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Interdiffusion in the solid couple AgI–CuI

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Interdiffusion measurements were calculated using the Boltzmann–Mattano analysis of concentration profiles and by following the thickness and resistance of the diffusion cell as a function of time. The results for the equimolar solid solution $Ag_{0.5}Cu_{0.5}I$ were coincident for the three methods, the values of the interdiffusion coefficients being of the order of 10^{-7} cm^2 s^{-1}, for the temperature range 570–620 K.

1. Introduction

In earlier papers [1, 2] the conduction characteristics of solid solutions of silver and copper (I) iodides of the general formula $Ag_{(1-x)}Cu_xI$ have been reported. These mixed solid electrolytes exhibit the property known as co-ionic conductivity, i.e. the current is carried either by Ag^+ or Cu^+ ions according to the value of x. Thus, when $x \geqslant 0.5$, the electrolyte is a Cu^+ conductor, changing to Ag^+ transport by $x < 0.5$. Brightwell *et al.* [3] and, more recently, Seydei and Suthanthiraraj [4] have presented structural and transport studies in the region $x \leqslant 0.25$ which agree with the above results.

The mixed electrolyte samples were prepared by bringing into contact pellets of the pure iodides at temperatures ranging from about 550 to about 750 K. The mixing process was then carried out by interdiffusion of silver and cuprous cations in a common matrix of iodide anions. It was found that the final composition of the mixture was dependent on the preparation form; in particular, when the pellets are left to interdiffuse between metallic copper discs, a stable composition of $x = 0.5$ is reached. As this ionic process is worthy of further consideration, in the present work the interdiffusion coefficient, $\tilde{D}$, was determined for the solid couple AgI–CuI.

Taking into account the cell geometry, the diffusional process can be considered as monodimensional and as occurring from a constant concentration source for both ions. In addition, the mixed iodide grows as a product layer separating the reactants. On this basis, the interdiffusion process was followed by three different methods: (a) determination of the concentration profiles at both sides of the original interface after a certain reaction time; (b) direct measurement of the advancement of the reaction front, by following the thickness of the product layer as a function of time; and (c) indirect determination of the product layer growth by means of resistivity measurements.

2. Experimental procedure

The interdiffusion couple was prepared by first pressing AgI powder in a mould and then adding CuI powder and pressing again, both at 2000 kg cm^{-2}, to give pellets of about 0.4 cm each. In this way, optimal contact between the reactant pellets was assured. The resulting tablet was sandwiched between two pure copper discs and put into a glass furnace under a pure nitrogen atmosphere. As mentioned above, under these conditions the composition tends to $AgCuI_2$. Silver iodide was synthesized from pro-analysi silver nitrate and potassium iodide. The cuprous iodide used was Ventron ultrapure. The working temperature covered the range between 570 and 625 K.

The thickness measurements were performed using a travelling microscope with a resolution of 20 μm. The resistance measurements were carried out with an A.C. bridge at 1000 Hz, using the copper discs as electrodes. The concentration profiles were obtained by means of electron probe microanalysis on transverse cuts of polymer-mounted samples.

3. Results

3.1. Concentration profiles

Fig. 1a shows typical concentration profiles obtained after diffusion for 1800 s at 578 K. The left side, corresponding to the CuI pellet is taken as zero length. The development of the profile along the length perpendicular to the interface shows first a zone of high constant copper concentration, whereas that of silver is very low. At about 700 μm the copper concentration starts to decrease and the silver one to increase, as expected. A concentration plateau at the equimolar composition is located between about 1200 and 1500 μm; this zone is clearly visible in micrographs or under the microscope as a darkened layer, a schematic drawing of which is shown in Fig. 1b. Thereafter, the profile shows another zone of about 0.40 Cu and 0.60 Ag, less visible under the microscope than the first

