Interdiffusion Studies of $NaNO_3$-$AgNO_3$ and $LiNO_3$-$AgNO_3$ Fused Salt Mixtures by Diaphragm Cell Method

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The interdiffusion coefficients of nitrate melts are determined by the diaphragm cell method. For the $NaNO_3$-$AgNO_3$ system at 290°C, the feasible composition range resulting from the phase diagram is $0.25 \leq x_2 \leq 1.0$ and for the $LiNO_3$-$AgNO_3$ system at 260°C, $0.1 \leq x_2 \leq 1.0$ (x_2 mole fraction of the silver nitrate). The concentration changes are followed by emf measurements depending on time and analyzed by a new plotting method.

The phenomenon of interdiffusion is investigated in the systems $NaNO_3$-$AgNO_3$ at 290°C in the composition range $0.25 \leq x_2 \leq 1.0$ (x_2 mole fraction of the silver nitrate) and $LiNO_3$-$AgNO_3$ at 260°C in the total composition range by the diaphragm cell method. These nitrate melts are especially suitable for the interdiffusion measurements carried out here, because they enable experiments to be conducted at relatively low temperatures; in addition, in the literature there are some results of interdiffusion measurements in the limiting composition range for $x_2 \rightarrow 0$, with which the interdiffusion coefficients determined in this work at higher concentrations can be compared.

The experimental temperature of each system is chosen so that nearly the whole composition range can be measured without any influence on the measurements by the onset of thermal decomposition of the silver nitrate at higher temperatures (>310°C). Accordingly, the feasible composition range results from the phase diagram of $NaNO_3$-$AgNO_3$ (*4*) and $LiNO_3$-$AgNO_3$ (*11*).

For diffusion experiments a diaphragm cell is used, which was proposed by Northrup and Anson (*7*) for the investigation of diffusion in aqueous solutions, and which was applied to molten salts by Laity and Miller (*5, 6*). The process of measurements is improved so that the measurements of the interdiffusion coefficients are possible over the total composition range. The evaluation of these measurements does not involve the approximations about the transport numbers of the investigated system, which were necessary for the method of Laity and Miller. In earlier experiments we measured the curve $\Phi(x_2)$ (the emf on dependence of the composition) (*10*). Now, we can follow concentration changes in the diaphragm cell by emf measurements directly without using transport numbers. The diaphragm cell and also the plotting method for the determination of the composition dependence on the time from measurements of the emf across the diaphragm cell are described in detail elsewhere (*8*). The accuracy of the experimental determinations is in the order of that of the emf measurements—about 1%.

The molten salts investigated are melts, which consist of three ion constituents or of two components in the sense of the Gibbs phase rule, which have a common cation or anion. For such melts the interdiffusion coefficient D is defined by the equation (*3*):

$$_{\omega}\vec{J}_n = -D \frac{1 - \omega_n}{\overline{V}(1 - x_n)} \text{ grad } x_n, \ (n = 1, 2) \tag{1}$$

in such a manner that the formula is valid for each reference system. ($_{\omega}\vec{J}_n$: diffusion flux density of component n in the reference system with the general reference velocity $\vec{\omega}$, ω_n: weight factor of the reference velocity, $\overline{V}$: molar volume, x_n: mole fraction of the component n). Equation 1 is *not* valid for molten salt mixtures with more than two independently migrating ion constituents (*9*).

After a short calculation the usual Fick law follows from Equation 1 with the mean volume velocity $\vec{w} = c_1 V_1 \vec{v}_1 + c_2 V_2 \vec{v}_2$ ($\vec{\omega} = \vec{w}$: reference velocity in the Fick reference system, c_i: molarity, V_i: partial molar volume and $\vec{v}_i$: average velocity of component i)

$$\overrightarrow{_wJ_1} = -D \text{ grad } c_1, \ \overrightarrow{_wJ_2} = -D \text{ grad } c_2 \tag{2}$$

The solution of this diffusion equation for the diaphragm cell used in this work is given by Gordon (*1*) as follows (*8*):

$$\ln \frac{\Delta c_0}{\Delta c_t} = \frac{1}{K} \left(\frac{1}{V'} + \frac{1}{V''} \right) Dt \tag{3}$$

(Δc_0 and Δc_t molarity difference of the silver nitrate between the two compartments of the cell at the time $t = 0$ and $t = t$, respectively, K cell constant, V' and V'' volume of the melt in the inner and outer compartment, respectively).

