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The solubility of a solid in a compressed gas is usually greater than the concentration which corresponds to its normal vapour pressure. This excess solubility may be expressed in terms of a virial expansion in which the successive coefficients represent the clustering of single gas molecules, pairs of gas molecules, etc., around one molecule of solute. If the molecules are non-polar, the second virial coefficient of such a system can be calculated from the properties of the pure substances and the principle of corresponding states. The higher coefficients may be calculated from an approximate extension of this law. Theoretical solubilities, calculated in this way, are compared with recent measurements of solubilities in compressed air and ethylene.

1. Introduction.—In the system formed by a pure solid in equilibrium with a gas an exact expression may be derived for the change with pressure of the concentrations in the gas phase. The system is an interesting one, since this change depends primarily on the forces, in the gas phase, between molecules of the solid component and molecules of the gaseous component. It is a useful way of measuring directly the forces between unlike molecules. Other ways depend usually upon the measuring of small differences between the properties of a solution and those of its pure components. Only the rate of diffusion of one gas into another has so far been used extensively to measure these forces directly.

2. Theory.—The Helmholtz free energy of one mole of a gas mixture may be written

$$\frac{F}{RT} = \sum_i x_i \left[\ln\left(\frac{x_i}{\phi_i V}\right) - 1 \right] + \sum_{l=2} \left(\frac{1}{l-1}\right)\frac{A_l}{V^{l-1}}, \qquad (2.1)$$

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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,

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

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 intermolecular 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

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

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

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,

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

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

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 relations between the critical constants and the intermolecular energy ϵ and collision diameter σ,

$$kT^c = 1\cdot28\, \epsilon, \qquad (3.5)$$

$$V^c = 1\cdot46\, (\tfrac{2}{3}\pi N\sigma^3). \qquad (3.6)$$

The critical constants used were : air ($132\cdot5^\circ$ K, $93\cdot4$ cm³/mole), carbon dioxide ($304\cdot2$, $94\cdot2$), ethylene ($282\cdot7$, 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 temperature 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
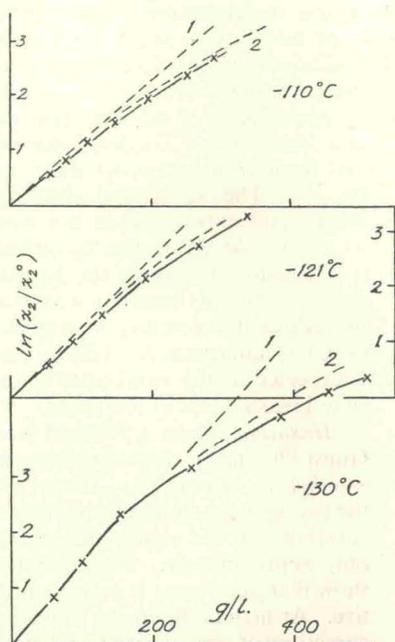
FIG. 1.—Graph of ln (x_2/x_2^0) against the density for the system carbon dioxide + air.[8]
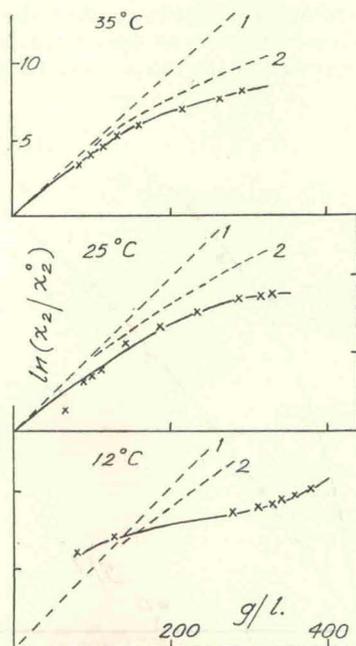
FIG. 2.—Graph of ln (x_2/x_2^0) against the density for the system naphthalene + ethylene.[9]
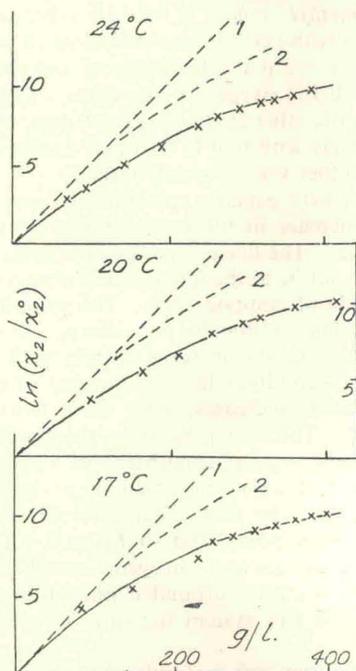
FIG. 3.—Graph of ln (x_2/x_2^0) against the density for the system hexachlorethane + ethylene.[10]
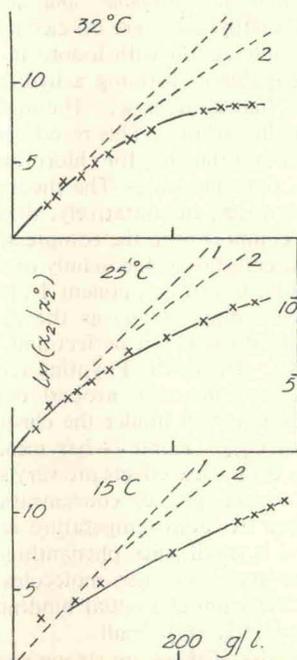
FIG. 4.—Graph of ln (x_2/x_2^0) against the density for the system p-chloro-iodo-benzene + ethylene.[11]

