of the equation given by Wagner [32]:

$$k_{\mathrm{p}}' = \tfrac{1}{2}\left(\frac{\tilde{V}z_2}{A_O}\right)^2 k_{\mathrm{p}}'' \qquad (11)$$

where $\tilde{V}$ is an equivalent volume of an oxide, z_2 is a valency of oxygen ($\equiv 2$); A_O atomic weight of oxygen.

The Fueki-Wagner method under discussion has been verified taking the $Co-Co_{1-y}O-O_2$

system as an example [13, 33-35]. This system has been chosen because cobaltous oxide is, as yet, the only material in which the structure, concentration and mobility of point defects have been studied in detail [36-43]. This oxide exhibits relatively large deviations from stoichiometry, originating from the existence of vacancies in the cation sublattice $(Co_{1-y}O)$, owing to which the defect concentration, its temperature and oxygen pressure dependence have been determined with relatively high accuracy by thermogravimetric techniques [37, 38, 42]. With equally high precision the self-diffusion coefficients of cobalt in this oxide have been determined, by radioisotopic methods, as being dependent on temperature and the equilibrium oxygen pressure [36-40]. This has been possible owing to the facts that on the one hand, mobility of cationic vacancies [41, 43] and their concentration are relatively high, which gives correspondingly high values of the self-diffusion coefficients of cobalt in this oxide, and on the other, the radioisotope of cobalt, ^{60}Co, shows a very long half-life time which facilitates accuracy of the results.

The kinetics of cobalt oxidation have been studied in the temperature range 950 to 1300°C and oxygen pressure range 10^{-5} to 1 atm with thermogravimetric [13, 33] and volumetric [34, 35] methods. Flat discs of spectrally pure cobalt were used in these studies, selecting the dimensions of the samples in such a way as to ensure full contact of the scale with the metallic core during the whole period of determination of the kinetic curve. In agreement with the results reported by the other authors [44-47] it has been found that oxidation of cobalt follows the parabolic rate law and growth of compact, mono-phasic scale, composed of $Co_{1-y}O$, proceeds by outward diffusion of the metal (a platinum marker at the metal/scale phase boundary).

Parabolic rate constants of oxidation were calculated taking into account the changes in the metallic core surface with the Mrowec-Stokłosa method [29]. The parabolic plots of cobalt oxidation at 1000°C for several oxygen pressures are presented in Fig. 2. The dependence of the parabolic rate constant on log oxygen pressure at this temperature is given in Fig. 3.

By graphical differentiation of this type of curve, plotted for several temperatures, the coefficients of D_{Co} as a function of temperature and oxygen pressure were calculated from
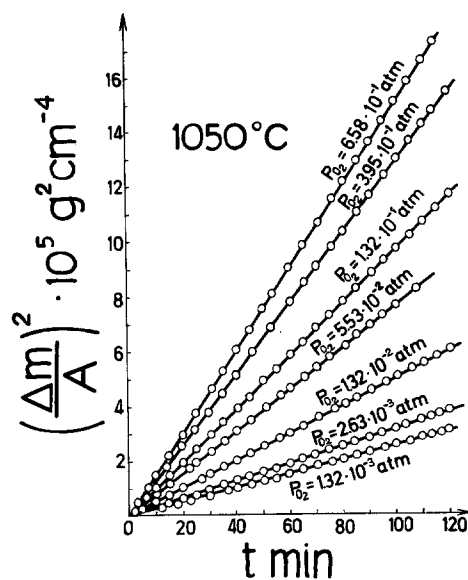

Figure 2 Parabolic plots of cobalt oxidation at 1050°C for several oxygen pressures.
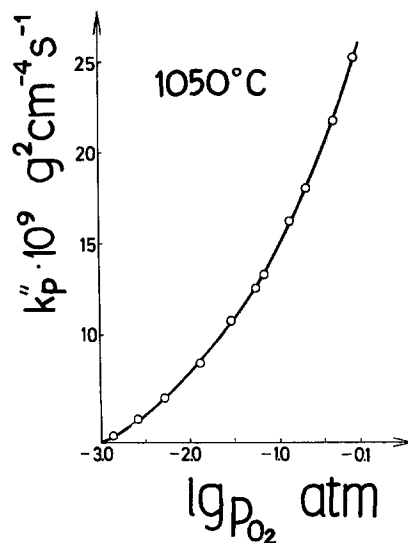

Figure 3 The oxygen pressure dependence of the parabolic rate constant of cobalt oxidation at 1050°C (semilogarithmic plot).

Equation 8. Selected results of these calculations are given in Fig. 4 in the Arrhenius system of co-ordinates for several values of oxygen pressure. For comparison, the same figure shows the results of radioisotopic studies of Chen et al. [40] and Carter and Richardson [36], taking into account the correlation effect. The tracer diffusion coefficients, $D_{Co}{}^t$, determined by these
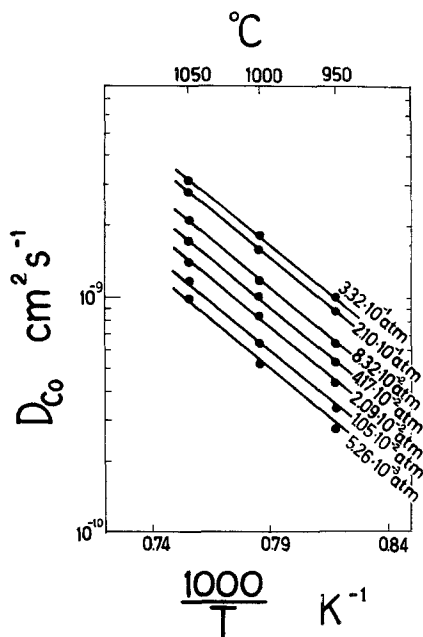
Figure 4 The temperature dependence of the self-diffusion coefficient of cobalt in cobaltous oxide for several oxygen pressures.

authors with the use of the radioisotope ^{60}Co, were transformed into self-diffusion coefficients, D_{Co}, using the equation:

$$D_{Co} = D_{Co}^t \frac{1}{f} \qquad (12)$$

assuming the correlation factor $f = 0.78$ [48].

