

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 $\times 10$ |
|---------------------------|---|---|--------------------------|---------------------------|
| $T = 714^\circ\text{K}$ | | | | |
| 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 \pm 1.3 | Av 1.03 \pm 0.06 | |
| $T = 701^\circ\text{K}$ | | | | |
| 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 \pm 0.9 | Av 1.07 \pm 0.04 | |
| $T = 679.5^\circ\text{K}$ | | | | |
| 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 \pm 1.1 | Av 1.09 \pm 0.09 | |
| $T = 663^\circ\text{K}$ | | | | |
| 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 \pm 1.3 | Av 1.11 \pm 0.10 | |
| $T = 642^\circ\text{K}$ | | | | |
| 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 \pm 0.9 | Av 1.06 \pm 0.07 | |
| $T = 629^\circ\text{K}$ | | | | |
| 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 \pm 1.3 | Av 1.09 \pm 0.08 | |

^a Temperatures are those of the fused salt.

quantity are included, as calculated from the naive model of Blander, Grimes, Smith, and Watson⁹

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

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 NaNO₃, 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 $K_{c, \text{exptl}}$ with $K_{c, \text{theor}}$ reveals $K_{c, \text{exptl}}$ to be from 18.1 (at 714°K) to 47.4 (at 629°K) times $K_{c, \text{theor}}$. 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 so-

lution 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 relationship¹¹

(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.

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

where $K_h' = 10^3 K_h \text{ mol l.}^{-1} \text{ atm}^{-1}$. This equation gives rise to a linear function¹²

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

in which ΔS_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

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

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

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

$$\Delta S_p^\circ = -15.0 \pm 0.1 \text{ eu} \quad (10)$$

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 ΔS_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

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

From this

$$\Delta S_c^\circ = -4.97 \pm 0.32 \text{ eu} \quad (12)$$

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 ΔS_p° using eq 7, all pressures were converted into fugacities by use of the approximation

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

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

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

$$\Delta S_p^\circ = -15.4 \pm 0.3 \text{ eu} \quad (15)$$

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

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

(-2.69 ± 0.08 using fugacities)

$$\Delta S_p^\circ = -16.6 \pm 0.1 \text{ eu} \quad (16b)$$

(-16.8 ± 0.1 using fugacities)

$$\Delta S_c^\circ = -6.78 \pm 0.18 \text{ eu} \quad (16c)$$

It is apparent from Table II, ref 2, and eq 14 and 16a that the temperature dependence of Ar solubility is

much less than 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 Zybko³ with the result: $K_h = (17.2 \pm 1.7) \times 10^{-7} \text{ mol cm}^{-3} \text{ atm}^{-1}$. 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 Watson⁹), 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 ($1.734 \times 10^{-24} \text{ cm}^3 \text{ molecule}^{-1}$ for N_2 , $1.626 \times 10^{-24} \text{ cm}^3 \text{ molecule}^{-1}$ 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 Lebowitz¹⁴ recognize

(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).