TABLE 3.—ACTIVATION VOLUMES AND ENERGIES FOR FUSED IODIDES

salt	temp./K	ΔV_κ/(cm^3/mol)	ΔV_Λ/(cm^3/mol)	$(E_\Lambda)_P$/(J/mol)	$(E_\Lambda)_V$/ (J/mol)	$(E_\Lambda)_V$/ $(E_\Lambda)_P$
LiI	798	-0.8 ± 0.3		7 570 [a]		
NaI	979	1.5 ± 0.2	4.8 ± 0.2	9 630 [b]	5830	0.60
	996	1.1 ± 0.4	4.5 ± 0.4	9 200$\pm$800 [c]		
	1053	0.6 ± 0.5	4.6 ± 0.5			
	1100	0.0 ± 0.6	4.5 ± 0.6			
	1125	-0.3 ± 0.6	4.5 ± 0.6			
KI	989	5.5 ± 1.0	9.7 ± 1.0	14 490 [b]	7350	0.51
	1034	4.9 ± 0.2	9.7 ± 0.2	14 500$\pm$1700 [c]		
	1069	4.6 ± 0.7	9.9 ± 0.7			
	1126	3.6 ± 0.5	9.7 ± 0.5			
RbI	978	7.0 ± 0.7		14 490 [b]	6730	0.46
	1030	5.8 ± 0.3		15 400$\pm$1900 [c]		
	1071	5.4 ± 1.1	11.4 ± 1.1			
	1100	5.2 ± 0.2				
CsI	952	8.0 ± 0.5	13.5 ± 0.5	15 890 [b]	8450	0.53
	1009	7.5 ± 0.3	13.5 ± 0.3	16 100$\pm$3500		
	1075	7.6 ± 1.4	14.3 ± 1.4			

[a] ref. (12); [b] ref. (13), (14); [c] this work.

THERMAL PRESSURE COEFFICIENTS $(\partial P/\partial T)_V$

Corrected values of $(\partial P/\partial T)_V$ and β have been calculated for AgCl, AgBr, CsCl and CsI, using eqn (3) and (4) and literature values of the expansivities.[9] $(\partial P/\partial T)_V$ and β were linear functions of temperature within experimental error. Values of A, B, C and D in the equations

$$(\partial P/\partial T)_V = A+BT;$$
$$\beta = C+DT$$

were obtained by least squares, and are presented in table 4. A compressibility value for CsCl reported by Bockris and Richards [10] lies within the standard deviation of our results.

TABLE 4.—LEAST-SQUARES VALUES OF THE PARAMETERS A, B, C AND D IN THE EQUATIONS $(\partial P/\partial T)_V = A+BT$ AND $\beta = C+DT$ (T = TEMPERATURE/K)

compound	A/ (bar/K)	10^2B/ bar	standard deviation/ (bar/K)	10^6C/ bar^{-1}	10^8D/ (bar^{-1} K^{-1})	standard deviation/ bar^{-1}
AgCl	54.4	-4.58	0.50	-8.86	2.38	0.23
AgBr	45.8	-3.63	0.25	-6.45	2.21	0.15
CsCl	20.5	-1.16	0.29	-28.8	7.34	1.6
CsI	5.26	$+0.029$	0.24	22.0	4.94	2.8

DISCUSSION

COMPARISON WITH PREVIOUS WORK

Bannard [17, 18] has measured the effect of pressure on the conductivities of fused NaCl, KCl, RbCl and CsCl over temperature and pressure ranges similar to those of the present work. He used an internally heated vessel, pressurized with argon. His isobaric plots of log x against $1/T$ show some scatter, which reflects the difficulty of obtaining a stable isothermal zone with this experimental arrangement. Within the combined limits of error, the two sets of results are in satisfactory agreement. Our conductivities at atmospheric pressure were within 15 % of those of Jaffe and van Artsdalen,[12] and our values of κ and $(E_\Lambda)_P$ were within 5 and 15 % of those reported recently by Zuca *et al.*[13, 14] Differences of a similar magnitude exist between the conductivities and " activation energies " reported by different workers,[12-14, 19] so these discrepancies are acceptable.