As seen from the data presented in Fig. 4, agreement between the values of self-diffusion coefficients of cobalt in cobaltous oxide determined indirectly by the Fueki-Wagner method and the values obtained in radioisotopic studies is very good.

To give a clearer illustration of this the results of kinetic and radioisotopic studies are shown below in the form of the empirical relations between the coefficient D_{Co} and temperature for an oxygen pressure of 0.2 atm.

$$\frac{D_{Co}^t}{f} = D_{Co} = 5.0 \times 10^{-3}$$

$$\exp\left(-\frac{38\,400}{RT}\right) cm^2 sec^{-1} \qquad (13)$$

(Chen *et al.*)

$$\frac{D_{Co}^t}{f} = D_{Co} = 5.2 \times 10^{-3}$$

$$\exp\left(-\frac{38\,000}{RT}\right) cm^2 sec^{-1} \qquad (14)$$

(Carter and Richardson)

$$D_{Co} = 5.0 \times 10^{-3}$$

$$\exp\left(-\frac{37\,800}{RT}\right) cm^2 sec^{-1} \qquad (15)$$

(Mrowec *et al.*)

Equations 13 and 14 present results of radioisotopic studies, the correlation effect being taken into account, and Equation 15 the data obtained by Fueki-Wagner method. The agreement presented above indicates that the kinetic method can be successfully applied to the determination of self-diffusion coefficients in metal oxides. It should be noted at the same time that the kinetic method is considerably simpler than radioisotopic methods and the results obtained by it are more accurate.
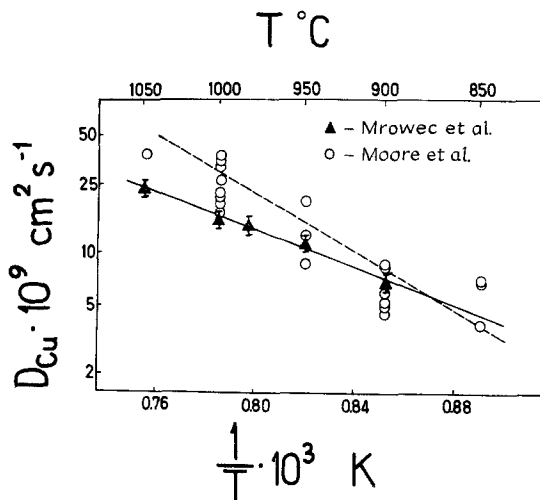

Figure 5 The temperature dependence of the self-diffusion coefficient of copper in cuprous oxide at an oxygen pressure of 1.3×10^{-4} atm.

In order to illustrate the precision of the kinetic method Fig. 5 show results of studies on self-diffusion of copper in cuprous oxide, $Cu_{2-y}O$, obtained with kinetic [12] and radioisotopic [49] methods. It follows from this plot that the error made in measurements with the latter method exceeds 50%. This is due among other factors, to the fact that the radioisotope ^{64}Cu has a very short half-life ($T_{1/2} = 12$ h). The results obtained with the kinetic method, on the other hand, show a reproducibility equally high as that reported for cobaltous oxide (where the maximum error does not exceed 5%).

Finally, it is worth mentioning that calculations of self-diffusion coefficients in metal oxides from kinetic measurements can be

TABLE I Self-diffusion coefficients of cobalt and copper in cobaltous and cuprous oxides calculated from kinetic data with the aid of Equations 8 and 16. Temperature for $Co_{1-y}O$ 1050°C; and for $Cu_{2-y}O$ 1000°C

Pressure $p_O/$ (arm)	$D_{Co} \times 10^9$ (cm^2 sec^{-1})		Pressure $p_O/$ (atm)	$D_{Cu} \times 10^8$ (cm^2 sec^{-1})	
	Values calculated with aid of			Values calculated with aid of:	
	Equation 8	Equation 16		Equation 8	Equation 16
2.63×10^{-3}	0.75	0.70	$6.6 \times 1L^{-3}$	4.6	4.2
$5.26 \times 1g^{-3}$	0.99	0.85	1.32×10^{-2}	5.4	5.2
1.05×10^{-2}	1.19	1.05	$2.63 \times 1L^{-2}$	6.1	6.3
2.09×10^2	1.40	1.27	$3.95 \times 1L^{-2}$	7.3	6.9
$4.17 \times 1L^{-2}$	1.72	1.53	$5.38 \times 1L^{-2}$	7.6	7.5
$8.32 \times 1L^{-2}$	2.14	1.86	$7.95 \times 1L^{-2}$	8.0	8.5
$2.10 \times 1L^{-1}$	2.80	2.42	$1.00 \times 1L^{-1}$	8.3	8.7
$3.32 \times 1L^{-1}$	3.04	2.71			

considerably simplified by assuming that the gradient of the defect concentration in the growing layer of the oxide scale on metal has a linear character. In this case, the Wagner equations (Equations 3 and 4) can be integrated to yield a simple relation between the parabolic rate constant of oxidation and self-diffusion coefficient of the more mobile component of the crystal lattice of the oxide [15, 18]:

$$k_p' = (1 + p)D \qquad (16)$$

where p is an effective charge of the defect with respect to the lattice, D is the self-diffusion coefficient of the metal, in the case of scales of $Me_{1-y}O$ and $Me_{1+y}O$ type, or the self-diffusion coefficient of oxygen in the case of scales with a defective anionic sublattice (MeO_{1-y} or MeO_{1+y}). Equation 16 is a modified form of the Mott-Gurney equation [50].

Engell [21], Pettit [22] and Mrowec [23-25] have shown that the gradient of defect concentration in the growing oxide layer on iron, cobalt, nickel and copper is linear as was anticipated. This gives grounds for the presumption that the linearity is a general rule and hence that a simplified form of Equation 16 can be used without limitations.

Table I shows selected values of self-diffusion coefficients of cobalt and copper in oxides of these metals calculated by the Fueki-Wagner method (Equation 8) and with the simplified Equation 16. It follows from this that both methods of calculation lead to practically the same results, which confirms the possibility of application of Equation 16.

