Thermal Diffusion in Molten Binary Mixtures of Silver Nitrate with Alkali Nitrates

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Thermal diffusion in the molten systems $LiNO_3-AgNO_3$, KNO_3-AgNO_3, $RbNO_3-AgNO_3$ and $CsNO_3-AgNO_3$ was detected by means of chemical analysis. Two types of cells were used: the elementary effect was measured directly in cells with vertical temperature gradients, and the coefficient of thermal diffusion (D') was estimated from the steady-state separation obtained in convection cells (horizontal temperature gradient). A discussion of possible sources of error shows for both methods that the results might be systematically lower than corresponding to ideal conditions. In all systems $AgNO_3$ was enriched at the cold side. There are indications that the Soret-coefficient varies with the composiiton of the mixture and the temperature. Thus for the $LiNO_3-AgNO_3$ system, depending on the conditions, the Soret coefficient ranged from 2×10^{-3} to 5.5×10^{-3} degr.$^{-1}$, while it was about 1.8×10^{-3} degr.$^{-1}$ over a wide concentration range for the KNO_3-AgNO_3 system, and about 1.3×10^{-3} degr.$^{-1}$ over the investigated ranges for the $RbNO_3-AgNO_3$ and $CsNO_3-AgNO_3$ systems.

Also isotope effects were measured with the convection cell, giving Soret-coefficients of the order of 10^{-5} to 4×10^{-5} degr.$^{-1}$ for $^6Li-^7Li$ as well as for $^{39}K-^{41}K$, which is in agreement with previous investigations.

Thermal diffusion can, in principle, be studied either by a direct (chemical or mass spectrometrical) analysis of the initial and final mixtures, or by following the change in a concentration dependent physical property such as the thermoelectric power or the refractive index. The latter methods have the advantage that the time-dependence of the process can be studied without disturbing the system. Furthermore, the methods usually are less tedious and ought to have a higher precision than a direct analysis, which on the other hand is the only method available for studying isotope effects (with the possible exception of the lightest elements). Regarding molten salts, direct analysis has been used to measure elementary effects [1–5] as well as enrichments in a convection cell [4, 6] while, to our knowledge, only one investigation of the change in thermoelectric power due to thermal diffusion has been reported so far [7].

In the present investigation direct analysis methods are used to study thermal diffusion in binary mixtures of $AgNO_3$ with $LiNO_3$, KNO_3, $RbNO_3$ and $CsNO_3$. (The phase diagrams of the chosen systems have at least one minimum, cf. Fig. 1, which is favourable due to the risk for thermal decomposition of nitrates at elevated temperatures. The omitted system with $NaNO_3$ has no minimum in its phase diagram.) The aim of the investigation is twofold: to determine the magnitude of the Soret coefficient over wide concentration ranges, and to study the reliability of direct analysis methods. In the last aspect the work reported here is supplemented by other investigations on binary mixtures of alkali nitrates [8] and of alkali sulfates [9], and on the isotope effect in pure lithium chloride [10].

Direct measurement of the elementary effect

The apparatus and procedure have been described previously [3, 5]. The bottom and top temperature of each cell was measured individually and repeatedly. Analytical grade chemicals were used without further purification. Except for some of the $LiNO_3-AgNO_3$ experiments, the chemical analysis was done with a

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[9] J.-E. Olsson and A. Lundén, unpublished.

[10] K. Wallin and A. Lundén, unpublished.

Perkin-Elmers model 303 atomic absorption spectrophotometer.

The Soret coefficient, σ, is calculated from the formula

$$\sigma = D'/D = \frac{1}{N_{\mathrm{T}}(1-N_{\mathrm{T}})} \cdot \frac{(N_{\mathrm{T}}-N_{\mathrm{B}})}{(t_{\mathrm{T}}-t_{\mathrm{B}})} \quad (1)$$

