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## Solubilities of Helium, Argon, and Nitrogen in Molten Nitrates at Pressures up to 1 kbar

BY B. CLEAVER AND D. E. MATHER \*

#### Dept. of Chemistry, The University, Southampton, SO9 5NH

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The following solubilities have been measured over a temperature range of 100 deg. and at pressures up to 1 kbar: He in LiNO<sub>3</sub> and NaNO<sub>3</sub>; Ar in LiNO<sub>3</sub>, NaNO<sub>3</sub>, RbNO<sub>3</sub> and AgNO<sub>3</sub>; N<sub>2</sub> in LiNO<sub>3</sub> and NaNO<sub>3</sub>. Henry's law was obeyed approximately in all systems. For Ar in NaNO<sub>3</sub>, which was studied most extensively, a plot of solubility against pressure showed curvature above 500 bar. This could be accounted for by allowing for gas imperfection and for the finite partial molar volume of the dissolved gas (estimated to be  $34\pm8$  ml/mol). The solubilities increased with rising temperature, with heats of solution in the range 13-20 kJ/mol. The standard entropies of solution were between -8 and -24 J K<sup>-1</sup> mol<sup>-1</sup>, referring to states of equal concentration in the gaseous and liquid phases. These entropies are more negative than those for solutions. For a given melt at a given temperature, the solubilities decreased with increasing size of the solute molecule, while for a given gas in a series of melts the solubilities were in the inverse sequence of the surface tensions. These trends are correctly predicted by a model in which the free energy of solution is equated to the work of formation of cavities in the melt to accommodate the gas molecules.

Most of the previous work on the solubility of gases in molten salts has been carried out at pressures below 2 bar, often using mixed melts of technological importance.<sup>1-8</sup> In the absence of strong solute-solvent interactions, heats of solution are generally positive and standard entropies of solution are in the range 0 to  $-6 \text{ J K}^{-1} \text{ mol}^{-1}$  (referring to equal concentrations of solute molecules in the gaseous and liquid phases).<sup>1, 5</sup> The solubilities of inert gases in a given melt follow the inverse sequence of solute molecular size.<sup>1</sup> Negative heats of solution are observed when strong interactions occur between the solute molecules and the ions in the melt.<sup>3, 4, 7, 8</sup> Only one group of workers has reported solubility measurements for gases in molten salts at high pressures,<sup>9-13</sup> and the results conflict with the trends described above. Ar and N<sub>2</sub> were reported to have negative heats of solution in fused NaNO<sub>3</sub>, and to be about an order of magnitude more soluble than in fluoride melts. The solubility sequence at  $369^{\circ}C$  was He>N<sub>2</sub>>Ar, which is not the size sequence. In view of these differences, we thought it desirable to repeat this work by a different method. We have measured the solubilities of He, Ar, and N<sub>2</sub> in LiNO<sub>3</sub> and NaNO<sub>3</sub>, and of Ar in RbNO<sub>3</sub> and AgNO<sub>3</sub>, at pressures up to 1 kbar. This extension of the pressure range permits the determination of the partial molar volume of the dissolved gas, in addition to the heat and entropy of solution. Inert gases have been used as pressure-transmitting media in studies of the pressure dependence of transport processes in molten salts <sup>10, 12, 14-18</sup> and the presence of dissolved gas has been a possible source of error.<sup>16-18</sup> The solubilities reported here provide a basis for estimation of the effect which dissolved gas might have on transport phenomena at high pressures. not reduct hod

#### EXPERIMENTAL

The melt was saturated by stirring it in contact with gas at high pressure. A sample of the saturated melt was isolated, and subsequently analyzed.

\*present address : Albright & Wilson, Ltd., Whitehaven, Cumberland

#### MATERIALS

Helium (99.8 %), nitrogen, and argon (both 99.9 %) were obtained from British Oxygen Company, and were not dried or otherwise purified before use. They were compressed from cylinder pressure to the working pressure by a diaphragm compressor (Pressure Prodducts (U.K.), model 3033), and came in contact only with stainless steel during this process. NaNO<sub>3</sub> (B.D.H., A.R., >99.5 %) and RbNO<sub>3</sub> (Johnson, Matthey and Co., 99.9 %) were fused, filtered through Pyrex frits, allowed to freeze, and stored *in vacuo*. AgNO<sub>3</sub> (Johnson, Matthey & Co., 99.9 %) was recrystallized once from distilled water. LiNO<sub>3</sub> (Johnson, Matthey & Co., 99.9 %) was recrystallized from distilled water, dried at 120°C and stored at 100°C in an air oven.

