

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/cm ³ $\times 10^4$	Henry's law const, K_h , moles/cm ³ atm $\times 10^7$	Dist coeff, $K_{e,\text{exptl}} \times 10$	Theor dist coeff, $K_{e,\text{theor}} \times 10$	Gas press, P , atm	Soly, C_d , moles/cm ³ $\times 10^4$	Henry's law const, K_h , moles/cm ³ atm $\times 10^7$	Dist coeff, $K_{e,\text{exptl}} \times 10$	Theor dist coeff, $K_{e,\text{theor}} \times 10$
$T = 727^\circ\text{K}$					$T = 669.5^\circ\text{K}$				
364	6.00	16.5	1.11	0.042	415	6.64	16.0	1.03	0.022
286	4.00	14.0	0.908		332	5.87	17.7	1.10	
227	3.11	13.7	0.869		258	4.64	18.0	1.08	
167	2.73	16.4	1.01		205	3.75	18.3	1.08	
	Av	15.2 \pm 1.2	Av 0.976	151	3.08	20.4	1.17		
					Av	18.1 \pm 1.2	Av 1.09		
$T = 718^\circ\text{K}$					$T = 655.5^\circ\text{K}$				
357	5.97	16.7	1.11	0.039	398	7.77	19.5	1.23	0.016
281	4.21	15.0	0.961		323	5.91	18.3	1.12	
223	3.37	15.1	0.949		251	4.71	18.7	1.10	
163	2.98	18.3 ^a	...		200	3.77	18.8	1.09	
	Av	15.6 \pm 0.8	Av 1.01	148	2.75	18.6	1.04		
					Av	18.8 \pm 0.3	Av 1.12		
$T = 696^\circ\text{K}$					$T = 641.5^\circ\text{K}$				
349	5.57	16.0	1.04	0.031	387	7.67	19.8	1.22	0.016
272	4.34	16.0	1.00		314	5.99	19.1	1.14	
217	3.24	14.9	0.915		244	4.94	20.2	1.17	
159	2.85	17.9	1.07		194	3.74	19.3	1.08	
	Av	16.2 \pm 1.0	Av 1.01	144	2.90	20.1	1.11		
					Av	19.7 \pm 0.4	Av 1.14		
$T = 686.5^\circ\text{K}$					$T = 628.5^\circ\text{K}$				
426	7.40	17.4	1.16	0.027	375	7.89	21.0	1.26	0.014
341	5.93	17.4	1.11		306	6.07	19.9	1.16	
266	4.66	17.5	1.08		238	4.76	20.0	1.12	
213	3.31	15.5	0.938		192	3.43	17.9 ^a	...	
155	2.91	18.8	1.10		140	2.82	20.1	1.08	
	Av	17.3 \pm 0.9	Av 1.08		Av	20.2 \pm 0.4	Av 1.16		

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

the empirical equation of Addison and Coldrey⁹ applied to fused NaNO_3

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

where t is temperature in degrees centigrade. An approximate close-packed radius of 2.00 Å 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_e for, say, 641.5°K . This naïve approach gives $r = 1.16$ Å, 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 $K_{h,\text{av}}$ 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.

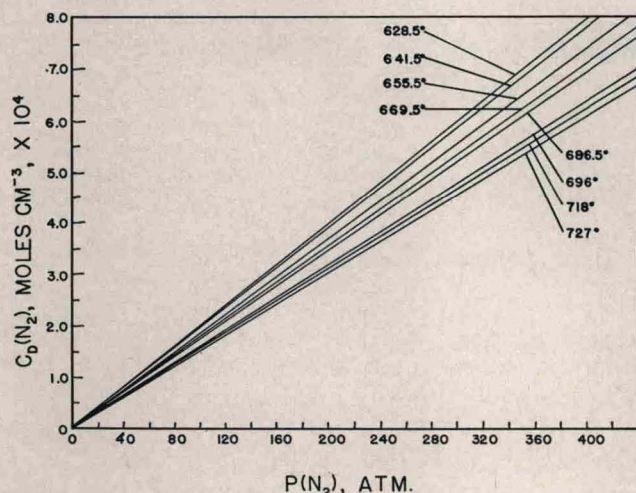


Figure 1. Solubility, C_d , vs. pressure, P , isotherms for nitrogen in fused sodium nitrate at various temperatures. See Table I for individual data points. All temperatures are in degrees Kelvin.

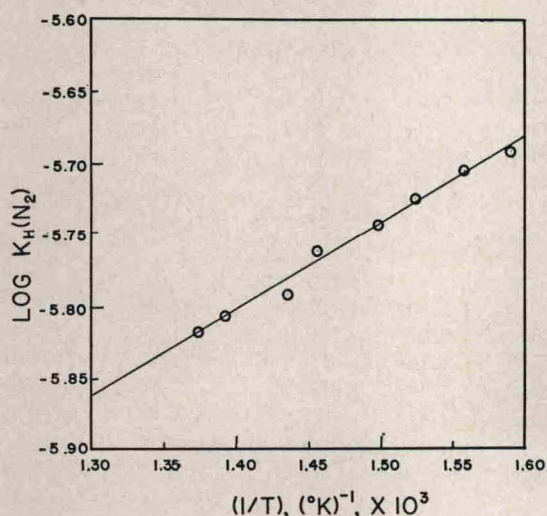


Figure 2. Common log of Henry's law constant, $\log K_h$ (where units of K_h are moles $\text{cm}^{-3} \text{atm}^{-1}$), vs. reciprocal absolute temperature, $1/T$, for nitrogen in fused sodium nitrate.

$1/T$ in $(^\circ\text{K})^{-1}$. 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 is⁴

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

where $K_h' = 1000K_h$ (i.e., K_h' is in units of moles $\text{l}^{-1} \text{atm}^{-1}$), ΔH is the heat of solution, and ΔS_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 $\Delta H = -2.73 \pm 0.09 \text{ kcal mole}^{-1}$ and $\Delta S_p^\circ = -16.6 \pm 0.1 \text{ eu}$, 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 $(K_{e,\text{exptl}}/K_{e,\text{theor}})$ ratios, $K_{e,\text{exptl}}(\text{av})$ being from 23 to 83 times greater than $K_{e,\text{theor}}$. 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 $-3.85 \text{ kcal mole}^{-1}$, for a 45 mole % of NaF in NaF-ZrF₄ mixture, to $-9.70 \text{ kcal mole}^{-1}$, for 80.5 mole % NaF. Our observed ΔH of $-2.73 \text{ kcal mole}^{-1}$ 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 ΔS_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).