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The High-Pressure Solubility of Nitrogen in Fused Sodium Nitrate.

Temperature and Pressure Dependences and the Heat and Entropy of Solution¹

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The solubility of nitrogen in fused sodium nitrate has been determined over a temperature range from 355 to 454° at pressures from 140 to 426 atm. Henry's law constants, K_h , were found for the resulting eight solubility-pressure isotherms. A plot of $\log K_h$ (with K_h in moles $\text{cm}^{-3} \text{ atm}^{-1}$) vs. $1/T$ yielded a straight line whose least-squares equation is $\log K_h = (597 \pm 19)(1/T) - (6.64 \pm 0.03)$. The heat and standard entropy of solution obtained from this equation are $-2.73 \pm 0.09 \text{ kcal mole}^{-1}$ and $-16.6 \pm 0.1 \text{ eu}$, respectively. The results are compared with those of other workers studying noble gas and hydrogen fluoride solubilities in molten fluoride mixtures. The results at 369° are also compared with earlier work of this laboratory involving helium and argon solubilities in fused sodium nitrate at the same temperature. Conclusions are drawn which compare the relative contributions of exothermic solvation effects and endothermic molecular cavity creation work in the liquid to the over-all heat of solution.

Introduction

In the simplified model of Blander, Grimes, Smith, and Watson,² the theoretical distribution coefficient, $K_{c,\text{theor}}$, for an inert gas in solution equilibrium with a fused salt is derived by equating 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. The derived relation is

$$K_{c,\text{theor}} = C_d/C_g = \exp(-kA\gamma_{\text{mic}}/RT) \quad (1)$$

where C_d and C_g are concentrations of the gas in the liquid and gas phases, respectively, A is the area of a hole created in the liquid by a gas molecule, γ_{mic} is a microscopic "surface tension" (generally taken as the macroscopic value), R is the gas constant, T is absolute temperature, and k is a conversion factor to obtain energy in calories. If the gas molecules are regarded as spherical, $kA = 18.08r^2$, where r is the effective molecular radius in Å. This model neglects solvation effects in comparison to the large endothermic work done against the high surface tension of a typical ionic liquid to accommodate a gas molecule. This approach is justified reasonably well by the cited authors'² observations of endothermic heats of solution for various

noble gases in molten fluoride mixtures. As the solvation effects, such as ion-induced dipole, become more pronounced, the associated exoenergetics would be expected to contribute to the over-all heat of solution to an ever-increasing extent. At some point, therefore, the solvation energy associated with a given solute may exceed the endoenergetics of molecular cavity creation, resulting in the more usually observed exothermic heat of solution. This effect would be even more enhanced if solvents of lower surface tensions were employed. Increasing solvation effects naturally bring about greater gas solubility at a given temperature and pressure, which in turn causes an increasing trend in the ratio $K_{c,\text{exptl}}/K_{c,\text{theor}}$.² Such was the case observed in ref 2 as solvation effects increased with increasing polarizability of the noble gas solute employed. Theoretical aspects of fused salt-gas solutions and their energetics have been amply reviewed and discussed by Stillinger.³

(1) This paper was presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) M. Blander, W. R. Grimes, N. V. Smith, and G. M. Watson, *J. Phys. Chem.*, **63**, 1164 (1959).

(3) F. H. Stillinger, Jr., "Equilibrium Theory of Pure Fused Salts," in "Fused Salt Chemistry," M. Blander, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 1-108.

In the later work of Shaffer, Grimes, and Watson⁴ on the solubility of HF in molten fluorides, the solvation effects obviously were dominant over the endothermic work against surface tension, resulting in fairly high solubilities and exothermic heats of solution.

In the present work we present the temperature and high-pressure dependences of the solubility of N₂ in fused NaNO₃, from which the heat and standard entropy of solution are calculated. It is shown that the solvation effects (probably ion-induced dipole in the main owing to the fairly polarizable N₂ molecule) are apparently dominant over the molecular cavity creation work done against the comparatively small surface tension of this melt. This results in a negative temperature coefficient of solubility, the associated exothermic heat of solution, and a negative standard entropy of solution of the same order of magnitude as that observed for the diatomic HF molecules cited in ref 4. Also, the results obtained at 642°K are compared with the data obtained by this laboratory for the solubilities of Ar^{5a} and He^{5b} in molten NaNO₃ at this temperature.

