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

Temperature and Pressure Dependences and the Heat and Entropy of Solution[1]

by James L. Copeland and Lawrence Seibles

Department of Chemistry, Kansas State University, Manhattan, Kansas 66504 (*Received November 15, 1965*)

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 cm^{-3} 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 ± 0.09 kcal mole^{-1} and -16.6 ± 0.1 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, $K_{c,theor}$, 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

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

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 A. 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 $K_{c,exptl}/K_{c,theor}$.[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 Watson[4] 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 N_2 in fused $NaNO_3$, 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 N_2 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 $NaNO_3$ 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 $NaNO_3$ and at least 99.98% pure (Bone Dry grade) N_2 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 $NaNO_3$ 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 N_2 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 N_2 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 N_2 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 $NaNO_3$ 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

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

where $d_{t,1}$ is the density at t°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 Welch[8]

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

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

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

(P is gas-saturating pressure in atmospheres), and distribution coefficients, K_c, 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).

Table I: Summary of Solubility–Temperature–Pressure Data for Nitrogen in Fused Sodium Nitrate. Temperatures Are Those of the Fused Salt

Gas press, P, atm	Soly, C_d, moles/cm³ $\times 10^4$	Henry's law const, K_h, moles/cm³ atm $\times 10^7$	Dist coeff, $K_{c.exptl} \times 10$	Theor dist coeff, $K_{c.theor} \times 10$
		$T = 727°K$		
364	6.00	16.5	1.11	
286	4.00	14.0	0.908	0.042
227	3.11	13.7	0.869	
167	2.73	16.4	1.01	
		Av 15.2 ± 1.2	Av 0.976	
		$T = 718°K$		
357	5.97	16.7	1.11	
281	4.21	15.0	0.961	0.039
223	3.37	15.1	0.949	
163	2.98	18.3[a]	...	
		Av 15.6 ± 0.8	Av 1.01	
		$T = 696°K$		
349	5.57	16.0	1.04	
272	4.34	16.0	1.00	0.031
217	3.24	14.9	0.915	
159	2.85	17.9	1.07	
		Av 16.2 ± 1.0	Av 1.01	
		$T = 686.5°K$		
426	7.40	17.4	1.16	
341	5.93	17.4	1.11	
266	4.66	17.5	1.08	0.027
213	3.31	15.5	0.938	
155	2.91	18.8	1.10	
		Av 17.3 ± 0.9	Av 1.08	

Gas press, P, atm	Soly, C_d, moles/cm³ $\times 10^4$	Henry's law const, K_h, moles/cm³ atm $\times 10^7$	Dist coeff, $K_{c.exptl} \times 10$	Theor dist coeff, $K_{c.theor} \times 10$
		$T = 669.5°K$		
415	6.64	16.0	1.03	
332	5.87	17.7	1.10	
258	4.64	18.0	1.08	0.022
205	3.75	18.3	1.08	
151	3.08	20.4	1.17	
		Av 18.1 ± 1.2	Av 1.09	
		$T = 655.5°K$		
398	7.77	19.5	1.23	
323	5.91	18.3	1.12	
251	4.71	18.7	1.10	0.016
200	3.77	18.8	1.09	
148	2.75	18.6	1.04	
		Av 18.8 ± 0.3	Av 1.12	
		$T = 641.5°K$		
387	7.67	19.8	1.22	
314	5.99	19.1	1.14	
244	4.94	20.2	1.17	0.016
194	3.74	19.3	1.08	
144	2.90	20.1	1.11	
		Av 19.7 ± 0.4	Av 1.14	
		$T = 628.5°K$		
375	7.89	21.0	1.26	
306	6.07	19.9	1.16	
238	4.76	20.0	1.12	0.014
192	3.43	17.9[a]	...	
140	2.82	20.1	1.08	
		Av 20.2 ± 0.4	Av 1.16	

[a] Data discarded from averaging according to Chauvenet's criterion.

the empirical equation of Addison and Coldrey[9] applied to fused NaNO₃

$$\gamma = 116.6 - 0.050(t - 308) \text{ dynes cm}^{-1} \quad (5)$$

where t is temperature in degrees centigrade. An approximate close-packed radius of 2.00 A was taken for the N_2 molecule regarded as a sphere.[10] It is interesting to perform a sample calculation for the expected value of r for N_2 using eq 1 with an experimental value of K_c for, say, 641.5°K. This naïve approach gives $r = 1.16$ A, a value which would appear to be too small, especially when Blander, *et al.*,[2] were forced to accept effectively *larger* radii than usual to obtain complete agreement of this theory with their

experiments. The errors recorded in Table I for the average Henry's law constants are the probable errors for a single observation.