It is worth mentioning that to calculate the diffusion coefficient from Equation 16 only the degree of defect ionization, p, is needed, per-

formance of the oxidation measurements at different oxygen pressures being unnecessary. Moreover, such calculations can be performed both for the scales of the p-type ($Me_{1-y}O$ or MeO_{1+y}) and n-type ($Me_{1+y}O$ or MeO_{1-y}), whereas the Fueki-Wagner method can be applied only to oxides of the p-type. On the other hand, one should remember that Equation 16 was obtained by assuming the linear distribution of defect concentration in the scale and can be applied only when this assumption is valid.

3. Two stage oxidation method

The methods of calculating self-diffusion coefficients of metal or oxygen in semiconducting oxides described above are based on the relationship which exists between the parabolic rate constant of growth of a compact oxide layer and the diffusion coefficient of this reagent which takes part in the process of matter transport through the scale. From the theory of diffusion in solids it follows that the self-diffusion coefficient is a product of two parameters: the defect diffusion coefficient, D_d, and their concentration expressed in molar fractions N_d [5, 6]:

$$D = D_d N_d . \qquad (17)$$

This relation pertains to the thermodynamic equilibrium between the crystal and its surroundings, i.e. to the gradientless conditions. In the growing scale, however, there exists a gradient of defect concentration, and since ionic and electronic defects possess opposite electric charges, their diffusion has an ambipolar character. Considerably more mobile electronic defects accelerate the diffusion of ionic defects and hence the diffusion coefficient of the latter is

larger. In these conditions the chemical diffusion coefficient is used, which is related to the defect diffusion coefficient by the following equation:

$$\tilde{D} = (1 + p)D_d . \qquad (18)$$

Comparing Equations 17 and 18 with Equation 16 the following relationship between the parabolic rate constant and chemical diffusion coefficient and concentration of defects in the scale is obtained:

$$k_p' = \tilde{D}N_d . \qquad (19)$$

It follows from the above equation that the parabolic rate constant, k_p' is a direct measure of a product of two important parameters which cannot be determined independently on the basis of conventional kinetic measurements. Rosenberg [51] has shown, however, that by carrying out the measurements of kinetic of metal oxidation in two stages – with an interval between them to allow the Me–MeO–O$_2$ system to reach the state of equilibrium – the chemical diffusion coefficient and the equilibrium defect concentration can be determined simultaneously. Application of this method is possible when the process of metal oxidation follows the parabolic rate law and when the scale formed on a metal is monophasic, compact and adheres closely to the metallic core. Growth of the scale occurs by diffusion of only one reagent – a metal or oxygen – when the type of defect structure must be known in order to anticipate which reagents take part in transport of matter through the scale. Finally, distribution of the defect concentration in the growing layer of the scale should have a linear character.

As seen from the above considerations the Rosenberg method requires the same conditions as the Fueki-Wagner method with the additional condition that the gradient of the defect concentration in the growing oxide layer is linear. As already mentioned there exist grounds for the assumption that the distribution of defect concentration in compact monophasic scale follows the parabolic rate law.

The principle of the Rosenberg's method is as follows. A metal is oxidized in isothermal and isobaric conditions in a system enabling continuous kinetic measurements to be made. After a compact oxide layer of thickness x_0 has been formed on the sample surface, the oxidation is terminated by removing oxygen from the reaction space. As a result the metal-scale-oxygen system passes spontaneously to equilibrium, the

partial pressure of oxygen in the apparatus being led to the value equal to the dissociation pressure of the oxide. In these conditions, the concentration of defects in the layer of oxide formed reaches the same value over its entire cross-section, corresponding to thermodynamic equilibrium with the metallic phase. This is illustrated schematically in Fig. 6.
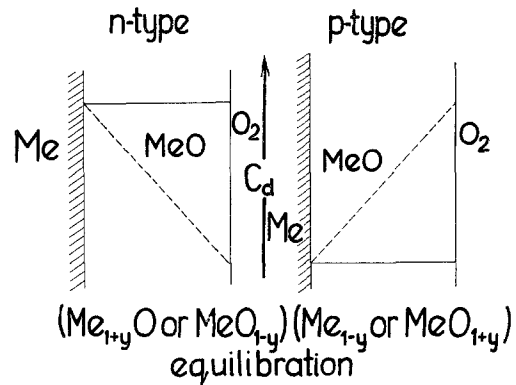

Figure 6 The distribution of defect concentration in oxide scales on metals after thermodynamic equilibrium in the Me–MeO–O$_2$ system was attained. Broken lines denote distribution of defect concentration in the scale before oxidation was interrupted.

After the process of homogenization has finished, oxygen is readmitted to the reaction space and measurement of further growth of the oxide layer is continued. Oxidation now takes place in an entirely different manner to that during the initial period of oxidation, i.e. before the break in the reaction. The scale layer has been saturated during the homogenization with the metal, which for p-type oxides corresponds to a minimal concentration of cationic vacancies or interstitial anions, and for n-type oxides to a maximal concentration of interstitial cations or anion vacancies. When oxygen is readmitted to the reaction space, the concentration of metal in the surface layer of the scale decreases rapidly due to the increase of cationic vacancies or interstitial anions (p-type oxides), or to the decrease in concentration of interstitial cations or anionic vacancies (n-type oxides). As the reaction proceeds, the concentration of defects is gradually changed, due to the diffusion processes, in the deeper layers of the scale, and leads eventually to restoration of the linear gradient of defect concentration in the scale which existed before the break in oxidation.
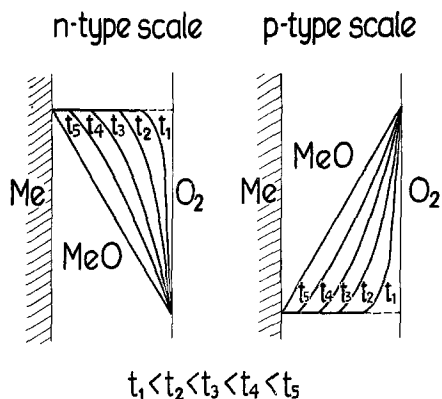
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n-type scale   p-type scale

$t_1 < t_2 < t_3 < t_4 < t_5$

Figure 7 Changes in the distribution of defect concentration in p- or n-type scale after readmittance of oxygen to the reaction space. Horizontal lines denote the distribution of defect concentration in the scale before the introduction of oxygen (equilibrium in the Me–MeO–O$_2$ system).

