Gravimetric Interdiffusion Measurements in Molten Halides at Temperatures up to 1000 °C

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The interdiffusion coefficient of bromide ions at low concentration in molten silver chloride has been measured with the gravimetric technique, and it can be "least-squares" fitted into the equation

$$D_{23}=6.58\times10^{-4}\exp\{-(4280\pm110)/R\,T\}\quad(503-820\ ^\circ\mathrm{C})$$

where D_{23} is expressed in $\mathrm{cm}^2\,\mathrm{s}^{-1}$ and $R\,T$ in cal equiv^{-1}. Friction coefficients as defined by Klemm do not indicate association between the chloride and bromide ions.

The interdiffusion coefficients of potassium ions in molten sodium chloride at 900 °C and of sodium ions in molten potassium chloride at 995 °C, both at low concentration, have been found to be approximately $2\times10^{-4}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$.

Interdiffusion measurements in halide mixtures have thus far been scarce because of the comparatively high melting points of these salts. It has been shown previously[1] that no systematic differences exist between the most frequently used interdiffusion techniques: the chronopotentiometric[2], the optical[3], the constant mass cell[4, 5], and the gravimetric[1, 6]. The latter method was chosen for the present work on halides since the gravimetric method is comparatively simple to modify for use at elevated temperatures.

Experimental

Commercially available, reagent grade salts were used after drying at 150 °C for 50 hours.

The general features of the gravimetric interdiffusion technique are described in detail elsewhere[6]. Commercial fritted quartz glass discs (diameter 20 mm, thickness 3.5 mm, porosity grade 4) were filled with a molten salt mixture which was allowed to diffuse out into another mixture with a different composition. In the final stage of the process the interdiffusion coefficient measured in this way corresponds to the composition that exists outside the disc[6]. The buoyancy of the disc during the diffusion was determined with an electrical balance, Mettler H2OE GD, connected to one channel of a potentiometric recorder Goerz Servogor 2. The temperature of the melt was measured with a Platinel[7] thermocouple connected to a Zeref[8] temperature reference chamber and the second channel on the recorder. Two different electrical furnaces were used: in the $AgCl-AgBr$ experiments a furnace with Kanthal[9] windings suitable for temperatures up to 800 °C, and in the $NaCl-KCl$ experiments a Nernst-Tammann furnace (type HTR 42, made by Rühstrat, Lenglern/Göttingen, BRD) designed for use at temperatures exceeding 2000 °C. The laboratory was thermostated and a constant heating current was fed to the furnaces. The temperature fluctuations during an experiment did not exceed 1 K.

Three heat radiation shields (two made of metal and one made of asbestos wood) were placed between the furnace and the balance. The radiated heat from the big furnace (full power dissipation 60 kVA) was also decreased by water cooling. Nevertheless, a vertical oscillatory motion of the balance with a period of about one minute was observed, partly caused by air draught and partly by convection in the melt. This disturbance was decreased but not completely eliminated by the thermal shields, and it could not be neglected above 800 °C. An averaging electronical filter[10] connected between the balance and the recorder was tried with good effect.

The graphite heating tube in the Nernst-Tammann furnace was closed in the bottom and continously flushed with argon gas. Air entering through the stirring rod holes in the furnace lid tended to oxidize the heating tube, and these holes had to be dispensed with.

The material that is diffusing out from the frit has to be swept away by some kind of stirring. The stirring is often accomplished by paddle-like stirring rods rotating at a speed which is usually determined by experience. In order to determine the adequate amount of stirring in the present set-up a series of experiments was performed in which the interdiffusion coefficient of silver ions in molten sodium nitrate was determined at 325 °C for different stirring rates.

The results are plotted in Figure 1. Each value is a mean of four different observations at the same stir-

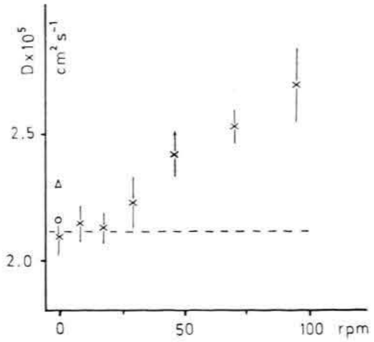

Fig. 1. The interdiffusion coefficient of Ag^+-ions in molten $NaNO_3$, as observed with the gravimetric technique using different stirring rates (×). For comparison, data observed with the porous frit technique[6] (○) and the optical technique[3] (△) are included. The dashed line shows the "best" value obtained by Mazzocchin et al.[22] by averaging.

ring rate. As a comparison, results obtained with other techniques are also given. It is found that the observed interdiffusion coefficient is constant up to a stirring rate of 30 rpm. In order to account for this fact an additional stirring mechanism must be operating, most likely being convection due to the unsymmetrical position of the salt containers inside the oven, the side of the container closest to the heating tube wall being hottest. Coarsely ground Pyrex glass powder floating on the salt melt followed this suggested flow pattern. The radial temperature gradient in the salt container which is necessary to maintain a sufficient amount of this kind of stirring was found to be 0.5 K cm^{-1} which gave a flow rate past the frit of 10 mm s^{-1}. A temperature gradient of this magnitude exists naturally in the salt containers when the present set-up is used and additional stirring is not necessary.

