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Thermodynamics of High-Temperature High-Pressure Solutions. Argon in Molten Sodium Nitrate[1]

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The solubility of Ar in molten $NaNO_3$ has been determined over a temperature range from 356 to 441° at pressures from 151 to 395 atm. Henry's law constants, K_h, and distribution coefficients, K_c, were found for the resulting six solubility–pressure isotherms. A plot of log K_h *vs.* $1/T$ yielded a value for the enthalpy of solution, ΔH, of -1.69 ± 0.21 kcal mole^{-1}. The standard entropy of solution, corresponding to a standard state of 1 *M* concentrations of gas in both the liquid and gaseous states, $\Delta S_c°$, resulted as -4.97 ± 0.32 eu from the intercept of a plot of log K_c *vs.* $1/T$. The results are compared to similar work in this laboratory involving N_2 in fused $NaNO_3$, where $\Delta H = -2.73 \pm 0.09$ kcal mol^{-1} and $\Delta S_c° = -6.78 \pm 0.18$ eu, and with low pressure work in molten fluoride systems performed in other laboratories where ΔH values were endothermic. Calculations of ΔH's of solution for both the Ar and N_2 work using approximate fugacities rather than pressures did not change the values appreciably, yielding -1.84 ± 0.21 kcal mol^{-1} for Ar in $NaNO_3$ and -2.69 ± 0.08 kcal mol^{-1} for N_2 in $NaNO_3$. 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. It is seen that predictions based on such a simple model conceived for the N_2 work are, for the most part, reasonably confirmed in the present investigation.

Introduction

In a previous paper the authors reported the results of a study of the temperature and high-pressure dependences of the solubility of N_2 in fused $NaNO_3$.[2] The system was found to possess an exothermic heat of solution and a rather high negative entropy of solution. A tentative simple model was advanced which

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[1] This work was presented in part at the Third Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., Nov 1967.

conceived of exothermic solvation effects dominating over endothermic work of molecular cavity creation necessary to accommodate a solute particle. It was predicted that a molecule of comparable size to N_2, but of less polarizability, such as Ar, should therefore be somewhat less soluble in $NaNO_3$ than is N_2, and should have a somewhat less exothermic heat of solution (if indeed exothermic at all). In addition, a monatomic gas, such as Ar, would be expected to suffer a less negative entropy of solution than did the diatomic N_2 molecules. The present investigation serves to confirm these predictions to a large degree.

Experimental Section and Data Treatment

The apparatus and procedure were the same as previously described.[2] Four separate runs were completed, each at salt temperatures of 714, 701, 679.5, 663, 642, and 629°K to yield six solubility–pressure isotherms consisting of four points apiece. The maximum Ar pressure for any experiment was 395 atm, and the minimum pressure was 151 atm for any run.

As in previous work,[2,3] 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 $NaNO_3$, $d_{t,p}$, at a given centigrade temperature, t, and piston pressure, P (atm), used for calculating the total volume of pure salt was obtained from the empirical equation

$$d_{t,p} = 2.134 - (7.03 \times 10^{-4})t + (3.9 \times 10^{-5})P \text{ g cm}^{-3} \quad (1)$$

where the temperature coefficient is from the work of Bloom, Knaggs, Molloy, and Welch,[4] and the pressure coefficient is based on the data of Owens.[5] An error, which should be well within the experimental error of the over-all procedure, probably persists as the result of using such pure-salt densities as estimates of the actual solution densities.

At the higher temperatures and pressures employed in this work (much above 600°K and 200 atm), use of the best P–$\bar{V}$–T data available (those compiled by Din[6]) would entail too extensive extrapolations for reasonably accurate estimates of the molar volumes of Ar. Therefore, the Beattie–Bridgeman equation was employed to find $\bar{V}$ at *all* temperatures and pressures used, for consistency. This equation is usually a quartic in $\bar{V}$[7]

$$0 = P\bar{V}^4 - RT\bar{V}^3 - (RTB_0 - Rc/T^2 - A_0)\bar{V}^2 + (RcB_0/T^2 - aA_0)\bar{V} - RcbB_0/T^2 \quad (2)$$

However, with numerical values for the constants for Ar of:[8] $A_0 = 1.2907$, $a = 0.02328$, $B_0 = 0.03931$, $b = 0$, and $c = 5.99 \times 10^4$, the equation reduces to a cubic in $\bar{V}$ for Ar since $b = 0$

$$f(\bar{V}) = P\bar{V}^3 - RT\bar{V}^2 - (RTB_0 - Rc/T^2 - A_0)\bar{V} + (RcB_0/T^2 - aA_0) = 0 \quad (3)$$