Figure 8 Paralinear course of oxidation after readmittance of oxygen to the reaction space.

Fig. 7 shows, schematically, successive stages of changes in the distribution of defects in the scale after readmitting oxygen to the reaction space.

Considering the process of the growth of the scale after the break in oxidation from the point of view of the diffusion theory, we can distinguish two limiting stages. In the first, the diffusion processes take place only in the external part of the scale layer whereas the internal part, close to the metallic phase, is in a state of thermodynamic equilibrium. Therefore, we consider this case to be diffusion in a sem-infinite system. It should be noted that at this stage of the reaction, only oxide is oxidized without involving a metallic base in the process of oxidation.

After restoration of the linear gradient of defect concentration in the scale, the oxidation process passes into the second stage. Diffusion in the scale takes place under steady state conditions if we neglect the fact that increment of the layer thickness, Δx, in this period is much smaller in comparison to the initial thickness $x_0 (\Delta x \ll x_0)$.

It follows from the above considerations that oxidation after readmitting oxygen to the reaction space has a paralinear character, as shown schematically in Fig. 8. In the initial period the scale behaves as a semi-infinite diffusion system, which binds oxygen at a rate determined by changes in defect concentration in this layer (parabolic course). In the later period of the reaction, on the other hand, the gradient of defect concentration in the scale reaches a
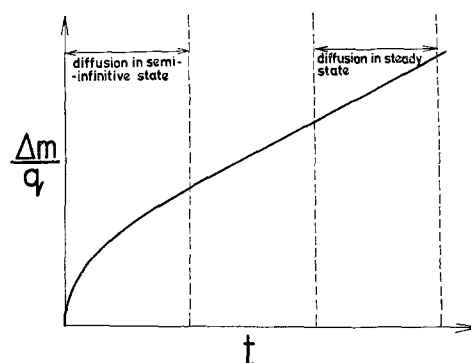
practically constant value, because the increment of the scale thickness at this stage of the process is negligibly small in comparison to the initial thickness x_0 (linear course).

The second Fick's law for the case under consideration was solved by Rosenberg. The complex equation obtained has two simple limiting solutions. The parabolic fragment of the kinetic curve, shown in Fig. 7, is described by the equation:

$$\left(\frac{\Delta m}{q}\right) = (1.128 \, C_d \tilde{D}) t^{1/2} \qquad (20)$$

The linear course of the reaction, observed in its further stages, is given by the equation:

$$\left(\frac{\Delta m}{q}\right) = \left(\frac{\tilde{D} C_d}{x_0}\right) t + \frac{x_0 C_d}{3} \qquad (21)$$

where $(\Delta m/q)$ is the mass of oxygen bound by a unit surface area, i.e. the unit weight gain of the sample under oxidation, C_d is the concentration of defects in the scale at the phase boundary at which they are formed: for p-type oxides this is the concentration of cation vacancies or interstitial anions in a crystal of the $Me_{1-y}O$ or MeO_{1+y} type which is in equilibrium with oxygen at the pressure at which the second stage of oxidation was carried out. In the case of an n-type oxide, on the other hand, this is a concentration of interstitial cations or anion vacancies in a crystal $Me_{1+y}O$ or MeO_{1-y} in equilibrium with the metallic phase, i.e. at an oxygen pressure equal to the dissociation pressure of a given oxide. (The concentration C_d is expressed in g or g atoms cm^{-3} depending on the units in which the weight gain, Δm, is given.)

Equation 20 describes correctly the parabolic

course of the reaction when the following condition

$$t \ll \frac{x_0^2}{\tilde{D}} \qquad (22)$$

whereas Equation 21 can be applied to the linear fragment of the kinetic curve when:

$$t > \frac{x_0^2}{2\tilde{D}} . \qquad (23)$$

The above given equations can be written in another form, which is more suitable for graphical interpretation:

$$\left(\frac{\Delta m}{q}\right) = k_p \, t^{1/2} + C_p \qquad (24)$$

and

$$\left(\frac{\Delta m}{q}\right) = k_1 t + (C_1 - C_p) \qquad (25)$$

where $k_p = 1.128 \, C_d \tilde{D}$, is a parabolic rate constant of the reaction in its initial period (semi-infinite system), $k_1 = \tilde{D} C_d / x_0$, is a linear rate constant of oxidation in the second stage (steady state conditions). Constant C_p is a measure of perturbations of the parabolic reaction course which may occur in the first moments after readmittance of oxygen to the reaction space.

Values of C_p different from zero may result, among the other factors, from a non-fixed oxygen pressure in the vicinity of the scale surface. Depending on the character of these perturbations, constant C_p may assume a positive or negative value: this is taken into account in the calculations. Constant C_i – after taking into account correction C_p – determines, the value of the expression $x_0 C_d / 3$.

The values of constants k_p and C_p can be determined from the initial section of the paralinear kinetic curve by plotting the kinetic data in the form $(\Delta m / q)$ versus $\sqrt{t}$. This plot should yield a straight line, the slope of which gives the value of k_p and the value of the ordinate axis at $t = 0$ determines the value of C_p as shown in Fig. 9. This plot enables the simultaneous determination of the time interval in which the process follows a parabolic rate law, i.e. the scale resembles a semi-infinite diffusion system. In the next stage, the curve gradually passes into its linear course which leads to positive deviations of the experimental points from the straight line (Fig. 9).
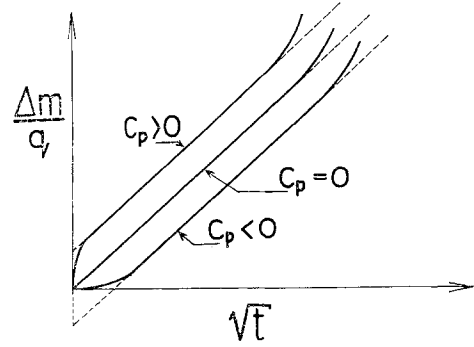

Figure 9 Parabolic plot of oxidation during the first stage of the reaction.