Figure 1 is a graph of the eight solubility–pressure isotherms, with temperatures as indicated in degrees Kelvin. The plots are drawn with slopes equal to the tabulated average K_h values. Individual points are not shown for the sake of avoiding confusion; they are available for graphing from Table I. Figure 2 depicts the relationship between the common log $K_{h,av}$ and

(9) C. C. Addison and J. M. Coldrey, *J. Chem. Soc.*, 468 (1961).

(10) W. J. Moore, "Physical Chemistry," 3rd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 229.
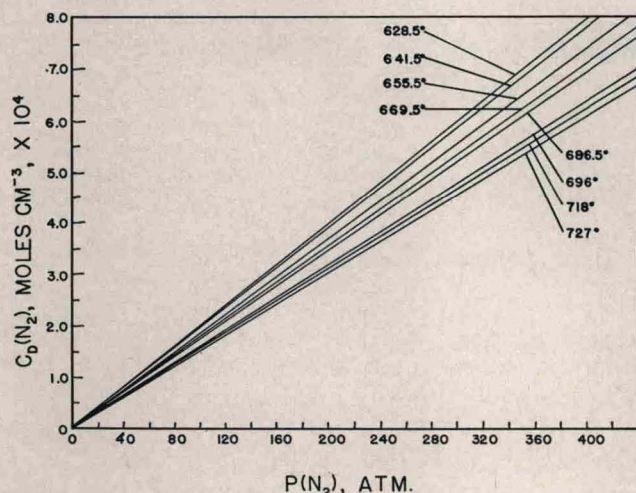
Figure 1. Solubility, C_d, vs. pressure, P, isotherms for nitrogen in fused sodium nitrate at various temperatures. See Table I for individual data points. All temperatures are in degrees Kelvin.
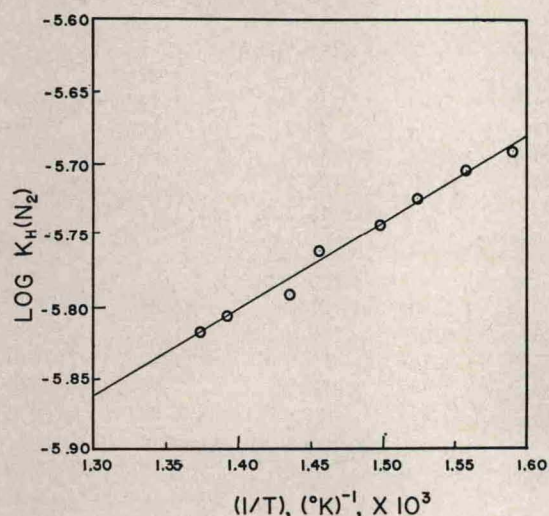

Figure 2. Common log of Henry's law constant, log K_h (where units of K_h are moles cm^{-3} atm^{-1}), vs. reciprocal absolute temperature, $1/T$, for nitrogen in fused sodium nitrate.

$1/T$ in $(°K)^{-1}$. The least-squares straight-line relationship for this graph is

$$\log K_h = (597 \pm 19)(1/T) - (6.64 \pm 0.03) \quad (6)$$

where the errors are the least-squares probable errors, and units of K_h are those of Table I. The theoretical thermodynamic equation for such a plot is[4]

$$\ln K_h' = -(\Delta H/R)(1/T) + \Delta S_p°/R \quad (7)$$

where $K_h' = 1000K_h$ (i.e., K_h' is in units of moles $l.^{-1}$ atm^{-1}), ΔH is the heat of solution, and $\Delta S_p°$ is the standard entropy of solution in terms of equal solute gas pressures inside and outside the liquid. Use of eq 6 and 7 leads to the experimental values $\Delta H = -2.73 \pm 0.09$ kcal $mole^{-1}$ and $\Delta S_p° = -16.6 \pm 0.1$ eu, where the errors are again probable errors.