The measurements are evaluated by Equation 3. We obtain the following results: In Table I the mole fraction of the silver nitrate is tabulated in the first column; the interdiffusion coefficients of the $NaNO_3$-$AgNO_3$ system are tabulated at 290°C in the second, and the interdiffusion coefficients of the system $LiNO_3$-$AgNO_3$ at 260°C in the third column.

In Figure 1 the interdiffusion coefficients of the $NaNO_3$-$AgNO_3$ system measured in this work at 290°C are compared with data from the literature measured by Gus-

Table I. Interdiffusion Coefficients D of $NaNO_3$-$AgNO_3$ System at 290°C and $LiNO_3$-$AgNO_3$ System at 260°C as Function of Mole Fraction x_2 of Silver Nitrate

x_2	$NaNO_3$-$AgNO_3$, $D \cdot 10^9/m^2\ sec^{-1}$	$LiNO_3$-$AgNO_3$, $D \cdot 10^9/m^2\ sec^{-1}$
0.10	...	1.30
0.20	...	1.14
0.25	1.94	...
0.30	1.87	1.05
0.35	1.80	...
0.40	1.75	1.11
0.45	1.70	...
0.50	1.65	1.29
0.55	1.62	...
0.60	1.60	1.55
0.65	1.63	...
0.70	1.77	1.87
0.75	1.94	...
0.80	2.14	2.23
0.85	2.37	...
0.90	2.62	2.63
0.95	2.88	...

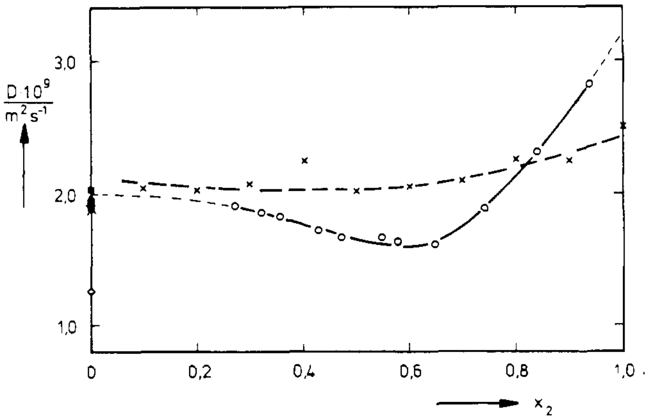

Figure 1. $NaNO_3$–$AgNO_3$: interdiffusion coefficients D as function of mole fraction x_2 of silver nitrate at 290°C, this work, compared with data from literature

○ This work
■ (*2*)
▲ (*5, 6*)
▼ (*15*)
✱ (*2*)
◇ (*12*)
x (*13*)

tafsson et al. (*2*) at 320°C by an optical method, Laity and Miller (*5, 6*) at 310°C with a diaphragm cell similar to the one used in this work, Thalmayer et al. (*15*) by a chronopotentiometric method, and Gustafsson et al. (*2*) at 310°C, again by an optical method. A widely different result was obtained by Sjöblom (*12*) at 320°C with a gravimetric method, which has more recently been improved. However, the values obtained at 320°C with the improved gravimetric method (*13*) agree only partially with our results. The values are more scattered and do not depend so much on the composition. Since the experimental temperature is 30°C higher than ours, higher values are to be expected, but presumably the higher temperature is also responsible for the increased scatter of the values because of incipient thermal decomposition.

In Figure 2 the results of measurements on the $LiNO_3$–$AgNO_3$ system at 260°C are plotted. The limiting value measured with the gravimetric method (*14*) lies, as would be expected from the arguments mentioned above, off the curve obtained in this work. There are no other data on this system in the literature.

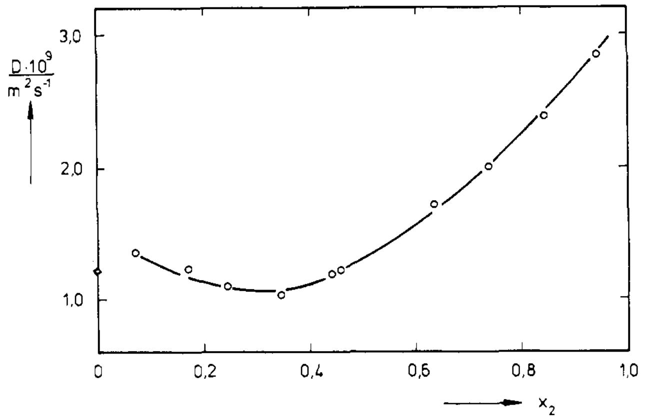

Figure 2. $LiNO_3$–$AgNO_3$: interdiffusion coefficients D as function of mole fraction x_2 of silver nitrate at 260°C

○ This work
◇ (*14*)

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