Constants k_1 and C_1 are determined from the linear section of the kinetic curve plotted in the form $(\Delta m / q)$ versus t (Fig. 10).
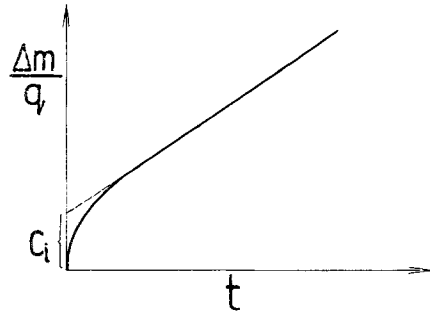

Figure 10 Paralinear course of oxidation over the whole stage of oxidation after readmittance of oxygen to the reaction space.

As k_p, k_1 and C_p and C_1 can all be determined from one kinetic curve, it may be possible to calculate, for given experimental conditions, the chemical diffusion coefficient and equilibrium concentration of defects in the oxide forming a scale, simultaneously. The lattice parameters are related to the empirical constants by the following equations:

$$\tilde{D} = \left(\frac{1.128 \, k_1 x_0}{k_p}\right)^2 \qquad (26)$$

$$C_d = \frac{(k_p/1.128)^2}{k_1 x_0} \qquad (27)$$

and

$$C_d = \frac{3(C_1 - C_p)}{x_0} . \qquad (28)$$

It can be seen from the above equations that if the parabolic and linear constants of the paralinear course of the reaction of further oxidation are known, this is sufficient information for determination of the values of both $\tilde{D}$ and C_d. The value of C_d can also be calculated from the values of C_l and C_p (Equation 28).

The correct values of $\tilde{D}$ and C_d from the kinetic method can be obtained if the following conditions are fulfilled:

1. The oxide layer is compact in its entire cross-section and adheres well to the metallic core in all the stages of the experiment.

2. Growth of scale follows a parabolic rate law.

3. The surface of the scale is smooth microscopically (the roughness coefficient $R \cong 1$).

4. The period of homogenization of the pre-oxidized sample of a metal exceeds the value of $x_0^2/\tilde{D}$. The measurement of k_p is performed over a time considerably shorter than $x_0^2/\tilde{D}$ and the measurement of k_l over a time longer than $x_0^2/2\tilde{D}$.

It follows from this that for rational planning of the experiments it is necessary to know the order of magnitude of $\tilde{D}$. If estimation of this value cannot be made, the appropriate thickness of the initial oxide layer, x_0, should be determined in preliminary measurements. This thickness should be selected in such a way that the period of the parabolic course of the reaction is sufficiently long to enable k_p to be determined with a high accuracy. On the other hand, this period cannot be too long because the increment in the scale thickness during the whole period of determination of the kinetic curve should be considerably smaller than x_0.

It can be shown that at the present stage in the development of the technique of kinetic measurements, the defect concentration in the scale can be determined even at such low defect concentration as 10^{15} cm^{-3}. This corresponds to concentrations of the order of 10^{-4} at % which is two orders of magnitude lower than the lowest concentrations measurable by the other methods.

Another advantage of the method under consideration results from the possibility of repeating the measurements of $\tilde{D}$ and C_d on the same sample, without removing it from the reaction space. After the first measurement of constants k_p, k_l, C_p and C_l at a given thickness of the oxide layer, x_0, oxygen can again be removed from the apparatus and after the homogenizing, the new cycle of the measure-

ments can be repeated, taking into account the small increase in the oxide layer. This cycle can be repeated several times not only for estimating the reproducibility of the measurements but also for determination of the dependence of D and C_d on temperature and oxygen pressure.

The method described above has been used for several systems [51-53, 8]. Comparison of these results with those obtained by the classical methods has been made recently by Fryt et al. [7, 9] for the Co–Co$_{1-y}$O–O$_2$ system. This system was selected for the same reasons as in the case of verification of the Fueki-Wagner method: not only has the self-diffusion coefficient of cobalt in this oxide been determined as a function of temperature and oxygen pressure [36, 40] but also the chemical diffusion coefficient [41, 43] and equilibrium concentration of defects [37-39, 42] in this oxide are known.

The studies were performed in a simple thermogravimetric apparatus [7] enabling continuous measurement of increase in weight of the oxidized sample with an accuracy of the order of 10^{-4} g. The required partial pressure of oxygen in the reaction space was provided by the appropriate composition of the argon-oxygen mixture, which under the pressure of 1 atm, passed through the apparatus with a flow rate of 20 l/h^{-1}. The experiments were performed in the temperature range 1000 to 1200°C and the oxygen pressure ranged from 3×10^{-3} to 1 atm.

The thickness of the initial layer of the oxide, x_0, was estimated, based on values of $\tilde{D}$ determined by Price and Wagner [41]. Depending on the reaction conditions, this thickness lay between 0.055 and 0.083 cm. The initial layer of oxide of required thickness x_0 was obtained by oxidation of the metal sample at a temperature of 1100 or 1200°C in a normal atmosphere. The temperature was then fixed at that of the following experiment and purified argon was passed through the reaction chamber. The partial pressure of oxygen in argon was about 10^{-6} atm, which was higher than the dissociation pressure of cobaltous oxide in this temperature range. However, under these conditions the oxidation process was hindered, as shown by the constant weight of the sample during treatment with argon. This is understandable as the oxidation process is practically stopped at that oxygen pressure which is close to the dissociation pressure of a given oxide. Thus, although from the thermodynamic point of view the Co–CoO–O$_2$ system

could not reach a state of equilibrium, for kinetic reasons, the defect concentration in cobaltous oxide was established at the value corresponding to equilibrium with metallic phase.

