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HAL Id: jpa-00225613
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Submitted on 1 Jan 1986

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A MODIFICATION OF DARKEN'S EQUATION FOR THE INTERDIFFUSION COEFFICIENT IN P-TYPE OXIDE SOLID SOLUTIONS

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Abstract - A modified form of Darken's equation for the interdiffusion coefficient is obtained for the case of solid solution oxides of the (A,B)O type by considering the effect of the difference between the diffusion coefficients of the two ions on the concentration of the lattice defects during equilibration.

I - INTRODUCTION

Interdiffusion experiments at constant temperature and oxygen activity between two oxides which are completely soluble can be used to obtain the interdiffusion coefficient of the system, which is a parameter describing the rate of mixing of the two components. The interdiffusion coefficient in binary metallic systems is related to other phenomenological parameters measured independently, i.e. the tracer-diffusion coefficients of the two components, through an equation originally derived by Darken /1/. Application of this equation to calculate the interdiffusion coefficient for binary-oxide solid solutions of the (A,B)O type has been shown to present some problems /2-4/. In fact diffusion in oxide systems is different from diffusion in metals due to requirement that electrical neutrality is maintained and due to the influence of a further parameter, the value of the oxygen activity. In fact, unless the tracer-diffusion coefficients of the two ions happen to be the same for equal values of the oxide composition and oxygen activity, the two ions will diffuse in opposite directions at different rates, producing a deviation of the concentration of vacancies from the corresponding equilibrium values in the two sides of the diffusion couple. This in turn produces local changes of the oxygen activity which affect the fluxes of the two ions, tending to avoid the production of large deviations from the equilibrium inside the sample. The formation of oxygen activity gradients connected with the different diffusivities of the cations in oxide solid solutions has been both proposed on theoretical grounds and confirmed experimentally /2-4/. The purpose of the present work is to take into account the development of oxygen...
activity gradients inside the diffusion couple in an interdiffusion experiment in an (A,B)O solid solution to obtain a modified form of Darken's equation.

To restrict the treatment, the oxides are assumed to have the same kind of electrical conductivity (p-type), to contain only metal vacancies as lattice defects and to form a complete series of solid solutions exhibiting ideal behavior: in addition, it is assumed that oxygen diffusivity is negligible with respect to that of the two metal components. All the previous conditions apply to the oxides considered here for numerical applications.

II - THEORY

The diffusion flux of the two types of ions A and B in an (A,B)O solid solution under the most general case involving the presence of gradients of oxygen activity and oxide composition has been given by C. Wagner /5/, in connection with the analysis of the parabolic growth of an (A,B)O oxide on a binary A-B alloy, in the form

\[ J_A = -c_M D_A \left( 1 - \xi \right) \left\{ \frac{\partial \ln a_{AO}}{\partial x} \right\} \]

and

\[ J_B = -c_M D_B \xi \left\{ \frac{\partial \ln a_{BO}}{\partial x} \right\} \]

where \( \xi \) is the mole fraction of BO in the mixed oxide, \( D_A \) and \( D_B \) are the diffusion coefficients of the two ions in the oxide solution, \( a_{AO} \) and \( a_{BO} \) and \( a_0 \) are the activities of AO, BO and oxygen in the oxide, respectively, and \( c_M \) is the overall metal concentration in (A,B)O expressed as moles per unit volume (cm\(^{-3}\)). The diffusion coefficients appearing in Eqs. (1) and (2) are considered to be the tracer-diffusion coefficients of the two ions, in agreement with the general expression of the inter-diffusion coefficient /6/, while the fluxes are given with respect to a local lattice plane. Assuming that the oxide solution is thermodynamically ideal (i.e. \( a_{AO} = (1 - \xi) \) and \( a_{BO} = \xi \)), Eqs. (1) and (2) reduce to

\[ J_A = c_M D_A \left\{ \frac{\partial \xi}{\partial x} + (1 - \xi) \frac{\partial \ln a_0}{\partial x} \right\} \]

and

\[ J_B = -c_M D_B \xi \left\{ \frac{\partial \xi}{\partial x} - \xi \frac{\partial \ln a_0}{\partial x} \right\} \]

It should be recalled that \( D_A \) and \( D_B \) in a mixed oxide will depend both on the oxygen activity and on the oxide composition /7/ mainly because they are proportional to the overall concentration of metal vacancies in p-type oxides.