#### APPARATUS

Fig. 1 shows a schematic drawing of the apparatus, and fig. 2 shows details of some of the components. The larger pressure vessel A was machined from a bar of Ninomic 90 (Henry



FIG. 1.-Schematic diagram of the apparaus (not to scale). The letters are referred to in the text.

Wiggin and Co.). The vessel dimensions were 2.5 cm int. diam., 7.6 cm ext. diam., and 60 cm long. The large vessel was connected via a valve B to a smaller vessel C, made from a creep-resisting steel (Firth Vickers, type 448). The screw and plug of this vessel were made from stainless alloys Rex 559 (Firth Vickers) and EN 58B, respectively. The plug was gold plated to facilitate sealing. A stainless steel clad chromel-alumel thermocouple was fitted through the upper opening of C. Electrical heating was applied to C and to the upper half of A, and also to the body of the valve B and the short tubes connecting it to the vessels. Cooling water was circulated through jackets at the lower end of A and on the stem and packing of B. The flange closure of A incorporated a rubber O-ring seal. The heater windings on A were shunted by rheostats, which were adjusted to give a constant temperature zone over the top 8 cm of the bore. The two vessels were maintained at the same temperature by automatic controllers, and the temperature of B was regulated manually.

The sensing elements for the controllers were small platinum resistance thermometers bound firmly to the outsides of A and C.

Inside vessel A was a stainless steel cup D (EN 58B) of capacity slightly greater than vessel C, connected by a drive rod to a d.c. motor E (with reduction gearing). This was in the cold part of the vessel, and caused the cup to rotate at 100 rev/min. The motor and cup



FIG. 2.—Detail of components of the high pressure apparatus. The letters are referred to in the text.

were mounted in housing made from EN 58B, the function of which was to support the components and also to fill the dead space inside the vessel. The junctions of two stainless steel clad chromel-alumel thermocouples (Spembley Technical Products Ltd.) were positioned inside the cup D, one at the top and one at the bottom, to indicate the temperature and check for the absence of a gradient. During runs, the temperature difference between the two junctions was not greater than 1 deg. The thermocouple connections through the lower flange of the vessel were made via cones of chromel and alumel, insulated from the flange by nylon sleeves. Chromel and alumel wires passed from the lower ends of the cones to the cold junctions, which were kept in ice. The pressure tubing connecting A to B had brazed to its lower end a length of stainless steel capillary tubing, which extended to within a few mm of the bottom of D. The working gas from the compressor G could be admitted to the apparatus through valve H, and the pressure could be read to  $\pm 10$  bar by the Bourdon gauge J (Budenberg Gauge Co. Ltd.). The gauge calibration was checked periodically against a dead weight tester. The apparatus could be evacuated, or vented to the atmosphere through valve K. The valves, tubing, and high pressure fittings were purchased from Pressure Products (U.K.) Ltd. The apparatus was mounted in a steel supporting frame, which was surrounded by a safety barrier made from  $\frac{3}{8}$  in. mild steel plate.

#### PROCEDURE

The vessels were sealed, and were evacuated through K with B open. B was then closed, and air admitted to the rest of the apparatus. The lower flange and the mechanisms attached

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to it were withdrawn from A. A sample of salt was placed in cup D, and melted. A piece of stainless steel gauze was slid over the two thermocouple junctions, which were then positioned in the melt. The gauze caused the melt to be stirred when the cup was rotated by the motor. The assembly was quickly inserted into A, which was at the working temperature, and the closure bolts were fastened. Air was flushed out of A, by alternately admitting the working gas through H and venting through K. The gas was then pumped in to the working pressure, with K closed, and the apparatus isolated by closing H. The stirrer motor was started, and the melt allowed to saturate. Trial experiments were performed on the system  $Ar + NaNO_3$  to find the time needed for saturation. The melt was exposed to the gas at 200 bar for times between 1 and 65 h. The amount of gas taken up reached a limiting value after 5 h, corresponding to a Henry constant  $K_H$  of  $1.07 \times 10^{-7}$  mol ml<sup>-1</sup> bar<sup>-1</sup>.