After homogenization, the stream of the argon-oxygen mixture was introduced into the reaction chamber and the kinetics of the scale growth were registered. After completing one cycle the system was again equilibrated and the measurement cycle was repeated at another oxygen pressure. The same procedure was applied to the whole temperature range studied and the measurements were repeated for several samples.
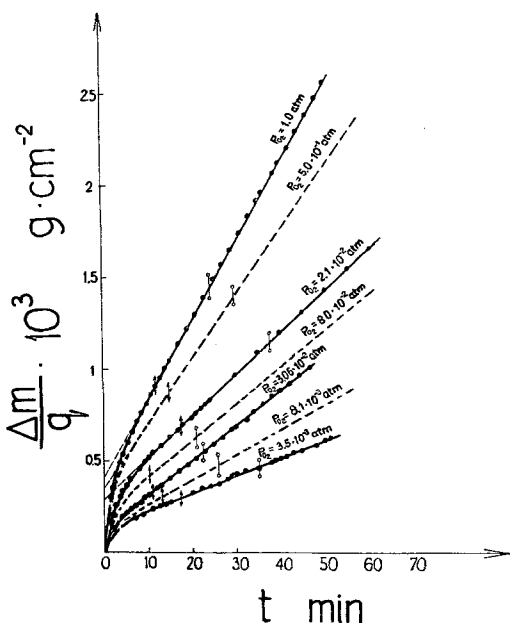
Figure 11 Paralinear course of oxidation of cobalt at 1200°C for several oxygen pressures after readmittance of oxygen gas to the reaction space.

Fig. 11 presents a set of curves obtained at 1200°C for several values of oxygen pressure. Similar results were obtained at other temperatures. As seen from the plot, the kinetic curves obtained have a paralinear character. The slope of linear sections of these curves may be used to calculate the constant k_1, and values of ordinates obtained at points of intersection of these straight lines with the ordinate axis gave values of C_1.

To determine the values of k_p and C_p the results of the measurements in the initial stage of oxidation were plotted in the parabolic system of ordinates [$(\Delta m/q)$ versus $\sqrt{t}$]. As seen from the plot in Fig. 12 the course of oxidation in this
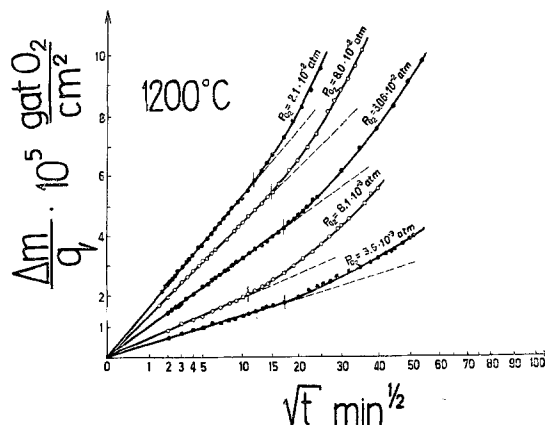

Figure 12 Parabolic plot of first stage oxidation of cobalt at 1200° C for several oxygen pressures, after readmittance of oxygen to the reaction space.

system of co-ordinates is linear and hence the values of k_p can be calculated from the slopes of these lines. In the case under study, $C_p = 0$. Using these values of k_p, k_1, C_p and C_1, concentrations of cation vacancies and chemical diffusion coefficients in cobaltous oxide were calculated using Equations 26 to 28 as a function of temperature and equilibrium oxygen pressure. Some results of these calculations are shown in Figs. 13 to 16. It follows from these plots that the defect concentration is a function of temperature and equilibrium pressure of oxygen as follows:

$$N_{V_{Co}} = 1.26 p_{O_2}^{1/3.85} \exp \left(\frac{12\,500}{RT} \right) \quad (29)$$

where $N_{V_{Co}}$ is the concentration of cationic vacancies in cobaltous oxide (in molar fractions).

The chemical diffusion coefficient, on the other hand, is independent of the oxygen pressure and is a function of temperature as follows:

$$\tilde{D}_{CoO} = 6.6 \times 10^{-3}$$
$$\exp \left(-\frac{24\,400}{RT} \right) cm^2 \, sec^{-1}. \quad (30)$$

Fisher and Tannhauser [42], Eror and Wagner [38] and Koel and Gellings [43] have determined the equilibrium concentration of cation vacancies in cobaltous oxide as being dependent on temperature and oxygen pressure from thermogravimetric measurements of deviations from stoichiometry in this oxide. In addition, Price and Wagner [41] and Koel and Gelling [43] have determined the chemical diffusion coefficient in cobaltous oxide and its temperature
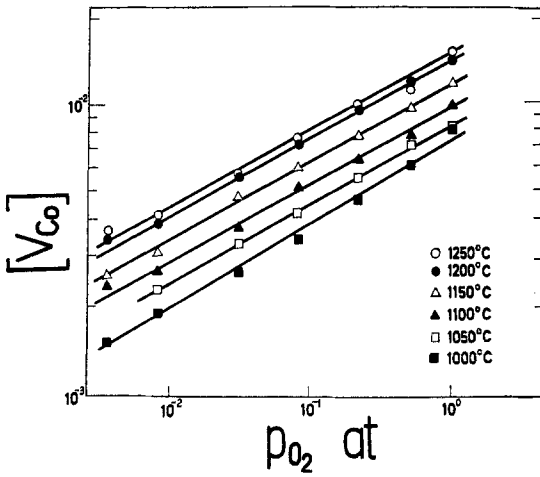
Figure 13 The dependence of equilibrium concentration of cation vacancies in cobaltous oxide on oxygen pressure for several temperatures.
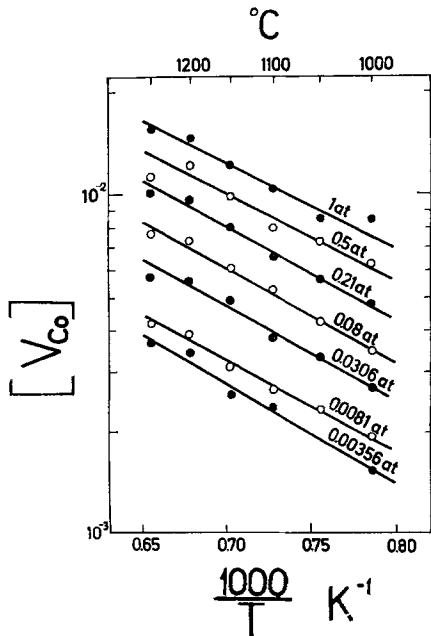