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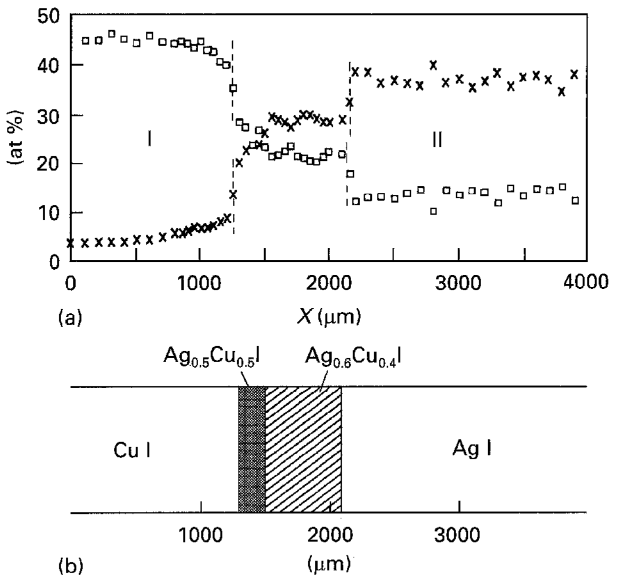

Figure 1 (a) Concentration profile after 1800 s at 578 K: (□) copper, (×) silver. (b) Schematic diagram of the interdiffusion zone.

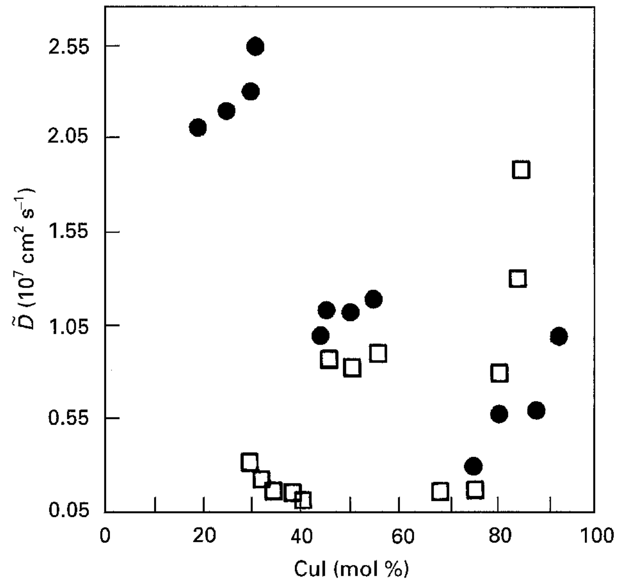

Figure 2 Interdiffusion coefficients as a function of composition at (□) 578 K, (●) 602 K.

one. Finally, on the right, a constant composition of about 0.74 Ag and 0.26 Cu is reached. Determinations carried out at 602 K after a shorter diffusion time gave similar results but with the equimolar composition zone extending over a shorter length.

It should be mentioned that some profiles obtained after diffusion at lower temperature show no discernible zone of equimolar composition. The micrographs showed no distinguishable interfacial darkened zone, but a pattern of more or less intermixed patches of copper and silver, extended over a length of about 40 μm.

From the obtained diffusion profiles, the interdiffusion coefficients were calculated as a function of composition, using the Boltzmann–Mattano method [5]. The following expression was used

$$\tilde{D} = \frac{-\int_{C=C_0}^{C} x \, \mathrm{d}c}{2t(\mathrm{d}C/\mathrm{d}x)_C} \tag{1}$$

where $\tilde{D}$ is the interdiffusion coefficient, C the concentration, x the distance and t the diffusion time. The integral term represents the area under the curve in a definite concentration interval. The derivative is taken at the concentration C at which the value of $\tilde{D}$ is calculated. For the calculations, a "Matano interface" should be defined in the desired concentration zone. In this case, two such planes are indicated in Fig. 1a. The obtained values for 578 and 602 K are plotted as a function of composition in Fig. 2. An estimated maximum error of 40% was assigned to these values, taking into account both the inaccuracy of the measurements and of the graphical integration of the area under the curve. For the sake of comparison, it may be mentioned that in recent similar determinations made in the study of the interfacial reaction between borosilicate and sapphire [6], the obtained interdiffusion coefficients are reported with a standard deviation of about 50%. Three different zones are to be seen in Fig. 2: two at the copper- and silver-rich sides, where the interdiffusion coefficients varied markedly with composition, and an intermediate one in which the composition is that of the expected reaction product, namely $Ag_{0.5}Cu_{0.5}I$, and where the $\tilde{D}$ values are practically constant. In this region the obtained average values are $(8.8 \pm 3.5)\,10^{-8}$ and $(1.1 \pm 0.4)\,10^{-7}\,\mathrm{cm^2\,s^{-1}}$ for 578 and 602 K, respectively.

