The discrepancies between theory and experiment may be ascribed to the neglect of temperature variation of elastic constants and other anharmonic effects. At lower temperature, the discrepancies are attributable to the coarseness of the frequency spectrum and the uncertainty in the electronic contribution to the specific heat. The disagreement is also partly attributable to the approximate description of electron-ion interaction and to the assumption of short range interatomic interaction in the theory. The analyses of phonon dispersion relations on Born-von Kármán force models show that atoms beyond the second neighbour interact appreciably, particularly in niobium.

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Interdiffusion Studies in Molten Alkali Nitrates

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Interdiffusion of anions in fused alkali nitrates has been studied with a plane source diffusion technique; the concentration gradients in the diffusion cell being measured with a wave-front-shearing interferometer. By choosing the same cations in the experiments the diffusional mixing of different anions at low concentrations into three alkali nitrates has been studied. The diffusion coefficients of F^- and Br^- in $LiNO_3$; F^-, Br^-, I^-, CO_3^{2-}, and SO_4^{2-} in $NaNO_3$; and I^- and CO_3^{2-} in $RbNO_3$ were obtained over a temperature range of some 100 °C above the melting point of the different solvents.

A development of experimental procedures has been in progress during the last couple of years, which enables the use of optical interferometry for studying density gradients at temperatures up to 800 °C [1–6]. As a part of this work a new method for studying interdiffusion has been suggested and proved successful. The experimental arrangement has resembled that of a plane diffusion source in a semiinfinite medium or often refered to as bottom layer diffusion. The initial plane source has been obtained by dropping a solid crystal to the bottom of a diffusion vessel containing the solvent. The melting points of the chosen solutes are generally much higher than those of the alkali nitrates used as solvents, which favourably eliminates an eventual partial disintegration of the crystal before reaching the bottom of the container. Because of the large density and refractive index differences between the solvents and solutes it has been possible of work with rather small crystals, which implies a very slight disturbance of the liquid at the beginning of the experiment because of the temperature difference between the solvent and the crystal being dropped from room temperature.

The concentration differences are given for a number of representative experiments in Table 1. The reason why it was possible to work with such low differences is the comparatively large dependence of refractive index on concentration. The dependence being estimated according to a theory given elsewhere [5]. The concentration increase due to the diffusing solute is so small that the diffusion coefficient may be considered as that at infinite dilution.

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Table 1. The concentration dependence of the refractive index $(\partial\mu/\partial c)$ is calculated from the molar refractivities and the densities of the pure components according to a theory suggested in reference [5]. The concentration of the diffusing substance is assumed to be zero in the equations. The mean concentrations $(\langle\bar{c}\rangle)$ are calculated for some typical experiments. The $\langle c\rangle$-values are given for the earliest possible time, which means that the concentration at any point in the cell is lower during most of the experiment. It has not been possible to obtain the necessary information on the molar refractivities for all the binary systems studied.

Diffusing ion	Solvent	Temp. °C	$(\partial\mu/\partial c)$ [cm^3/g]	Mean concentration difference $\langle(\bar{c})\rangle$ mole %
Br^-	$LiNO_3$	258.4	+ 0,06659	0.23
Br^-	$LiNO_3$	307.5	+ 0,06499	0.25
F^-	$NaNO_3$	319.9	− 0.05295	0.09
F^-	$NaNO_3$	374,8	− 0.05194	0.59
Br^-	$NaNO_3$	320.6	+ 0.06358	0.21
Br^-	$NaNO_3$	393.8	+ 0.06298	0.15
SO_4^{2-}	$NaNO_3$	320.5	+ 0.01531	0.18
SO_4^{2-}	$NaNO_3$	374.2	+ 0,01543	0.33

Experimental Procedure

The shearing interferometer consisted of a single Savart plate working in the polarized light from a He−Ne gas laser. The shearing corresponded to a vertical displacement of about 1 mm in the plane of the diffusion vessel. The interferograms where recorded with a Nikon-F camera equipped with an electric feeding system which allowed an automatic triggering of the shutter every second minute. The times between successive exposures were thus controlled by a synchronous motor and a micro-switch. The diffusion chamber measured: 3 mm × 30 mm (parallel with the optical axis) × 22 mm. A very narrow diffusion cell is preferable to prevent convection but at the same time the interference fringes must have a proper extention. Without making any extensive investigation we beleave this cell to be a good compromise. The temperature was controlled within ± 0.2 K during the experiments.

The crystals to be dropped into the diffusion cell were generally obtained by cutting a small piece of the premelted material. This proved to be important in order that the crystal would pass through the solvent as fast as possible.

Results and Discussion

The diffusion coefficients were calculated from the interferograms as described earlier [4, 5]. Our results are summarized in Tables 2 through 6. The probable errors given in Table 5 are calculated from least square fits of $\ln D$ versus T^{-1}. In this calculation the errors of the diffusion coefficients (D) and not the errors of $\ln D$ were assumed to be the same over the entire temperature range. This was done by applying proper weights to the $\ln D$-values at the calculations.