where N is the mole fraction of the alkali nitrate and t is the temperature, with subscripts T and B referring to the top and bottom, respectively. With this definition the Soret coefficient becomes positive, when $AgNO_3$ is enriched at the cold side. The Soret coefficient is to be considered as a purely phenomenological quantity, corresponding to the ratio between the coefficient of thermal diffusion, D', and the ordinary diffusion coefficient, D (see e. g. cit. [11]). The measured separation, and thus the calculated σ, might be influenced by a number of disturbances, which will be discussed below. If convection occurs during the experiment, the effective diffusion coefficient D_{eff} becomes larger than D, i. e. the measured Soret coefficients become systematically too low. Although it is tedious in practice, this disturbance is in principle detectable by making a number of experiments of short duration in order to see whether the measured characteristic time becomes lower than that estimated as $\Theta = 4\, d^2/\pi^2 D$ (l. c. [5]), where d is the distance, about 35 mm, over which we have a temperature gradient. (It is assumed that the salt volume at the top of the cell is so large that the change in N_{T} is negligible.) For most of our experiments the duration was about 120 hours, i. e. of the order of Θ estimated for 200 °C and $2\,\Theta$ at our highest temperatures. It can thus be argued that the duration of our experiments should have been longer, but we wanted to reduce the possible influence of thermal decomposition upon our experiments.

For the interpretation of the experiments it is instructive to consider the possible sources of disturbance:

1. Convection will occur if there is a horizontal temperature gradient within the cell. Such a gradient might be present in the upper part of the cell, where heat is transferred both by radiation from the upper metal plate of the furnace and by (unsymmetrical) direct contact between the glass cell and the metal plate. Although it is difficult to estimate the magnitude of the convection caused by inhomogenities in the horizontal temperature distribution, we believe that its contribution is small in our experimental arrangement [12].

2. Another source of convection is the density variations that follow the inevitable temperature fluctuations during the experiment [13]. However, an estimation shows that this contribution to D_{eff} is negligible in our experiments.

3. Nordén and Lodding have recently estimated the mixing that occurs during the quenching and solidification of a melt in a capillary [14]. The latter contribution is proportional to the volume change on solidification, which in our case is strongly dependent on the composition of the mixture; for the pure alkali nitrates it covers the range from 21.4% ($LiNO_3$) to −0.23% ($RbNO_3$) (l. c. [15]). According to this estimation the mixing that takes place is proportional to the radius of the cell tube and inversely proportional to the square root of the time it takes to cool and solidify. In experiments of our type, it might be expected that about half the obtained separation can be lost due to an inappropriate quenching technique [16]. We preferred to isolate from each other the two parts that were to be analysed, by blowing an air stream against the cell near the positions where we intended to cut the cell afterwards [3].

4. A certain fractionation of the components of a mixture occurs during the solidification, and if the cooling is slow, this can cause a great difference in composition between the salt in different parts of the cell. Thus for this reason rapid quenching is preferable, while the opposite was the case for the disturbance discussed above.

5. Nagaura and Sasaki claim to have found that gravitation caused an enrichment of the heavy component in the bottom of a vertical cell [2], and they preferred to use a horizontal cell. However, it is reason to doubt their interpretation, since estimations

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[11] H. J. V. Tyrrell, Diffusion and Heat Flow in Liquids, Butterworths, London 1961, p. 43.

[12] The effect of convection on the steady state has been estimated for aqueous solutions in cells of a geometry different from ours; J. N. Agar and J. C. R. Turner, Proc. Roy. Soc. London A, **255**, 307 [1960].

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[15] H. Schinke and F. Sauerwald, Z. Anorg. Allg. Chem. **304**, 25 [1960].

[16] When using a long capillary technique for self-diffusion measurements, L. E. Wallin, Z. Naturforschg. **17a**, 191 [1962], estimated the displacement that occured during a slow cooling of the melt.

under reasonable assumptions show clearly that gravitation effects should be negligible for "particles" of the size of the ions in a molten salt.

6. Although thermal diffusion normally causes an enrichment of the heavy component at the cold side, the opposite occurs in some cases, which might lead to a higher density at the hot than at the cold side, and thus to convection in the cell, cf. our previous discussion of the forgotten effect [6]. However, due to the decrease of the corresponding pure salt densities with increasing temperature, a certain enrichment of $AgNO_3$ in the upper part of our cells should be permissible, and Soret coefficients of the order of 10^{-3} degr.$^{-1}$ in either direction are, in principle, measurable.

7. Thermal decomposition of either or both components can give spurious results. We first intended to use metal cells, but since a considerable decomposition of $AgNO_3$ occured in them, we used glass cells for all the experiments reported here.

8. The separation will be suppressed if gas bubbles (decomposition products or due to a bad filling procedure) are trapped in the cell.

