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Effect of Pressure on Electrical Conductivities of Fused Alkali Metal Halides and Silver Halides

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The electrical conductivities of the following fused salts were measured at temperatures up to 860°C and over a pressure range 1-1000 bar: the chlorides, bromides and iodides of the five alkali metals; silver chloride, silver bromide. The volumes $\Delta V_{\Lambda} = -RT(\partial \ln \Lambda/\partial P)_T$ were calculated to be independent of temperature for each salt. ΔV_{Λ} was zero for the lithium halides, and increased as the ions were changed in the sequences $\mathrm{Li}^+ \rightarrow \mathrm{Cs}^+$ or $\mathrm{Cl}^- \rightarrow \mathrm{I}^-$. The ΔV_{Λ} values were used to find the temperature dependence of conductivity at constant density from that at constant pressure. The results are not consistent with the free volume theory, or with the hole theory of Bockris and Hooper. However, the observed trends are in qualitative accord with the Rice-Allnatt statistical theory of transport in liquids. This theory was used to calculate the conductivity of fused potassium chloride and its pressure and temperature dependence, using ionic pair correlation functions obtained in a computer-simulated ionic dynamics experiment. The results are in moderate agreement with experiment.

We have reported measurements of the pressure dependence of electrical conductivity for fused nitrates and for other salts containing polyatomic anions.^{1, 2} Although the "activation volume", defined by

$$\Delta V_{\Lambda} = -RT(\partial \ln \Lambda / \partial P)_T, \tag{1}$$

varied in a systematic way as the cation and anion sizes were changed, interpretation of the results in terms of ionic interactions was complicated by the non-spherical shape of the anions. More detailed discussion becomes possible if the ions in the melt are spherical; an effective pair potential can then be written in which the internuclear distance is the only variable.³⁻⁶ The fused alkali halides satisfy this requirement; they are the simplest of ionic liquids, occupying a position in relation to fused salts similar to that of the liquid rare gases in the field of molecular fluids.

We report measurements of the isothermal pressure dependence of conductivity for the fused alkali metal chlorides, bromides and iodides, and silver chloride and bromide. An externally heated pressure vessel was used, and the pressure-transmitting fluid was argon. This arrangement allowed stable pressure and temperature conditions to be established in the zone containing the conductivity cell. We have derived the temperature dependence of conductivity at constant density from that at constant pressure, using the equation ¹

$$(\partial \ln \Lambda / \partial T)_V = (\partial \ln \Lambda / \partial T)_P + (\partial \ln \Lambda / \partial P)_T (\partial P / \partial T)_V.$$
(2)

Values of $(\partial P/\partial T)_V$ were either measured directly or were calculated from published values of expansivity α and compressibility β by the expression

$$\left(\frac{\partial P}{\partial T}\right)_{V} = -\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P} / \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T} = \frac{\alpha}{\beta}.$$
(3)

EXPERIMENTAL

MATERIALS

AgCl and AgBr were prepared in a dark room, by treating aqueous AgNO₃ solution (B.D.H., A.R.) with HCl or HBr solution (B.D.H., A.R.). The precipitates were collected and washed with dilute HCl or HBr, followed by distilled water. They were dried in an air oven at 150°C for several days. KCl, KBr, KI, NaCl and NaBr (B.D.H., A.R.) were recrystallized from distilled water. The solutions were evaporated to dryness at 80°C, and the salts were finally dried by gradually heating them to 300°C over 48 h. NaI, RbCl, RbI, CsCl, CsBr and CsI were similarly prepared from B.D.H. reagent-grade chemicals (99 % pure). LiCl, LiBr, and LiI were made by treating a filtered solution of Li₂CO₃ with HCl, HBr or HI (A.R.). The solutions were evaporated to dryness at 80°C, and the solids were dried under vacuum as the temperature was slowly raised to 100°C over 24 h and then to 350°C over 24 h. Solutions of all alkali halides gave a neutral reaction both before and after conductivity measurements.

