For polycrystalline monoclinic lithium sulphate a constant coefficient of thermal expansion, $(22 \pm 1) \times 10^{-6}$ degr.$^{-1}$, is obtained over the range $200-550$ °C, and it appears as if the coefficient might be slightly lower in the region between 200 °C and room temperature. The thermal expansion of monoclinic lithium sulphate has been estimated previously by Pistorius[6], who measured the powder diffraction pattern at 500 °C. From a comparison with the somewhat inaccurate room-temperature values of the unit-cell constants, he concluded that the thermal expansion takes place mainly along the c-axis. The difference between the quoted unit cell volumes at 500 °C and room temperature corresponds to an average coefficient of (linear) thermal expansion of 39×10^{-6} degr.$^{-1}$, which is higher than our result given above.

For cubic lithium sulphate the contraction measurements give a coefficient of thermal expansion of $(43 \pm 3) \times 10^{-6}$ degr.$^{-1}$ for the range $600-750$ °C. This coefficient of thermal expansion can be used to recalculate the above mentioned activation energy of the equivalent conductivity. For the entity ΛT (product of conductivity and absolute temperature) the activation energy is now obtained as

$$Q_{\Lambda T} = 10\,360 \pm 700 \text{ cal/equiv.},$$

which is about 2% higher than the published value[2].

From the present experiments the volume change at the transition point is estimated to 4.2%. This corresponds to a volume change,

$$\Delta V_{\mathrm{tr}} = 2.2 \text{ cm}^3\text{/mole}.$$

This result is in good agreement with the volume change Pistorius calculates from the pressure-temperature curve and the heat of reaction by applying the Clausius-Clapeyron relation (2.2 ± 1 cm^3/mole), while the obtains 0.9 ± 0.6 cm^3/mole from the unit cell volumes measured by high-temperature X-ray diffractometry[6].

We are indebted to Dr. A. Lundén for helpful discussions during this investigation. This work was financially supported by “Ollie och Elof Ericssons stiftelse”.

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[6] C. W. F. T. Pistorius, Z. Phys. Chem. NF **28**, 262 [1961].

A Plane Source Method for Measuring Interdiffusion Coefficients of Transparent Liquids

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A bottom layer diffusion technique is described, where an experiment is initiated by dropping a crystal of the diffusing substance to the bottom of a properly designed container for the liquid. It is shown that this technique is comparable to any other method from point of view of accuracy while the experimental procedure is extremely simple. The technique is tested at room temperature on two aqueous solutions with widely different diffusion coefficients. It is also applied to the determination of the interdiffusion coefficient of the silver ion in the three molten salts: sodium, potassium, and rubidium nitrate.

Optical methods have proved to be very useful in the study of liquid diffusion at room temperature because of their accuracy and the possibility to follow the process for a long period of time. The great amount of information which can be obtained from one particular experiment contributes to an important check of the internal consistency of the data which is necessary if the presence of convective motions in the liquid is to be ruled out. Since the problem of using optical techniques at high temperatures has been solved[1, 2], it seems to be a rather straightforward application to measure interdiffusion coefficients of transparent liquids. This would, however, be a very difficult technical problem if one would try to use any of the conventional “draw-slide”, “sliding-solvent”, or “flowing-junction” cells in order to approximate the initial condition of a sharp interface in an infinite medium[3]. A procedure which ought to be more attractive is the one described by Ljunggren and Lamm[4] who injected a concentrated

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[1] L. W. Wendelöv, L.-E. Wallin, and S. E. Gustafsson, Z. Naturforsch. **22 a**, 1180 [1967].

[2] S. E. Gustafsson, N.-O. Halling, and R. A. E. Kjellander, Z. Naturforsch. **23 a**, 44 [1968].

[3] O. Bryngdahl, Acta Chem. Scand. **12**, 684 [1958].