Table 2. Diffusion of Br^- at low concentration in molten $LiNO_3$.

Temp. °C	$D \times 10^5$ [cm^2/s]
258.4	0.44
284.9	0.47
285.4	0.54
307.4	0.73
350.9	0.93
350.9	1.06

When comparing the apparent activation energies of Table 5 with previously published data [5] for systems with common anions, the similarity despite the difference in size of the diffusing ions is surprising. The activation energies for large ions are only some 30 percent higher than those of small ones. There is a slight tendency of increasing activation energies towards higher volumes of the ions, which is seen from the measurements in sodium nitrate. The in-

Table 3. Diffusion of F^-, Br^-, I^-, CO_3^{2-}, and SO_4^{2-} at low concentrations in molten $NaNO_3$.

F^-		Br^-		I^-		CO_3^{2-}		SO_4^{2-}	
Temp. °C	$D \times 10^5$ cm^2/s	Temp. °C	$D \times 10^5$ cm^2/s	Temp. °C	$D \times 10^5$ cm^2/s	Temp. °C	$D \times 10^5$ cm^2/s	Temp. °C	$D \times 10^5$ cm^2/s
319.9	0.54	320.5	1.10	320.1	0.96	320.6	0.42	320.5	0.53
320.6	0.68	320.6	0.96	320.6	1.03	320.6	0.52	320.7	0.36
341.8	0.72	334.8	1.28	341.4	1.32	360.8	0.69	320.7	0.53
342.5	0.87	335.1	1.30	341.6	1.35	361.1	0.66	341.2	0.62
362.1	0.80	361.5	1.38	346.2	1.46	374.9	0.73	341.5	0.59
362.1	0.83	362.1	1.40	346.5	1.34	374.9	0.74	361.0	0.70
374.8	0.92	374.9	1.66	362.2	1.54	—	—	361.1	0.67
374.8	1.07	393.1	1.81	362.7	1.43	—	—	374.2	0.81
—	—	393.8	1.60	362.8	1.41	—	—	374.2	0.82
—	—	—	—	374.8	1.56	—	—	—	—
—	—	—	—	388.4	1.71	—	—	—	—

Table 4. Diffusion of I^- and CO_3^{2-} at low concentrations in molten $RbNO_3$.

I^-		CO_3^{2-}	
Temp. °C	$D \times 10^5$ cm²/s	Temp. °C	$D \times 10^5$ cm²/s
327,7	0.70	327.5	0.33
364.9	0.94	327.8	0.35
395.5	1.21	328.3	0.40
395.5	1.24	363.4	0.51
		364.0	0.52
		395.6	0.60
		395.8	0.62

Table 5. Activation energies of diffusion (kcal/mole) in Arrhenius presentations.

Diffusing ion	$LiNO_3$	$NaNO_3$	$RbNO_3$
F^-	—	6.0 ± 0.9	—
Br^-	6.4 ± 0.5	4.9 ± 0.5	—
I^-	—	5.2 ± 0.5	6.7 ± 0.2
CO_3^{2-}	—	5.9 ± 0.7	6.0 ± 0.5
SO_4^{2-}	—	7.0 ± 1.0	—

fluence of the cations on the diffusion of anions does not appear to be of any particular importance as judged from these measurements. However, the limited temperature range of the measurements, because of thermal decomposition, is a serious difficulty in obtaining precise activation energies for systems containing molten alkali nitrates.

Table 6. Diffusion coefficients (10^{-5} cm²/sec) at the melting points of the solvents.

Diffusing ion	$LiNO_3$	$NaNO_3$	$RbNO_3$
F^-	—	0.58	—
Br^-	0.40	1.00	—
I^-	—	0.99	0.58
CO_3^{2-}	—	0.43	0.32
SO_4^{2-}	—	0.43	

In Table 6 we have given the diffusion coefficients calculated at the melting point of the three solvents. The tendency, if any, among the coefficients is towards lower diffusion rates when the size increases. The diffusion coefficients in sodium nitrate are significantly larger than those in lithium- and rubidium nitrate. In this respect the size of the cation is important. The smallest and largest cation radii give a lower diffusion rate. This may be intelligible from the point of view of "fitting" in the liquid quasi "lattice". The cations may thus work as a "lubricant".

We believe that the kind of measurements which is presented in this work is important primarily because of the possibility to get a more complete picture of the interactions that restrict the diffusion in fused salts, since most of the earlier efforts has been devoted to the study of interdiffusion of two constituents with common anions but different cations. Another important aspect of this work is that the experimental technique using optical interferometry has proved to be a very convenient one for interdiffusion studies in these particular molten salt systems.

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