COMPARISON WITH THE HOLE THEORY

The hole theory of Bockris and Hooper [20] is based on a model suggested by Fürth.[21] Liquids are supposed to contain " holes " of volume distributed about a most probable value of $0.68\,(kT/\sigma)^{\frac{3}{2}}$, where σ is the surface tension. Diffusion occurs by jumps of ions into neighbouring holes, the jump distance being approximately the ionic diameter. It is stated [20] that the molar enthalpy of formation of a mole of holes of radius r is $4\pi r^2\sigma N$ (eqn 9, ref. (20)). Blander [22] has pointed out that this is the *free energy* of hole formation, and the subsequent conclusion, that the enthalpy of hole formation is $3.55\,RT_m$ (T_m = melting point), is therefore invalid. The use of the Stokes–Einstein equation in the derivation is also questionable. The experimental " activation energy ", defined by the Arrhenius equation $D = D_0 \exp[-(\Delta E_D)_P/RT]$, is identified with the sum of the enthalpy of hole formation ΔH_h and the enthalpy of activation for jumping ΔH_j^*. It is then assumed that ΔH_j^* is small compared with ΔH_h, so that $(\Delta E_D)_P \approx \Delta H_\mathrm{h}$. In a later paper,[23] Nagarajan and Bockris identify ΔE_j^* ($\approx \Delta H_\mathrm{j}^*$) with the Arrhenius energy at constant volume $(\Delta E_D)_V$. In another analysis relating to conductivity,[24] it is assumed that $\Delta H_\mathrm{j}^* \approx 0.1\,\Delta H_\mathrm{h}$, and comparison of the equation for equivalent conductivity derived from the hole theory with the Arrhenius equation $\Lambda = A \exp[-(E_\Lambda)_P/RT]$ indicates that $(\Delta H_\mathrm{h}+\Delta H_\mathrm{j}^*) \approx \Delta H_\mathrm{h} = (E_\Lambda)_P+RT$. At constant volume, it is implied that $(E_\Lambda)_V+RT = \Delta H_\mathrm{j}^* \approx 0$, i.e., $(E_\Lambda)_V \approx -RT$. In this paper the quantity $4\pi r^2\sigma N$ is correctly identified as the molar free energy of hole formation, but the enthalpy of hole formation is then derived as $\Delta H_\mathrm{h} = 4\pi r^2(\sigma - T\mathrm{d}\sigma/\mathrm{d}T)N$, which is incorrect because it overlooks the temperature dependence of the average hole radius r. This mistake is repeated in another paper on self-diffusion.[25]

Thus, the analysis used by Bockris *et al.* in deriving their expressions for the enthalpy of hole formation contain serious errors. Reference to tables 1, 2 and 3 shows that the assumption that $(E_\Lambda)_V \ll (E_\Lambda)_P$ (or $(E)_V \approx -RT$) is also grossly wrong. In fact $(E_\Lambda)_V \approx (E_\Lambda)_P$ for the lithium halides, and falls to about $0.5\,(E_\Lambda)_P$ for the halides of the heavier alkali metals and silver. $(E_\Lambda)_V$ is approximately equal to $+RT$ for most of the salts studied, except the silver halides.

Molecular dynamics calculations for the hard-sphere fluid [26] have indicated that the supposition that diffusion occurs principally by jumps of the order of a molecular diameter is also unrealistic.

COMPARISON WITH THE FREE VOLUME THEORY

In its original form,[27] the free volume theory of Cohen and Turnbull related to hard sphere fluids, in which all non-overlapping configurations are assumed to have the same energy. Diffusion is supposed to occur only if a void of volume greater than a critical value v^* arises next to the diffusing molecule. The diffusion coefficient is given by

$$D = gau \exp(-\gamma v^*/v_\mathrm{f}) \tag{9}$$