DISCUSSION

In most of the systems considered in part 1 the solid had a very small vapour pressure at the temperature of the solubility measurements. Even at the lowest pressures investigated the concentration of solute in the gas phase was therefore small and it was thus possible to neglect both the effect of the solute on the density of the gas phase and the interactions between solute molecules in calculating the solubility. These conditions do not apply to the systems reported here, as the vapour pressure of xenon at 155° K is 380 mm Hg and that of carbon dioxide at 190° K is 500 mm Hg; also, the present measurements covered the lower part of the solubility isotherm (cf. fig. 2) in which the concentration decreases with increasing pressure and high concentrations were therefore found at the lower pressures.

The effect of the solute on the density of the gas phase is eliminated, and the calculation is put into terms of a directly observed quantity, if the equation of state of the mixed gas phase is expressed as a power series in pressure instead of density. The high concentration of solute necessitates the retention of terms in B_{22} and C_{222} in that equation of state. (B_{22} is the second and C_{222} the third virial coefficient of the pure component 2.) It will still be possible to use in the final equation the virial coefficients calculated by the method of Lennard-Jones if suitable transformations between the pressure and volume virial coefficients are introduced (see eqn. (4)).

The equilibrium between a pure solid and a mixed gas phase is given by [7]

$$RT \ln \frac{x_2}{x_2^\circ} = RT \ln \frac{Px_2}{p_2^\circ} = - \int_0^P \left[\left(\frac{\partial V}{\partial n_2} \right) - \frac{RT}{P} \right] dP + \int_0^{P_2^\circ} \left[\frac{V_2}{n_2} - \frac{RT}{p_2} \right] dP_2$$
$$+ \int_{P_2^\circ}^P V_2^s dP. \tag{1}$$

If the equation of state of the mixed gas phase is

$$\frac{V_m}{N} = \frac{RT}{p} + \frac{\beta_m}{RT} + \frac{\gamma_m}{(RT)^2} P, \tag{2}$$

where subscript m refers to the mixture and $N = n_1 + n_2$, and if the compressibility of the solid of molar volume V_2^s is neglected, it is found that

$$RT \ln \frac{x_2}{x_2^\circ} = - \frac{P}{RT} \left(\beta_m + N \frac{\partial \beta_m}{\partial n_2} \right) - \tfrac{1}{2} \left(\frac{P}{RT} \right)^2 \left(\gamma_m + N \frac{\partial \gamma_m}{\partial n_2} \right)$$
$$+ \frac{\beta_{22}}{RT} p_2^\circ + \tfrac{1}{2} \gamma_{222} \left(\frac{P_2^\circ}{RT} \right)^2 + V_2^s (P - p_2^\circ). \tag{3}$$

On introducing the transformations

$$\beta_m = RT\, B_m,$$
$$\gamma_m = RT(C_m - B_m^2), \tag{4}$$

where B_m and C_m are the virial coefficients in the volume equation of state,

$$PV_m = RT(1 + B_m/V_m + C_m/V_m^2 + \ldots)$$

and carrying out the differentiations in (3), eqn. (5) is obtained.

$$\ln \frac{x_2}{x_2^\circ} = \frac{V_2^s(P - p_2^\circ)}{RT} + (x_1^2 B_{11} - 2x_1^2 B_{12} + x_2^2 B_{22} - 2x_2 B_{22}) \frac{P}{RT}$$
$$- x_1^4 3 B_{11}^2 - x_1^3 (2C_{111} + 4B_{11}B_{12}) + x_1^2 3 C_{112} + x_1^3 x_2 12 B_{11}B_{12}$$
$$- x_1^2 x_2 (6C_{112} + 4B_{11}B_{22} + 8B_{12}^2) + x_1 x_2 6 C_{122} - x_1 x_2^2 (6C_{122} + 12 B_{12} B_{22})$$
$$+ x_1 x_2^3 12 B_{12} B_{22} + x_1^2 x_2^2 (12 B_{12}^2 + 6 B_{11} B_{22}) + x_2^4 3 B_{22}^2$$
$$- x_2^3 (2C_{222} + 4B_{22}^2) + x_2 3 C_{222}] \tfrac{1}{2} \left(\frac{P}{RT} \right)^2$$
$$+ B_{22} \frac{P_2^\circ}{RT} + \tfrac{1}{2} (C_{222} - B_{22}^2) \left(\frac{p_2^\circ}{RT} \right)^2, \tag{5}$$