HIGH PRESSURE APPARATUS

The pressure vessel was made from Nimonic 105 (H. Wiggin & Co., Hereford, England). It was of 2.5 cm i.d., 7.5 cm o.d. and 75 cm long, and was mounted vertically. The upper end was heated by an external furnace. The furnace windings were in three sections, which were shunted by rheostats. These were adjusted to give an isothermal zone of length 6 cm, the centre of which was 12 cm from the top of the bore. The temperature profile in this zone did not change when the pressure was raised from atmospheric to 1000 bar. At the lower end, the vessel was cooled by a water jacket, below which was a flange closure and rubber O-ring seal. The lower flange carried a port for admission of argon, and six electrical terminals insulated by conical Nylon sleeves. Four of these terminals were of mild steel, and were used to make connections to the conductance cell; the remaining two were of chromel and alumel, and were connected internally and externally to wires of these metals. The internal wires were insulated with alumina sleeving. The thermocouple junction was positioned opposite the centre of the conductivity cell, and was protected by a silica sheath. An isothermal pressure change of 1000 bar causes the e.m.f. of the chromel-alumel couple to change by less than 5 μ V.⁷ Neglect of this would cause an error of 0.1 K in temperature measurement, which is negligible. Pressures were measured to ± 5 bar with a Bourdon gauge (Budenberg Gauge Co., Ltd.) which was calibrated against a dead-weight tester. Argon (99.9 %) was taken directly from cylinders and compressed to the working pressure by a diaphragm compressor (Pressure Products Ltd., model 3033).

CONDUCTANCE CELLS AND BRIDGES

Various conductance cells were used, employing Pyrex, silica, hot pressed alumina or sapphire as construction material, with platinum electrodes (see fig. 1). For each cell, diffusion of dissolved gas from the exposed surface of the melt into the region between the electrodes was hindered by restricting the intervening melt to a narrow annular space between the cell and the tube surrounding it. Pyrex cells (fig. 1a) were used for the silver halides, silica cells (fig. 1b) for the halides of Na, K, Rb and Cs, and alumina or sapphire cells (fig. 1c) for the lithium halides. The cell was held in a stainless steel or silica cup, positioned in the isothermal zone of the pressure vessel. The cup was supported on a column of pyrophyllite spacers, threaded onto a central rod of stainless steel. An inverted silica tube was placed over the cell, with the open end extending downwards into the cold part of the vessel. This tube protected the walls of the pressure vessel from attack by corrosive salt vapours.

Conductances were measured with a transformer ratio-arm bridge (Wayne-Kerr, type B221), with external audio-oscillator and tuned amplifier and null detector, or with a Jones bridge which has been described previously.¹ The lead resistances were determined as a function of temperature and pressure, and appropriate corrections were applied. Conductance measurements were made over a range of frequencies (2-10 kHz) and were corrected to infinite frequency.¹ The frequency dependence was generally less than 1 % over this range, and was independent of temperature and pressure for a given salt and cell.





FIG. 1.—Conductance cells. (a) Pyrex cell; A, platinum electrodes; B, porosity 3 frit; C, Pyrex tube. (b) Silica cell; A, platinum leads; B, stainless steel cup; C, silica tube; D, platinum container and electrode; E, silica capillary. (c) Alumina or sapphire cell; A, alumina bead fused on; B, alumina or sapphire capillary; C, alumina tube; D, platinum container and electrode; E, inner platinum electrode.

PROCEDURE FOR CONDUCTANCE MEASUREMENTS

The cell was loaded with dried, powdered salt, and was put into the cup on the pyrophyllite support column. The silica tube was placed over this, and the whole unit was pushed up into the pressure vessel (which was at the required working temperature). The vessel was sealed, and a suitable time was allowed for the cell and vessel to reach temperature equilibrium (*ca.* 1 h). The pressure was raised in stages to 1000 bar, and then reduced again to atmospheric, readings being taken at each pressure. A complete pressure cycle lasted about 90 min, after which time the melt was allowed to degas at atmospheric pressure for 2-3 h. At the end of a set of experiments, the contents of the cell were dissolved in water and treated with phenolphthalein, to confirm the absence of hydrolysis or oxidation products.