[4] S. Ljunggren and O. Lamm, Acta Chem. Scand. **11**, 340 [1957].

solution at the bottom of a cell and thereby created an initial condition which resembles bottom layer diffusion. No matter which experimental procedure is used we must realize that there is an unwanted departure from ideal conditions in the liquid at the start of the diffusion experiment. This is usually taken care of by some kind of zero time correction. A detailed mathematical consideration of various initial conditions and their importance in plane source diffusion experiments is given elsewhere[5]. Because of the possibility to correct for even a rather serious disturbance at the start of the experiment as long as all the diffusing material is concentrated in a thin layer at the bottom it is possible simply to drop a crystal of the diffusing substance to the bottom of the cell, where it dissolves and starts diffusing into the solvent above. This procedure requires of course that the density of the crystal is so much higher than that of the liquid that the amount of material being dissolved before the crystal reaches the bottom is negligible.

In our experiments with potassium chloride and cadmium sulphate diffusing in water and silver ions diffusing in different alkali nitrates we have learned that by a proper choice of the crystal size the disturbance at the start is so small that it is completely covered by he experimental uncertainty in the determination of the diffusion coefficient from the interferograms. When an optical method is used to record the concentration distribution the starting conditions can be checked very carefully and it turned out that when in a few cases a very small amount of material was left behind the falling crystal in the liquid, it reached the bottom in a few seconds because of the higher density of this concentrated liquid. Due to the extremely simple experimental procedure we beleave that this is an ideal technique in routine analyses especially at high temperatures, where the simplicity is particularly important.

Theory of the Method

In order to understand the interferograms we must calculate the optical path of a light beam traversing the cell at an arbitrary level x.

Ljunggren and Lamm assumed that as soon as the concentrated solution was ejected in the cell, all the diffusing material was instantaneously distributed to form a thin layer at the bottom of the cell at zero time. This assumption enabled them to use the simple plane source solution of Fick's second law to describe the concentration distribution. Their assumption may be very justified but since the optical path

$$R(x,t) = \int_0^L \mu \, \mathrm{d}z \qquad (1)$$

is obtained by integrating the refractive index μ over the length L of the cell in the direction z of the optical axis, a rapid distribution of the material along the optical axis is not even necessary for the mentioned plane source solution at a level x, multiplied by L and $\partial\mu/\partial c$, to represent $R(x,t) - R(x,0)$. The only indispensable condition is that the time t_0 at which the injected material has dissolved and spread perpendicular to the optical axis is small compared with the time t at which the optical path is recorded. If this condition is fulfillled, one has

$$R(x,t) = \mu_0 L + (\partial\mu/\partial c)\, M (\pi D t)^{-\frac{1}{2}} \cdot \exp(-x^2/4\,D\,t) \qquad (2)$$

where μ is taken to be

$$\mu = \mu_0 + (\partial\mu/\partial c)\, c$$

with constant concentration dependence $(\partial\mu/\partial c)$, and where M is the total amount of solute supplied to the bottom divided by the cell width.

In order to investigate how the diffusing substance was distributed over the bottom, we dropped a crystal into a very wide cell and followed the process from the very beginning. It turned out that the substance spread over a large area of the bottom (about 7 cm^2 when using a 5 mg crystal) befor the diffusion became the dominating process. This observation shows that if the cell is made sufficiently narrow the amount of material per unit length across the cell is constant, which is a necessary condition for Eq. (2) to hold. We designed cells with two different cross sections, A: 50×5 mm^2 and B: 40×3 mm^2, which both turned out to work very well. The larger dimension was oriented along the optical axis.

For the experiments we have been using a wave-front-shearing interferometer[6] which has proven to be a very reliable and versatile tool to record optical path differences. If b is the shear of the wave-fronts

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[5] L.-E. Wallin and S. E. Gustafsson, to be published.

