# Interdiffusion and Selfdiffusion in Binary Mixtures of Molten Salts

Carl-Axel Sjöblom

Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

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Mutual diffusion coefficients in two fused salt systems have been measured with the gravimetric porous frit technique. The system $AgNO_3-KNO_3$ has been investigated for the composition range 50−75 mole % $AgNO_3$, and the system $AgNO_3-NaNO_3$ for mixtures rich in $NaNO_3$. The self-diffusion coefficient of the $Ag^+$-ion in $AgNO_3-KNO_3$ has been measured with the porous frit technique. A comparison with results obtained by other workers is made.

The gravimetric method was first introduced by Schulze[1], and it was reinvented by Wall, Grieger, and Childers[2], who tested it on diffusion of electrolytes. Since then, it has been used by several investigators for a number of diffusion studies in aqueous solutions[3−7]. It is a relatively simple and fast method, and an application to molten salt mixtures would be very valuable, since only two other methods have been used for measuring interdiffusion coefficients in such systems. Of these, the chronopotentiometric technique[8] is restricted to very low concentrations of the electroactive ion in the inactive "solvent". Recently, Laity and Miller[9] have used a constant mass diffusion cell devised by Stokes[10]. They investigated the $AgNO_3-NaNO_3$ system for mixtures rich in $NaNO_3$. Their method might be used for higher $AgNO_3$ concentrations also, but no experiments of this kind have yet been reported. The present investigation is intended to show, that the use of the gravimetric porous frit method can be extended to molten salt mixtures, and that the method is capable of measuring the dependence of the diffusion coefficient on the composition of the melt.

## Outline of the Method

A fritted glass disc is filled with a molten salt mixture. The disc is suspended in a large salt volume of another composition, and the apparent weight $w(t)$, $t =$ time, of the disc is measured with a balance as the interdiffusion proceeds. If the diffusion coefficient is a constant, it can be shown[2] that after some time

$$w(t)-w(\infty) \sim \exp\{-\pi^2 D\, t/(4\, L^2)\},$$

i. e., $S \equiv \mathrm{d}\,{}^{10}\log|w(t)-w(\infty)|/\mathrm{d}t = -D/k$,

where $w(\infty)$ is the final apparent weight of the disc, $2\,L$ is the "effective" thickness of the disc, $D$ is the diffusion coefficient, $S$ is the "slope", and $k$ is the slope constant. For the derivation of the first equation it is assumed that the disc is a cylinder with sealed edges, but it has been shown[11], that the second equation becomes valid also for a frit of arbitrary shape after a sufficiently long time (10 minutes in the present investigation). Thus a plot of ${}^{10}\log|w(t)-w(\infty)|$ versus $t$ gives a straight line with a slope $S$. Wall and Wendt[12] have investigated the case when $D$ varies with concentration, and they have found, that the above equation gives a value of $D$ corresponding to the composition of the large volume outside the frit, i. e. the final composition inside the frit. A good approximation is obtained if the average slope of the experimental curve is taken when

$$\frac{D\,t}{L^2} > 0.3 \quad \text{and} \quad \left|\frac{w(t)-w(\infty)}{w(0)-w(\infty)}\right| < 0.4\,.$$

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[1] G. Schulze, Z. Phys. Chem. **89**, 168 [1914].

[2] F. T. Wall, P. F. Grieger, and C. W. Childers, J. Amer. Chem. Soc. **74**, 3562 [1952].

[3] F. T. Wall and C. W. Childers, J. Amer. Chem. Soc. **75**, 3550 [1953].

[4] G. B. Taylor and F. T. Wall, J. Amer. Chem. Soc. **75**, 6340 [1953].

[5] M. E. Baur, C. W. Garland, and W. H. Stockmayer, J. Amer. Chem. Soc. **81**, 3147 [1959].

[6] A. E. Marcinkowsky, F. Nelson, and K. A. Kraus, J. Phys. Chem. **69**, 303 [1965].

[7] C. W. Garland, S. Tong, and W. H. Stockmayer, J. Phys. Chem. **69**, 1718 [1965].

