

where a is the molecular diameter, u is the gas kinetic velocity, γ is a geometric factor of about unity and v_f is the free volume per molecule. v^* is expected to be of similar magnitude as the molecular volume. At constant volume, D is predicted to vary as $T^{\frac{1}{2}}$, i.e., v^* and v_f are functions of density only. This is equivalent to $(\Delta E_D)_V = \frac{1}{2}RT$, and assuming that D and Λ are related by the Nernst-Einstein equation, the corresponding prediction for the equivalent conductivity²⁸ is $(E_\Lambda)_V = -\frac{1}{2}RT$. This is at variance with our results, which indicate that $(E_\Lambda)_V \approx RT$. The free volume theory is also at variance with the work of Alder and Einwohner,²⁶ since it requires a maximum in the free path distribution at a distance $\approx a$. Eqn (9) was also reported to be inconsistent with the experimentally-determined temperature and pressure coefficients of self-diffusion in liquid Ar, Kr, Xe and CH₄.²⁹

COMPARISON WITH THE SMALL STEP-DIFFUSION MODEL OF RICE AND ALLNATT

Rice³⁰ has pointed out that there are fundamental objections to treating transport in dense media by versions of the transition state theory. The small step diffusion theory of Rice and Allnatt^{31, 32} provides an alternative approach. In this theory, each molecule undergoes a sequence of "hard" binary collisions, between which a quasi-Brownian motion occurs as a result of the fluctuating "soft" force field of the surrounding molecules. Assuming no cross correlation between the hard and soft forces,³³ the theory gives rise to expressions for a friction coefficient ζ , which can be written as a sum of hard³⁴ and soft contributions:

$$\zeta = \zeta^{(H)} + \zeta^{(S)}. \quad (10)$$

Berne and Rice^{35, 36} have extended the Rice-Allnatt theory to apply to molten salts. The self-diffusion coefficients D_+ , D_- in an alkali halide melt can be expressed in terms of the particle number density ρ , the hard-core collision distance $\sigma_{\alpha\beta}$, the normalized 2-body distribution function $g_{\alpha\beta}(\sigma_{\alpha\beta})$ evaluated at distance $\sigma_{\alpha\beta}$ and the reduced mass $\mu_{\alpha\beta}$ of the pair of ions α and β , using the equations^{37, 38}

$$D_+ = kT/(\zeta_+^{(H)} + \zeta_+^{(S)}), \quad (11)$$

$$\begin{aligned} \zeta_+^{(H)} &= \zeta_{+-}^{(H)} + \zeta_{++}^{(H)} \\ &= (8/3)\rho(2\pi kT)^{\frac{1}{2}}[\sigma_{+-}^2 g_{+-}(\sigma_{+-})\mu_{+-}^{\frac{1}{2}} + \sigma_{++}^2 g_{++}(\sigma_{++})\mu_{++}^{\frac{1}{2}}], \end{aligned} \quad (12)$$

$$\begin{aligned} \zeta_+^{(S)} &= \zeta_{+-}^{(S)} + \zeta_{++}^{(S)} \\ &= [K_{+-} + 2K_{++}]^{\frac{1}{2}} \left[1 + \frac{K_{+-}}{(K_{+-} + 2K_{++})^{\frac{1}{2}}(K_{+-} + 2K_{--})^{\frac{1}{2}}} \right]^{\frac{1}{2}}, \end{aligned} \quad (13)$$

where the K are given by

$$K_{\alpha\beta} = (\rho\mu_{\alpha\beta}/3) \int_{\sigma_{\alpha\beta}}^{\infty} \nabla^2 U(r) g_{\alpha\beta}(r) d^3r. \quad (14)$$

Expressions for D_- , $\zeta_-^{(H)}$ and $\zeta_-^{(S)}$ are obtained by interchanging $+$ and $-$ subscripts in eqn (11)-(13). The equivalent conductivity Λ is related to D_+ and D_- by

$$\Lambda/F^2 = [(D_+ + D_-)/RT](1 - \Delta), \quad (15)$$

where

$$\Delta = (4\pi\rho/3kT) \int_{\sigma_{+-}}^{\infty} (dU^*/dr) g_{+-}(r) r^3 dr. \quad (16)$$

In (16), U^* is the non-coulombic part of the anion-cation pair-potential function.