Of the disturbances dicussed above, No. 4 (and 5) would give a greater separation than due to thermal diffusion, while it is reduced by Nos. 1, 2, 3, 6 and 8. (No. 7 might cause errors in either direction.) Summarizing, if systematical errors exist, it is likely that the measured Soret coefficient is lower than the true one. Most of our cells had a diameter of 2.6 mm, but we also used some 1.6 mm cells. Since there was no detectable difference between the results obtained with the two types of cells, this is an indication that the disturbances $1-3$, which all increase with increasing cell diameter, are negligible in comparison with the spread in results that is expected from the inaccuracy of the chemical analysis.

Measurements with a convection cell (Thermogravitational column)

In addition to the previous measurements on $LiNO_3-AgNO_3$ mixtures [6], two more experiments have been made with a convection cell [8]. The performance of such cells has been treated theoretically by several authors, see e. g. cit. [17], whereby a number of simplifications are used. Thus it is assumed that the viscosity (η), diffusion coefficient (D), coefficient of thermal expansion (β) and Soret coefficient (σ) all are independent of both temperature (T) and concentration, and that the density (ϱ) is a linear function of the concentration. It is a common practice to use a "mass fixed frame of reference" when deriving the formulas [17], and the concentrations are expressed as mass fractions (w). Furthermore, vertical diffusion is neglected in comparison with the flow due to convection, and the calculations are usually made under the assumption that the upper and lower reservoirs have equal volumes. The obtained formulas for the concentrations at the top and the bottom of the cell as a function of the time are awkward to use, but they can be simplified for the limiting cases of short or long running times. Thus, in the early stages the changes in concentration should be a linear function of time, and the Soret coefficient can be calculated from the proportionality constant. However, in practice this method to determine σ requires a frequent taking of samples followed by an analysis with sufficient accuracy to detect small concentration changes. For the other limiting case, the steady state, the relation between a parameter A^* and the concentrations w_U, w_L and w_0 (the subscripts standing for upper, lower and initial, respectively) can be approximated in different ways [17]. Thus for dilute solutions we obtain

$$w_U/w_L = \exp(2\,A^*) \tag{2}$$

or if we introduce the separation factor, Q, which is most commonly used for isotope enrichment experiments [3]

$$Q = \frac{w_U(1-w_L)}{w_L(1-w_U)} = \exp(2\,A^*)\,. \tag{2 a}$$

For more concentrated solutions the simplest expressions are obtained when using the tangential approximation [17]:

$$\frac{w_U}{w_0} = 1 - \frac{1-w_0}{1-2\,w_0}\,\frac{\varrho_L}{\bar{\varrho}}\tanh(1-2\,w_0)\,A^*\,, \tag{3 a}$$

$$\frac{w_L}{w_0} = 1 + \frac{1-w_0}{1-2\,w_0}\,\frac{\varrho_U}{\bar{\varrho}}\tanh(1-2\,w_0)\,A^* \tag{3 b}$$

with $\bar{\varrho} = \frac{1}{2}(\varrho_U + \varrho_L)$.

The coefficient of thermal diffusion (D') can now be calculated:

$$D' = \frac{A^*\,\beta\,\varrho\,g\,a^4}{252\,\eta\,h} \tag{4}$$

where a = plate separation, g = gravitational acceleration and h = height of diffusion cell. The results are often expressed in terms of the Soret coefficient $\sigma = D'/D$.

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[17] Ref. [11], p. 205.

The accuracy of the obtained coefficients of thermal diffusion is of course affected by the numerous approximations made in the derivation of the formulas, but it is to be expected that the experimental sources of error are at least as important, and the results with this method should always be considered as semiquantitive. Either when working with liquids or gases, a serious problem is that parasitic circulating loops can develop in a thermogravitational column, thus reducing the separation below what predicted by theory. Such deviations from the theoretical circulation pattern might be caused by existing inhomogenities in the temperature distribution and the plate separation, a. Since the latter parameter appears as a^4 in Eq. (4) the difficulties associated with the determination of the plate separation might well alone introduce an error exceeding a factor of two in the calculated coefficient of thermal diffusion. When applying Eq. (4) to our results, η, β, ϱ and D were calculated from pure salt data [18, 19] under the assumption of a linear dependence upon composition [20].