[8] J. M. Wood, 11th Meeting of the Electrochem. Soc., Washington, D.C., May 1957. — H. A. Laitinen and W. S. Ferguson, Anal. Chem. **29**, 4 [1957]. — H. A. Laitinen and H. C. Gaur, Anal. Chim. Acta **18**, 1 [1958]. — D. Inman and J. O'M. Bockris, J. Electroanal. Chem. **3**, 126 [1962]. — C. E. Thalmayer, S. Bruckenstein, and D. M. Gruen, J. Inorg. Nucl. Chem. **26**, 347 [1964].

[9] R. W. Laity and M. P. Miller, J. Phys. Chem. **68**, 2145 [1964].

[10] R. H. Stokes, J. Amer. Chem. Soc. **72**, 763 [1950].

[11] F. Grün and C. Blatter, J. Amer. Chem. Soc. **80**, 3838 [1958].

[12] F. T. Wall and R. C. Wendt, J. Phys. Chem. **62**, 1581 [1958].

These requirements were always fulfilled in the present work. The experimental points tend to scatter when $\left|\frac{w(t)-w(\infty)}{w(0)-w(\infty)}\right| < 0.1$. Points below this limit were not used in the calculations.

If $D$ is known, the effective length $2\,L$ and the tortuosity factor $L_0$, (effective length/actual length), can be calculated from the slope

$$S = -\pi^2 D/(2.30 \times 4\,L^2).$$

The same factor $L_0$ can be obtained from resistance calibrations[13, 14].

## Experimental

Merck and May & Baker reagent grade salts were used, not further purified. They were dried for more than 24 hours at 130 °C before use.

The diffusion setup consists of a Mettler H15GD analytical balance placed on a rigid stand made of steel and concrete. The furnace (Fig. 1) is situated below the balance and contains two 100 ml Pyrex glass beakers filled with salt mixtures of different composition. (It is not necessary to make the composition difference so small, that the diffusion coefficient can be considered as a constant.) The frit is suspended from the balance with a fine platinum wire reaching through holes in the stand and in the top of the furnace down into one of the beakers. The beakers can be smoothly moved vertically with a mechanical device (a „lift", Fig. 1) and their positions can be interchanged below the frit. The distance between the surface of the melt and the frit is reproducible within 0.2 mm.

The frit is a commercial sintered Pyrex glass disc, Jobling 3610/62, 20 mm POR 4, with unsealed edges. The total volume of the pores inside a disc is about 0.35 cm³. The density of the melt is greater than

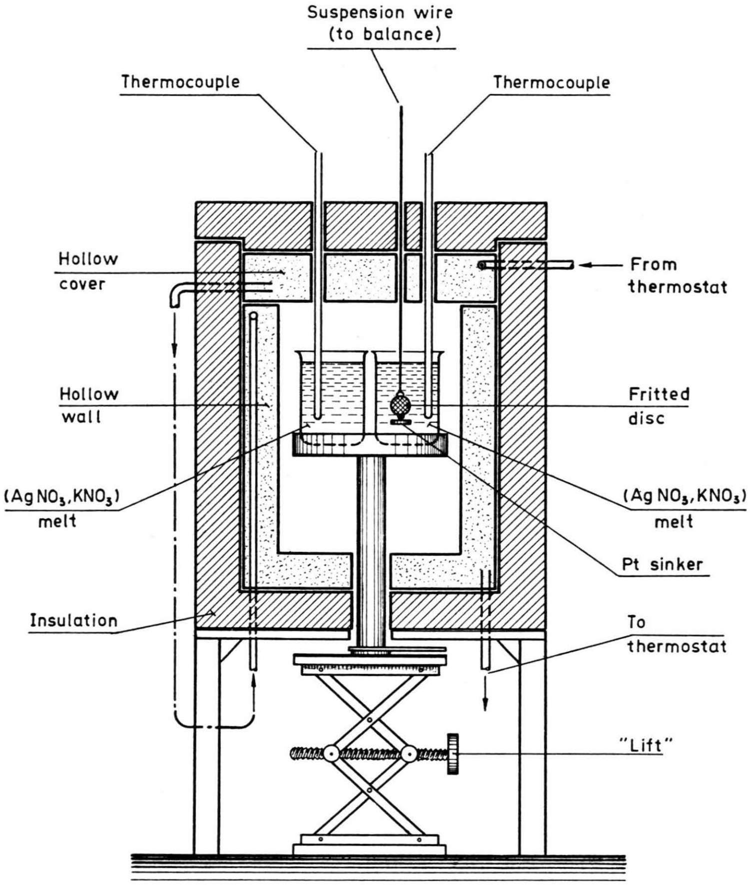

Fig. 1. Furnace design.