MEASUREMENT OF $(\partial P / \partial T)_V$

Thermal pressure coefficients were calculated from literature values of the expansivity and compressibility for most of the compounds studied, using eqn (3). $(\partial P/\partial T)_V$ was measured directly for AgCl, AgBr and CsI, for which no compressibility data were available, and also for CsCl. A pyknometric method was used, the pyknometers being made from Pyrex for AgCl and AgBr (fig. 2a) and from silica for CsCl and CsI (fig. 2b). In each version, a capillary stem of length 10 cm and 1 mm i.d. was provided, to reduce the rate of diffusion of dissolved gas from the meniscus into the bulb. The Pyrex cell had a platinum wire sealed through the bottom, and a second wire could be inserted into the top of the capillary. In the silica cell, a twin-bore capillary was used, into which wires were inserted to different depths. In both cases, contact between the meniscus and the upper probe was indicated by an abrupt drop in the electrical resistance between the probes. The cells were filled by charging the upper chamber with purified, powdered salt. The salt was melted, and forced into the lower bulb. The filling chamber was then broken off, the probe wires were inserted and the cell was mounted inside the pressure vessel. The temperature was raised slowly (2-3 K/min) until the meniscus contacted the upper probe. The temperature was noted, and the pressure was increased to a new value. The temperature was again raised slowly, until contact with the upper probe was re-established. This situation could be detected with a precision which varied from $\pm \frac{1}{4}$ K to ± 1 K. These operations were repeated until the pressure reached 1000 bar. Checks were made for the absence of irreversible effects due to leakage, evaporation, chemical change or gas dissolution. Plots of P against T were straight lines within

experimental error. The slopes of these lines correspond to the condition of constant meniscus position, and require correction to allow for the change in the volume of the pyknometer with pressure. If $(\partial P/\partial T)^{\text{obs}}$ is the observed slope, $(\partial P/\partial T)_V$ for the melt can be found using the equation

$$\left(\frac{\partial P}{\partial T}\right)_{V} = \left(\frac{\partial P}{\partial T}\right)^{\text{obs}} \left(1 - \frac{\beta_{\text{c}}}{\beta_{\text{m}}}\right) = \left(\frac{\partial P}{\partial T}\right)^{\text{obs}} / \left[1 + \frac{\beta_{\text{c}}}{\alpha_{\text{m}}} \left(\frac{\partial P}{\partial T}\right)^{\text{obs}}\right],\tag{4}$$

where subscripts m and c refer to the melt and the container material respectively. β_c has been measured between room temperature and 400°C for Pyrex and silica.⁸ For use in eqn





(4), these results were extrapolated to higher temperatures (500°C for Pyrex, 800°C for silica). Uncertainty in β_c represents the greatest source of error in the experiments; the total uncertainty in $(\partial P/\partial T)_V$ is estimated to be $\pm 4\%$.

RESULTS

CONDUCTANCE MEASUREMENTS

Following established practice,⁹ we describe the experimental temperature and pressure coefficients of conductivity using the Arrhenius equation and the terminology of the transition state theory. We restrict our use of the terms "activation volume" and "activation energy" to refer simply to the quantities defined operationally by eqn (1), (5) and (7). We do not believe that the transition state theory is applicable to ion migration in fused salts, and do not intend to imply that ΔV , E_P and E_V relate to the formation of a transition state.

Isothermal plots of ln x against pressure for the alkali halides and silver halides were linear within experimental error. A selection of these plots is presented in fig. 3-5. Straight lines were fitted by least squares, and the "activation volume" ΔV_{κ} was found using the equation

$$\Delta V_{\kappa} = -RT(\partial \ln \kappa / \partial P)_{T}.$$
(5)



FIG. 3.—Isothermal plots of log_{10} (conductivity) against pressure for fused alkali metal chlorides. For ease of presentation, the isotherms have been positioned arbitrarily on the log κ axis. A, LiCl at 968 K; B, NaCl at 1098 K; C, KCl at 1065 K; D, RbCl at 1070 K; E, CsCl at 1074 K. •, increasing pressure; \blacktriangle , decreasing pressure.



FIG. 4.—Isothermal plots of $\log_{10}(\text{conductivity})$ against pressure for fused alkali metal bromides. The isotherms have been positioned arbitrarily on the $\log \kappa$ axis. A, LiBr at 870 K; B, NaBr at 1062 K; C, KBr at 1050 K; D, RbBr at 1075 K; E, CsBr at 1069 K. \bullet , increasing pressure; \blacktriangle , decreasing pressure.



FIG. 5.—Isothermal plots of log₁₀(conductivity) against pressure for fused alkali metal iodides. The isotherms have been positioned arbitrarily on the log κ axis. A, LiI at 798 K; B, NaI at 1053 K; C, KI at 1069 K; D, RbI at 1071 K; E, CsI at 1075 K. ●, increasing pressure; ▲, decreasing pressure.