where P = total pressure of the system,

$p_2°$ = saturated vapour pressure of the solid at temperature T,

$V_2{}^s$ = mole volume of the solid,

x_1 and x_2 are mole fractions.

The virial coefficients of the mixture are given in terms of those of the pure components by

$$B_m = \sum_i \sum_j x_i x_j B_{ij},$$

$$C_m = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk},$$

and were calculated by the Lennard-Jones (12:6) potential as in part 1, except that in the present case the interaction parameters of the pure components were known and there was no need to invoke the principle of corresponding states to find them. The parameters of the second mixed virial coefficient are given by

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{\frac{1}{2}},$$
$$b_{12}^{\circ\,\frac{1}{3}} = \tfrac{1}{2}(b_{11}^{\circ})^{\frac{1}{3}} + \tfrac{1}{2}(b_{22}^{\circ})^{\frac{1}{3}}, \tag{6}$$

and those of the third mixed virial coefficients by

$$\epsilon_{112} = \epsilon_{11}^{\frac{2}{3}}\epsilon_{22}^{\frac{1}{3}}; \quad \epsilon_{122} = \epsilon_{11}^{\frac{1}{3}}\epsilon_{22}^{\frac{2}{3}};$$

$$(b_{112}^{\circ})^{\frac{1}{3}} = \tfrac{2}{3}(b_{11}^{\circ})^{\frac{1}{3}} + \tfrac{1}{3}(b_{22}^{\circ})^{\frac{1}{3}}; \quad (b_{122}^{\circ})^{\frac{1}{3}} = \tfrac{1}{3}(b_{11}^{\circ})^{\frac{1}{3}} + \tfrac{2}{3}(b_{22}^{\circ})^{\frac{1}{3}}. \tag{7}$$

Eqn. (7) has recently been shown to give a good approximation to the exact value of the mixed coefficients.[8] The parameters for the pure components are given in table 1.
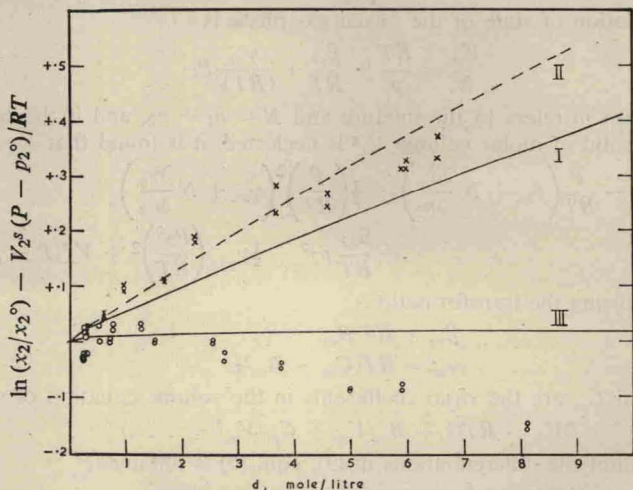

FIG. 4.—Solubility functions of CO_2 systems, 190° K.
Curves calculated by eqn. (5), points, experimental values.
I, $CO_2 + H_2$, using parameters of table 1.
II, $CO_2 + H_2$, using parameters of ref. (10).
III, $CO_2 + He$.

Eqn. (5) cannot be solved explicitly but can readily be solved by iteration. If $x_2°$ is taken as an initial value for x_2 and a first approximation is calculated by the simple formula (2.8) of part 1, it is usually sufficient to carry out a single calculation with (5) to obtain a final value of ln $(x_2/x_2°)$ to four significant figures.