Figure 14 The Arrhenius plot of the temperature dependence of the equilibrium concentration of defects in cobaltous oxide for several oxygen pressures.

dependence using a thermogravimetric method and by electrical conductivity measurements. The results of these studies can be summarized in the form of the following empirical equations:

$$N_{V_{Co}} = 0.94 \times 10^{-1} p_{O_2}^{1/3.86}$$
$$\exp\left(-\frac{7200}{RT}\right) \qquad (31)$$

(Tannhauser and Fisher)

$$N_{V_{Co}} = 0.95 \times 10^{-1} p_{O_2}^{1/3.8}$$
$$\exp\left(-\frac{6500}{RT}\right) \qquad (32)$$

(Eror and Wagner)

$$N_{V_{Co}} = 1.45 \times 10^{-1} p_{O_2}^{1/4.0}$$
$$\exp\left(-\frac{7800}{RT}\right) \qquad (33)$$

(Koel and Gellings)

$$\tilde{D}_{CoO} = 4.33 \times 10^{-3}$$
$$\exp\left(-\frac{24\,000}{RT}\right) \text{ cm}^2 \text{ sec}^{-1} \qquad (34)$$

(Price and Wagner)

$$\tilde{D}_{CoO} = 8.3 \times 10^{-3}$$
$$\exp\left(-\frac{24\,000}{RT}\right) \text{ cm}^2 \text{ sec}^{-1} \qquad (35)$$

(Koel and Gellings)

Comparison of Equation 30 with Equations 34 and 35 shows a good agreement between the results of studies on the chemical diffusion obtained with kinetic and classical methods. The results of studies on the defect concentration show that the agreement is only observed for the dependence of this concentration on the oxygen pressure (practically the same exponents at the oxygen pressure in Equations 29 and 31 to 33). The heat of defect formation determined by the kinetic method (Equation 29) is, however, considerably higher than that determined by the classical method. This is probably due to the fact that the kinetic method gives the total concentration of defects, whereas with the other methods only the concentration of the predominant defects, related to the deviation from stoichiometry, is determined. This problem was the subject of a previous paper [54].

It has been mentioned previously that the self-diffusion coefficient of a metal or oxygen in oxides is related to the chemical diffusion coefficient and equilibrium defect concentration by a simple equation (Equation 1). For the case

under discussion, this equation can be written in the following form:

$$D_{Co} = \frac{\tilde{D}_{CoO}\, N_{Co}}{1 + p}. \qquad (36)$$
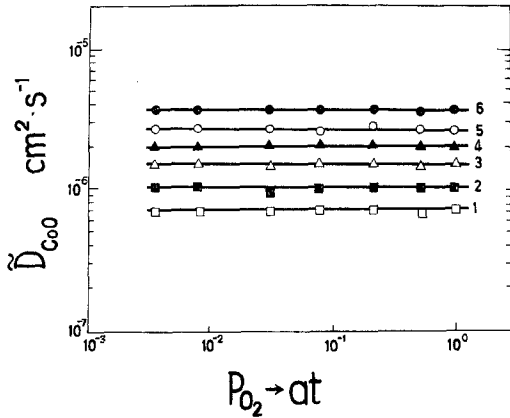

Figure 15 The dependence of the chemical diffusion coefficient in cobaltous oxide on oxygen pressure for several temperatures.
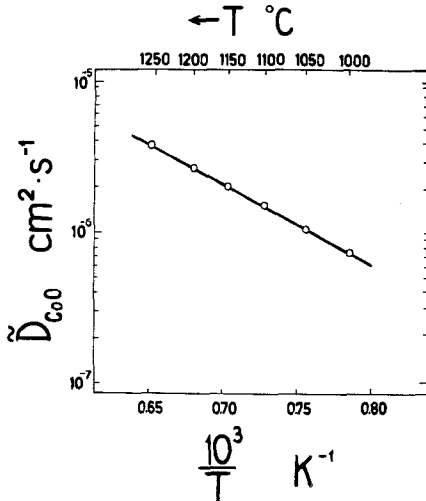

Figure 16 The Arrhenius plot of the temperature dependence of the chemical diffusion coefficient in cobaltous oxide.

In the range of temperatures and oxygen pressures studied cation vacancies in cobaltous oxide are singly ionized (the exponent at the oxygen pressure in Equations 29 and 31 to 33 being close to $\frac{1}{4}$). Hence $p = 1$ and Equation 36 assumes the form:

$$D_{Co} = \frac{1}{2}\tilde{D}_{CoO} N_{Co}. \qquad (37)$$

Replacing $\tilde{D}_{CoO}$ and N_{Co} in Equation 37 by

Equations 29 and 30 one obtains the following equation for the dependence of the self-diffusion coefficient of cobalt in cobaltous oxide on the oxygen pressure and temperature:

$$D_{Co} = 8.3 \times 10^{-3} p_{O_2}{}^{1/3.85}$$
$$\exp\left(-\frac{37\,800}{RT}\right) \text{cm}^2\,\text{sec}^{-1} \qquad (38)$$

As already mentioned, the self-diffusion coefficient of cobalt in $Co_{1-y}O$ has been determined with high accuracy over a wide range of temperatures and oxygen pressures by Carter and Richardson [36] and recently by Chen *et al.* [40] by radioisotope methods. Since Chen *et al.* carried out their measurements at only one value of the oxygen pressure, equal to 0.21 atm, comparison of the results obtained with those of the radioisotope methods has been limited to this value of oxygen pressure only. Empirical Equation 38 assumes for this case the following form ($p_{O_2} = 0.21$ atm):

$$D_{Co} = 5.2 \times 10^{-3}$$
$$\exp\left(-\frac{37\,800}{RT}\right) \text{cm}^2\,\text{sec}^{-1} \qquad (39)$$

(Mrowec *et al.*, two stage kinetic method)

The results of Chen *et al.* [40] and Carter and Richardson [36] for the same value of oxygen pressure, can be written as:

$$D_{Co} = 5.0 \times 10^{-3}$$
$$\exp\left(-\frac{38\,400}{RT}\right) \text{cm}^2\,\text{sec}^{-1} \qquad (40)$$

