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The Solubility of Argon to 451 Atmospheres in Fused Sodium Nitrate at 369°

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The solubility of argon in fused sodium nitrate at 369° has been determined to a maximum saturating pressure of 451 atm. The relationship between solubility and saturating pressure is linear and thus obeys Henry's law. The experimental solubility equation is $C_d = (17.2 \times 10^{-7})P \pm 0.41 \times 10^{-4}$ mole of Ar (cm.^{3} of melt)$^{-1}$ where P is saturating pressure in atm. The Henry's law constant is given by $K = (17.2 \pm 1.7) \times 10^{-7}$ mole of Ar (cm.^{3} of melt)$^{-1}$ atm.$^{-1}$. The Henry's law constant in terms of the ratio of concentration of Ar in the liquid phase to its concentration in the gas phase has a value in fair agreement with simple theory. Two extreme possibilities for probable distribution of the gaseous atoms throughout the liquid salt are briefly discussed in terms of the free volume theory of liquids.

The inherent simplicity of solutions of gases in simple molten salts makes them of great interest to theoreticians concerned with structures of such melts. Solutions of noble gases constitute the simplest such systems because of the relatively weak interactions of the gaseous atoms with the ionic liquid. A relatively complicated theoretical expression for predicting Henry's law constants for such solutions has already been developed.[1] However, relatively few data are presently available to aid the theoretical situation, and most of these data are for noble gas solubilities in a few mixtures of molten fluorides.[2–4] In addition, these data are for only a few atmospheres of saturating gas pressure.

The purpose of this paper is to present results of measurements of the solubility of Ar in molten $NaNO_3$ at 369° at relatively high pressures (up to 451 atm.) and the Henry's law constant calculated therefrom. It is shown that this constant is in fair agreement with the order of magnitude predicted by Blander, *et al.*, from their simplified theoretical treatment.[3]

Experimental Section

Reagent grade $NaNO_3$ from Baker and Adamson and from Fisher was employed. The Baker and Adamson salt was used without purification other than drying. The Fisher chemical was also dried, but exhibited traces of a residue which was insoluble in the fused salt. This residue eventually settled, and the pure molten salt was then decanted. Argon was obtained from the National Cylinder Gas Co. and had a stated purity of 99.999%. It was used without further purification.

A 500-ml. capacity Inconel metal bomb, Type A243HC5 of the Parr Instrument Co., was fitted with two CONAX thermocouple glands packed with a natural magnesium silicate. Each of these glands contained a chromel–alumel thermocouple. One thermocouple junction was positioned centrally in the lower half of the bomb and the other junction was located similarly in the upper half of the system. Both junctions were protected against salt corrosion by Pyrex tubes. The accuracy of each of the thermocouples was ±0.5°. The bomb was further equipped with a 0–8000 p.s.i.g. Supergauge manufactured by the U. S. Gauge Division of Ametek. The accuracy of this gauge, as quoted by the manufacturer, was ±40 p.s.i., or slightly better than ±3 atm.

To determine the solubility of Ar in fused $NaNO_3$ at a given saturating pressure, the following procedure was employed. The effective empty volume of the bomb, containing a Pyrex liner and thermocouples, was taken as the average of several measurements of the volume of water required to fill the closed bomb

(1) H. Reiss, *et al.*, *J. Chem. Phys.*, **32**, 119 (1960).

(2) W. R. Grimes, N. V. Smith, and G. M. Watson, *J. Phys. Chem.*, **62**, 862 (1958).

(3) M. Blander, W. R. Grimes, N. V. Smith, and G. M. Watson, *ibid.*, **63**, 1164 (1959).

(4) G. M. Watson, *et al.*, *J. Chem. Eng. Data*, **7**, 285 (1962).