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[13] C. A. Sjöblom and A. Lundén, Z. Naturforschg. **18 a**, 942 [1963].

[14] R. K. Schofield and C. Dakshinamurti, Discussions Faraday Soc. **3**, 56 [1936]. — L. J. Klinkenberg, Bull. Geol. Soc. Amer. **62**, 559 [1951]. — P. C. Carman, Flow of Gases through Porous Media, Butterworths, London 1956, p. 46.

that of the glass, therefore a small platinum sinker is fixed to a small eye at the lower edge of the disc.

Two different furnaces were used. One furnace was heated with silicone fluid, which was pumped through the hollow top cover and inner walls (Fig. 1). The fluid was heated in a high temperature thermostat (Bühler Superthermostat). When temperature equilibrium has been established, no temperature differences can be detected in the utilized part of the furnace (measuring accuracy 0.2 °C). This design could be used up to 200 °C. The other furnace was wire-wound in a conventional way, and the maximum temperature difference was here less than 1 °C. The temperature of the melts was measured with a calibrated thermocouple connected to a Philips potentiometric recorder, type PR 2210/A 21. Constant temperature (± 0.5 °C) was maintained in the baths by a temperature controller, type West Gardsman JP.

The balance was enclosed into a wooden box to avoid attack by salt vapours. Thermostatted air was circulated in the box.

The furnace is replaced with a water thermostat during the calibration runs. The frits are filled with 1-m. KCl solution, which diffuses out into destilled water at $(25.00 \pm 0.02)$ °C. Since the diffusion coefficient is known [15], a slope constant can be obtained for each disc.

For filling, the frit is immersed extremely slowly into one of the melts by rising the beakers with the lift (it takes about one hour). Due to capillary forces, the frit is nearly filled already before it is entirely immersed into the melt, but it takes nearly two weeks in the melt until the apparent weight becomes constant (cf. ref. [3]).

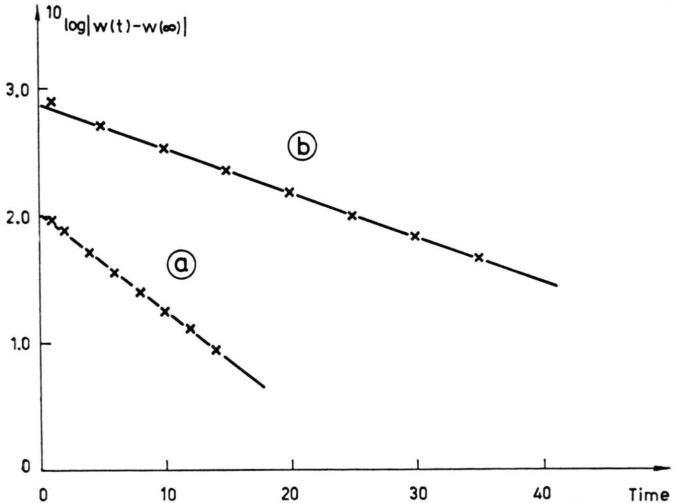

Fig. 2. Plot of $^{10}\log \mid w(t) - w(\infty) \mid$ versus time. Curve a: calibration run, slope $-7.83 \times 10^{-2}\ \text{min}^{-1}$; curve b: salt experiment, slope $-3.52 \times 10^{-2}\ \text{min}^{-1}$.

The interdiffusion is started by interchanging the positions of the beakers. Since it makes no difference in the calculations if the denser mixture "diffuses out" from the frit or into it, two different interdiffusion coefficients, corresponding to the two different mixtures, can be measured. A typical experimental diffusion curve is shown in Fig. 2 along with the corresponding calibration curve. The linearity of the plot is excellent after a few minutes.

## Stirring

End effects have been discussed recently by Nanis, Richards, and Bockris [16], who use an empirical relation established for aqueous dye solutions in order to calculate the $\Delta l$-effect in molten salt experiments, and by Spedding and Mills [17].

Previous workers using the gravimetric porous-frit technique in aqueous solutions, have found that no stirring is necessary in order to avoid end effects. A similar conclusion was arrived at by Gergely et al. [18], who solved the diffusion equation for the boundary conditions appropriate to a microcapillary method without stirring (convection neglected). They found, that the effective length of the capillary could be obtained from calibration runs with solutions having a known diffusion coefficient. Therefore it seems to be a well-established fact that "stirring" by convection, free diffusion and oscillations during weighing is adequate for gravimetric measurements in aqueous solutions.