FIG. 3.—Apparatus used to measure the amount of gas recovered from the melt.

In a second experiment, the melt was exposed to the gas at 640 bar for 8 h. The pressure was then reduced to 200 bar, and stirring continued for a further 12 h. The Henry constant at the end of this time was  $1.05 \times 10^{-7}$  mol ml<sup>-1</sup> bar<sup>-1</sup>. This confirms that equilibrium had been reached in the first experiment. In all subsequent runs, 12 h was chosen as a sufficient and convenient time for saturation. At the end of this time, the motor was turned off and the pressure and temperature noted. Valve B was then opened slowly. The gas pressure in A forced melt up the delivery tube F into vessel C, which was completely filled in a few seconds. B was then closed again, isolating a sample of saturated melt in C. The pressure was released from A, the bolts removed and the inner assembly withdrawn. The cup D, the drive shaft and the upper part of the support housing were removed, and were replaced by the stainless steel cup L (see fig. 2). The modified assembly was replaced in A. The glass apparatus shown in fig. 3 was then attached to the low pressure side of valve K. The volumes of the glass bulbs and the glass tubing had previously been determined (the latter as a function of mercury height in the manometer). K was opened, and vessel A, the Toepler pump, the glass bulbs, and the manometer were evacuated through M. All taps were then closed. Valve B was opened, and evolution of gas caused the melt in C to be ejected down tube F into the cup L. (L was made bigger than the original cup D, because some frothing appeared to occur at this stage. Re-use of D sometimes resulted in spillage.) The evolved gas was transferred to the system of bulbs by means of the Toepler pump, a sufficient number of bulbs being used to give a final pressure just below atmospheric. The

temperature in the insulated box containing the bulbs was noted, and the pressure read from the manometer. The number of moles of gas recovered was calculated from the pressure, volume and temperature. Vessel A was re-opened, and the salt in L weighed. The solubility was expressed in moles of gas per ml melt, using published density data <sup>19</sup> to calculate the volume of the melt.

#### ERRORS

The above procedure is based on the assumption that vessel A remained vacuum-tight during the degassing process. Tests showed that a slow leakage of air into the apparatus did occur at this stage. In all the measurements reported here, this leakage rate was measured after A had been evacuated and before the saturated salt was released from C. The process of degassing the melt and transferring the gas to the glass bulbs was timed, and a correction applied. This could not be done with complete certainty, because the pressure inside A fluctuated as gas was evolved from the melt and removed by the Toepler pump. In fig. 4-7, the upper and lower ends of the vertical bars correspond respectively to uncorrected data and data corrected for ingress of air at the rate which would apply if the vessel had been under vacuum throughout the degassing operation. The amount of air entering was approximately the same for each determination, so this source of error is relatively less important the higher the solubility of the gas.

Another possible source of error was formation of gas by chemical decomposition of the melt. Oxygen and oxides of nitrogen might possibly be formed in this way. The gas recovered from molten  $AgNO_3$  was transferred into a bulb containing alkaline pyrogallol solution before its volume was determined. For the alkali nitrate melts, the volume of recovered gas was the same before and after exposure to alkaline pyrogallol solution, showing that no oxygen was present.

#### RESULTS

Fig. 4-7 show gas solubility plotted against pressure for the systems studied, and fig. 4 includes plots of log  $K_{\rm H}$  against 1/T for the three gases in sodium nitrate. The solubility isotherms are approximately linear in all cases, although some show curvature towards the pressure axis at the higher pressures. Because of this,  $K_{\rm H}$  was evaluated by fitting a straight line to the data in the range 0-500 bar. Table 1 gives the values of  $K_{\rm H}$ , the heat of solution  $\Delta H$ , (=  $-R\partial \ln K_{\rm H}/\partial(1/T)$ ), and the standard entropy of solution  $\Delta S^{\circ}$  for each system. Following Blander,<sup>2</sup> we have chosen standard states in which the solute is at the same concentration in the gas phase and