During an interdiffusion experiment, two samples of solid solution with different composition (but each homogeneous per se) and with a constant common value of the oxygen activity are brought together under a constant oxygen activity in the gas phase in equilibrium with the \( a_0 \) in the oxides. Diffusion between the two regions takes place due to the difference in oxide composition. In principle, the two fluxes are given by

\[ J_A = c_M D_A (\partial \xi / \partial x) \quad \text{and} \quad J_B = -c_M D_B (\partial \xi / \partial x) \]

so that the two fluxes should differ if \( D_A \neq D_B \). However this condition leads to a situation of non equilibrium concerning the concentration of defects in the various regions of the sample. The extreme case for this is when the faster diffusing ion
(say A) corresponds to an oxide having a higher concentration of defects under a given temperature and oxygen activity. In fact, in this case, A will diffuse away from regions of concentrations of A higher than the average final value \( \xi \) more rapidly than the slower diffusing species B will diffuse in. As a result, the concentration of metal vacancies will rise in the A-rich regions, where it should instead decrease as a result of the increase of the concentration of B. The opposite situation will occur in regions containing a concentration of A lower than the average, where the concentration of vacancies will decrease as a result of the diffusion process. In this way, a deviation from the condition of equilibrium for the concentration of vacancies will be produced on both sides of the sample. In principle, vacancies could be destroyed in regions where they are supersaturated, and could be created where their concentration is below equilibrium, but these processes are not important in oxides /3,4/. The local change in the concentration of vacancies can be interpreted as a corresponding change in the oxygen activity. In fact, an oxygen activity gradient has been shown to be produced in diffusion couples in systems of this kind /2-4/, and it has been proposed that this is such that to make \( J_A \approx -J_B /2-4/ \) Use A of this condition in conjunction with the general expression for the two fluxes given above yields

\[
\frac{D_A - D_B}{aE/a_x} = - \left[ \frac{D_A(1 - \xi) + D_B \xi}{a \ln a_0} \right]
\]

from which, after rearrangement, the ratio between the gradients of \( \ln a_0 \) and \( \xi \) is obtained in the form

\[
\frac{a \ln a_0}{a \xi} = \frac{D_B - D_A}{D_A(1 - \xi) + D_B \xi} = \alpha
\]

Under this condition, the two fluxes then become

\[
J_A = c_M D_A \left[ 1 + (1 - \xi) \alpha \right] \left( \frac{aE/a_x}{a \ln a_0} \right)
\]

and

\[
J_B = -c_M D_B \left[ 1 - \alpha \xi \right] \left( \frac{aE/a_x}{a \ln a_0} \right)
\]

The interdiffusion coefficient for the system is defined by the equation /8/

\[
D(I) = \frac{1}{c_M} \left( \frac{J_A \xi - J_B(1 - \xi)}{aE/a_x} \right)
\]

which, upon introduction of Eqs. (5) and (6), becomes

\[
D(I) = D_A \xi + D_B(1 - \xi) + \alpha \xi(1 - \xi)(D_A - D_B)
\]

The normal expression of the interdiffusion coefficient, neglecting the factor \( S \) arising from the vacancy flow effect, which is usually considered very close to one /2-4,6/, is

\[
D(I) = \left[ D_A \xi + D_B(1 - \xi) \right] \left( 1 + \frac{a \ln \gamma}{a \ln x_i} \right)
\]

where the factor

\[
\phi = 1 + \left( \frac{a \ln \gamma}{a \ln x_i} \right)
\]

(with \( \gamma_i \) = activity coefficient of the component \( i \) (A or B) and \( x_i \), its mole fraction) is the so-called thermodynamic factor. In the case of an ideal solution this factor is considered equal to one not only for a binary system A-B, but also for a ternary system such as a solid solution between A0 and B0 /2-4/. The expression obtained above differs from the usual form of Darken's equation, in which \( \phi \) is considered equal to one, by the presence of the correction term

\[
\beta = \alpha \xi(1 - \xi)(D_A - D_B).
\]
It is seen immediately that this term is equal to zero when $D_A = D_B$, but that it is always negative when $D_A \neq D_B$, thus making $D(I)$ calculated according to Eq. (7) always smaller than the value given by Darken's equation.

It is also interesting to point out that, according to the expression of $\alpha$ reported above, the gradient of oxygen activity will have the same sign as that of $\xi$ if $D_A > D_B$, but opposite to it if $D_B < D_A$. For p-type oxides containing metal vacancies as the prevailing defects this implies that in the first instance there will be a net flux of vacancies from a region of high $a$ values (high concentrations of B) to that of low $a_0$ values (small concentrations of B), and a net metal flux in the opposite direction. This will thus produce a decrease of the flux of B and an increase of that of A until they are almost equal. The opposite situation occurs if $D_B < D_A$ since in this case the gradient of $a_0$ will increase the flux of B and decrease that of A.