3.2. Thickness of the product layer as a function of time

As mentioned above, the product layer is clearly seen as a dark zone in the transverse cuts of the diffusion cells, which allowed the determination of thickness as a function of diffusion time by means of a travelling microscope. Assuming complete diffusion control, the layer growth should be inversely proportional to its own thickness, L, which leads to the well-known parabolic rate law

$$L^2 = 2kt \tag{2}$$

where t is the diffusion time and k the corresponding rate constant. As a typical example, the results obtained at 588 K are presented in Fig. 3, which shows that the points fit a straight line when plotted according to Equation 2. The slope yields a value of the rate constant $k = (1 \pm 0.13)\,10^{-7}\,\mathrm{cm^2\,s^{-1}}$. Similar behaviour was found for runs made at 578, 602 and 619 K. From the obtained rate constants, the corresponding interdiffusion coefficients for the equimolar composition were calculated, as explained in the next section, where the complete set of results is presented.

3.3. Thickness of product layer from resistance measurements

From another point of view, the system may be considered as a set of variable resistors connected in series. Thus, at constant temperature, the total resistance at time t, R_t, may be expressed as a sum of terms given by

$$R_t = R_{\mathrm{AgI}} + R_{\mathrm{P}} + R_{\mathrm{CuI}} \tag{3}$$

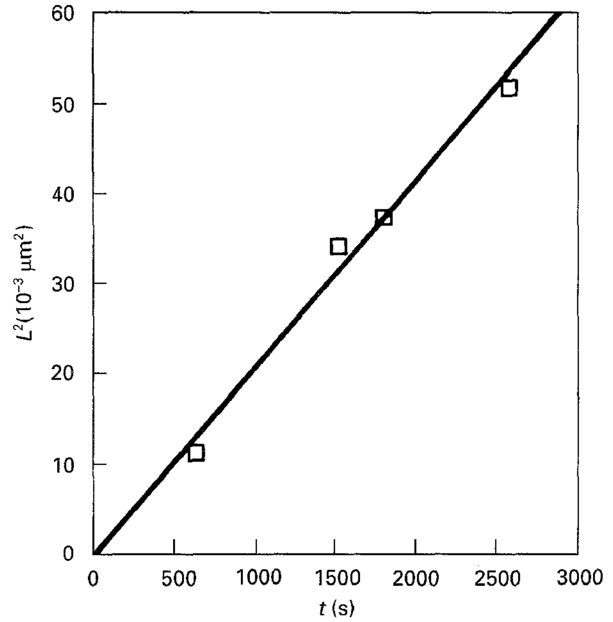

Figure 3 Thickness of the $Ag_{0.5}Cu_{0.5}I$ layer against diffusion time, at 588 K.

where R_P represents the resistance of the product layer, and R_{AgI} and R_{CuI} correspond to the resistances of the layers of AgI and CuI, respectively. By expressing the resistances in terms of the dimensions and conductivities, the following equation results

$$R_t = L_{AgI}/(A\,\sigma_{AgI}) + L_P/(A\,\sigma_P) + L_{CuI}/(A\,\sigma_{CuI}) \quad (4)$$

where L and σ are the thickness and conductivity, respectively, of the subindexed layer, and A represents the common area.

