where $\alpha_p T/\beta_T = \pi + p$. π is the so-called internal pressure related to the mechanical coefficients of the liquid by the relationship (Rowlinson, 1969)

$$\pi + p = \left[\left(\frac{\partial E}{\partial V}\right)_T + p\right] = \frac{\alpha_p T}{\beta_T} = \gamma_V T, \tag{11}$$

where $\gamma_V = (\partial p/\partial T)_V$. The paucity of literature values of α_p and β_T for all molten salts is reflected in the large uncertainties of the derived isochoric enthalpies and volumes of activation given in Tables 2 and 3. Nevertheless, it is to be noted that $(E_\Lambda^\ddagger)_V$ is considerably less than $(E_\Lambda^\ddagger)_p$. The ratio $(E_\Lambda^\ddagger)_V/(E_\Lambda^\ddagger)_p \approx 0{\cdot}4$ at atmospheric pressure compares with that of Barton *et al.* for $CsNO_3$ of 0·45. [Their figures for the nitrates have been modified slightly by recent (unpublished) compressibility data obtained in this laboratory.] Furthermore, the value of $\Delta V_\Lambda^\ddagger$ for CsCl is somewhat larger than for $CsNO_3$ (8·9 ml mole^{-1} at 450°C), although, because these quantities are temperature dependent, no significance can be attached to this difference. However, the importance of the actual geometry of the ions is suggested by the ascending values of $\Delta V_\Lambda^\ddagger$ through the nitrate series, and it is likely that a similar trend will be found for the chlorides.

The transport properties of molten salts have frequently been interpreted in terms of the density-fluctuation hole model developed by Bockris and coworkers (Bockris and Hooper, 1961; Bockris and Richards, 1957; Bockris *et al.*, 1960). They separated the activation enthalpy and activation volume into components for hole formation and the jump process, i.e.

$$\Delta H^\ddagger = \Delta H_h^\ddagger + \Delta H_j^\ddagger \tag{12}$$

and

$$\Delta V^\ddagger = \Delta V_h^\ddagger + \Delta V_j^\ddagger . \tag{13}$$

Extending the hydrodynamic model of Fürth (1941), they obtained for the enthalpy of hole formation ΔH_h and most probable hole volume ΔV_h:

$$\Delta H_h = 3{\cdot}74RT \tag{14}$$

$$\Delta V_h = 0{\cdot}68\left(\frac{RT}{\gamma}\right)^{3/2} \tag{15}$$

where here γ is the surface tension. Their derivation of these quantities has been questioned (see, for example, Yosim and Reiss, 1968), but Nagarajan and Bockris (1966) have, nevertheless, argued strongly for this model from diffusion studies on molten salts as a function of temperature and pressure. The present measurements of jump enthalpy and volume are, according to Bockris *et al.*, overall values which include a term for the formation of holes as well as a term for the activated jump over a barrier. Subtraction of the calculated values for the formation of holes, according to Equations (14) and (15), gives negative values for the jump activation enthalpy and the jump activation volume, which are clearly impossible.

The 'free-volume' model (Cohen and Turnbull, 1959) predicts a ratio $(E_\Lambda^\ddagger)_V/(E_\Lambda^\ddagger)_p$ close to zero. If any of the alkali chlorides were to exhibit a purely free-volume dependence of the conductivity, it would be the large-cation caesium salt. However, for CsCl the ratio is 0·4 and evidently a more complex description is indicated. A comparison of the experimental values with the predictions of more refined models of transport will be made elsewhere, especially when conductance measurements on the remaining alkali chlorides are available.

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