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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 NaNO₃ 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 NaNO₃ 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 $\pm 0.5^{\circ}$. 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).

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 NaNO₃ 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 NaNO3 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 NaNO₃ 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 NaNO₃, 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

 Table I:
 Summary of Solubility of Ar in Molten

 NaNO₃ at 369° vs. Saturating Pressure of Ar Data

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

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, $C_{\rm d}$

(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).

 $C_{\rm d} = (17.2 \times 10^{-7})P \pm 0.41 \times 10^{-4} \text{ mole of Ar}$ (cm,³ of melt)⁻¹ (1)

where P is the saturating pressure in atm., and the error is the probable error calculated with respect to the best straight line. The Henry's law constant is the average slope

$$K = (17.2 \pm 1.7) \times 10^{-7} \text{ mole of Ar (cm.}^3 \text{ of } melt)^{-1} \text{ atm.}^{-1} (2)$$

where the error is the probable error of the slope. This value for K is in good agreement with the first crude results reported earlier by this laboratory.⁹ If this constant is converted to $K_c = C_d/C_g$ (where C_d and C_g denote concentrations of Ar in the liquid and gas phases, respectively), then (approximately)

$$K_{\rm c} = 86 \times 10^{-3} \tag{3}$$

It is assumed that C_d is small enough to render the solution ideal, so that the activity of Ar therein may be equated to its concentration. Furthermore, ideal gas behavior is assumed for Ar at the high temperature, in spite of its pressure, so that its fugacity may be equated to pressure. The latter assumption involves errors of about 9.3% in the molar volume of Ar at the maximum employed pressure of 451 atm., and of about 2% at the lowest pressure of 70 atm., as deduced from Din's compilation.⁶

The simplified solubility model of Blander, *et al.*, equates the free energy of solution of the gas to the free energy of formation of holes the size of the gas molecules in a continuous fluid having the same surface tension as the solvent.³ Their derived relation for K_e is

$$K_{\rm c} = \exp\left[-kA\gamma_{\rm mic}/RT\right] \tag{4}$$

where A is the area of a hole created by a gas molecule, γ_{mic} is a microscopic "surface tension," R is the gas constant, T is the absolute temperature, and k is a conversion factor to obtain energy in calories. For spherical gas atoms, $kA = 18.08r^2$, where r is the atomic radius of the gas in Å. γ_{mic} is taken to be the same as that of the macroscopic fluid. For fused NaNO₃ at 369°, $\gamma = 109.7$ dynes cm.^{-1,10} The atomic radius of Ar is taken as r = 1.92 Å.³ Equation 4 with these values gives a calculated K_c of 3.3×10^{-3} . Thus our experimental K_c agrees to an order of magnitude with the calculated value to about the same extent as did some of the results of Blander, *et al.*,³ and Watson, $et al.^4$

Two interesting extreme possibilities may exist for probable distribution of Ar atoms throughout the liquid NaNO₃. One possibility is that the gaseous atoms take up holes of their own creation in the liquid. In this case, the volume of the solution would be expected to be greater than that of the pure solvent by an amount roughly equal to the total volume of the solute particles (about 3 cm.3 for the highest solubility observed in this work at 451 atm.). Unfortunately, measurements of such possible volume changes could not be made with the present apparatus. Another extreme possibility is that the solute atoms predominantly occupy existing free volume (as holes) in the liquid. In the hole theory of fused salts, the volume increase on melting is attributed almost entirely to holes.¹¹ Thus such free volume amounts to about 4.32 cm.³ mole⁻¹ for fused NaNO₃.¹² In this case, but little volume difference would be expected between the pure solvent and solution, especially in view of the relatively weak solvent-solute interactions. A third possibility, of course, is a combination of these two cases. If the availability of liquid free volume provides for enhanced solubility to some extent, then the solubility of Ar at an equivalent temperature in LiNO₃ should be greater than in NaNO₃ by virtue of a larger free volume for the former salt (about $6.84 \text{ cm.}^3 \text{ mole}^{-1 \text{ 12}}$). Similarly, the solubility should be less in KNO₃ (free volume of about 1.73 cm.³ mole⁻¹¹²), etc. Such studies are being undertaken in this laboratory in conjunction with conductance measurements on the solutions.9 It is hoped that the conductance measurements will help to elucidate the mechanism of solute distribution in such liquids.

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