					$(E_A)_V/$	$(E_A)_V$
salt	temp./K	$\Delta V_{\kappa}/(\mathrm{cm}^3/\mathrm{mol})$	$\Delta V_A / (\text{cm}^3/\text{mol})$	$(E_A)_P/(J/mol)$	(J/mol)	$(E_A)_P$
LiCl	916	-2.4 ± 0.6	-0.8 ± 0.6	8440 a	8560	1.01
	921	-1.5 ± 0.3	0.1 ± 0.3			
	921	-2.2 ± 0.4	-0.6 ± 0.4			
	968	-1.2 ± 0.7	0.5+0.7			
	973	-1.4 ± 0.7	0.4 ± 0.7			
NaCl	1098	03 + 12	30 ± 12	10 590 b	5960	0.56
Itaci	1133	1.1+2.9	4.1+2.9	$9300+800^{c}$	0,000	AnA
		Christian Press		04-5.6		
KCl	1065	2.9 ± 0.2	6.3 ± 0.2	14 110 ^b	7310	0.52
	1093	2.7 ± 0.1	6.2 ± 0.1	14000 ± 5700	c	
	1129	2.2 ± 0.1	6.2 ± 0.1			
RbCl	1009	4.1 ± 0.4		15 680 b	8020	0.51
	1045	4.3 ± 0.3		16400 + 1900	с	
	1070	4.0 + 0.5	8.0 ± 0.5	n of temperatur		
	1114	4.1 ± 1.5	7 10.61			
CeCl	044	61+03	03+03	16 740 b	8490	0.51
CSCI	083	58+03	91+03	15800 ± 1500	c	0.51
	1034	45 ± 10	86+10	15 000 1 1500		
	1074	4.5 ± 0.3	91 ± 03			
	1120	4.5 10.5	0.7 ± 0.6			
	1129	4.4 1 0.0	9.7 _ 0.0			
AgCl	745	1.1 ± 0.1	1.7 ± 0.1	5130 d	2780	0.54
	755	0.9 ± 0.1	1.5 ± 0.1	4 700± 540 °		
	774	0.9 ± 0.2	1.5 ± 0.2			

TABLE 1.—ACTIVATION VOLUMES AND ENERGIES FOR FUSED CHLORIDES

^a ref. (12); ^b ref. (13), (14); ^c this work; ^d ref. (15).

Values of ΔV_{κ} are listed in tables 1-3. The uncertainties quoted correspond to 95 % confidence limits. The "activation volume" ΔV_{Λ} , defined by eqn (1), was calculated from ΔV_{κ} using eqn (6),