TABLE 1.—SOLUBILITY DATA FOR HELIUM, ARGON AND NITROGEN IN MOLTEN ALKALI NITRATES

				surface 19		
temp.	$10^{7} K_{\rm H}$	$\Delta H$	$\Delta S^{\circ}$	tension	K <sub>H</sub> (expt.)	$\Delta H(\text{expt.})$
(°C)	(mol ml <sup>-1</sup> bar <sup>-1</sup> )	(kJ/mol)	(J K <sup>-1</sup> mol <sup>-1</sup> )	(dyne/cm)	K <sub>H</sub> (calc.)	$\Delta H(\text{calc.})$
332	$1.86 \pm 0.3$	13.4	-17.4	- 115	0.12	1.2
391	$2.32 \pm 0.3$			113	0.13	
441	$2.80 \pm 0.3$			111	0.14	
331	$0.64 \pm 0.15$	15.8	-21.7	- 115	1.9	0.53
410	0.90±0.15			112	1.3	
440	$1.04 \pm 0.15$			111	1.2	
331	$0.50 \pm 0.15$	16.0	-23.6	115	2.6	0.51
390	$0.64 \pm 0.15$			113	1.7	
449	0.84±0.15			111	1.3	
270	$1.51 \pm 0.4$		1	114	0.11	_
273	0.91±0.2	14.0	-19.3	114	4.5	0.45
307	$1.09 \pm 0.15$			113	3.5	
277	0.73 ±0.1	· · · · · · · · · · · · · · · · · · ·		114	6.3	
331	$1.30 \pm 0.2$	20.1	-8.6	107	2.6	0.62
440	$2.40 \pm 0.2$			100	1.5	
234	$0.19 \pm 0.05$		6 201 IOI 80	147	12.9	
	temp. (°C) 332 391 441 331 410 440 331 390 449 270 273 307 277 331 440 234	$\begin{array}{c c} temp. & 10^7 K_{\rm H} \\ (^{\circ}{\rm C}{\rm C}{\rm (mol\ ml^{-1}\ bar^{-1})} \\ 332 & 1.86\pm0.3 \\ 391 & 2.32\pm0.3 \\ 441 & 2.80\pm0.3 \\ 331 & 0.64\pm0.15 \\ 410 & 0.90\pm0.15 \\ 410 & 1.04\pm0.15 \\ 331 & 0.50\pm0.15 \\ 390 & 0.64\pm0.15 \\ 390 & 0.64\pm0.15 \\ 270 & 1.51\pm0.4 \\ 273 & 0.91\pm0.2 \\ 307 & 1.09\pm0.15 \\ 277 & 0.73\pm0.1 \\ 331 & 1.30\pm0.2 \\ 440 & 2.40\pm0.2 \\ 234 & 0.19\pm0.05 \\ \end{array}$	temp. $10^7 K_H$ $\Delta H$ (°C)         (mol ml <sup>-1</sup> bar <sup>-1</sup> )         (kJ/mol)           332 $1.86 \pm 0.3$ $13.4$ 391 $2.32 \pm 0.3$ $13.4$ 391 $2.32 \pm 0.3$ $13.4$ 331 $0.64 \pm 0.15$ $15.8$ 410 $0.90 \pm 0.15$ $140$ 440 $1.04 \pm 0.15$ $15.8$ 410 $0.90 \pm 0.15$ $16.0$ 390 $0.64 \pm 0.15$ $16.0$ 390 $0.64 \pm 0.15$ $12.12 \pm 0.02$ 270 $1.51 \pm 0.4$ 273 $0.91 \pm 0.2$ $14.0$ 307 $1.09 \pm 0.15$ -           277 $0.73 \pm 0.1$ 331 $1.30 \pm 0.2$ $20.1$ 440 $2.40 \pm 0.2$ 234	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$



FIG. 4(a).—Solubility isotherms for the system He+NaNO<sub>3</sub>. ■, 441°C; ▲, 391°C; ●, 332°C.

in the solution. The standard entropy of solution is derived from the heat of solution using the expression

$$\Delta S^{\circ} = (\Delta H/T) + \mathbf{R} \ln (C_d/C_g),$$

where  $C_d$  and  $C_g$  are the concentrations of gas atoms in the solution and in the gas phase respectively.