It is also possible to obtain Eq. (7) for $D(I)$ by starting from the definition of the interdiffusion coefficient but taking into account the correct values for the thermodynamic factors for the two metal ions in the solid solution. In fact, as shown elsewhere [9], the thermodynamic factors for the metal ions A and B in an oxide solid solution are not always equal to one, and in general they differ from each other, the actual values depending on the oxygen activity, on the oxide composition and also on the ratio between the gradients of these two variables. This result shows clearly that the error connected with the use of Darken's equation for the estimate of $D(I)$ from the tracer-diffusion coefficients of A and B depends on the approximation of considering the thermodynamic factors of the two ions equal to each other and equal to one. In fact, as shown elsewhere [9], one obtains $D_A = D_B = 1$ only when diffusion in the mixed oxide occurs as a result of the presence of gradients of oxide composition under constant oxygen activity. In the interdiffusion experiments however this simple condition does not apply, as examined above, so that the two thermodynamic factors are no longer equal to one.

III - NUMERICAL APPLICATIONS

The equations derived in the previous section are applied here to a specific system for which all the relevant data have been measured, i.e., solid solutions between NiO and CoO. In this case the limiting pure oxides are p-type semiconductors containing metal vacancies [10], while the behavior of the two oxide components in the solid solution is practically ideal [11].

The interdiffusion coefficient in NiO-CoO solid solutions has been measured at different temperatures [11], but simultaneous direct measurements of the tracer-diffusion coefficient of the two cations $D_{Ni}$ and $D_{Co}$ have been carried out only at 1300°C and 1445°C [2]; therefore comparison between calculated and experimental values can be carried out only at these temperatures.

The tracer-diffusion coefficients of Ni and Co at 1300°C at the oxygen activity of air have been measured for selected values of the mole fraction of Co in the mixed oxide. In the following, Ni is considered as A and Co as the B ion. The tracer-diffusion coefficients can be expressed as functions of $\xi$ in the form [2]

$$D_{Ni} = D_0^{Ni} \exp(a_1 \xi + b_1 \xi^2)$$

$$D_{Co} = D_0^{Co} \exp(a_2 \xi + b_2 \xi^2)$$

where $D_0^{Ni}$ and $D_0^{Co}$ are the values of $D_{Ni}$ and $D_{Co}$ at $\xi = 0$.

Values of $a_1$, $b_1$, $a_2$, and $b_2$ given by Chen et al. [2] do not represent the actual data very well; it is found that better agreement with the experimental data is obtained by using instead slightly modified values, which are

$a_1 = 5.653; \quad b_1 = -1.444; \quad a_2 = 5.9681; \quad b_2 = -1.6195$

Use of these expressions for $D_{Ni}$ and $D_{Co}$ as functions of $\xi$ allows one to evaluate $\alpha$ and then $D(I)$ as functions of $\xi$. The results of the calculation are reported in Fig. 1 along with the curve of $D(I)$ corresponding to Darken's equation and with the expe-
Experimental data from Stiglich et al. /11/. Experimental data at temperatures of 1299° (two sets) and of 1307°C (one set) have been reported together. It is seen that the curve of $D(1)$ calculated according to Eq. (7) is clearly lower than that corresponding to Darken's curve, the difference being largest around $\xi = 0.5$, because the correction term of Eq. (7) reduces to zero at $\xi = 0$ and $\xi = 1$. The experimental data of $D(1)$ are too low for $\xi = 0.51$ and particularly for $\xi = 0.76$ because in the last instance the data for $\xi = 0.76$ fall below the smallest $D$, i.e. $D_{Ni}$. However, the agreement with the experimental value of $D(1)$ at 1307°C is rather good. Even if the difference between the two curves for $D(1)$ is limited, the change produced by the correction term is in the correct direction. In addition, it can be stressed that the importance of the correction is related to the difference between the two diffusion coefficients, being proportional to $(D_B - D_A)^2$. Thus the effect of this term is relatively low in this case where $D_B/D_A$ is rather small (from 2.1 to 2.42), but it should be more important when $D_B/D_A$ is very different from the unity.

The expressions given for the two tracer-diffusion coefficients at 1445°C are sufficiently correct. Fig. 1 shows the curves for $D(1)$ according to Darken's equation and according to Eq. (7) also at this temperature. In this case the difference between the two curves of $D(1)$ is smaller than that at 1300°C because the $D_B/D_A$ ratio is also smaller. At this temperature the agreement between the experimental and calculated data for $D(1)$ is better than that at 1300°C.

Fig. 1 - Interdiffusion coefficients $D(1)$ at 1300 and 1445°C in air versus $\xi$.
Curves a: calculated from Eq. (8); curves b: calculated from Eq. (7); ●, △ and ▲: experimental data from Stiglich et al. /11/ at 1436, 1307 and 1299°C, respectively.

REFERENCES

/1/ Darken, L., Trans. AIME 175 (1948) 184.