[6] E. Ingelstam, Ark. Fys. **9**, 197 [1954].

in the cell plane, we get the path difference

$$\Delta R = R(x+b/2,t) - R(x-b/2,t)$$
$$=(\partial\mu/\partial c)\, M(\pi D t)^{-\frac{1}{2}} \cdot \{\exp[-(x+b/2)^2/4Dt] - \exp[-(x-b/2)^2/4Dt]\}\,. \qquad (4)$$

When calculating the diffusion coefficient we have used the fact that ΔR has the same value for two fringes, which are symmetrically located relative to the minimum (cf. Fig. 1). This gives

$$D t[{}_{10}\log \sinh(b\, x_i/4Dt) - {}_{10}\log \sinh(b\, x_j/4Dt)] - 0.10857\,(x_i^2 - x_j^2) = 0 \qquad (5)$$

where i and j denote the two fringes. The calculation of he diffusion coefficient must here be done by iteration. If we choose a small shear and disregard the early interferograms when the gradient is comparatively high we can get a good approximation by assuming that $\partial R/\partial x = \Delta R/b$. Using the same fringes as above we get

$$D = 0.10857\,(x_i^2 - x_j^2)/[t \cdot {}_{10}\log(x_i/x_j)]\,. \qquad (6)$$

In our measurements Eqs. (5) and (6) have given D-values within one percent from each other. If some other way of combining the fringes is used, the equations will take a slightly different form.

We have here shown that it is possible to determine the diffusion coefficient knowing the positions of two fringes and the time from the start of the experiment. It is also obvious that we can obtain $(\partial\mu/\partial c)$ if the wave-length of the light (λ) and the total amount of diffusing substance per unit length (M) are known. Using Eq. (4) we get

$$(\partial\mu/\partial c) = k\,\lambda(\pi D t)^{\frac{1}{2}} \cdot M^{-1}\{\exp[-(x_j+b/2)^2/4Dt] - \exp[-(x_j-b/2)^2/4Dt] - \exp[-(x_{j+k}+b/2)^2/4Dt] + \exp[-(x_{j+k}-b/2)^2/4Dt]\}^{-1} \qquad (7)$$

where k is an arbitrary integer depending upon the choice of the fringe pairs, which are assumed to be situated on the same side of the minimum of the ΔR-function (cf. Fig. 1).

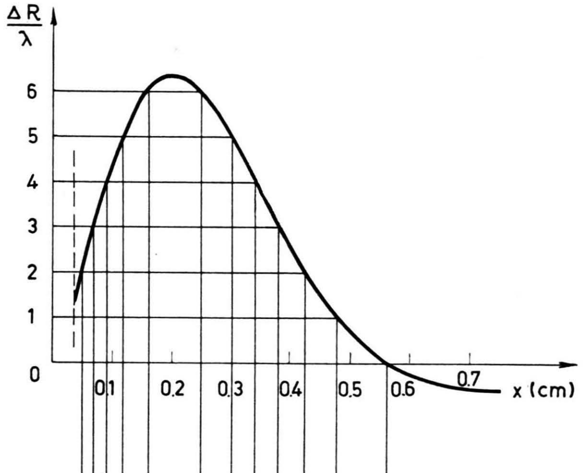

Fig. 1. The optical path difference as a function of the x-coordinate with the resulting interferogram below. The shear is taken to be 0.07 cm and $D \cdot t$ to be 2×10^{-2} cm^2. A possible linear gradient introduced by the optical system, giving a vertical displacement of the curve, is also indicated.

Experimental

A detailed description of the furnace, the interferometer, the temperature recording, and the purity of the salts is given elsewhere [2, 7].

The cells were made of stainless steel with hand lapped end surfaces in order to ensure no leakage during the diffusion. The height of both cells was over 22 mm, so that the diffusion could be considered to proceed in a semi-infinite medium for a long time.

When preparing the silver nitrate crystals we used salt that was premelted in order to get solid crystals of well defined shape without trapped air or moisture. This would escape as gas bubbles when the crystal reaches the bottom and disturbe the starting conditions. The mass of the crystals, which proved not to be very critical, was in these experiments varied between 2 and 10 mg.