At the temperatures of the present work, the conductivity of silver iodide is much higher than those of the other participants. Thus, the first term on the right of Equation 4 may be taken as negligible, because its thickness change during the runs was no more than 20%. In turn, the thickness of the CuI pellet may be expressed as the difference between its original value, L^0, and the portion which becomes part of the product layer, which may be taken as $L_P/2$, i.e. $L_{CuI} = L^0 - L_P/2$. Introducing this expression into Equation 4 results

$$R_t = L_P/(A\sigma_P) + L^0/(A\sigma_{CuI}) - L_P/(2A\sigma_{CuI}) \quad (5)$$

As before, the growth of the product layer should follow the parabolic law, i.e.

$$L_P = k'^{1/2}\,t^{1/2} \quad (6)$$

where $k' = 2\,k$ of Equation 2. Introducing Equation 6 into Equation 5, the following expression for the electrical resistance of the diffusion cell as a function of time is obtained

$$R_t = L^0/(A\sigma_{CuI}) + [(1/\sigma_P - 1/2\,\sigma_{CuI})\,k'^{1/2}/A]t^{1/2} \quad (7)$$

In this way, a linear relationship between the cell resistance and the square root of time is expected. In Fig. 4 the experimental resistance values at 588 and 571 K are plotted as R against $t^{1/2}$. It is seen that after an initial sharp decrease of the resistance, the points fit a straight line. From the slopes of those straight lines the values of k' were calculated by means of Equation 7. For instance, at 588 K, using $\sigma_P = 0.4\ \Omega^{-1}\,cm^{-1}$; $\sigma_{CuI} = 1.6 \times 10^{-3}\ \Omega^{-1}\,cm^{-1}$ and $A = 0.71\ cm^2$ a value of $k' = (2.07 \pm 0.4)\,10^{-7}\,cm^2\,s^{-1}$ or $k = (1 \pm 0.2)\,10^{-7}\ cm^2\,s^{-1}$ is obtained, in good agreement with that resulting from the thickness measurements.

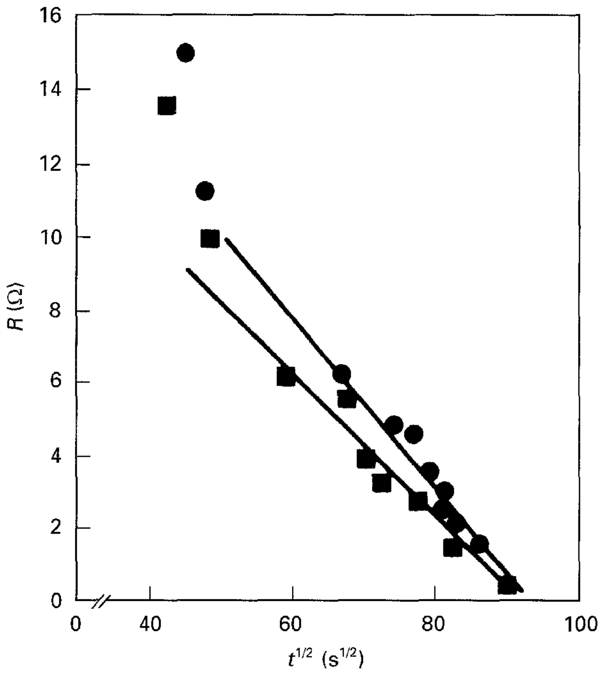

Figure 4 Resistance of the diffusion cell against the square root of time at (●) 588 K, (■) 571 K.

Further, from the k' values, it is possible to calculate the $\tilde{D}$ values for the molar composition of 50 mol% AgI–50 mol% CuI, according to the following reasoning. First, the thickness, L, at time, t, can be expressed as the ratio between the volume and surface area of the product layer, which, introducing the density, δ, gives

$$L = m/(\delta\,A) = n\,PM/(\delta\,A) \quad (8)$$

where m is the mass of formed product, n the corresponding number of moles and PM its molar mass. In turn, n is also the total number of moles which have diffused during time t through the original contact area, i.e. at $x = 0$. The flux at that point can be obtained by regarding the diffusional process as semi-infinite from a source of constant concentration, C_0, for which the corresponding solution of Fick's Second Law [7], yields the expression for the concentration profile as

$$C(x, t) = C_0/2[1 - \mathrm{erf}(x/2D^{1/2}t^{1/2})] \quad (9)$$

whereas the local concentration gradient is given by

$$\delta C/\delta x = -\,C_0/2(\pi D t)^{1/2}\exp(-\,x^2/4Dt) \quad (10)$$

Equation 10 can be used to calculate the number of diffused moles per unit area at $x = 0$, by integrating the flux $J_{(x=0)} = -\,D\delta C/\delta x$ between $t = 0$ and t, which gives

$$n/A = 2C_S(D\,t)^{1/2}/\pi^{1/2} \quad (11)$$

where C_S is the product concentration at the interface, i.e. that of the equimolar mixture.

