where x_i is the mole fraction of species i, and ϕ_i is its translational partition function, omitting the volume factor. V is the molar volume of the mixture and A_l are virial coefficients given by

$$A_2 = \sum_i \sum_j x_i x_j B_{ij},$$

$$A_3 = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk}, \quad \text{etc.} \tag{2.2}$$

Eqn. (2.1) and (2.2) are a generalization of eqn. (704.3) of Fowler and Guggenheim.[1] The chemical potential of component i is given by

$$\frac{\mu_i}{RT} = \ln\left(\frac{x_i}{\phi_i V}\right) + \sum_{l=2}\left(\frac{l}{l-1}\right)\frac{A_l^i}{V^{l-1}}, \tag{2.3}$$

where

$$A_2^i = \sum_j x_j B_{ij},$$

$$A_3^i = \sum_j \sum_k x_j x_k C_{ijk}. \tag{2.4}$$

If this component is present as a pure solid then its chemical potential in that phase is given by

$$\mu_i^s/RT = -\ln f_i^s + (pV_i^s/RT), \tag{2.5}$$

where f_i^s is the partition function of the molecule in the solid, p is the total pressure, and V_i^s is the molar volume of the solid. This equation is derived by Fowler and Guggenheim,[1] (eqn. (513·5)). The last term is of this form whether the added gas be perfect or not. This effect of the applied pressure was first discussed by Poynting, and the term is usually known by his name. Consider now a gas (component 1) added to a solid in equilibrium with its vapour (component 2). The chemical potentials of (2.3) and (2.5) are now equal and the pressure may be written in terms of the volume by means of the virial equation of state, which may be derived from (2.1). First, if there is no added gas ($x_1 = 0$),

$$-\ln V_2 = \ln(\phi_2/f_2^s) + (V_2^s - 2B_{22})/V_2$$
$$+ (V_2^s B_{22} - \tfrac{3}{2} C_{222})/V_2^2 + \quad \text{etc.,} \tag{2.6}$$

where V_2 is the molar volume of the pure saturated vapour. Secondly, if the added gas is present at such high concentration that $x_1 \approx 1$, then

$$\ln(x_2/V) = \ln(\phi_2/f_2^s) + (V_2^s - 2B_{12})/V$$
$$+ (V_2^s B_{11} - \tfrac{3}{2} C_{112})/V^2 + \quad \text{etc.,} \tag{2.7}$$

where V is again the molar volume of the mixture. By subtracting (2.6) from (2.7) and neglecting terms in $1/V_2$ and its powers on the right-hand side, since $V_2 \gg V$, then

$$\ln(x_2 V_2/V) = \ln(x_2/x_2^0) = (V_2^s - 2B_{12})/V + (V_2^s B_{11} - \tfrac{3}{2} C_{112})/V^2$$
$$+ (V_2^s C_{111} - \tfrac{4}{3} D_{1112})/V^3 + \quad \text{etc.,} \tag{2.8}$$

where x_2^0 is the mole fraction which component 2 would have if its concentration in the mixture was that of the pure saturated vapour. The terms on the right hand side fall into two groups. Those with V_2^s as a factor are the Poynting terms. All but the first disappear if the added gas is perfect. The terms in B_{12}, C_{112}, D_{1112}, etc., represent the interaction in the gas phase of one molecule of the solid with one molecule, pairs of molecules, etc., of the added gas. Of the virial coefficients in (2·8), B_{11} and B_{12} are negative for all the systems considered here, and the rest are probably positive. Thus the numerator of the first term is positive,

the second negative and the third of uncertain sign. This equation may be written in a shorter form which represents Poynting's term more accurately,

$$\ln (x_2/x_2^0) = (pV_2^s/RT) - 2B_{12}/V - \tfrac{3}{2}C_{112}/V^2 - \tfrac{4}{3}D_{1112}/V^3 \text{ etc.} \quad (2.9)$$

However, (2.8) rather than (2.9), is used in this paper. The coefficient D_{1112} cannot be calculated and so the series must be stopped at the second term of (2.8). It is better to make a consistent approximation by neglecting all terms in $1/V^3$, rather than to retain some and omit others.

3. THE CALCULATION OF THE VIRIAL COEFFICIENTS.—If x_2/x_2^0 has been measured at low pressures then B_{12} can be calculated from the limiting slope of (2.8) at zero density. This has been done by Robin and Vodar [2] from measurements [3] of the solubility of solid iodine in compressed carbon dioxide. However, the second and higher terms in (2.8) are not negligible for the systems discussed here. We have therefore calculated the virial coefficients entirely from the properties of the pure components to give theoretical expressions for the solubility, x_2/x_2^0, which are compared with the experimental results.

The calculations are based upon two assumptions—first, that all the inter-molecular potentials are of the form which lead to the principal of corresponding states, and secondly, that interactions between pairs of unlike molecules can be related to those between pairs of like molecules by defining characteristic critical temperatures and volumes by

$$(T_{12}^c) = (T_1^c)^{\frac{1}{2}}(T_2^c)^{\frac{1}{2}}, \quad (3.1)$$

$$(V_{12}^c)^{\frac{1}{3}} = \tfrac{1}{2}(V_1^c)^{\frac{1}{3}} + \tfrac{1}{2}(V_2^c)^{\frac{1}{3}}. \quad (3.2)$$

These two assumptions have been justified for the calculation of B_{12} of non-polar gases.[4,5] Such an extension of the principle of corresponding states to mixtures cannot be exact for the higher coefficients, C_{112}, D_{1112}, etc., but it may be shown (Rowlinson, unpublished) that a first approximation to these coefficients, for molecules of not too dissimilar sizes and energies, is obtained by defining, for the nth coefficient,

$$(T_{11--2}^c) = (T_1^c)^{(n-1)/n} \cdot (T_2^c)^{1/n} \quad (3.3)$$

$$(V_{11--2}^c) = (n-1/n)(V_1^c)^{\frac{1}{3}} + (1/n)(V_2^c)^{\frac{1}{3}}. \quad (3.4)$$

The coefficient B_{12} could be calculated [4] from T_{12}^c, V_{12}^c and experimental values of B_{11}. This cannot conveniently be done for C_{112} as there are not accurate enough measurements of C_{111}. We have therefore calculated all three coefficients from tables computed [6] for the 12,6 potential of Lennard-Jones, using these re-lations between the critical constants and the intermolecular energy ϵ and collision diameter σ,

$$kT^c = 1 \cdot 28 \, \epsilon, \quad (3.5)$$

$$V^c = 1 \cdot 46 \, (\tfrac{2}{3}\pi N\sigma^3). \quad (3.6)$$

The critical constants used were : air (132·5° K, 93·4 cm³/mole), carbon dioxide (304·2, 94·2), ethylene (282·7, 130), naphthalene (753, 408), hexachlorethane (712, 470), p-chloro-iodobenzene (748, 346). The constants for the last two compounds are only approximate. They are estimated from boiling points and liquid densities by the principle of corresponding states and by the empirical rule of Meissner and Redding.[7] In place of the molar volume of the mixture in (2.8), the molar volume of the pure added gas at the same pressure and tem-perature is used. This leads to a little error at high densities but does not affect the limiting slope at low densities.

4. COMPARISON WITH EXPERIMENT.—*The system carbon dioxide + air.*—This has recently been studied by Webster [8] at several temperatures near the critical point of air. Fig. 1 shows $\ln (x_2/x_2^0)$ plotted against the density of air for three temperatures above the critical ($-141°$ C). It is seen that the agreement with