FIG. 4(c).—Solubility isotherms for the system N<sub>2</sub>+NaNO<sub>3</sub>. ■, 449°C; ▲, 390°C; ●, 331°C.



FIG. 4(d).—Plots of ln ( $K_{\rm H}$ ) against 1/T for He, Ar and N<sub>2</sub> in NaNO<sub>3</sub>.



FIG. 5(a).—Solubility isotherm for the system  $He+LiNO_3$ .



FIG. 5(b).—Solubility isotherms for the system  $Ar+LiNO_3$ .  $\blacktriangle$ , 307°C;  $\bullet$ , 273°C.



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### COMPARISON WITH PREVIOUS WORK

The Henry's constants in table 1 are lower than those reported by Copeland et al.<sup>9-13</sup> by about an order of magnitude for He, Ar and N<sub>2</sub> in NaNO<sub>3</sub>, and by more than two orders of magnitude for Ar in AgNO<sub>3</sub>. Furthermore, we find the heats of solution for Ar and N<sub>2</sub> in NaNO<sub>3</sub> to be positive, not negative as reported by Copeland.<sup>13, 14</sup> Measurements by Field<sup>20</sup> on He, Ar and N<sub>2</sub> in NaNO<sub>3</sub> below 2 bar gave results for  $K_{\rm H}$  and  $\Delta H$  in fairly good agreement with ours. Apart from Copeland's work, negative values of  $\Delta H$  have previously been found only when the solute gas interacts strongly with the solvent ions, e.g., in the systems  $HF + NaF/ZrF_{4}$ ,<sup>3</sup> HF+LiF/BeF<sub>2</sub>,<sup>4</sup> NH<sub>3</sub>+LiNO<sub>3</sub><sup>7</sup> and H<sub>2</sub>O+alkali metal nitrates.<sup>8</sup> Copeland attributes his negative  $\Delta H$  values to ion + induced dipole interactions between solvent and solute,<sup>13</sup> but the concepts of free energy and enthalpy have been confused in his arguments. The technique involved equilibration of known quantities of gas and melt in a heated pressure vessel, and measurement of the final pressure. The Beattie-Bridgeman equation <sup>21</sup> was then used to calculate the number of moles of gas present in the gas phase, which was subtracted from the number originally admitted to give the amount of gas dissolved. The solubility was thus obtained by subtraction of two quantities of similar magnitude. Errors may have arisen from temperature gradients, or thermal expansion of the pressure vessel.<sup>22</sup>

#### DISCUSSION

### EVALUATION OF THE PARTIAL MOLAR VOLUME OF THE DISSOLVED GAS

For most of the plots of solubility against pressure shown in fig. 4-7, some curvature towards the pressure axis is discernible. This is particularly clear for the system  $Ar + NaNO_3$  (fig. 4b), but tends to be obscured by the experimental scatter in the other cases. At least three causes of curvature may be identified : (i) deviations from the ideal gas equation in the gas phase; (ii) the partial molar volume of the dissolved gas becomes significant in comparison to the molar volume in the gas phase as the gas pressure is increased; (iii) deviations from Raoult's law for the solvent. (iii) is probably less important than (i) or (ii), since the solubility is only about 1 mol % at the highest pressures used. Molten salt solvents generally conform to Raoult's law at this concentration.<sup>23</sup> An expression for solubility as a function of pressure is obtained by integration of a standard equation <sup>24</sup> which takes account of (ii) :

$$\left(\frac{\partial \ln C_d}{\partial P}\right)_T = \left(\frac{V_g - V_d}{RT}\right),\tag{1}$$

where  $v_g$  is the gas molar volume and  $\bar{v}_d$  is the partial molar volume of the dissolved gas. If  $\bar{v}_d$  is assumed independent of pressure and concentration over the experimental range, and use is made of the fact that  $\lim_{P \to 0} (C_d/P) = K_{\rm H}$ , integration of (1) gives