All these results can be criticized, since conditions applicable to aqueous solutions do not necessarily apply to molten salts even with identical Reynold's numbers. During the present investigation it was found that, although unstirred interdiffusion runs gave reproducible results too [19], these results were considerably lower than those of the present investigation. This discrepancy is probably caused by a build-up (in the unstirred runs) of a region near the frit with a density different from that of the bulk. Since the average thickness of the frits used in the interdiffusion runs was 2 mm, the build-up corresponds to a $\Delta l$ of about 0.7 mm. This is not unreasonable in view of the 20 mm diameter of the frits. Control experiments on diffusion of 1-m. KCl solution in water show, on the other hand, excellent agreement between runs with and without stirring.

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[15] L. J. Gosting, J. Amer. Chem. Soc. **72**, 4418 [1950].

[16] L. Nanis, S. R. Richards, and J. O'M. Bockris, Rev. Sci. Instr. **36**, 673 [1965].

[17] P. L. Spedding and R. Mills, J. Elctrochem. Soc. **112**, 594 [1965].

[18] J. Gergely, J. Tamàs, A. Vértes, and S. Lengyel, Acta Chim. Hung. **39**, 423 [1963].

[19] C.-A. Sjöblom and A. Lundén, Z. Naturforschg. **20 a**, 632 [1965].

Any excessive motion of the large salt volume will affect the accuracy of the readings on the balance. Therefore the possible amount of stirring is limited in a gravimetric experiment. The stirring was performed during periods of 30 seconds, after which the liquid was allowed to come to rest. Before each stirring period a reading was taken on the balance. Experiments with intervals of one, two and five minutes between the stirring periods were made, and the experimental diffusion coefficient was independent of the amount of stirring in these cases. This fact was regarded as an indication that end-effects are negligible in the present work. The mean flow rate past the cell was 1 mm/s, and it was obtained by operating the arresting knob of the balance, thus gently making the frit to oscillate vertically.

Experiments on aqueous solutions can give valuable clues to possible improvements of the experimental techniques for molten salts, but there are potential dangers if the results are transformed uncritically, as can be realized from the need of stirring when making gravimetric diffusion measurements in melts. (When the flow rate past the capillary mouth is zero, the Reynold's numbers are identical in the melt and in the aqueous solution, and this fact might lead to the erroneous conclusion that stirring is unnecessary in both cases.)

## Results and Discussion

Calibration results for frits with different linear dimensions are given in Table 1. Since this method measures a diffusion coefficient corresponding to the outside bath concentration, identical slopes are obtained (within experimental error) when the frits are filled with 1-m. KCl and 0.4-m. KCl. The reproducibility ($\pm 3\%$) is linked to the accuracy of the balance.

| Frit | Frit concn. (m) | Porosity (%) | Slope $\times 10^2$ ($\text{min}^{-1}$) | Tortuosity factor | $k$ ($\text{cm}^2 \text{min s}^{-1}$) | Average $k$ |
|---|---|---|---|---|---|---|
| A | 1.0 | 42 | $-7.33$ | 1.27 | 2.51 | 2.58 |
| A | 1.0 | | $-7.00$ | 1.30 | 2.61 | |
| A | 1.0 | | $-7.15$ | 1.29 | 2.57 | |
| A | 0.4 | | $-6.90$ | 1.32 | 2.66 | |
| A | 0.4 | | $-7.15$ | 1.29 | 2.57 | |
| B | 1.0 | 39 | $-4.80$ | 1.29 | 3.83 | 3.77 |
| B | 1.0 | | $-4.80$ | 1.29 | 3.83 | |
| B | 1.0 | | $-4.85$ | 1.28 | 3.79 | |
| B | 0.4 | | $-5.03$ | 1.26 | 3.67 | |
| B | 0.4 | | $-4.90$ | 1.27 | 3.75 | |
| C | 1.0 | 38 | $-4.70$ | 1.27 | 3.91 | 3.96 |
| C | 0.4 | | $-4.65$ | 1.28 | 3.95 | |
| C | 0.4 | | $-4.58$ | 1.29 | 4.02 | |
| D | 1.0 | 43 | $-8.03$ | 1.25 | 2.29 | 2.32 |
| D | 1.0 | | $-7.83$ | 1.26 | 2.35 | |
| E | 1.0 | 45 | $-8.08$ | 1.25 | 2.27 | 2.30 |
| E | 1.0 | | $-7.89$ | 1.26 | 2.33 | |
| F | 1.0 | 45 | $-7.45$ | 1.27 | 2.47 | 2.41 |
| F | 1.0 | | $-7.83$ | 1.24 | 2.35 | |
| G | 1.0 | 52 | $-4.75$ | 1.26 | 3.87 | 3.85 |
| G | 1.0 | | $-4.80$ | 1.26 | 3.83 | |