$\bar{V}$ (in l. mole^{-1}) was found for every P–T pair employed in this work by programming an IBM-1410 to calculate $\bar{V}$ from eq 3 by the Newton–Raphson method. Ideal gas values for $\bar{V}$ were used as beginning trial values. Generally, only four iterations were required by the computer to produce an acceptable value of $\bar{V}$, but in a very few cases five such iterations were necessary. (An acceptable value of $\bar{V}$ was taken to have been attained when the absolute value of $[f(\bar{V})/(\mathrm{d}f(\bar{V})/\mathrm{d})\bar{V}]/\bar{V}$ was less than 10^{-5}.) To test the accuracy of solutions so obtained for the high-temperature and pressure region, some calculated $\bar{V}$ values were compared to Din's literature values[6] at the upper end of his table. Table I compares these calculated $\bar{V}$ quantities with their corresponding literature values. It is seen from this table that the agreement of the $\bar{V}$ values is good. We assumed, therefore, that the Beattie–Bridgeman calculations of $\bar{V}$ for Ar would satisfy our needs in this work.

Table I: Comparison of Some $\bar{V}_{\text{lit}}$[6] and $\bar{V}_{\text{calcd}}$ Values for Argon Obtained by Computer Solutions of the Beattie–Bridgeman Equation

P, atm	T, °K	$\bar{V}_{\text{calcd}}$, l. mole^{-1}	$\bar{V}_{\text{lit}}$, l. mole^{-1}	% diff
180	550	0.2630	0.2622	0.305
180	600	0.2877	0.2864	0.454
200	550	0.2381	0.2371	0.422
200	600	0.2605	0.2590	0.580

Average Henry's law constants, K_h, and distribution coefficients, K_c, where

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

$$K_c = C_d/C_g \text{ (unitless)} \quad (4b)$$

(C_d = concentration of gas in dissolved phase, C_g = concentration of gas in gaseous phase) were calculated for each solubility–pressure isotherm.

Results

Table II summarizes the experimental temperatures, pressures, solubilities, Henry's law constants, and distribution coefficients. Theoretical values of the latter

(2) J. L. Copeland and L. Seibles, *J. Phys. Chem.*, **70**, 1811 (1966).

(3) J. L. Copeland and W. C. Zybko, *ibid.*, **69**, 3631 (1965).

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

(5) B. B. Owens, *J. Chem. Phys.*, **44**, 3918 (1966).

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

(7) C. E. Holley, Jr., W. J. Worlton, and R. K. Zeigler, Project LA-2271, Los Alamos Scientific Laboratory of the University of California, Los Alamos, N. M., 1959.

(8) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. 1, Longmans, Green and Co., Ltd., London, 1949, p 726.

Table II: Summary of Solubility–Temperature–Pressure Data for Argon in Fused Sodium Nitrate[a]

P, atm	C_d, moles/cm^3 $\times 10^4$	K_h, moles/cm^3 atm $\times 10^7$	$K_{c,\,expt} \times 10$	$K_{c,\,theor} \times 10$
		$T = 714°K$		
395	6.07	15.4	0.979	0.057
306	4.75	15.5	0.963	
226	4.25	18.8	1.14	
175	3.05	17.4	1.03	
		Av 16.8 ± 1.3	Av 1.03 ± 0.06	
		$T = 701°K$		
382	6.73	17.6	1.10	0.051
299	4.86	16.3	0.990	
223	4.04	18.1	1.08	
170	3.22	19.0	1.09	
		Av 17.7 ± 0.9	Av 1.07 ± 0.04	
		$T = 679.5°K$		
363	7.44	20.5	1.24	0.041
285	5.13	18.0	1.06	
214	4.02	18.8	1.08	
166	2.86	17.2	0.970	
		Av 18.6 ± 1.1	Av 1.09 ± 0.09	
		$T = 663°K$		
353	7.34	20.8	1.22	0.034
276	5.48	19.9	1.14	
207	4.19	20.3	1.14	
162	2.73	16.9	0.925	
		Av 19.5 ± 1.3	Av 1.11 ± 0.10	
		$T = 642°K$		
341	6.81	20.0	1.13	0.027
265	5.20	19.6	1.09	
200	3.92	19.6	1.07	
156	2.73	17.5	0.932	
		Av 19.2 ± 0.9	Av 1.06 ± 0.07	
		$T = 629°K$		
333	6.65	20.0	1.11	0.023
255	5.78	22.7	1.23	
196	3.74	19.1	1.02	
151	2.86	18.9	0.983	
		Av 20.2 ± 1.3	Av 1.09 ± 0.08	

[a] Temperatures are those of the fused salt.

quantity are included, as calculated from the naive model of Blander, Grimes, Smith, and Watson[9]

$$K_{c,\,theor} = \exp(-18.08r^2\gamma/RT) \qquad (5)$$

where r is taken as the close-packed radius of the Ar atom, 1.92 Å,[9] and γ is the surface tension of molten $NaNO_3$, calculated as a function of temperature from the work of Addison and Coldrey.[10] The errors in Table II are the probable errors for a single observation. Comparison of $K_{c,exptl}$ with $K_{c,theor}$ reveals $K_{c,exptl}$ to be from 18.1 (at 714°K) to 47.4 (at 629°K) times $K_{c,theor}$. Part of the increasingly poor agreement of these two values with lower temperatures stems from the fact that eq 5 conforms to endothermic heats of solution with positive temperature coefficients of solubility, while the present work indicates a negative temperature coefficient of solubility with an exothermic solution enthalpy.