$$\ln C_d = \ln K_{\rm H} + \ln f - (P\bar{v}_d/RT), \qquad (2)$$

where f is the fugacity of the gas. Eqn (2) is the Kritchevsky-Kasarnovsky equation,<sup>25</sup> and indicates that a plot of  $\ln (f/C_d)$  against P should be a straight line of slope  $\bar{v}_d/RT$  and intercept  $-\ln K_{\rm H}$ . Values of PV/RT for argon were available <sup>26</sup> at 400°C, for 27 pressures in the range 42-776 bar. The fugacity was evaluated graphically for a series of pressures, using the formula,

$$\ln \frac{f}{P} = \int_{0}^{P} \left[ \frac{P'V}{RT} - 1 \right] d \ln P'.$$

A plot of  $\ln (f/P)$  against P had only slight curvature, and a short extrapolation allowed values of f to be obtained over the pressure range of the solubility measurements. The solubility data for Ar+NaNO<sub>3</sub> at 410°C were adjusted to 400°C, using the van't Hoff equation with  $\Delta H = 15.8$  kJ/mol (see table 1). A plot of log  $(f/C_d)$  against P is shown in fig. 8. A straight line was fitted to the points by least squares, and  $\bar{v}_d$  and  $K_{\rm H}$  were found from the slope and intercept. The values were :  $\bar{v}_d = 34\pm8$  ml/mol and  $K_{\rm H} = (1.0\pm0.1) \times 10^{-7}$  mol ml<sup>-1</sup> bar<sup>-1</sup> at 410°C, where the intervals quoted correspond to 95 % confidence limits. These values are not materially altered if the calculation is restricted to the pressure range 0-776 bar. Similar plots (not shown) were made for Ar+NaNO<sub>3</sub> at 440°C, Ar+NaNO<sub>3</sub> at 331°C and Ar+RbNO<sub>3</sub> at 440°C, and yielded values for  $\bar{v}_d$  of  $26\pm13$ ,  $30\pm13$  and  $34\pm13$  mol/mol, respectively. The corresponding  $K_{\rm H}$  values were  $(1.1\pm0.2)\times10^{-7}$ ,  $(0.65\pm0.1)\times10^{-7}$  and  $(2.9\pm0.5)\times10^{-7}$  mol ml<sup>-1</sup> bar<sup>-1</sup>. For N<sub>2</sub>+NaNO<sub>3</sub> at 390°C, the same procedure gave  $\bar{v}_d = 46\pm40$  ml/mol and  $K_{\rm H} = (0.8\pm0.5)\times10^{-7}$  mol ml<sup>-1</sup> bar<sup>-1</sup>. The PVT data used for N<sub>2</sub> were those of Bartlett.<sup>27</sup> The poorer precision of the results for Ar+RbNO<sub>3</sub> and N<sub>2</sub>+NaNO<sub>3</sub> reflects the fact that fewer data points were available for these systems. The fact that straight lines are obtained



FIG. 8.—Plot of log  $(f/C_d)$  against pressure for the system Ar+NaNO<sub>3</sub> at 400°C.

when  $\ln(f/C_d)$  is plotted against P is evidence that the solvent is not deviating from Raoult's law as the solute concentration increases. Such deviations would lead to curvature in these plots.

In table 1,  $K_{\rm H}$  was evaluated from the slope of the best straight line through the origin of an isothermal plot of  $C_d$  against P, over the range 0-500 bar. This corressonds to the approximation  $\ln (f/P) - (P\bar{v}_d/RT) = 0$  (cf. eqn (2)). Since the  $K_{\rm H}$  values in table 1 agree with those derived using eqn (2) within the combined limits of error, the use of the simpler procedure is justified in the general case.

Smith and Walkley <sup>28</sup> described a simple method for estimating the partial molar volume of a solute gas from a knowledge of the volume  $v_0$  of the gas at 0 K and the thermal pressure coefficient of the solvent  $(\partial P/\partial T)_v$ . Their formula is

$$\bar{v}_d = v_0 \left[ 1 - \frac{R}{\bar{v}_d} \left( \frac{\partial P}{\partial T} \right)_v^{-1} \right]^{-3}.$$
(3)