Alkali	initial conc. mole-%	Temperature top °C	Temperature bottom °C	Number of cells considered	Number of cells excluded	Soret coeff. $\sigma \cdot 10^3$ degr.$^{-1}$
Li	5	249	222	7	1	5.5 ± 0.9
	10	248	223	7	1	5.5 ± 0.7
	23	284	194	4		2.3 ± 0.4
	25	290	267	1	2	3.1
	60	285	220	4		2.0 ± 0.2
	60	322	261	2	2	2.1 ± 0.1
K	10	339	264	10		1.4 ± 0.2
	20	312	196	8		1.7 ± 0.2
	30	304	194	8		2.4 ± 0.5
	39	282	192	4	1	1.7 ± 0.2
	45	298	192	4		1.4 ± 0.2
	60	339	262	4		0.7 ± 0.1
Rb	10	332	258	3	1	1.2 ± 0.1
	34	297	185	5		1.1 ± 0.2
	40	302	194	2	2	1.1 ± 0.1
	45	307	178	2		1.5 ± 0.5
	64	305	179	1	1	1.4
	80	343	265	2	2	1.4 ± 0.3
Cs	17.5	291	191	3		1.3 ± 0.2
	32.5	284	187	2	1	1.1 ± 0.3

Table 1. Investigation of the elementary effect with cells having a vertical temperature gradient. The quoted errors are standard deviations of the mean.

Alkali ion	Alkali mole-%	Plate separation mm	Temperature high °C	Temperature low °C	Soret coefficient Cations $\sigma \cdot 10^3$	Soret coefficient Alkali isotopes $\sigma \cdot 10^5$
Li	20	0.57	313	257	0.7	4.0
	40	0.64	310	252	3.3	2.0
	40	0.57	328	270	1.6	1.1
	60	0.57	316	278	1.4	3.8
	80	0.57	317	272	0.9	3.8
	80	0.45	315	276	0.9	0.8
K	39	0.49	225	202	2.0	4.5

Table 2. Experiments with convection cell. The temperatures at the salt-metal interfaces are estimated, cf. cit. [6].

Results and discussion

The results obtained with elementary effect cells are summarized in Table 1 and those with convection cells in Table 2. In the former case 83 measurements are considered [21], while 14 were excluded since they deviated significantly from those considered. Of the excluded ones, only three were much (more than a factor of two) higher than the accepted ones, while thus eleven were very low or even of the opposite sign. This unsymmetry of the deviations might be taken as an indication of the importance of large errors in the analysis relative to the systematical errors discussed above [21]. For the convection cells the Soret coefficient listed in Table 2 is the average of calculations using the tangential approximation for the top and bottom part respectively, cf. Eq. (3). The results obtained by (3 a) and (3 b) showed fair agreement for some of the cells, while for one cell (cell with $a = 0.64$ mm), the results for the two cases deviated by as much as a factor of five. It is difficult to say to what extent the deviations between (3 a) and (3 b) calculations are due to errors in the chemical analysis, differences between compartment volumes or parasitic convection loops. For all cells a calculation was also made with Eq. (2 a), and although its basic assumption of dilute solutions were not fulfilled, the results with (2 a) differed only a few percent from the average

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[18] G. J. Janz, A. T. Ward and R. D. Reeves, Molten Salt Data (U.S.-AFOSR No. 64-0039); Rensselaer Polytechnic Institute Technical Bulletin Series, Troy, N.Y. 1964.

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

[20] When evaluating isotope separations the corresponding cation diffusion coefficient of the pure salt was used.

[21] For the experiments with 10−30% KNO_3 the samples from each cell were analysed at 2 or 3 different occasions, while we normally only made one analysis per cell. However, in cases where strongly deviating results were obtained, these could normally be confirmed by a second analysis, when it was possible to make one.

of (3 a) and (3 b). Thus we conclude that it is sufficient to use the simpler Eq. (2 a) for molten salt mixtures at all concentrations, since the obtained Soret coefficients are, anyhow, only to be considered as semi-quantitative, at best. Eq. (2 a) was also used to evaluate the isotope effects for lithium and potassium.

Although it is to be remembered that, as shown above, existing systematic errors would tend to give too low Soret coefficients for both types of cells, the fair agreement between the two methods justifies considering the accuracy of the results as being better than 50%, with a possible exception for the $LiNO_3 - AgNO_3$ system. For three of the investigated systems wide concentration ranges are covered, cf. Fig. 1, where the temperature ranges of the experiments are plotted in the phase diagrams of the systems.