To compare our results with those of workers experimenting on other systems at pressures from 0 to 1 or 2 atm, an enthalpy of solution was calculated from the relationship[11]

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

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

(11) M. Blander in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, Inc., New York, N. Y., 1964 pp 230–233.

$$d \ln K_h'/d(1/T) = -\Delta H/R \qquad (6)$$

where $K_h' = 10^3 K_h$ mol l.$^{-1}$ atm^{-1}. This equation gives rise to a linear function[12]

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

in which $\Delta S_p°$ is a standard entropy corresponding to a standard state of the gas at 1 atm both inside and outside the melt. In the present work, a least-squares plot of log K_h *vs.* $1/T$ gives

$$\log K_h = (370 \pm 45)(1/T) - (6.28 \pm 0.02) \qquad (8)$$

This equation, modified to ln K_h' in eq 7, yields

$$\Delta H = -1.69 \pm 0.21 \text{ kcal mol}^{-1} \qquad (9)$$

$$\Delta S_p° = -15.0 \pm 0.1 \text{ eu} \qquad (10)$$

A more satisfactory form for the standard entropy of solution is obtainable from the intercept of an equation of the form of eq 7 using ln K_c rather than ln K_h'.[11,13] The $\Delta S_c°$ so obtained corresponds to a standard state of the gas at 1 mol l.$^{-1}$ in both phases. A least-squares plot of log K_c *vs.* $1/T$ for this work gives

$$\log K_c = (78 \pm 46)(1/T) - (1.08 \pm 0.07) \qquad (11)$$

From this

$$\Delta S_c° = -4.97 \pm 0.32 \text{ eu} \qquad (12)$$

All errors are least-squares probable errors.

Minor errors persist as a result of the use of gas pressures rather than fugacities. In a recalculation of ΔH and $\Delta S_p°$ using eq 7, all pressures were converted into fugacities by use of the approximation

$$f = P^2\bar{V}/RT_g \qquad (13)$$

where T_g is the gas temperature, and all K_h values were accordingly recomputed. The revised values of the thermodynamic properties then resulted as

$$\Delta H = -1.84 \pm 0.21 \text{ kcal mol}^{-1} \qquad (14)$$

$$\Delta S_p° = -15.4 \pm 0.3 \text{ eu} \qquad (15)$$

When these values are taken with their probable errors and are compared to eq 9 and 10, it is obvious that the two set of results, one based on pressures and the other on fugacities, overlap with their probable error brackets.

The results of this work are to be compared to those for N_2 in $NaNO_3$,[2] for which

$$\Delta H = -2.73 \pm 0.09 \text{ kcal mol}^{-1} \qquad (16a)$$

(-2.69 ± 0.08 using fugacities)

$$\Delta S_p° = -16.6 \pm 0.1 \text{ eu} \qquad (16b)$$

(-16.8 ± 0.1 using fugacities)

$$\Delta S_c° = -6.78 \pm 0.18 \text{ eu} \qquad (16c)$$

It is apparent from Table II, ref 2, and eq 14 and 16a that the temperature dependence of Ar solubility is much less that that for N_2. Indeed, the Ar solubility temperature dependence is so slight that at 642°K the probable error in the average K_h causes it to fall slightly below that for 663°K, when the trend is for gently increasing K_h values with decreasing temperature. The scatter of such data about a small slope is even more pronounced for the average K_c values at different temperatures. Measurements in this work were not carried above 441° and 395 atm because of safety limitations on the equipment at such high temperature–pressure combinations.

A single solubility isotherm at 642°K for Ar in $NaNO_3$ was determined earlier by Copeland and Zybko[3] with the result: $K_h = (17.2 \pm 1.7) \times 10^{-7}$ mol cm^{-3} atm^{-1}. The present work value at 642°K of $(19.2 \pm 0.9) \times 10^{-7}$ is seen to overlap with the earlier value when the probable error brackets are considered.