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Eqn (3) was derived by treating the gas as a hard-sphere fluid, and calculating the volume for which the gas pressure was equal to the internal pressure of the solvent. This volume was equated to  $\bar{v}_d$ . Values of  $v_0$  may be found either from the volumes of solidified gases, or from molecular diameters obtained from second virial coefficients or from gas viscosities. Calculated values of  $\bar{v}_d$  were in good agreement with experiment for simple solute molecules in a range of organic solvents. Eqn (3) has been used to calculate  $\bar{v}_d$  for argon, nitrogen, and some other gases in molten nitrates (see table 2). The results agree with those derived from our solubility data, within experimental error. No figures are tabulated for helium, as quantum effects make it difficult to assign a value to  $v_0$ ; the liquid molar volume is 27.4 ml/mol at 1.2 K,<sup>29</sup> but the molar volume estimated from the molecular diameter is only 10 ml/mol.<sup>30</sup> For NaNO<sub>3</sub> as solvent, these values of  $v_0$  give  $\bar{v}_d = 39$  and 21 ml/mol respectively. Table 2 shows that for a given gas,  $\bar{v}_d$  is less in molten nitrates than in organic solvents. This reflects the higher internal pressure of the former group of liquids, for which  $T(\partial P/\partial T)_v$  is in the range 10-12 kbar.<sup>31</sup> Eqn (3) requires that, if  $(\partial P/\partial T)_v$  is positive,  $\bar{v}_d$  must be greater than  $v_0$ . This is confirmed by the experimental data for organic liquids, and by the more limited data for molten salts. The suggestion 9, 32 that dissolved gas molecules might "fill up the holes" in the melt is not supported, as it would require  $\bar{v}_d \sim 0$ .

solvent	solute	$v_0 (ml/mol)$ (a,b)	$v_d(ml/mol)$ (calc., eqn (3)) (expt.)		
C7F16	Ar	25	53	54ª	
CCl4	Ar	25	44	44a	
NaNO <sub>3</sub>	Ar	25	37	34+8 <sup>c</sup>	
AgNO <sub>3</sub>	Ar	25	36	_	
CsNO <sub>3</sub>	Ar	25	41		
NaNO <sub>3</sub>	N <sub>2</sub>	32	44	46±404	
NaNO <sub>3</sub>	02	28	40	_	
NaNO <sub>3</sub>	CH₄	35	47		
NaNO <sub>3</sub>	CF <sub>4</sub>	63	76	-	
NaNO <sub>3</sub>	Cl <sub>2</sub>	41	53	-	

#### EFFECT OF DISSOLVED GASES ON TRANSPORT PROPERTIES

An applied pressure of 1 kbar changes the electrical conductivity of molten alkali nitrates by between 1 % (LiNO<sub>3</sub>) and 12 % (CsNO<sub>3</sub>).<sup>18</sup> Considering argon or nitrogen as pressurizing gases, dissolution of gas to the equilibrium concentration at this pressure would cause a further change in conductivity by simple dilution. Assuming no change in ion mobility when the gas dissolves, the conductivity decrease is estimated to be not more than 1 %, based on the solubilities and partial molar volumes in tables 1 and 2. It seems likely that the ion mobilities would increase, rather than decrease, when dilution occurs: this is observed when water is added to molten LiClO<sub>3</sub>,<sup>33</sup> and when p-xylene is added to molten tetra-n-amyl ammonium thiocyanate.<sup>34</sup> The net decrease in conductivity when argon or nitrogen dissolve isothermally in a nitrate melt at 1 kbar is therefore unlikely to exceed 1 %, which corresponds to a change of +0.6 ml/mol in the specific conductance activation volume  $\Delta V_{\kappa}$ . This is much less than the reported difference between the "gas-free" and "gas-saturated" values of  $\Delta V_{\kappa}$  for sodium nitrate,<sup>18</sup> which may have other experimental causes. The "gas-free" value has been confirmed independently.<sup>35</sup>

# COMPARISON OF EXPERIMENTAL $K_{\rm H}$ and $\Delta H$ values with those predicted by blander's theory

Blander <sup>2</sup> has used a theory originally proposed by Uhlig <sup>36</sup> to estimate the solubilities and heats of solution of inert gases in fluoride melts. The dissolution process is considered in three stages : (i) the gas is expanded from concentration  $C_g$  to concentration  $C_d$ . The free energy change is  $\Delta G_1 = \mathbf{R}T \ln (C_d/C_g)$ . (ii) The gas molecules are contracted to points and mixed with the liquid. The free energy change is  $\Delta G_2$ . (iii) The gas molecules are expanded to their proper size. The work required to create the cavities in the melt to accommodate the molecules is  $\Delta G_3 = 4\pi r^2 N\gamma$ , where *r* is the radius of the gas molecule and  $\gamma$  is the surface tension of the melt, here considered as a continuum.