Neglecting the pressure dependence of Δ , the trends in our results can be accounted for qualitatively by eqn (11)-(15). The only pressure-dependent terms in these equations are the number density ρ and the two-body radial distribution function $g(r)$. The pressure dependence of ρ is measured as the isothermal compressibility β , values of which are listed in Table 5 for the alkali halides. β is relatively small for the

TABLE 5.—ISOTHERMAL COMPRESSIBILITIES OF THE FUSED ALKALI HALIDES AND SILVER HALIDES AT 1073 ($10^6\beta$, bar $^{-1}$)

	Cl	Br	I
Li	24.7	29.4	—
Na	28.7	33.6	47.3
K	38.4	43.8	59.9
Rb	44.5*	53.4*	67.3*
Cs	51.2	67.1	75
Ag	16.7†	17.3†	—

* ref. (11); † this work; all other values, ref. (10).

lithium salts, and increases when the size of either ion is increased. Correspondingly, the hard and soft friction coefficients, and therefore D_+ , D_- and Λ , should show greater pressure dependence with increasing ion size, as observed. A similar trend is to be expected from the integral term in eqn (14), which contributes to the soft friction coefficients. This integral is determined almost completely in the range of r values for which the curvature of the pair potential is large. For KCl, the integral has converged when $r = 5 \times 10^{-10}$ m. This range includes the first peak in the two-particle radial distribution function $g(r)$. Increasing pressure is expected to increase the area under this peak, both for like and unlike ion interactions. This ordering effect of pressure will be greatest for the most compressible salts. For lithium salts, in which anion-anion contact probably occurs, the effect of pressure on $g_{+-}(r)$ will be relatively slight, the main result of compression being to increase the area of the first peak of $g_{--}(r)$. For salts of the heavier alkali metals, both like and unlike radial distribution functions should be increased by pressure in the range $r = 0.5 \times 10^{-10}$ m, causing relatively larger changes in D_+ , D_- and Λ . Thus the theory successfully accounts for the trends in our results.

QUANTITATIVE CALCULATIONS BASED ON THE RICE-ALLNATT THEORY

Singer and Woodcock^{39, 40} have performed Monte Carlo and ionic dynamics calculations on fused KCl and other alkali halides. The pair potentials used were of the form

$$U_{\alpha\beta}(r) = (z_\alpha z_\beta e^2)/r + b_{\alpha\beta} \exp [B_{\alpha\beta}(S_{\alpha\beta} - r)] - C_{\alpha\beta}/r^6 - D_{\alpha\beta}/r^8, \quad (17)$$

where z_α and z_β are the ion valencies. The constants $b_{\alpha\beta}$, $B_{\alpha\beta}$, $S_{\alpha\beta}$, $C_{\alpha\beta}$ and $D_{\alpha\beta}$ were taken from the literature.^{3, 6, 41, 42} For KCl, calculations were carried out at two pressures for each of two temperatures. The normalized radial distribution functions $g_{+-}(r)$, $g_{++}(r)$ and $g_{--}(r)$ were obtained under each set of conditions, for values of r in the range 0.10×10^{-10} m. We have used these radial distribution functions and pair potentials to evaluate the integrals in eqn (14), and so have found K_{+-} , K_{++} , K_{--} and the soft friction coefficients. The hard-friction coefficients were evaluated using eqn (12). The diffusion coefficients were then calculated at each temperature and pressure, and the "activation energy" $(\Delta E_D)_\rho$ and "activation volume" ΔV_D were derived using the Arrhenius equation and an equation similar to (1). (We use these terms