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simply as convenient ways to express the temperature and pressure coefficients of diffusion.) The results of these calculations are shown in tables 6 and 7. The hard-core repulsion parameters used in the calculations were (in 10^{-10} m): $\sigma_{+-} = 3.0$; $\sigma_{++} = 2.9$; $\sigma_{--} = 3.2$. Similar calculations of friction coefficients for fused alkali halides are reported by Ichikawa and Shimoji,³⁷ but they used pair distribution

TABLE 6.—CALCULATED FRICTION COEFFICIENTS AND DIFFUSION COEFFICIENTS IN FUSED KCl

TIV	pressure/	ζ(H) +-	ζ(Η)	ζ(Η)	$\zeta(S)$	ζ(S) ++	ζ <u>(S)</u>	D+	D_
1043	-0.9	5 61	0.002	0.05	7 34	0.82	0.90	1 04	$(cm^2 s^{-1})$
1043	2.4	6.19	0.001	0.03	8.13	0.79	0.93	0.95	0.95
1306	-0.03	5.06	0.01	0.07	7.58	0.65	0.63	1.35	1.34
1306	1.44	4.95	0.01	0.08	7.86	0.71	0.68	1.33	1.32
1073*	0.0	4.9	1.2	1.1	10.2	2.2	1.4	the state of the s	and the second

* values calculated by Ichikawa and Shimoji.37

functions obtained by resolution of the mean distribution function derived from X-ray diffraction experiments.⁴³ The resolution is subject to considerable uncertainty,⁴⁴ which can lead to significant errors because the $K_{\alpha\beta}$ of eqn (13) and (14) are very sensitive to the shapes of the g(r) curves in the range $r = 2.5 \times 10^{-10}$ m.

TABLE 7.—CALCULATED AND OBSERVED DIFFUSION COEFFICIENTS, ACTIVATION ENERGIES AND ACTIVATION VOLUMES IN FUSED KCI: THE VALUES LISTED ARE FOR ATMOSPHERIC PRESSURE, UNLESS OTHERWISE STATED

T/K	source	$\frac{10^4 D_+}{(cm^2/s)}$	$\frac{10^4 D_{-}}{(cm^2/s)}$	$(\Delta E_D)_+/$ (kJ/mol)	$(\Delta_{ED})_{-}/$ (kJ/mol)	$(\Delta V_D)_+/$ (cm ³ /mol)	$(\Delta V_D)_{-}/(\text{cm}^3/\text{mol})$
1043	expt. 25	0.66	0.59	29	30		0.1 - 1
1043	calc.	1.01	1.01	13	13	2.4	2.4
	(this work)†						
1043	calc. (LVW)*	0.75	0.75	26	26	anne <u>n</u> ste	
1306	expt.25	1.29	1.18	29	30	1/10-3	s to make
1306	calc.	1.35	1.34	13	13	1.3	1.3
	(this work)†						ni kom
1273	calc. (LVW) 40	1.30	1.30	26	26	4.6	4.6
1273	calc. (LVW)*	0.92	0.92			±1.5	+1.5
(p = 8)						second sufficient	
kbar)							

* personal communication, L. V. Woodcock.

† interpolated from the data in table 5, assuming log D to be a linear function of pressure.

Table 6 shows that the hard and soft anion-cation interactions make the main contribution to the friction coefficients, with smaller but significant contributions from the soft anion-anion and cation-cation interactions. A plot (not shown) of the integrand of eqn (14) against r indicates that the integral has converged when $r = 4 \times 10^{-10}$ m, which is consistent with Rice's assertion that the transport properties of fused salts are determined largely by short-range forces.⁴ If the attractive terms in the pair potential are omitted, leaving only the exponential repulsive term in eqn (17), the effect is to reduce the calculated diffusion coefficients by only 4 %. The principal factor determining the transport properties is therefore the shape of the repulsive part of the pair potential. The role of the attractive forces is indirect, in that they determine g(r). Because $\zeta_{++}^{(s)} \approx \zeta_{-}^{(s)}$, and both are an order of magnitude smaller than $\zeta_{+-}^{(s)}$, the calculated D_+ and D_- are practically equal to each other under