Since the gas is in equilibrium with the liquid, the sum of these free energy changes is zero. If no chemical interaction occurs between the gas molecules and the ions in the melt,  $\Delta G_2$  may be neglected and

$$RT\ln\left(C_d/C_a\right) = -4\pi r^2 N\gamma. \tag{4}$$

Eqn (4) may be used to calculate the solubility of the gas at different temperatures, using experimental values of the surface tension. The heat of solution can be calculated from the temperature dependence of the solubility. This has been done for the systems studied here, and the results are included in table 1. The radii used in the calculations were <sup>2, 11</sup> (in units of  $10^{-10}$  m): He, 1.22; Ar, 1.92; N<sub>2</sub>, 2.00. This simple model predicts the solubilities to within an order of magnitude, and gives the heats of solution to within a factor of 2. The agreement is about as good as that obtained by Blander *et al.*,<sup>2</sup> and confirms the general validity of the model for inert gas solutions. The observed trends in our results are correctly predicted, i.e., (i) for a given gas and melt, the solubilities of a series of gases follow the inverse sequence of the molecular diameters. (ii) For a given gas dissolving in a series of melts, the solubilities increase with decreasing surface tension. This is exemplified by the series Ar+AgNO<sub>3</sub>, Ar+NaNO<sub>3</sub>, Ar+LiNO<sub>3</sub>, Ar+RbNO<sub>3</sub> (see table 1).

A feature of the results is that  $K_{\rm H}$  (expt.)/ $K_{\rm H}$  (calc.) is about 0.1 for He + NaNO<sub>3</sub> and for He + LiNO<sub>3</sub>. Blander <sup>2</sup> obtained a similarly low value for this ratio for He + NaF/ZrF<sub>4</sub>. As he suggests, this may reflect thermal motion of the gas atom in its cavity, so that the cavity radius is larger than the radius of the gas atom deduced from gas phase studies.

The broad agreement between theory and experiment increases the confidence with which the theory may be used to estimate gas solubilities in systems which have not been studied experimentally. Conversely, if experimental results differ greatly from the predicted values (e.g., if the solubility is more than a decade higher than predicted, or if  $\Delta H$  is negative), this may be taken as an indication that the free energy term  $\Delta G_2$  is not negligible.

#### STANDARD ENTROPIES OF SOLUTION

Entropies of solution have been calculated from the experimental results for those systems which have been studied over a temperature range, and are listed in table 1.  $\Delta S^{\circ}$  is negative, and takes values between -8 and  $-24 \text{ J K}^{-1} \text{ mol}^{-1}$ . These are more negative than the corresponding entropy changes for inert gases dissolving in NaF/ZrF<sub>4</sub><sup>-1</sup> ( $\Delta S^{\circ} = 0$  to  $-6 \text{ J K}^{-1} \text{ mol}^{-1}$ ), for CO<sub>2</sub> in alkali halide melts <sup>5</sup> ( $\Delta S^{\circ} =$ -2.5 to  $-5 \text{ J K}^{-1} \text{ mol}^{-1}$ ), or for inert gases in benzene ( $\Delta S^{\circ} = -4$  to  $-7 \text{ J K}^{-1} \text{ mol}^{-1}$ ),

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but less negative than for inert gases in water <sup>38</sup> ( $\Delta S^{\circ} = -54 \,\mathrm{J}\,\mathrm{K}^{-1}\,\mathrm{mol}^{-1}$  for He, and  $-82 \text{ J K}^{-1} \text{ mol}^{-1}$  for argon, at 25°C). The large, negative values for aqueous solutions are generally attributed to structuring of the water surrounding the gas molecule, to give an ice-like cage. For nitrate melts, the fact that  $\Delta S^{\circ}$  is more negative than it is for halide solvents may possibly be due to some restriction of the rotational movement of the nitrate ions near the gas molecules.

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