TABLE I Parabolic rate constants and interdiffusion coefficients for $Ag_{0.5}Cu_{0.5}I$ obtained from resistance and thickness measurements

T (°K)	k' (10^{-7} cm^2 s^{-1})	D(10^{-7} cm^2 s^{-1})
571 Resistance	0.99	0.77 ± 0.15
588	2.07	1.60 ± 0.30
603	3.10	2.40 ± 0.48
578 Thickness	1.80	1.40 ± 0.18
588	2.00	1.60 ± 0.21
602	2.20	1.70 ± 0.22
619	9.10	7.10 ± 0.92

Introducing Equation 11 into Equation 8, gives

$$L = 2\, C_S (D\,t)^{1/2}\, PM/\pi^{1/2}\, \delta \qquad (12)$$

In the present case, the product ($C_S PM$) equals the density of the product layer. Thus, from Equations 6 and 12, the relationship between the parabolic rate constant and $\tilde{D}$ is obtained as

$$\tilde{D} = k'\pi/4 \qquad (13)$$

Using this equation, the interdiffusion coefficients for the equimolar composition from both the resistance and thickness measurements were calculated. The obtained values are assembled in Table I. An experimental error of 20% was estimated for the interdiffusion coefficients obtained from the resistance measurements and of 13% for those resulting from thickness determinations.

4. Discussion

The general shape of the concentration profiles indicates a higher contribution of the copper ion diffusivity, because a higher copper concentration at the silver-rich side is found than the silver concentration at the copper-rich side, i.e., in the same time, more copper than silver has diffused through the interfacial zone. This is in agreement with the above-mentioned co-ionic conductivity characteristic of the solid solution.

For the variation of D upon composition, it is possible to compare the trend of the copper-rich side with known values for dilute solutions of AgI in CuI [8], which is in the order of $\sim 10^{-6}$ for $T = 583$ K. In fact, the extrapolation to dilute solutions of AgI in CuI of the data shown in Fig. 4 yields a value near to 10^{-6} cm^2 s^{-1}.

A feature which may require some explanation is the behaviour shown by the resistance measurements, Fig. 4. The faster resistance decay found at short time could be explained by a lack of homogeneity in the first stages of product formation. In fact, as mentioned above, the reacting interface at low temperature, i.e. at low reaction extent, shows not a well-defined product layer, but an irregular one. In addition, the $\tilde{D}$ values obtained at 486 K are almost two orders of magnitude lower than those obtained in the measurements made at higher temperatures. It may thus be reasonable to assume that a certain time must transpire before the product layer is formed along the entire reacting interface, and that this time should be the shorter the larger is the temperature.

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References

1. J. C. BAZÁN and J. A. SCHMIDT, *J. Appl. Electrchem.* **6** (1976) 411.
2. J. C. BAZÁN, J. A. SCHMIDT and R. S. PETTIGROSSO de MIRAGLIA, *Sol. State Ionics* **6** (1982) 171.
3. J. W. BRIGHTWELL, C. N. BUCKLEY and B. RAY, *ibid.* **15** (1985) 331.
4. M. K. P. SEYDEI and S. A. SUTHANTHIRARAJ, *J. Mater. Sci.* **28** (1993) 3519.
5. Y. ADDA and J. PHILIBERT, "La Diffusion dans les Solide", Vol. I (Presses Universitaires de France, Paris, 1966) Ch. 1, p. 16.
6. J. H. JEAN and T. K. GUPTA, *J. Mater. Res.* **7** (1992) 2514.
7. J. CRANK, "The Mathematics of Diffusion", 2nd Edn (Clarendon Press, Oxford, 1975) p. 32.
8. W. JOST, "Diffusion in Solids, Liquids, Gases", 3rd Edn (Academic Press, New York, 1960) p. 199.

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