Full line, experimental; dashed line (1), calculated from first term of (2.8); dashed line (2), calculated from first two terms of (2.8).

experiment is excellent. Both the initial slope and the curvature of the experimental line are well reproduced. It is concluded that in this simple system the properties of the solution can be calculated satisfactorily from the properties of the pure substances alone.

Naphthalene + ethylene (Diepen and Scheffer [9]).—The experimental and theoretical curves are shown in fig. 2. The agreement between theory and experiment is not now so exact. At 35° C the agreement is satisfactory except at the highest densities, but it becomes worse as the critical temperature of ethylene (9° C) is approached. This is not unexpected as the virial equation of state breaks down at this point.

Hexachlorethane + ethylene (van Gunst [10]) and p-*chloro-iodobenzene + ethylene* (Ewald [11]).—These are the two systems in which the critical constants of the solids are known only approximately. Fig. 3 and 4 show that agreement is only qualitative. At high densities the increased curvature of the experimental lines is probably due to the higher terms in (2·8) which have been neglected in these calculations.

FIG. 5.—Graph of ln (x_2/x_2^0) against the density for the systems iodoform + propane (curve 1) and iodoform + dimethyl ether (curve 2).

Iodoform + propane and iodoform + dimethyl ether (Ewald [11]).—Propane and dimethyl ether are iso-electronic molecules with very similar critical constants. Their interaction with iodoform was studied to see if the hydrogen of iodoform was capable of forming a hydrogen bond with the oxygen of the ether. Fig. 5 shows that is the case. The interaction with the ether is much greater than with the hydrocarbon. This result agrees qualitatively with that of Fox and Lambert [5] who found that B_{12} for chloroform + diethyl ether was unusually large.

5. CONCLUSIONS.—The theory put forward here explains qualitatively, and in simple cases, quantitatively, the very great increase in the concentration of the solid component in the compressed gas mixture. The linear increase in ln (x_2/x_2^0) at low densities is due mainly to the term B_{12}, that is, to the independent clustering of molecules of component 1 about a molecule of component 2. The solubility increases more slowly as the density rises. This is due to two effects. First, the added gas is not perfect and so its pressure does not increase linearly with its density. Hence the Poynting term is lower. Secondly, when the number of gas molecules clustering around one solid molecule increases, then their mutual interactions will hinder the clustering process. This is expressed by the positive sign of C_{112}. Robin [12] has measured the solubility of phenanthrene in nitrogen where both these effects are very small, and so ln (x_2/x_2^0) is proportional to density up to much greater concentrations than usual. The first effect is small since nitrogen at room temperature is near to its Boyle point, and so $B_{11} \approx 0$. The second is small since phenanthrene is a large molecule and nitrogen a small one, and so more nitrogen molecules than usual can cluster around a phenanthrene molecule without mutual hindrance. That is, in this system the ratio C_{112}/B_{12}^2 is apparently very small.

Finally, if there are strong specific forces between one molecule of the gas and one of the solid then the initial slope of ln (x_2/x_2^0) will be greater than the principle of corresponding states would indicate.

1 Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge, 1939).
2 Robin and Vodar, *J. Physique Rad.*, 1952, **13**, 264.
3 Braune and Strassmann, *Z. physik. Chem.*, 1929, **143**, 225.
4 Guggenheim and McGlasham, *Proc. Roy. Soc. A*, 1951, **206**, 448.
5 Fox and Lambert, *Proc. Roy. Soc. A*, 1951, **210**, 557.
6 Bird, Spotz and Hirschfelder, *J. Chem. Physics*, 1950, **18**, 1395; and private communication.
7 Meissner and Redding, *Ind. Eng. Chem.*, 1942, **34**, 524.
8 Webster, *Proc. Roy. Soc. A*, 1952, **214**, 61.
9 Diepen and Scheffer, *J. Amer. Chem. Soc.*, 1948, **70**, 4085.
10 van Gunst, *Thesis* (Delft, 1950).
11 Ewald, *Thesis* (Manchester, 1952), to be published.
12 Robin, *J. Chim. Physique*, 1951, **48**, 415, 501.