Table 1. Calibration results. The average thickness of the fritted discs is 2 mm, the average diameter of the frits A–C is 30 mm and of the frits D–G 20 mm.

The experimental interdiffusion coefficient in the system $AgNO_3-KNO_3$ was measured over the composition range 50–75 mole % $AgNO_3$ between 172 and 245 °C and in the system $AgNO_3-NaNO_3$ for mixtures rich in $NaNO_3$ at 320 °C. The results are given in Table 2. In order to see if the obtained interdiffusion coefficients had a reasonable magnitude, the self-diffusion (tracer diffusion) coefficient of the $Ag^+$-ion in $AgNO_3-KNO_3$ was measured with a previously described technique [13, 20]. These results are given in Table 3. A "least squares" calculation [21] shows that the interdiffusion data are well described by an Arrhenius equation,

$$D = D_0 \exp\{-Q/(R\,T)\}.$$

If the same type of equation is postulated for the self-diffusion coefficients, rough values for the activation energies [22] can be obtained. The obtained energies of activation for diffusion (given in table 4) are of the same order of magnitude as those for self-diffusion in molten $AgNO_3$ and $KNO_3$ [23]. Our interdiffusion and tracer diffusion coefficients in $AgNO_3-KNO_3$ at 220 °C are plotted versus composition in Figure 3, which shows, that the gravimetric method is able to measure variations in $D$ with concentration. The plot indicates, that there might be a minimum at 65 mole % $AgNO_3$, where

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[20] S. Djordjevic and G. J. Hills, Trans. Faraday Soc. **56**, 269 [1960].

[21] A. Hald, Statistical Theory with Engineering Applications, John Wiley & Sons, New York 1952, p. 522.

[22] The concept of "activation energy" has been discussed by A. Lundén, Z. Naturforschg. **19 a**, 400 [1964].

[23] A. S. Dworkin, R. B. Escue, and E. R. Van Artsdalen, J. Phys. Chem. **64**, 872 [1960].

| Frit | Mixture | Mole% $AgNO_3$ | Slope $\times 10^2$ $min^{-1}$ | $D_{12} \times 10^6$ $cm^2 s^{-1}$ | Temp. °C |
|---|---|---|---|---|---|
| G | $AgNO_3$–$NaNO_3$ | 0 | − 3.26 | 12.9 | 319 |
| G | | 0 | − 3.29 | 12.6 | 319 |
| D | | 0 | − 5.51 | 12.8 | 321 |
| D | | 0 | − 5.64 | 13.1 | 322 |
| D | | 0 | − 5.77 | 13.4 | 322 |
| G | $AgNO_3$–$NaNO_3$ | 10 | − 3.50 | 13.4 | 320 |
| G | | 10 | − 3.43 | 13.2 | 320 |
| D | | 10 | − 5.78 | 13.4 | 320 |
| D | | 10 | − 5.94 | 13.8 | 321 |
| D | | 10 | − 5.95 | 13.8 | 323 |
| F | $AgNO_3$–$KNO_3$ | 50 | − 2.31 | 5.57 | 182 |
| F | | 50 | − 2.34 | 5.63 | 182 |
| F | | 50 | − 3.52 | 8.48 | 209 |
| F | | 50 | − 3.66 | 8.82 | 209 |
| F | | 50 | − 5.30 | 12.8 | 240 |
| F | | 50 | − 5.34 | 12.9 | 240 |
| E | $AgNO_3$–$KNO_3$ | 61 | − 2.44 | 5.60 | 172 |
| E | | 61 | − 2.25 | 5.18 | 172 |
| E | | 61 | − 3.55 | 8.17 | 213 |
| E | | 61 | − 3.51 | 8.07 | 214 |
| E | | 61 | − 5.22 | 12.0 | 245 |
| E | | 61 | − 5.15 | 11.8 | 245 |
| F | $AgNO_3$–$KNO_3$ | 65 | − 2.42 | 5.83 | 182 |
| F | | 65 | − 2.41 | 5.81 | 182 |
| F | | 65 | − 3.33 | 8.02 | 209 |
| F | | 65 | − 3.34 | 8.04 | 209 |
| F | | 65 | − 4.46 | 10.8 | 240 |
| F | | 65 | − 4.80 | 11.6 | 241 |
| E | $AgNO_3$–$KNO_3$ | 75 | − 2.16 | 4.97 | 172 |
| E | | 75 | − 2.11 | 4.95 | 172 |
| E | | 75 | − 3.66 | 8.41 | 214 |
| E | | 75 | − 3.79 | 8.72 | 214 |
| E | | 75 | − 5.37 | 12.4 | 245 |
| E | | 75 | − 5.67 | 13.0 | 245 |

