

temperature in the insulated box containing the bulbs was noted, and the pressure read from the manometer. The number of moles of gas recovered was calculated from the pressure, volume and temperature. Vessel A was re-opened, and the salt in L weighed. The solubility was expressed in moles of gas per ml melt, using published density data¹⁹ to calculate the volume of the melt.

ERRORS

The above procedure is based on the assumption that vessel A remained vacuum-tight during the degassing process. Tests showed that a slow leakage of air into the apparatus did occur at this stage. In all the measurements reported here, this leakage rate was measured after A had been evacuated and before the saturated salt was released from C. The process of degassing the melt and transferring the gas to the glass bulbs was timed, and a correction applied. This could not be done with complete certainty, because the pressure inside A fluctuated as gas was evolved from the melt and removed by the Toepler pump. In fig. 4-7, the upper and lower ends of the vertical bars correspond respectively to uncorrected data and data corrected for ingress of air at the rate which would apply if the vessel had been under vacuum throughout the degassing operation. The amount of air entering was approximately the same for each determination, so this source of error is relatively less important the higher the solubility of the gas.

Another possible source of error was formation of gas by chemical decomposition of the melt. Oxygen and oxides of nitrogen might possibly be formed in this way. The gas recovered from molten AgNO_3 was transferred into a bulb containing alkaline pyrogallol solution before its volume was determined. For the alkali nitrate melts, the volume of recovered gas was the same before and after exposure to alkaline pyrogallol solution, showing that no oxygen was present.

RESULTS

Fig. 4-7 show gas solubility plotted against pressure for the systems studied, and fig. 4 includes plots of $\log K_H$ against $1/T$ for the three gases in sodium nitrate. The solubility isotherms are approximately linear in all cases, although some show curvature towards the pressure axis at the higher pressures. Because of this, K_H was evaluated by fitting a straight line to the data in the range 0-500 bar. Table 1 gives the values of K_H , the heat of solution ΔH , ($= -R\partial \ln K_H / \partial (1/T)$), and the standard entropy of solution ΔS° for each system. Following Blander,² we have chosen standard states in which the solute is at the same concentration in the gas phase and

TABLE 1.—SOLUBILITY DATA FOR HELIUM, ARGON AND NITROGEN IN MOLTEN ALKALI NITRATES

system	temp. (°C)	$10^7 K_H$ (mol ml ⁻¹ bar ⁻¹)	ΔH (kJ/mol)	ΔS° (J K ⁻¹ mol ⁻¹)	surface ¹⁹ tension (dyne/cm)	K_H (expt.) K_H (calc.)	ΔH (expt.) ΔH (calc.)
He + NaNO ₃	332	1.86 ± 0.3	13.4	-17.4	115	0.12	1.2
	391	2.32 ± 0.3			113	0.13	
	441	2.80 ± 0.3			111	0.14	
Ar + NaNO ₃	331	0.64 ± 0.15	15.8	-21.7	115	1.9	0.53
	410	0.90 ± 0.15			112	1.3	
	440	1.04 ± 0.15			111	1.2	
N ₂ + NaNO ₃	331	0.50 ± 0.15	16.0	-23.6	115	2.6	0.51
	390	0.64 ± 0.15			113	1.7	
	449	0.84 ± 0.15			111	1.3	
He + LiNO ₃	270	1.51 ± 0.4	—	—	114	0.11	—
Ar + LiNO ₃	273	0.91 ± 0.2	14.0	-19.3	114	4.5	0.45
	307	1.09 ± 0.15			113	3.5	
N ₂ + LiNO ₃	277	0.73 ± 0.1	—	—	114	6.3	—
Ar + RbNO ₃	331	1.30 ± 0.2	20.1	-8.6	107	2.6	0.62
	440	2.40 ± 0.2			100	1.5	
Ar + AgNO ₃	234	0.19 ± 0.05	—	—	147	12.9	—

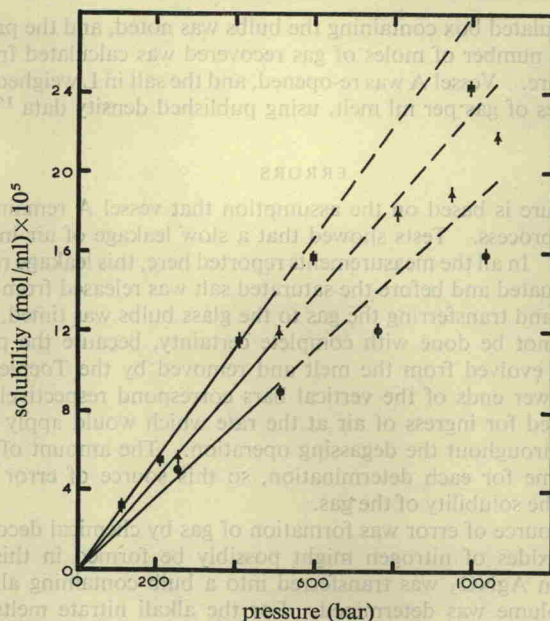


FIG. 4(a).—Solubility isotherms for the system He+NaNO₃. ■, 441°C; ▲, 391°C; ●, 332°C.

in the solution. The standard entropy of solution is derived from the heat of solution using the expression

$$\Delta S^\circ = (\Delta H/T) + R \ln (C_a/C_g),$$

where C_a and C_g are the concentrations of gas atoms in the solution and in the gas phase respectively.

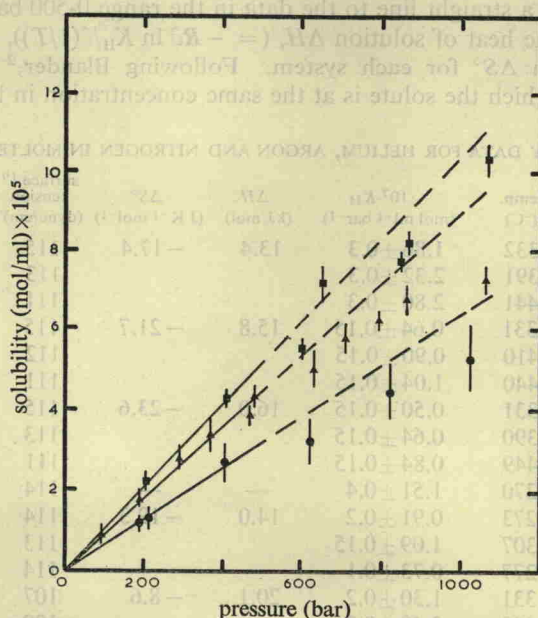


FIG. 4(b).—Solubility isotherms for the system Ar+NaNO₃. ■, 440°C; ▲, 410°C; ●, 331°C.