Experimental Section

The basic apparatus and method for determining high-pressure solubilities of inert gases in fused salts have already been discussed.^{5a}

In the present work, Baker and Adamson Reagent grade NaNO₃ and at least 99.98% pure (Bone Dry grade) N₂ from the National Cylinder Gas Co. were employed. To remove moisture, the salt was fused and allowed to solidify in a porcelain casserole contained in a desiccator. The solid block of NaNO₃ was then finely pulverized, and about 400 g of the powder was weighed to the nearest 0.5 g into a Pyrex bomb liner. The salt-charged liner was enclosed in the bomb, and the basic procedure outlined in ref 5a was followed using N₂ as the "inert" gas. However, in this work, the bomb assembly was heated to an initial fused-salt temperature of 454° (except in one run when the pressure involved would have been too high for safety), and the equilibrium gas temperature and pressure were noted. The temperature was then lowered to a salt temperature of 445°, the system was frequently agitated to ensure equilibrium and to avoid supersaturation of the melt, and the new equilibrium gas temperature and pressure were observed. This stepwise procedure was continued for salt temperatures of 423, 413.5, 396.5, 382.5, 368.5, and 355.5°. This experiment was repeated five times for the same eight temperatures, each time with a different starting pressure of N₂ at room temperature. These runs yielded eight solubility isotherms, each consisting of

four or five solubility-pressure points. The maximum pressure for any experiment was 426 atm, and the minimum pressure for any run was 140 atm. Molar volumes of N₂ at the various gas temperatures and pressures were obtained from graphs of the P - \bar{V} - T data compilation of Din.⁶

As in previous work,⁵ the decrease in moles of the gas phase in the system, between a given high temperature and room temperature, was attributed to gas solubility in the melt. The density of liquid NaNO₃ at a given temperature and pressure, $d_{t,p}$, used for calculating the total volume of the pure salt, was obtained from the following empirical equation for the density in the absence of a gas phase

$$d_{t,p} = d_{t,1} + (3.9 \times 10^{-5})P \text{ g cm}^{-3} \quad (2)$$

where $d_{t,1}$ is the density at $t^\circ\text{C}$ and 1 atm, and P is piston pressure in atmospheres. This relationship is based on the density-piston pressure data of Owens.⁷ The density $d_{t,1}$ is obtainable from the empirical relation of Bloom, Knaggs, Molloy, and Welch⁸

$$d_{t,1} = 2.134 - (7.03 \times 10^{-4})t \text{ g cm}^{-3} \quad (3)$$

A minor error persists, of course, as a result of using such pure salt densities as estimates of the actual dilute solution densities. It is thought that this error is well within the experimental error of the procedure. The maximum error in a pressure measurement is slightly less than ± 3 atm, as quoted by the gauge manufacturer.^{5a}

Average Henry's law constants, K_h , where

$$K_h = C_d/P \text{ moles of gas cm}^{-3} \text{ atm}^{-1} \quad (4)$$

(P is gas-saturating pressure in atmospheres), and distribution coefficients, K_e , were calculated for each solubility-pressure isotherm.

Results

Table I summarizes the experimental pressures, solubilities, Henry's law constants, and distribution coefficients. In addition, theoretical values of the latter quantity are included, as calculated from eq 1. Surface tension values used in eq 1 were calculated from

(4) J. H. Shaffer, W. R. Grimes, and G. M. Watson, *J. Phys. Chem.*, **63**, 1999 (1959).

(5) (a) J. L. Copeland and W. C. Zybko, *ibid.*, **69**, 3631 (1965); (b) J. L. Copeland and W. C. Zybko, *ibid.*, **70**, 181 (1966).

(6) F. Din, "Thermodynamic Functions of Gases," Vol. 3, Butterworth and Co., Ltd., London, 1961, pp 146-150.

(7) B. B. Owens, private communication to J. L. C., 1965.

(8) H. Bloom, I. W. Knaggs, J. J. Molloy, and D. Welch, *Trans. Faraday Soc.*, **49**, 1458 (1953).