$$\Delta V_{\Lambda} = \Delta V_{\kappa} + \beta R T. \tag{6}$$

TABLE 2.—ACTIVATION VOLUMES AND ENERGIES FOR FUSED BROMIDES

salt	temp./K	$\Delta V_{\kappa}/(\text{cm}^3/\text{mol})$	$\Delta V_A/(\text{cm}^3/\text{mol})$	$(E_A)_P/(J/mol)$	$(E_A)_V$ (J/mol)	$(E_A)_V $ $(E_A)_P$
LiBr	869 870 914 922	-1.9 ± 0.7 -1.4 ± 0.4 -2.3 ± 0.8 -1.9 ± 0.4	$\begin{array}{r} -0.3 \pm 0.7 \\ 0.2 \pm 0.4 \\ -0.5 \pm 0.8 \\ -0.1 \pm 0.4 \end{array}$	8 860 <i>ª</i> 9 850±800 <i>°</i>	9060	1.02
NaBr	1047 1062 1094 1119 1131 1145	$\begin{array}{c} 0.3 \pm 0.3 \\ 0.3 \pm 0.1 \\ 0.0 \pm 0.1 \\ -0.3 \pm 0.3 \\ -0.2 \pm 0.2 \\ -0.3 \pm 0.3 \end{array}$	$\begin{array}{c} 3.1 \pm 0.3 \\ 3.2 \pm 0.1 \\ 3.1 \pm 0.1 \\ 3.0 \pm 0.3 \\ 3.2 \pm 0.2 \\ 3.2 \pm 0.3 \end{array}$	9 920 ^b 9 800±700 ^c	6410	0.65
KBr	1015 1050 1105	3.9 ± 0.5 3.7 ± 0.3 3.2 ± 0.3	$7.2 \pm 0.5 \\ 7.4 \pm 0.3 \\ 7.5 \pm 0.3$	15 580 ^b 15 100±4 800 ^c	8350	0.54
RbBr	988 999 1008 1075 1122	$5.5 \pm 0.5 \\ 5.2 \pm 0.5 \\ 5.0 \pm 0.5 \\ 4.3 \pm 0.5 \\ 3.8 \pm 0.4$	9.1±0.5	15 500 ^b 13 300±2 700 ^c	7930	0.51
CsBr	956 1002 1069 1098 1128	$\begin{array}{c} 6.3 \pm 0.4 \\ 5.7 \pm 0.1 \\ 5.5 \pm 0.3 \\ 5.2 \pm 0.1 \\ 5.1 \pm 0.6 \end{array}$	$\begin{array}{c} 10.6 \pm 0.4 \\ 10.6 \pm 0.1 \\ 11.5 \pm 0.3 \\ 11.6 \pm 0.1 \\ 12.1 \pm 0.6 \end{array}$	16 410 ^b 15 500 <u>±</u> 700 ^c	8880	0.54
AgBr	727 753 791 813 850	$\begin{array}{c} 0.7 {\pm} 0.2 \\ 0.6 {\pm} 0.2 \\ 0.5 {\pm} 0.5 \\ 0.4 {\pm} 0.2 \\ 0.6 {\pm} 0.5 \end{array}$	$\begin{array}{c} 1.3 \pm 0.2 \\ 1.2 \pm 0.2 \\ 1.2 \pm 0.5 \\ 1.2 \pm 0.2 \\ 1.5 \pm 0.5 \end{array}$	4 620 ^d 4 680±200 ^c	2840	0.61

^a ref. (12); ^b ref. (13), (14); ^c this work; ^d ref. (16).

 ΔV_{Λ} is independent of temperature within experimental error. We define "activation energies" corresponding to constant pressure and constant volume conditions by eqn (7),

$$(E_{\Lambda})_{P} = -R[\partial \ln \Lambda / \partial (1/T)]_{P}; (E_{\Lambda})_{V} = -R[\partial \ln \Lambda / \partial (1/T)]_{V}.$$
(7)

Using eqn (2), these energies are related by

$$(E_{\Lambda})_{V} = (E_{\Lambda})_{P} - T(\partial P/\partial T)_{V} \Delta V_{\Lambda}$$
(8)

 $(E_{\Lambda})_{V}$ was calculated for each salt. For the alkali halides other than CsCl and CsI, $(\partial P/\partial T)_{V}$ was calculated using eqn (3) and literature values of expansivity ⁹ and compressibility.^{10, 11} The $(E_{\Lambda})_{P}$ values used in eqn (8) were also taken from the literature. Values of ΔV_{κ} , ΔV_{Λ} , $(E_{\Lambda})_{P}$, $(E_{\Lambda})_{V}$ and $(E_{\Lambda})_{V}/(E_{\Lambda})_{P}$ are listed in tables 1-3.

salt	temp./K	$\Delta V_{\rm re}/({\rm cm}^3/{\rm mol})$	$\Delta V_A/(\text{cm}^3/\text{mol})$	$(E_A)_{\mathcal{P}}/(J/mol)$	$(E_A)_V/$ (J/mol)	$(E_A)_V $ $(E_A)_P$
LiI	798	-0.8 ± 0.3		7 570 ª	CI	~ <i>I</i> /I
NaI	979 996 1053 1100 1125	$1.5 \pm 0.2 \\ 1.1 \pm 0.4 \\ 0.6 \pm 0.5 \\ 0.0 \pm 0.6 \\ -0.3 \pm 0.6$	$\begin{array}{c} 4.8 \pm 0.2 \\ 4.5 \pm 0.4 \\ 4.6 \pm 0.5 \\ 4.5 \pm 0.6 \\ 4.5 \pm 0.6 \end{array}$	9 630 ^b 9 200 <u>±</u> 800 ^c	5830	0.60
KI	989 1034 1069 1126	5.5 ± 1.0 4.9 ± 0.2 4.6 ± 0.7 3.6 ± 0.5	9.7 ± 1.0 9.7 ± 0.2 9.9 ± 0.7 9.7 ± 0.5	14 490 ^b 14 500 <u>+</u> 1700 ^c	7350	0.51
RbI	978 1030 1071 1100	7.0 ± 0.7 5.8 ± 0.3 5.4 ± 1.1 5.2 ± 0.2	11.4±1.1	14 490 ^b 15 400±1900 ^c	6730	0.46
CsI	952 1009 1075	8.0 ± 0.5 7.5 ± 0.3 7.6 ± 1.4	13.5 ± 0.5 13.5 ± 0.3 14.3 ± 1.4	15 890 ^b 16 100±3500	8450	0.53