Results and Discussion

In the theoretical part we assumed that the concentration could be considered independent of the horizontal transverse coordinate, if the cell is sufficiently narrow. This assumption can be checked directly by looking at the fringes, which otherwise would show a curvature. As can be seen from the interferograms of Fig. 2 the fringes are perfectly straight although the cell in this particular case was 0.5 cm wide. As a matter of fact the fringes become perfectly straight within about one minute after the start of an experiment or almost as soon as the

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[7] L. W. Wendelöv, S. E. Gustafsson, N.-O. Halling, and R. A. E. Kjellander, Z. Naturforsch. **22 a**, 1363 [1967].

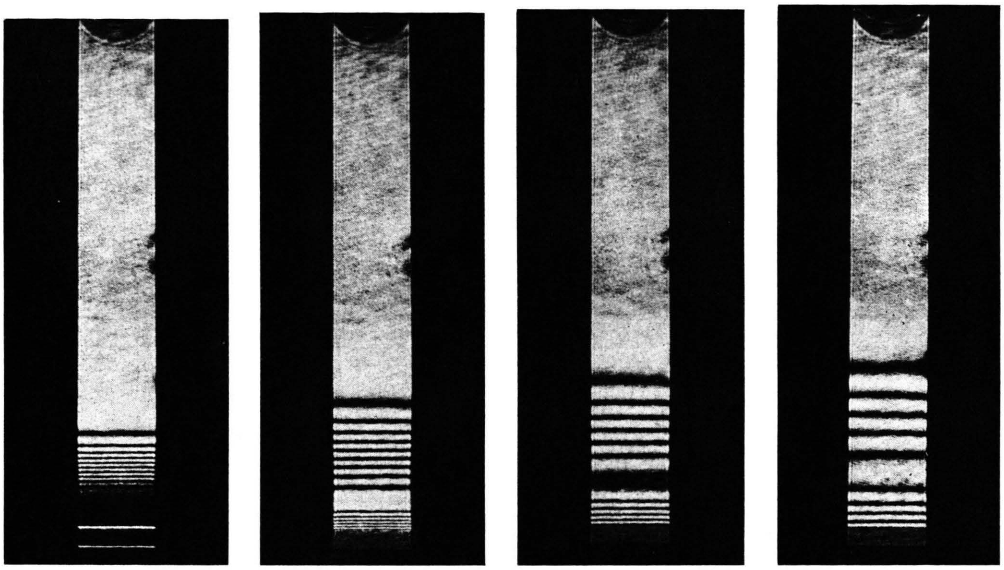

Fig. 2. Interferograms recorded at four different times of an experiment where the silver ion is diffusing into sodium nitrate at a temperature of 316.1 °C. The cell width is 0.514 cm, the shear 0.07 cm, and the mass of the crystal 3.34 mg.

crystal is dissolved. This shows that the assumption is well justified.

A different kind of curvature of the fringes can be observed if convection is created in the cell, for instance by an unwanted temperature gradient. In this case the fringes are bending irregularly and are neither straight nor stably curved. The absence of curvature can actually be used as a very good indication that convection does not disturbe the process. Because of the possibility to observe the whole experiment visually or to record it photographically, this is an important feature of the optical techniques at high temperatures.

In Table 1 we have given the results from a number of separate experiments at room temperature, which show both the accuracy and the reproducibility of this "dropped crystal technique". The $CdSO_4$ experiments were performed with cell A and the KCl experiments with cell B. In Table 2 the results of a series of measurements on three molten salt systems are presented. Here we have also given the results from a few measurements at approximately the same temperature in order to show that the technique works with the same reproducibility in both temperature ranges. Including all our measurements we get an average of the mean deviations which amounts to 1.6 precent, which compares very favourably with the errors from any other experimental technique. There is some difference in the mean deviations between the values of the potassium nitrate and the rubidium nitrate systems. This is probably due to the fact that we worked with slightly less shear, 0.07 cm, in the first case compared with 0.11 cm in the second one, which prevented us from following the diffusion over the same extended period of time in the first case. The values given for the sodium nitrate system are averages of a number of measurements at five predetermined temperatures.

