Gas press, P, atm	Soly, $C_{\rm d}$, moles/cm ³ $\times 10^4$	Henry's law const, $K_{\rm h}$, moles/cm ³ atm $ imes 10^7$	Dist coeff, $K_{c,exptl} \times 10$	Theor dist coeff, $K_{\rm c,theor} imes 10$	Gas press, P, atm	Soly, $C_{\rm d}$, moles/cm ³ $\times 10^4$	Henry's law const, $K_{\rm h}$, moles/cm ³ atm $\times 10^7$	Dist coeff, $K_{c,exptl} \times 10$	Theor dist coeff, $K_{\rm c,theor} imes 10$
$T = 727 ^{\circ}\mathrm{K}$					$T = 669.5^{\circ} \mathrm{K}$				
364	6.00	16.5	1.11		415	6.64	16.0	1.03	
286	4.00	14.0	0.908	0.042	332	5.87	17.7	1.10	
227	3.11	13.7	0.869		258	4.64	18.0	1.08	0.022
167	2.73	16.4	1.01		205	3.75	18.3	1.08	
		Av $15.2 \pm$	Av 0.976		151	3.08	20.4	1.17	
		1.2	111 0.010				Av $\overline{18.1} \pm$	Av 1.09	
		7 710	77				1.2		
257	5 07	$T = 718^{\circ}$	1 11		$T = 655.5^{\circ} \mathrm{K}$				
991	0.97	15.0	0.061	0.030	308	7 77	I = 0.00.0	1 93	
201	3 37	15.1	0.901	0.000	393	5 01	18.3	1.25	
163	2 08	18 34	0.010		251	4 71	18.7	1.10	0.016
100	2.00	Are 15 6 -	Arr 1 01		200	3 77	18.8	1.09	0.010
		AV 15.0 ±	AV 1.01		148	2.75	18.6	1.04	
		0.8					Av 18 8 +	Av 1 12	
	$T = 696 ^{\circ}\mathrm{K}$						0.3	AV 1.12	
349	5.57	16.0	1.04				0.0		
272	4.34	16.0	1.00	0.031			$T = 641.5^{\circ}\mathrm{K}$		
217	3.24	14.9	0.915		387	7.67	19.8	1.22	
159	2.85	17.9	1.07		314	5.99	19.1	1.14	
		Av 16.2 \pm	Av 1.01		244	4.94	20.2	1.17	0.016
		1.0			194	3.74	19.3	1.08	
T - 686 5°K					144	2.90	20.1	1.11	
196	I = 080.3 K						Av 19.7 \pm	Av 1.14	
241	5.03	17.4	1 11				0.4		
266	4 66	17.5	1.08	0.027			T = 628.5	°K	
213	3 31	15.5	0.938	0.021	375	7.89	21.0	1.26	
155	2.91	18.8	1.10		306	6.07	19.9	1.16	
200		Av 17 3 +	Av 1 08		238	4.76	20.0	1.12	0.014
		AV 11.5 1	AV 1.00		192	3.43	17.9ª		
		0.0			140	2.82	20.1	1.08	
						and the second	Av 20 2 +	Av 1.16	
							0.4		
a Data	discarded from	om averaging	according to	Chauvenet's crit	terion.				

 Table I:
 Summary of Solubility-Temperature-Pressure Data for Nitrogen in Fused Sodium Nitrate.
 Temperatures

 Are Those of the Fused Salt
 Solubility-Temperature-Pressure Data for Nitrogen in Fused Solubility-Temperatures
 Solubility-Temperature-Pressure Data for Nitrogen in Fused Solubility-Temperatures

the empirical equation of Addison and Coldrey⁹ applied to fused NaNO₃

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

where t is temperature in degrees centigrade. An approximate close-packed radius of 2.00 A was taken for the N₂ molecule regarded as a sphere.¹⁰ It is interesting to perform a sample calculation for the expected value of r for N₂ 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

 $\log K_{\rm h} = (597 \pm 19)(1/T) - (6.64 \pm 0.03) \quad (6)$

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 is⁴

$$\ln K_{\rm h}' = -(\Delta H/R)(1/T) + \Delta S_{\rm p}^{\circ}/R \tag{7}$$

where $K_{\rm h}' = 1000 K_{\rm h}$ (*i.e.*, $K_{\rm h}'$ is in units of moles $1.^{-1}$ atm⁻¹), ΔH is the heat of solution, and $\Delta S_{\rm p}^{\circ}$ 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 $\Delta S_p^{\circ} = -16.6 \pm 0.1$ eu, where the errors are again probable errors.

Discussion

The negative temperature coefficient of solubility for N₂ in fused NaNO₃ 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, $K_{\rm c.exptl}(av)$ being from 23 to 83 times greater than $K_{\rm c, theor}$. 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-ZrF₄ mixture, to -9.70 kcal mole⁻¹, for 80.5 mole % NaF. Our observed ΔH of -2.73kcal mole $^{-1}$ is somewhat smaller than the lowest such value for the HF work, implying less exothermic solvation effects for N₂ in NaNO₃ 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 $\Delta S_{\rm p}^{\circ}$ 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 N₂ 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).