According to the solution of the diffusion equation[6, 11] the buoyancy (apparent weight) of the frit during the final stage of the diffusion follows the equation

$$w(t) = w(\infty) + k' \exp\{-k D t\} \qquad (1)$$

where $w(t)$ and $w(\infty)$ are buoyancies at time t and infinite time, respectively, and k' and k are constants (k is the calibration constant of the frit obtained by diffusion in an aqueous solution). In order to obtain good accuracy in D, $w(\infty)$ must be known with good accuracy also, which means that the experimental conditions (in particular temperature) must be kept within narrow limits for a considerable length of time. An alternative evaluation method is obtained by taking the derivative of Eq. (1) with respect to time

$$\mathrm{d}w(t)/\mathrm{d}t = -k k' D \exp\{-k D t\} . \qquad (2)$$

The time for an experiment will be shorter, since there is no need to know $w(\infty)$, and this fact may be valuable at high temperatures where salt volatility and corrosion may pose problems. Comparisons between the results obtained using Eq. (1) and Eq. (2) respectively on the same experiment show (as expected) a very good agreement, but it is felt at this stage that at moderately high temperatures the best results are obtained using Equation (1).

It is known[12] that fused quartz is attacked by chloride melts, in particular sodium chloride, at high temperatures. The salt containers were therefore made of aluminium oxide for this series. Fritted alumina discs were tried, but we had to return to fused quartz in order to obtain a sufficient wetting of the frits (the initial filling of the frits is obtained by capillary forces). The corrosion of the quartz frit was decreased by keeping it in the potassium chloride melt until the first interdiffusion run was to start. Salt was gradually lost from the containers by evaporation, particularly above 900 °C, limiting the duration of an experimental series to less than 80 hours.

Results and Discussion

The observed interdiffusion coefficients of bromide ions in molten silver chloride are plotted in Figure 2. The results were obtained using a frit

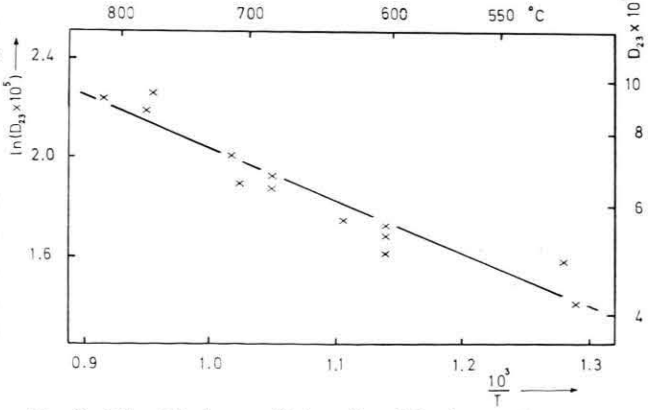

Fig. 2. The diffusion coefficient D_{23} of Br^--ions at low concentration in molten AgCl as observed with the gravimetric technique. The line corresponds to the adopted linear regression.

filling consisting of 10 mole% silver bromide and 90 mole% silver chloride which diffused out into pure silver chloride. No "hydrostatic" flow due to the density difference could be observed. The results can be represented in the temperature interval 503 – 820 °C by an Arrhenius equation, obtained by linear regression:

$$D_{23} = 6.58 \times 10^{-4} \exp\{-(4280 \pm 110)/RT\}$$

where D_{23} is expressed in $\mathrm{cm^2\,s^{-1}}$ and RT in calories equivalent^{-1}. The given error is a standard deviation. The standard error of estimate[13] in D_{23} is less than 8%.

The difference between the densities of sodium chloride and potassium chloride (1.50 and 1.45 $\mathrm{g\,cm^{-3}}$ respectively, at 900 °C[14]) is quite small. In order to obtain a sufficient buoyancy change during the diffusion the frit had to be filled with one of the pure components which diffused out into the other component. The readings were made using the electronic averaging filter. Two major experimental problems remained: melt evaporation and frit corrosion. These problems led to a gradual decrease of the observed D value and to a termination of the series when an unsufficient amount of salt remained. The interdiffusion coefficient at low concentration of sodium ions in molten potassium chloride was found to be $(2.0 \pm 0.6) \times 10^{-4}\,\mathrm{cm^2\,s^{-1}}$ at 995 °C (mean of four values) and of potassium ions in molten sodium chloride $2.0 \times 10^{-4}\,\mathrm{cm^2\,s^{-1}}$ at 900 °C (only two determinations were successful in this case).

The results from the silver chloride – silver bromide experiments can be used in order to draw conclusions about the ionic interactions if the Klemm friction coefficients[15] are used as described before[16]. Using equivalent conductance data tabulated by Janz[17] the following anion-anion friction coefficients can be calculated: at 500 °C 1.6×10^{-8} and at 800 °C $0.8 \times 10^{-8}\,\mathrm{J\,s\,cm^{-2}\,mole^{-1}}$, which indicates that the mixture behaves "normally" (no association of the anions).

The observed interdiffusion coefficient of potassium ions in fused sodium chloride is higher than the value according to Törklep[18] ($1.2 \times 10^{-4}\,\mathrm{cm^2\,s^{-1}}$ at 850 °C), but the error margins are wide in both cases and they may easily overlap. The data by Bockris et al.[19] using the conventional capillary method are lower still, but these data have been calculated assuming a considerable Δl-effect and correcting mathematically for it, an approach which has been criticized[20].

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