(Chen *et al.*, radioisotopic method)

$$D_{Co} = 5.2 \times 10^{-3}$$
$$\exp\left(-\frac{38\,000}{RT}\right) \text{cm}^2\,\text{sec}^{-1} \qquad (41)$$

(Carter and Richardson, radioisotopic method)

Finally, it is worth comparing the data given above with Equation 15 which gives the temperature dependence of D_{Co} for the oxygen pressure of 0.21 atm, as determined by the Fueki-Wagner method:

$$D_{Co} = 5.0 \times 10^{-3}$$
$$\exp\left(=\frac{37\,800}{RT}\right) \text{cm}^2\,\text{sec}^{-1} \qquad (42)$$

(Mrowec *et al.* differential kinetic method)

Comparison of Equation 30 with Equations 34 and 35, and Equations 39 and 42 with Equa-
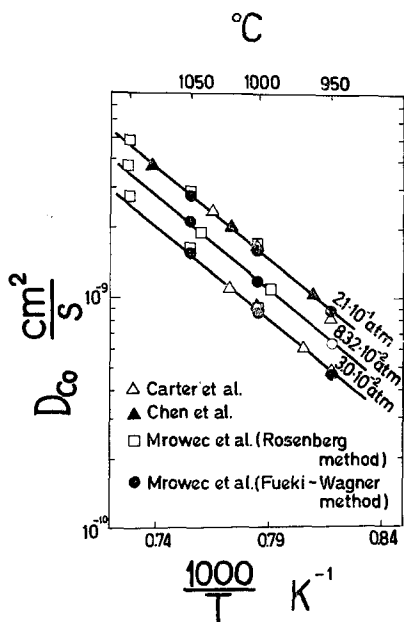
Figure 17 Temperature dependence of the self-diffusion coefficient of cobalt in cobaltous oxide for several oxygen pressures in Arrhenius system of co-ordinates.
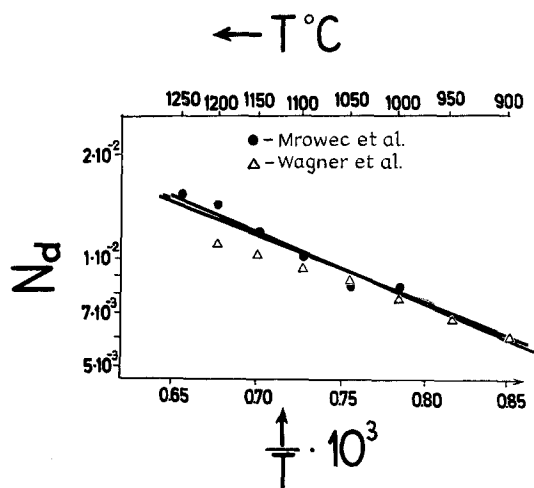

Figure 18 Temperature dependence of the equilibrium defect concentration in cobaltous oxide.

tions 40 and 41 shows an exceptionally good agreement between the data of chemical diffusion coefficients and self-diffusion coefficients obtained using kinetic and classical methods. This agreement pertains not only to the values of activation energies of the diffusion of cation vacancies and cobalt ions in cobaltous oxide, but also to the absolute values of $\tilde{D}_{CoO}$ and D_{Co} in the entire range of temperatures and oxygen

pressures studied. Practically identical values of pre-exponential factors in Equations 39 to 42.

Figs. 17 and 18 give the results obtained by different authors in studies on defect concentrations and self-diffusion coefficients for a wide range of temperatures and oxygen pressures. The plots shown in these figures confirm the agreement between the results obtained with kinetic and other methods.

4. Conclusions

The discussion presented above leads to the following conclusions on the possibility of applying kinetic methods to the study of the concentrations and mobility of point defects in metal oxides:

1. There exist two new methods for studying self-diffusion coefficients of a metal or oxygen in semiconducting oxides, based on measurements of the kinetics of metal oxidation. These methods can be used when an oxide layer, formed on the metal surface, is compact, closely adherent to the metallic core and its growth is governed by a parabolic rate law. In these cases the parabolic rate constant of oxidation can be used in calculations of the self-diffusion coefficient of this component of the oxide, the diffusion of which is responsible for the growth of the oxide layer.

2. When the studied oxide is a p-type semiconductor with the deficit of a metal ($Me_{1-y}O$), then the self-diffusion coefficient of a metal can be determined as being dependent on the oxygen pressure and temperature by both the Fueki-Wagner and Rosenberg methods. This also applies to studies of self-diffusion coefficients of oxygen in p-type oxides with an excess of oxygen (MeO_{1+y}). The coefficient D_{Me} or D_0 determined under these conditions corresponds to the equilibrium of the oxide with oxygen at the oxygen pressure at which the oxidation process was carried out.

3. In the case of oxides of n-type with an excess of metal ($Me_{1+y}O$) or deficit of oxygen (MeO_{1-y}) the Fueki-Wagner method cannot be used, because the rate of growth of this type of scale is practically independent of the oxygen pressure over wide limits. In this case, the self-diffusion coefficient of metal or oxygen may be determined by the Rosenberg method or calculated directly from the parabolic rate constant with the aid of the modified Mott-Gurney equation. In this latter case, it is necessary to know the degree of ionization of defects involved in diffusion of the metal or oxygen ions. The self-

diffusion coefficient determined in this way corresponds to equilibrium of the studied oxide with the metallic phase.

4. The Rosenberg method, consisting of a two-stage oxidation, enables the simultaneous determination of chemical and self-diffusion coefficients and defect concentration from one kinetic curve. The measurement can, moreover, be repeated on the same sample without removing it from the reaction space. It should also be noted that the defects (the concentration of which is determined by the Rosenberg method) comprise both extrinsic defects responsible for the deviation from stoichiometry and intrinsic ones (Frenkel and Schottky type defects).

5. Kinetic methods are considerably simpler than classical radioisotope methods and results of these measurements have a higher accuracy than the classical methods. Hence kinetic methods should be generally applied in studies of concentration and mobility of point defects in metal oxides, in particular in those compounds in which determination of these parameters by classical methods is very difficult or impossible.

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