Table 2. Experimental results, interdiffusion.

| Mole% $AgNO_3$ | Temp °C | Time sec | $l$ cm | $L_0$ | $I/I_0$ | $D_{Ag} \times 10^6$ $cm^2 s^{-1}$ |
|---|---|---|---|---|---|---|
| 50 | 180 | 9790 | 1.12 | 1.42 | 0.506 | 8.65 |
| 50 | 230 | 8640 | 1.06 | 1.46 | 0.343 | 16.4 |
| 61 | 187 | 6000 | 0.99 | 1.36 | 0.584 | 7.56 |
| 61 | 188 | 16590 | 0.98 | 1.31 | 0.347 | 6.94 |
| 61 | 237 | 5750 | 0.96 | 1.43 | 0.533 | 9.85 |
| 65 | 178 | 11640 | 1.05 | 1.46 | 0.517 | 6.32 |
| 65 | 225 | 5290 | 0.95 | 1.37 | 0.560 | 8.81 |
| 75 | 184 | 8420 | 1.08 | 1.40 | 0.623 | 5.45 |
| 75 | 234 | 4500 | 1.05 | 1.47 | 0.552 | 14.2 |

Table 3. Experimental results, self-diffusion of the $Ag^+$-ion in molten $AgNO_3-KNO_3$. $l$=length of the (cylindrical) frit.

| Mole% $AgNO_3$ | Activation energy (cal $mole^{-1}$) Interdiffusion | Self- diffusion |
|---|---|---|
| 0 | | 4970 (ref. [23]) |
| 50 | 6810 ± 170 | 5700 |
| 61 | 4910 ± 310 | 2900 |
| 65 | 5190 ± 180 | 3200 |
| 75 | 5870 ± 170 | 7500 |
| 100 | | 3730 (ref. [23]) |

Table 4. Activation energies for interdiffusion and self-diffusion in molten $AgNO_3-KNO_3$. The stated errors are standard deviations, obtained acording to ref. [21].

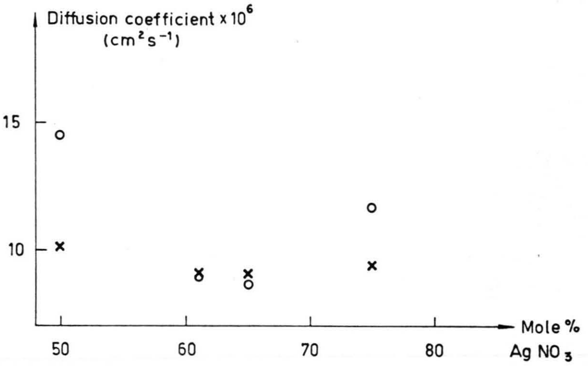

Fig. 3. The interdiffusion (×) and self-diffusion (○) coefficients in $AgNO_3-KNO_3$ as a function of composition at 220 °C.

POLYAKOV [24] claims to have found a minimum both for viscosity and electrical conductivity.

Both interdiffusion and self-diffusion coefficients are of the same order of magnitude in the $AgNO_3-KNO_3$ mixture. Moreover, if the self-diffusion coefficients measured by the conventional capillary technique [23] for the pure nitrates are extrapolated to 220 °C one obtains $D_K = 4.6 \times 10^{-6}$ and $D_{Ag} = 1.1 \times 10^{-5}$ $cm^2 s^{-1}$. Since the interdiffusion coefficient is expected to fall between these values, the result for the $AgNO_3-KNO_3$ system is very reasonable.

