Offprinted from the *Transactions of The Faraday Society*.
No. 574, Vol. 66, Part 10, October, 1970

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

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Received 24*th February*, 1970

The following solubilities have been measured over a temperature range of 100 deg. and at pressures up to 1 kbar: He in $LiNO_3$ and $NaNO_3$; Ar in $LiNO_3$, $NaNO_3$, $RbNO_3$ and $AgNO_3$; N_2 in $LiNO_3$ and $NaNO_3$. Henry's law was obeyed approximately in all systems. For Ar in $NaNO_3$, 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 ± 8 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^{-1} mol^{-1}, referring to states of equal concentration in the gaseous and liquid phases. These entropies are more negative than those for solutions of the same gases in organic solvents or in molten halides, but less negative than for aqueous 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.[1-8] 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 J K^{-1} mol^{-1} (referring to equal concentrations of solute molecules in the gaseous and liquid phases).[1, 5] The solubilities of inert gases in a given melt follow the inverse sequence of solute molecular size.[1] Negative heats of solution are observed when strong interactions occur between the solute molecules and the ions in the melt.[3, 4, 7, 8] Only one group of workers has reported solubility measurements for gases in molten salts at high pressures,[9-13] and the results conflict with the trends described above. Ar and N_2 were reported to have negative heats of solution in fused $NaNO_3$, and to be about an order of magnitude more soluble than in fluoride melts. The solubility sequence at 369°C was $He > N_2 > Ar$, 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_2 in $LiNO_3$ and $NaNO_3$, and of Ar in $RbNO_3$ and $AgNO_3$, 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 [10, 12, 14-18] and the presence of dissolved gas has been a possible source of error.[16-18] The solubilities reported here provide a basis for estimation of the effect which dissolved gas might have on transport phenomena at high pressures.

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.

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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 Products (U.K.), model 3033), and came in contact only with stainless steel during this process. $NaNO_3$ (B.D.H., A.R., $>$99.5 %) and $RbNO_3$ (Johnson, Matthey and Co., 99.9 %) were fused, filtered through Pyrex frits, allowed to freeze, and stored *in vacuo*. $AgNO_3$ (Johnson, Matthey & Co., 99.9 %) was recrystallized once from distilled water. $LiNO_3$ (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 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.

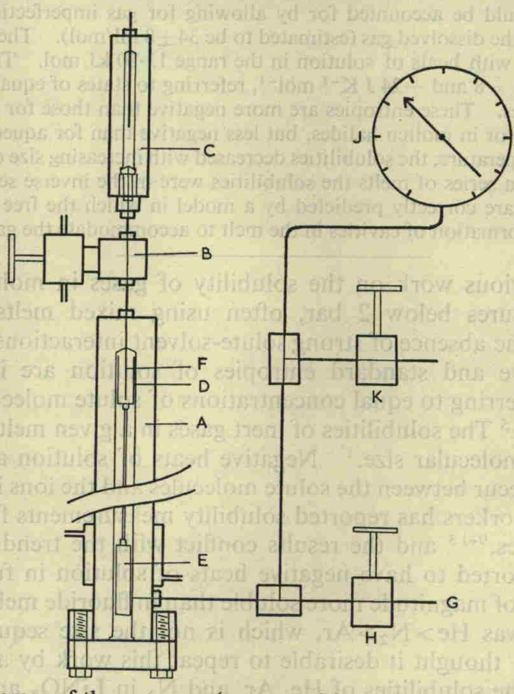

FIG. 1.—Schematic diagram of the apparaus (not to scale). The letters are referred to in the text.