Temperature °C	Concentration mole/liter	Diffusion coefficient $\times 10^5$ cm²/s Measured	Lit.[8,9]	Deviation %
		$CdSO_4$ in H_2O		
22.0	0.02	0.576	0.575	+ 0.2
22.0	0.02	0.570	0.575	− 0.9
22.0	0.02	0.588	0.575	+ 2.2
		KCl in H_2O		
21.6	0.06	1.643	1.697	− 3.2
21.6	0.06	1.640	1.697	− 3.4
21.7	0.06	1.712	1.701	+ 0.6

Table 1. Diffusion coefficients of two electrolyte solutions at room temperature. The concentration is estimated at $x=\sqrt{2\,D\,t}=0.5$ cm (inflexion point of concentration curve).

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[8] L. G. LONGSWORTH, in: The Structure of Electrolytic Solutions, W. J. HAMER, Ed., John Wiley & Sons, Inc., New York, N.Y., 1959.

[9] H. S. HARNED and R. L. NUTTALL, J. Am. Chem. Soc. **71,** 1460 [1949].

	Temperature °C	Diffusion coefficient $\times 10^5$ cm^2/s
$AgNO_3-NaNO_3$	313.4	2.01
	319.2	2.03
	332.4	2.21
	355.0	2.69
	382.8	3.32
$AgNO_3-KNO_3$	341.8	1.94
	342.0	1.78
	351.6	1.94
	352.6	2.10
	367.9	2.38
	368.3	2.39
	368.5	2.49
	378.0	2.53
	378.2	2.46
$AgNO_3-RbNO_3$	323.3	1.48
	323.3	1.50
	332.2	1.62
	332.5	1.68
	345.4	1.87
	345.8	1.89
	353.4	1.95
	353.4	1.97
	365.0	2.12

Table 2. Diffusion coefficients of silver ions in three molten alkali nitrates.

Unfortunately there are very few interdiffusion coefficients of molten salts available and the agreement between different determinations is sometimes very poor. This can be seen from Table 3 where we have made a comparison between our results and previously published diffusion coefficients. Evidently new and reliable techniques for this kind of measurements are needed. We feel that this work is a contribution to the accomplishment of this end.

Temperature °C	Diffusion coefficient $\times 10^5$ cm^2/s This work	Literature	Reference
320	2.05	1.28	10
310	1.89	1.93	11
310	1.89	1.96	12

Table 3. A comparison between the present determination of the diffusion coefficient of the silver ion in sodium nitrate and previously published values.

Solvent	Conventional calculation $D_0 \times 10^3$ cm^2/s	Q cal/mole	Modified calculation $D_0 \times 10^3$ cm^2/s	Q cal/mole	Standard deviation of the Q-value cal/mole
$NaNO_3$	2.59	5690	2.82	5800	340
KNO_3	5.76	7010	5.02	6830	800
$RbNO_3$	3.92	6590	3.46	6440	340

Table 4. The activation energies (Q) for silver ions diffusing in three different alkali nitrates calculated from the fromula $D=D_0 \cdot \exp(-Q/R\,T)$.

In Table 4 the activation energies Q (assuming an Arrhenius equation) are given together with the probable errors. Because of the tendency of thermal decomposition of silver nitrate we had to restrict the temperature range and therefore got a corresponding uncertainty in the activation energies. Two different estimates are given. In the first one we have used the conventional method of calculating the Q-values by assuming that the $\ln D$-values are normally distributed. This is, however, not generally in agreement with the experimental situation, where rather the D-values themselves are likely to be normally distributed. This is taken care of by assigning a proper weight to the experimental points[13]. If the spread in the measurements is small as in our case, the different ways of calculation do not give very different results. In more unfavourable cases, however, a discrepancy of 5 to 15 precent is not unusual, and as much as 30 percent has been noted.