In the $AgNO_3-NaNO_3$ system, a comparison can be made with the results of LAITY and MILLER [9]. Their experimental values (mole-fixed) range from 1.74 to $2.17 \times 10^{-5}$ $cm^2 s^{-1}$ at 310 °C. The present results are about 30% lower than these, and much lower than the 1911 figures of HARRISON [25], whose method, however, probably suffers from convective mixing of the solutions. The difference between LAITY

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[24] V. D. POLYAKOV, Izv. Sektora Fiz. Khim. Analiza, Inst. Obshch. Neorgan. Khim. Akad. Nauk SSSR **26**, 149 [1955].

[25] L. H. HARRISON, Thesis, University of Munich, 1911, and A. H. HÖCHBERG, Thesis, University of Frankfurt, 1915, both given in W. JOST, Diffusion in Solids, Liquids, Gases, Academic Press, New York, N.Y. 1960, p. 478.

and MILLER's and the present values can be attributed to several factors:

1. End effects arising from the different stirring methods might be important. Since in the present investigation the same method was used both for calibration and experiment, it is reasonable to assume, that $\Delta l$-effects (if any) will cancel out (provided adequate stirring is applied). LAITY and MILLER measured the resistance across the diaphragm of an 0.1-m. KCl solution to obtain the cell constant. Since their calibration method is unaffected by $\Delta l$-effects, any such effects during the experiment will make the obtained diffusion coefficients too high. A comparison between the results of the unstirred [19] and the stirred gravimetric interdiffusion runs on $AgNO_3 - KNO_3$ shows, that a correct choice of flow rate past the frit is very important. Unsuitable flow conditions may give rise to considerable $\Delta l$-effects [17].

2. Fritted Pyrex glass discs were used in both investigations. Our frits have a mean pore diameter of 10 $\mu$m, which is a very large distance compared with the dimensions of the diffusing units, even if they are assumed to be globules consisting of about a hundred atoms. For some experiments with the conventional open-ended capillary method with molten metals, a change in capillary diameter from 0.8 to 0.4 mm was found to decrease the self-diffusion coefficient about 30% for potassium [26] while no such effect was found for lithium [27]. It is suspected that the "wall-effect" found in the first case is at least partially due to chemical exchange between the melt and the capillary walls. Similar wall-effects migh affect one or both of the interdiffusion methods [28].

3. There might occur a demixing effect during the filling process of the discs, thus causing the effective thickness of the disc to be different in the melt and in the aqueous solution. This assumption is, however, contradicted by the fact, that the total weight change during an experiment is always in excellent agreement with the value calculated from the porosity of the frit and the density difference between the melts.

4. HONIG [29] has found reactions between an $AgNO_3$ melt and the glass fibre paper which he used for "electrodiffusion" measurements. In our tracer diffusion experiments, on the other hand, only a negligible part (less than 0.3%) of the $Ag^{110m}$ activity stuck to the frits. Neither could any silver discoloration of the frits be detected after any of the experiments.

The reproducibility of the present method is considerably better than that of the previous [9] one, the maximum spread being $\pm 4\%$. At present, a certain systematic difference exists between our results and those of LAITY and MILLER, and it is difficult to decide which method that is capable to yield the most "correct" values. It is safe to conclude, however, that both methods are capable to give results of the correct order of magnitude, and that the results by HARRISON [25] are much too high. Further refinements of the experimental techniques will certainly remove the remaining discrepancies between the two latest methods.

I am indebted to Dr. A. LUNDÉN for encouraging discussions and helpful criticism of the manuscript, and to Mr. W. PARKER for making the radioactive samples. This work has been supported by "Magn. Bergvalls Stiftelse".

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[26] J. ROHLIN and A. LODDING, Z. Naturforschg. **17 a**, 1081 [1962].

[27] A. OTT and A. LODDING, Z. Naturforschg. **20 a**, 1578 [1965].

[28] Work is in progress at this laboratory to investigate if fritted-disc methods for diffusion measurements in molten salts are affected by wall-effects.

[29] E. P. HONIG, Thesis, University of Amsterdam 1964.