

A plot of  $\ln(f/P)$  against  $P$  had only slight curvature, and a short extrapolation allowed values of  $f$  to be obtained over the pressure range of the solubility measurements. The solubility data for Ar+NaNO<sub>3</sub> at 410°C were adjusted to 400°C, using the van't Hoff equation with  $\Delta H = 15.8$  kJ/mol (see table 1). A plot of  $\log(f/C_d)$  against  $P$  is shown in fig. 8. A straight line was fitted to the points by least squares, and  $\bar{v}_d$  and  $K_H$  were found from the slope and intercept. The values were:  $\bar{v}_d = 34 \pm 8$  ml/mol and  $K_H = (1.0 \pm 0.1) \times 10^{-7}$  mol ml<sup>-1</sup> bar<sup>-1</sup> at 410°C, where the intervals quoted correspond to 95 % confidence limits. These values are not materially altered if the calculation is restricted to the pressure range 0-776 bar. Similar plots (not shown) were made for Ar+NaNO<sub>3</sub> at 440°C, Ar+NaNO<sub>3</sub> at 331°C and Ar+RbNO<sub>3</sub> at 440°C, and yielded values for  $\bar{v}_d$  of  $26 \pm 13$ ,  $30 \pm 13$  and  $34 \pm 13$  mol/mol, respectively. The corresponding  $K_H$  values were  $(1.1 \pm 0.2) \times 10^{-7}$ ,  $(0.65 \pm 0.1) \times 10^{-7}$  and  $(2.9 \pm 0.5) \times 10^{-7}$  mol ml<sup>-1</sup> bar<sup>-1</sup>. For N<sub>2</sub>+NaNO<sub>3</sub> at 390°C, the same procedure gave  $\bar{v}_d = 46 \pm 40$  ml/mol and  $K_H = (0.8 \pm 0.5) \times 10^{-7}$  mol ml<sup>-1</sup> bar<sup>-1</sup>. The PVT data used for N<sub>2</sub> were those of Bartlett.<sup>27</sup> The poorer precision of the results for Ar+RbNO<sub>3</sub> and N<sub>2</sub>+NaNO<sub>3</sub> reflects the fact that fewer data points were available for these systems. The fact that straight lines are obtained

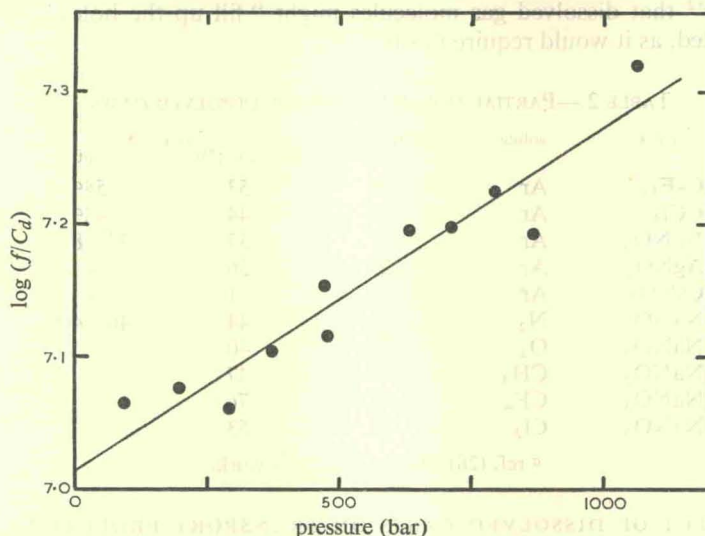


FIG. 8.—Plot of  $\log(f/C_d)$  against pressure for the system Ar+NaNO<sub>3</sub> at 400°C.

when  $\ln(f/C_d)$  is plotted against  $P$  is evidence that the solvent is not deviating from Raoult's law as the solute concentration increases. Such deviations would lead to curvature in these plots.

In table 1,  $K_H$  was evaluated from the slope of the best straight line through the origin of an isothermal plot of  $C_d$  against  $P$ , over the range 0-500 bar. This corresponds to the approximation  $\ln(f/P) - (P\bar{v}_d/RT) = 0$  (cf. eqn (2)). Since the  $K_H$  values in table 1 agree with those derived using eqn (2) within the combined limits of error, the use of the simpler procedure is justified in the general case.