The concentration dependence of the refractive index $(\partial\mu/\partial c)$ was measured in two series of experiments to show that the equations derived are applicable and give reproducible results. This quantity is of special importance in optical measurements of the thermal diffusion constants. $(\partial\mu/\partial c)$ in the $AgNO_3-NaNO_3$ system was found to be 0.058 cm^3/g and in $AgNO_3-KNO_3$ 0.064 cm^3/g independent of the temperature. It is only necessary to know the wave length and the total amount of material per unit length (M), cf. Eq. (7). The width can be measured directly on the interferograms if the magnification is known. It is not possible to increase the optical path by extending the cell along the optical axis as long as the width and the amount of material is kept constant. A too short cell is, however, not desirable because of the higher concentration differences within the cell.

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[11] C. E. Thalmayer, S. Bruckenstein, and D. M. Gruen, J. Inorg. Nucl. Chem. **26**, 347 [1964].

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The measuring technique for diffusion coefficients which is outlined in this work is beleaved to be very suitable for routine analyses of many binary systems. It is of course necessary that $(\partial\mu/\partial c)$ is not too small as in most isotopic mixtures. If the "dropped crystal technique" cannot be used it may be possible to design an apparatus where the diffusing substance is transferred by other means to the bottom of the cell even at high temperatures.

Acknowledgement

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On Noble Gas Anomalies in the Great Namaqualand Troilite

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The abundances and isotopic composition of the stable noble gases were measured in a troilite nodule from the Great Namaqualand fine octahedrite. Helium, neon and argon show a significant spallation component. The major anomalies in krypton and xenon are from neutron capture on selenium and tellurium and from the decay of extinct I^{129}. The abundances of tellurium, iodine and uranium in the troilite were determined by neutron activation analyses and compared with the xenon anomalies. The results indicate that part of the excess Xe^{129} is from neutron capture on tellurium and the remainder is due to the retention of radiogenic Xe^{129} from the decay of extinct I^{129}, about 200 million years after an initial $I^{129}/I^{127} = 3 \times 10^{-3}$.

Although there have been many reports on the isotopic composition of the heavy noble gases in stone meteorites, relatively few studies have been reported on the abundances of the heavy noble gas isotopes in iron meteorites. Reynolds [1] reported the abundances of four xenon isotopes in Sardis troilite and three xenon isotopes in Sardis iron. Only recently have complete xenon and krypton spectra been reported for two iron meteorites; Costilla Peak iron [2] and Canyon Diablo graphite [3].

The isotopic anomalies observed in these two samples showed remarkably few similarities. Both the xenon and krypton spectra in Costilla Peak were characterized by a large spallation component. Radiogenic Xe^{129} could not be positively identified, but an upper limit of 2.2×10^{-13} cc STP radiogenic Xe^{129} per gram of Costilla Peak iron was established. In contrast to this the xenon and krypton spectra in Canyon Diablo graphite showed only a small spallation component but contained major anomalies due to neutron capture reactions on bromine and iodine. The amount of radiogenic Xe^{129} in Canyon Diablo graphite, 8.5×10^{-10} cc STP per gram, was greater than had been reported in any stone meteorite except Renazzo and Abee.

The iodine abundance have been measured for both the Sardis troilite [4] and the Canyon Diablo graphite [5]. The ratio of radiogenic Xe^{129} to iodine in the graphite is about 350 times the value of this ratio in the troilite. This suggests that the Canyon Diablo graphite began to retain the gaseous decay product of 17 million year (m. y.) I^{129} about the same time as the chondrites, but almost 150 m. y. before the Sardis troilite.

Due to the scarcity of noble gas data on the iron meteorites and the great differences in the krypton and xenon anomalies in the above-mentioned reports, it was decided to investigate the noble gases and the tellurium, iodine and uranium abundances from a single troilite nodule. The sample used for this study was provided by the museum of the University of Missouri at Rolla.

Hey [6] lists fifteen synonyms which have been used for the Great Namaqualand meteorite. Wasson [7] determined the concentration of Ga and Ge in this meteorite (under the synonym, Gibeon) and classi-

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