Discussion

Although experimental errors are sizable, some tenuous comparisons and conclusions can still be made. Comparison of the ΔH's of solution for Ar and N_2 from relations 14 and 16a shows that Ar in $NaNO_3$ is only about 0.68 times as exothermic as is N_2 in the melt. As pointed out earlier, the temperature dependence of Ar solubility is but very slight. This was predicted by Copeland and Seibles.[2] In the latter paper, endothermic work of molecular cavity creation against surface tension, to accommodate a solute molecule in the liquid (the basic model of Blander, Grimes, Smith, and Watson[9]), was deemed smaller in magnitude than exothermic solvation effects for N_2 and probably Ar. This was a result of the relatively low surface tension of $NaNO_3$. Furthermore, the cavity creation work was thought to be about the same for N_2 and Ar, in view of their similar molecular radii (2.00 Å for N_2, 1.92 Å for Ar). On the basis of this model, Ar was predicted to be somewhat less soluble in $NaNO_3$ and less exothermic in its enthalpy of solution than is N_2, basically as a result of the smaller molecular polarizability of Ar (1.734×10^{-24} cm^3 molecule^{-1} for N_2, 1.626×10^{-24} cm^3 molecule^{-1} for Ar).[2] This would lead to somewhat less ion-induced dipole interactions for Ar than for N_2, giving slightly less Ar solubility and exothermic solution heat, all other factors being considered equal. Actually, Table II compared to the N_2 data of ref 2 indicates that the absolute solubilities of Ar in $NaNO_3$ (as exemplified by the K_h values) are not significantly different from those of N_2 in the solvent after all. The main difference appears in the relative ΔH values for these gases.

Reiss, Frisch, Helfand, and Lebowitz[14] recognize

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

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

[14] H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.*, **32**, 119 (1960).

three contributions to the isothermal reversible work, W_c, required to transfer a gas molecule to the interior of a liquid phase

$$W_c = Y_1 + Y_2 + Y_3 \qquad (17)$$

Y_1 is the molecular cavity creation work which may be roughly approximated as

$$Y_1 \simeq 4\pi\gamma r^2 + 4\pi P r^3/3 \qquad (18)$$

(where r is the radius of the created hole) if the microscopic surface tension, γ, can be considered curvature independent. Y_2 is a complicated term for the energy of interaction, involving pair correlation functions acting in the molten salt between solute molecules and ions, and neglecting polarization forces. It is predominantly exothermic. The term Y_3 is the exothermic polarization energy involving the solute molecule of polarizability α and the mean-square electric field, $\langle E^2 \rangle$, it experiences.

$$Y_3 = -(^1/_2)\,\alpha\langle E^2 \rangle \qquad (19)$$

Blander, Grimes, Smith, and Watson[9] ignored the exothermic Y_2 and Y_3 terms in comparison to the large Y_1 work necessary to accommodate a gas molecule against the high surface tensions of their fluoride melts. They also neglected the second term in Y_1, since the pressures, P, that they used were small, and they tacitly assumed γ to be curvature independent, as well as to be approximately the same as the macroscopic surface tension. Thus, eq 5 was conceived.

In the present work with Ar, it is apparent that the Y_2 and Y_3 exoenergetic terms are not insignificant in comparison to Y_1, as was found also in the N_2 solubility work.[2] Thus, choosing as an example from Table II a pressure of 395 atm and a temperature of 714°K, the Y_1 term results as approximately 7.65 kcal mol^{-1}. From the observed heat of solution of Ar of -1.84 kcal mol^{-1}, we conclude that the $Y_2 + Y_3$ exothermic sum should exceed Y_1 in magnitude by about 1.84 kcal mol^{-1}. Of the Y_2 and Y_3 terms, it is apparent from eq 19 that the Y_3 polarization energy should be larger the greater the α of a solute molecule in the given solvent presenting a fixed $\langle E^2 \rangle$. Thus, at least Y_3 correlates with the observed greater exothermic heat of solution for the more polarizable N_2 molecule in fused $NaNO_3$ than for the less polarizable Ar molecule in the same solvent. Again, the endothermic Y_1 term should be nearly the same for both molecules in this system. At this point, it is still impossible to draw any quantitative conclusions as to the relative contributions of the extremely complex Y_2 interaction term applied to these two solutes.

As in the N_2 work, the $\Delta S_c°$ value for solution of -4.97 eu for Ar indicates an unusual environment and set of interactions for the Ar molecule in $NaNO_3$. This is not quite so pronounced as the -6.78 eu for N_2 in the system. However, as mentioned earlier,[2] rotational degrees of freedom exist for N_2, and these may be affected in solution, whereas such cannot be the case for atomic Ar. While the value -4.97 eu for Ar is certainly unusually large in magnitude for such a gas, it is not without precedent, since Watson, Evans, Grimes, and Smith[13] did observe an unusual standard solution entropy of -4.2 eu for both Ar and Ne in a 64–36 mol % LiF–BeF_2 molten solvent. Helium and Xe in the same solvent gave rise to values of -3.4 and -3.1 eu, respectively.

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