Discussion

The negative temperature coefficient of solubility for N_2 in fused $NaNO_3$ and the attendant exothermic heat of solution leave no doubt that solvation effects in this system are of greater importance than solute molecule cavity creation work. This is also amply demonstrated by the large $(K_{c,exptl}/K_{c,theor})$ ratios, $K_{c,exptl}(av)$ being from 23 to 83 times greater than $K_{c,theor}$. Prior work on solubilities of the noble gases in molten fluorides has usually resulted in this ratio being less than unity, with the smallest values for the less polarizable gases such as He and Ne.[2,11] In some of these cases, with the more polarizable gases such as Ar and Xe, the ratio sometimes was slightly greater than unity, presumably owing to the effect of greater ion–induced dipole interactions in augmenting the solubility.

In the HF work,[4] the experimental heat of solution ranged from -3.85 kcal $mole^{-1}$, for a 45 mole $\%$ of NaF in $NaF-ZrF_4$ mixture, to -9.70 kcal $mole^{-1}$, for 80.5 mole $\%$ NaF. Our observed ΔH of -2.73 kcal $mole^{-1}$ is somewhat smaller than the lowest such value for the HF work, implying less exothermic solvation effects for N_2 in $NaNO_3$ than what occur in the HF systems. This is to be expected in view of the additional exoenergetic contribution of ion–permanent dipole interactions which must occur in the latter system. Also, the Henry's law constants observed in the HF work are about 10 times greater than our observed values, which again may be attributable in part to such ion–dipole solvation effects. In addition, the relatively high stability of NaF–HF complexes is thought to increase solubility of the HF and to make the heat of solution still more negative.[4]

The $\Delta S_p°$ entropies of solution found in the HF work vary from -14.0 eu, for the 45 mole $\%$ NaF system, to -15.2 eu, for the 80.5 mole $\%$ NaF solution.[4] Our value of -16.6 eu therefore appears to be in line with these values for other diatomic molecules. These standard entropies of solution for HF and N_2 diatomic molecules are noticeably more negative than values obtained for monatomic noble gas molecules in fluoride melts.[2,12] This observation was predicted in view of

(11) G. M. Watson, R. B. Evans, III, W. R. Grimes, and N. V. Smith, J. Chem. Eng. Data, 7, 285 (1962).

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

rotational degrees of freedom being accessible to diatomic molecules but not to spherically symmetric rare gas atoms.[2]

Copeland and Zybko have observed Henry's law constants for high-pressure solubilities of Ar and He in molten $NaNO_3$ at 642°K.[5] For Ar, $K_{h,Ar} = (17.2 \pm 1.7) \times 10^{-7}$ mole cm^{-3} atm^{-1}, and for He, $K_{h,He} = (22.7 \pm 0.7) \times 10^{-7}$ mole cm^{-3} atm^{-1}. The close-packed "spherical" radius of the N_2 molecule is very nearly the same as that of Ar (1.92 A²). Thus, the cavity creation work done against the *comparatively small* surface tension of $NaNO_3$ by either gas would be expected to be small and approximately the same for each. However, the polarizability of N_2 is 1.734×10^{-24} cm^3 $molecule^{-1}$ as compared to 1.626×10^{-24} cm^3 $molecule^{-1}$ for Ar.[13] On this basis, one would expect slightly greater ion–induced dipole solvation effects for N_2 than for Ar, which would tend to make the former slightly more soluble if all other effects are nearly equal. The polarizability of He is only about 0.2036×10^{-24} cm^3 $molecule^{-1}$,[13] and its close-packed radius is about 1.22 A.[2] Thus, much less work against surface tension is required to create a hole for a He atom than for either N_2 or Ar. However, solvation effects for He would be practically nonexistent. It would appear, therefore, that the slightly greater solubility of He might be primarily the result of the relative ease of introducing such a small atom into the liquid, in spite of the partially compensating solvation effects which exist for the larger solute molecules.

(13) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd ed, Pergamon Press, Oxford, 1961, p 383.