Smith and Walkley<sup>28</sup> described a simple method for estimating the partial molar volume of a solute gas from a knowledge of the volume  $v_0$  of the gas at 0 K and the thermal pressure coefficient of the solvent  $(\partial P/\partial T)_v$ . Their formula is

$$\bar{v}_d = v_0 \left[ 1 - \frac{R}{\bar{v}_d} \left( \frac{\partial P}{\partial T} \right)_v^{-1} \right]^{-3} \quad (3)$$



Eqn (3) was derived by treating the gas as a hard-sphere fluid, and calculating the volume for which the gas pressure was equal to the internal pressure of the solvent. This volume was equated to  $\bar{v}_d$ . Values of  $v_0$  may be found either from the volumes of solidified gases, or from molecular diameters obtained from second virial coefficients or from gas viscosities. Calculated values of  $\bar{v}_d$  were in good agreement with experiment for simple solute molecules in a range of organic solvents. Eqn (3) has been used to calculate  $\bar{v}_d$  for argon, nitrogen, and some other gases in molten nitrates (see table 2). The results agree with those derived from our solubility data, within experimental error. No figures are tabulated for helium, as quantum effects make it difficult to assign a value to  $v_0$ ; the liquid molar volume is 27.4 ml/mol at 1.2 K,<sup>29</sup> but the molar volume estimated from the molecular diameter is only 10 ml/mol.<sup>30</sup> For  $\text{NaNO}_3$  as solvent, these values of  $v_0$  give  $\bar{v}_d = 39$  and 21 ml/mol respectively. Table 2 shows that for a given gas,  $\bar{v}_d$  is less in molten nitrates than in organic solvents. This reflects the higher internal pressure of the former group of liquids, for which  $T(\partial P/\partial T)_v$  is in the range 10-12 kbar.<sup>31</sup> Eqn (3) requires that, if  $(\partial P/\partial T)_v$  is positive,  $\bar{v}_d$  must be greater than  $v_0$ . This is confirmed by the experimental data for organic liquids, and by the more limited data for molten salts. The suggestion<sup>9, 32</sup> that dissolved gas molecules might "fill up the holes" in the melt is not supported, as it would require  $\bar{v}_d \sim 0$ .

TABLE 2.—PARTIAL MOLAR VOLUMES OF DISSOLVED GASES

solvent	solute	$v_0$ (ml/mol) (a,b)	$\bar{v}_d$ (ml/mol)	
			(calc., eqn (3))	(expt.)
$\text{C}_7\text{F}_{16}$	Ar	25	53	54 <sup>a</sup>
$\text{CCl}_4$	Ar	25	44	44 <sup>a</sup>
$\text{NaNO}_3$	Ar	25	37	34 + 8 <sup>c</sup>
$\text{AgNO}_3$	Ar	25	36	—
$\text{CsNO}_3$	Ar	25	41	—
$\text{NaNO}_3$	$\text{N}_2$	32	44	46 ± 40 <sup>c</sup>
$\text{NaNO}_3$	$\text{O}_2$	28	40	—
$\text{NaNO}_3$	$\text{CH}_4$	35	47	—
$\text{NaNO}_3$	$\text{CF}_4$	63	76	—
$\text{NaNO}_3$	$\text{Cl}_2$	41	53	—

<sup>a</sup> ref. (28); <sup>b</sup> ref. (30); <sup>c</sup> this work.

## EFFECT OF DISSOLVED GASES ON TRANSPORT PROPERTIES

An applied pressure of 1 kbar changes the electrical conductivity of molten alkali nitrates by between 1 % ( $\text{LiNO}_3$ ) and 12 % ( $\text{CsNO}_3$ ).<sup>18</sup> Considering argon or nitrogen as pressurizing gases, dissolution of gas to the equilibrium concentration at this pressure would cause a further change in conductivity by simple dilution. Assuming no change in ion mobility when the gas dissolves, the conductivity decrease is estimated to be not more than 1 %, based on the solubilities and partial molar volumes in tables 1 and 2. It seems likely that the ion mobilities would increase, rather than decrease, when dilution occurs: this is observed when water is added to molten  $\text{LiClO}_4$ ,<sup>33</sup> and when p-xylene is added to molten tetra-n-amy ammonium thiocyanate.<sup>34</sup> The net decrease in conductivity when argon or nitrogen dissolve isothermally in a nitrate melt at 1 kbar is therefore unlikely to exceed 1 %, which corresponds to a change of +0.6 ml/mol in the specific conductance activation volume  $\Delta V_\kappa$ . This is much less than the reported difference between the "gas-free" and "gas-saturated" values of  $\Delta V_\kappa$  for sodium nitrate,<sup>18</sup> which may have other experimental causes. The "gas-free" value has been confirmed independently.<sup>35</sup>