TABLE 3.—ACTIVATION VOLUMES AND ENERGIES FOR FUSED IODIDES

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

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

Corrected values of $(\partial P/\partial T)_{\nu}$ and β have been calculated for AgCl, AgBr, CsCl and CsI, using eqn (3) and (4) and literature values of the expansivities.⁹ $(\partial P/\partial T)_{\nu}$ 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 $\beta = C + DT (T = \text{temperature/K})$

compound	A/ (bar/K)	10 ² <i>B</i> / bar	standard deviation/ (bar/K)	106C/ bar-1	$\frac{10^8 D}{(bar^{-1} K^{-1})}$	standard deviation/ bar ⁻¹
AgC1	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 Hooper²⁰ 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 $D = D_0 \exp$ $[-(\Delta E_{\rm D})_{\rm P}/RT]$, is identified with the sum of the enthalpy of hole formation $\Delta H_{\rm h}$ and the enthalpy of activation for jumping ΔH_j^* . It is then assumed that ΔH_j^* is small compared with $\Delta H_{\rm h}$, so that $(\Delta E_D)_P \approx \Delta H_{\rm h}$. In a later paper,²³ Nagarajan and Bockris identify $\Delta E_i^* (\approx \Delta H_i^*)$ with the Arrhenius energy at constant volume $(\Delta E_D)_V$. In another analysis relating to conductivity,²⁴ it is assumed that $\Delta H_i^* \approx 0.1 \Delta H_h$, 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 $(\Delta H_{\rm h} + \Delta H_{\rm i}^*) \approx$ $\Delta H_{\rm h} = (E_{\Lambda})_P + RT$. At constant volume, it is implied that $(E_{\Lambda})_V + RT = \Delta H_{\rm i}^* \approx 0$, 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 $\Delta H_{\rm h} = 4\pi r^2 (\sigma - T d\sigma/dT)N$, 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

$$D = gau \exp\left(-\gamma v^*/v_{\rm f}\right)$$

(9)

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 conductivity 28 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

Rice ³⁰ 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 hard ³⁴ and soft contributions:

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

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}

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

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

$$= \left[K_{+-} + 2K_{++}\right]^{\frac{1}{2}} \left[1 + \frac{K_{+-}}{(K_{+-} + 2K_{++})^{\frac{1}{2}}(K_{+-} + 2K_{--})^{\frac{1}{2}}}\right]^{\frac{1}{2}}, \quad (13)$$

where the K are given by

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

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

where

$$\Delta = (4\pi\rho/3kT) \int_{\sigma_{+-}}^{\infty} (\mathrm{d}U^*/\mathrm{d}r)g_{+-}(r)r^3 \,\mathrm{d}r.$$
(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 $(10^6\beta, bar^{-1})$

	CI	Br	tinteth internit
Lingow	24.7	29.4	(he mpare
Na	28.7	33.6	47.3
K	38.4	43.8	59.9
Rb Old	44.5*	53.4*	67.3*
Cs	51.2	67.1	75
Ag	16.7†	17.3†	and the second

* 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 twoparticle 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 an ion-anion contact probably occurs, the effect of pressure on $q_{+-}(r)$ will be relatively slight, the main result of compression being to increase the area of the first peak of $q_{-}(r)$. 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

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

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

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

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).

The silver and sodium ions are of approximately equal size (the radii are 0.95 and 1.13×10^{-10} m, respectively ⁴⁵), but the compressibilities of the silver compounds are only about one-half those of the sodium salts at the same temperature (see table 5). The differences between the ΔV_{Λ} values are therefore consistent with the arguments advanced above. However, there is evidence that the fused silver halides do not have 100 % ionic character,^{46, 47} and probably the covalent contribution to the bonding is pressure dependent.⁴⁸ The application of the Rice-Allnatt theory in these circumstances is open to objection. Similar considerations would apply to the fused thallous halides.49

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