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all conditions. The calculated $(\Delta E_D)_+$ and $(\Delta E_D)_-$ are also equal, as is often observed in practice.²⁵ However, the calculated "activation energies" are about one-half of the experimental ones; D_+ and D_- are 50-70 % too high at 1043 K, but only 5-15 % too high at 1306 K. This is consistent with the weakness of eqn (14), which underestimates the negative contributions to the momentum autocorrelation function. This would cause the calculated diffusion coefficient to be too high, but the error would become less serious with decreasing density. For the same reason, the theory should underestimate the reduction in D_+ and D_- as the pressure is increased at constant temperature, i.e., the calculated ΔV_D values are expected to be too small. There are no directly measured experimental values with which they can be compared, but we may use the results from Singer and Woodcock's ionic dynamics calculations for this purpose. These are included in table 7, and are indeed greater than our calculated values. We note that $(\Delta V_D)_+$ and $(\Delta V_D)_-$ are smaller than ΔV_A , which implies that deviations from the Nernst-Einstein equation become greater as the pressure is increased at constant temperature.

THE NERNST-EINSTEIN DEVIATION PARAMETER Δ

The integration in eqn (16) was performed numerically, but satisfactory values of Δ were not obtained. From published values ^{9, 25} of Λ , D_+ and D_- , Δ is found to be +0.22 at the melting point of KCl. Our calculated values are shown below, for various choices of the lower limit of the integral in (16):

$\sigma_{\pm-}/10^{-10} \text{ m}$	3.0	3.1	3.2	3.4	3.6	3.8
Δ	-8.5	-5.5	-3.5	-1.4	-0.49	-0.11

These values have the wrong sign, and are much too high for any reasonable value of σ_{+-} (3.0-3.2 × 10⁻¹⁰ m). This reflects the great sensitivity of the integral of (16) to the form of the pair-potential function. The integrand changes sign from + to - as r increases through the value corresponding to the potential minimum (r_{min}) . For reasonable values of Δ to be obtained, the negative contribution to the integral (for $\sigma < r < r_{\min}$) has to be numerically slightly less than the positive contribution (for $r_{\min} < r < \infty$). For this to be so, r_{\min} must coincide approximately with the first peak in a plot of g(r) against r. For KCl, this occurs at $r = 3.0 \times 10^{-10}$ m. This condition is not fulfilled by the non-coulombic part of the pair potential used here, for which the minimum is at $r = 4.8 \times 10^{-10}$ m. The situation could be rectified by including further attractive terms in the pair potential. If the coulomb term is included, r_{\min} is reduced to 2.7×10^{-10} m, but the integral in (16) then diverges. The inclusion of an r^{-4} term, to allow for ion-induced dipole interactions, would change r_{\min} in the required direction, but such terms are not pairwise additive. The diffusion coefficients, which depend on the second derivative of the pair-potential function, are insensitive to the position of the potential minimum. This integral is determined largely in the range $r = 2.4 \times 10^{-10}$ m, where $(d^2 U/dr^2)$ is always positive. The main factor determining this integral is the repulsive term of the pair potential, and the inclusion or omission of attractive terms is of relatively little significance.

Thus, apart from the difficulty of obtaining a reasonable value of the Nernst-Einstein deviation parameter, the Rice-Allnatt theory provides a satisfactory, semiquantitative account of the conductivity of fused KCl, as a function of temperature and pressure.

SILVER HALIDES

Tables 1 and 2 show that ΔV_{Λ} for AgCl and AgBr is 1.6 and 1.2 cm³/mol respectively, i.e., smaller than the values for the corresponding sodium salts (*ca.* 3 cm³/mol).

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