completely through a small orifice in the bomb's head which normally accommodates the pressure gauge. This volume generally resulted as about 430 cm.^{3} with a maximum error of ± 1 cm.^{3}. A correction factor of 2 cm.^{3} was added to this volume to account for the volume of the Bourdon tube of the pressure gauge. A sample of dry $NaNO_3$ of from about 350 to 450 g. was weighed into the Pyrex liner to the nearest 0.5 g. The volume of the solid salt was calculated using a density of 2.261 g. cm.$^{-3}$.[5] The bomb, containing the salt, was sealed and evacuated, and Ar was admitted at room temperature to some desired pressure. When pressure equilibrium was attained at room temperature, the number of moles of Ar introduced was calculated from the equilibrium pressure, temperature, and gas volume by interpolation of detailed plots of the P–$\bar{V}$–T data compiled by Din.[6] The bomb was then heated in a vertical furnace to a fused $NaNO_3$ temperature of 369°, as indicated by the lower thermocouple within the liquid phase. At this temperature the liquid salt occupied about one-half of the bomb liner (about 200–250 cm.^{3} of liquid). Solution equilibrium was assumed to exist at the saturation pressure indicated and at a salt temperature of 369° when no discernible pressure change was observed for at least 24 hr., during which time the system was often agitated. The temperature of the salt was assumed to be uniform at 369° since agitation caused no perceptible change in the lower thermocouple's reading. The number of moles of gaseous Ar remaining was calculated from the new equilibrium gas pressure, volume, and temperature (indicated by the upper thermocouple located centrally in the gas phase) with the aid of the same graphs of Din's compilation. The final gas volume was the initial room temperature value corrected to the nearest 1 cm.^{3} for the increase in volume of the liquid $NaNO_3$ and its compression. A density of 1.875 g. cm.$^{-3}$, taken from the data of Bloom, *et al.*,[7] was used for the calculation of the volume of fused salt. Compression of the melt was found by interpolation of the data of Bockris and Richards for the isothermal compressibility coefficients of fused salts.[8] Thermal expansions of the bomb, Pyrex liner, and thermocouples were ignored in view of their minuteness. Finally, the decrease in moles of gaseous Ar was attributed to its solubility in the melt, which was then calculated.

Results and Discussion

Figure 1 is a graph of the solubility of Ar in fused $NaNO_3$, at 369°, *vs.* saturating pressure to an upper value of 451 atm. Table I summarizes these data. Corrections for slightly lower gas temperatures,

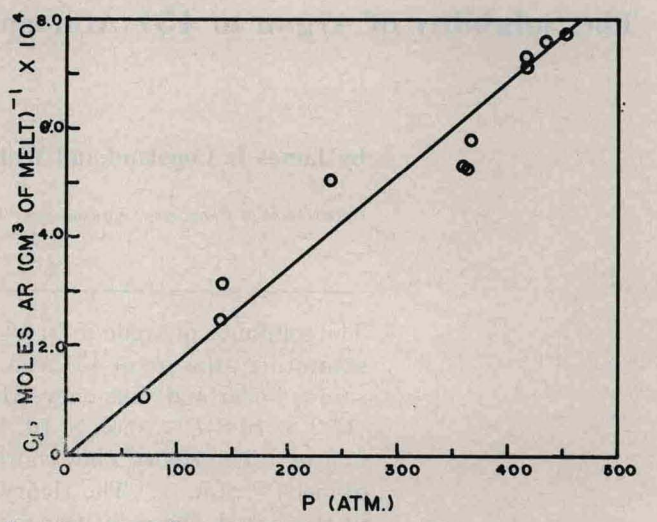

Figure 1. Solubility of argon in molten sodium nitrate at 369°, C_d, *vs.* saturating pressure of argon, P.

relative to the salt at 369°, were found not to affect the points above 200 atm. significantly and were therefore not applied thereto. Such corrections, however, were necessary for points below 200 atm. The maximum error in pressure is slightly better than ± 3 atm. for each point. The relationship appears linear and thus obeys Henry's law. The average slope calculated from these data yields the equation for solubility, C_d

Table I: Summary of Solubility of Ar in Molten $NaNO_3$ at 369° *vs.* Saturating Pressure of Ar Data

Saturating pressure, P, atm.	Solubility, C_d, moles of Ar (cm.^{3} of melt)$^{-1}$ × 10^4
70	1.10
139	2.50
140	3.16
238	5.07
359	5.35
362	5.31
366	5.81
416	7.33
417	7.16
434	7.63
451	7.78

(5) "Handbook of Chemistry and Physics," 40th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1958–1959, p. 657.

(6) F. Din, "Thermodynamic Functions of Gases," Vol. 2, Butterworth and Co., Ltd., London, 1962, pp. 192, 193.

(7) H. Bloom, *et al.*, *Trans. Faraday Soc.*, **49**, 1458 (1953).

(8) J. O'M. Bockris and N. E. Richards, *Proc. Roy. Soc.* (London), **A241**, 44 (1957).