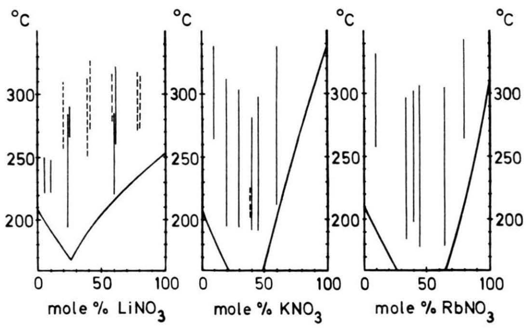

Fig. 1. Phase diagrams of the systems $AgNO_3-LiNO_3$, $AgNO_3-KNO_3$ and $AgNO_3-RbNO_3$ with the temperature ranges of our experiments indicated. The solid lines correspond to measurements of the elementary effect and dashed lines to experiments with a convection cell. Regarding the remaining system $AgNO_3-CsNO_3$, the measurements were made at concentrations corresponding to the two minima of this phase diagram.

Regarding the $LiNO_3 - AgNO_3$ system, the highest Soret coefficients, about 5.5×10^{-3} degr.$^{-1}$. are obtained for the combination of low $LiNO_3$ concentrations and low temperatures, while the Soret coefficient is of the order of 2×10^{-3} degr.$^{-1}$ for the other quoted experiments with higher concentrations and temperatures. Of the elementary effect measurements quoted in Table 1, those at 60% $LiNO_3$ belong to an early investigation [22], in which 52 more cells were analysed. Many of these cells gave Soret coefficients of about 2×10^{-3} degr.$^{-1}$, but there might be reason to suspect that thermal decomposition caused spurious results for at least some of the cells in the old investigation, (negative Soret coefficients were obtained at concentrations where the convection cells gave enrichment of $AgNO_3$ in the "normal" direction) so we find it safest not to draw definite conclusions from our results about possible temperature and concentration dependences in the system $LiNO_3 - AgNO_3$.

For the system $KNO_3 - AgNO_3$ the Soret coefficient obtained at 60%, seems to deviate significantly from the values obtained at lower concentrations. The temperature range covered at 60% was the same as at 10%, while the concentrations 20 – 45%, for which the Soret coefficients do not differ significantly from an average value of 1.8×10^{-3} degr.$^{-1}$, were investigated at lower temperatures. From this it might seem more plausible to suggest the existence of a concentration rather than a temperature effect.

For $RbNO_3 - AgNO_3$ the results over the whole concentration range 10 – 80% fit well with an average of 1.3×10^{-3} degr.$^{-1}$, and also the results for the $CsNO_3 - AgNO_3$ system fall near this value for the Soret coefficient.

The main reason to measure isotope effects in the present investigation is that this gives a possibility to establish the direction of the elementary effect in a convection cell [6]. However, it is worth noting that the obtained Soret coefficients for $^6Li - ^7Li$ and $^{39}K - ^{41}K$ are in agreement with previous studies of isotope effects in pure $LiNO_3$ and KNO_3 (l. c. [5]).

Summarizing, the present investigation gives the required information on the order of magnitude for thermal diffusion in alkali nitrate – silver nitrate mixtures. When comparing the investigated systems, the Soret coefficient tends to decrease with increasing mass of the alkali cation, which might be expected. However, it should be remembered that the mass of a Cs^+ ion is greater than that of an Ag^+ ion, while on the other hand only Li^+ (and Na^+) ions have a smaller radius than Ag^+. If a "density" (proportional to the mass divided by the cube of the ionic radius) is calculated, this entity becomes about twice as high for Ag^+ as for the alkali ions, while

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[22] In this investigation the chemical analysis was done gravimetrically, i. e. AgCl was precipitated and the filtrate was converted to Li_2SO_4. In order to obtain a sufficient amount of salt for the samples, the bottom of the tube was widened to a bulb. In most of these experiments the top temperature was about 320 °C. The durations were chosen over a wide range, up to 765 hours.

there is no systematics regarding the "densities" of the alkali ions [23]. When interpreting our results for solid sulfates with a fcc structure [9], the possibility of a correlation between thermal diffusion and ionic mobility will be discussed. However, comparisons between available data on electric conductivities of molten nitrates and our results suggest that the transport mechanism can be different in an electrical and a thermal gradient. Regarding thermal diffusion, the present experiments indicate that concentration or temperature effects probably exist in at least some nitrate systems, but the definite establishment of such effects with the methods used in the present investigation would be very laborious, and it is our hope that other methods can be developed that are more suitable for a detailed study of thermal diffusion in molten salts.

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[23] The estimated ionic radii refer to solid halides, but their use in the discusion of other solids as well as of melts is generally accepted. There are considerable differences between the sets of ionic radii obtained by different authors, cf. M. P. Tosi, Solid State Phys. **16**, 1 [1964].