

THE SOLUBILITY OF SOLIDS IN GASES

PART 3.—THE SOLUBILITY OF SOLID XENON AND SOLID CARBON DIOXIDE

BY A. H. EWALD*

Chemistry Division, National Research Council, Ottawa, Canada

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The solubility of solid xenon in compressed nitrogen, hydrogen and helium has been measured in order to test the theory describing this solubility in terms of van der Waals' interactions in the gas phase. Using only published values of the interaction parameters of the pure components the calculated solubility was found to be in good agreement with experimental results, except for the system with helium in which, it is suggested, a solid solution may be formed. The solubility of solid carbon dioxide was measured in hydrogen and helium. The solubility in hydrogen was found to be greater than the calculated values, indicating a carbon dioxide + hydrogen interaction in excess of ordinary van der Waals' forces.

In part 1 of this series¹ it was shown that the solubility of a solid in a compressed gas could be calculated in terms of van der Waals' interactions in the gas phase, and could be expressed in a power series in $1/V$ and the virial coefficients of the mixed gas phase. The theory of corresponding states was used to find the interaction parameters of the Lennard-Jones (12 : 6) potential and to calculate the virial

* Present Address : C.S.I.R.O. 'Division of Industrial Chemistry, High Pressure Laboratory, Sydney University, Australia.

coefficients. It was shown that the expression for $\ln(x_2/x_2^\circ)$ takes a particularly simple form if the total solubility is small. (x_2 is the actual mole fraction of the solid component 2 in the gas phase while x_2° is the mole fraction it would have if its concentration in the mixture were that of the pure saturated vapour of the solid.) The solubilities thus calculated were shown to be in qualitative agreement with experimental results.

The experimental solubility data which were then available were not very well suited to test the theory, as the components involved did not meet the assumptions of either the principle of corresponding states or the Lennard-Jones (12:6) potential very well. The present work was undertaken to obtain experimental data for systems to which the theory could be applied with greater confidence. Most suitable for this purpose are systems consisting of simple molecules for which the interaction parameters of the pure components are already known. Solid xenon provides an almost ideal component from this point of view and its solubility was therefore measured in compressed helium, hydrogen and nitrogen.

Recent measurements of the second virial coefficient of carbon dioxide² have suggested that, in contrast to the rare gases, carbon dioxide has a directional force field which may be described in terms of a molecular quadrupole.¹¹ In addition to the ordinary van der Waals interaction one would therefore expect a more specific interaction of carbon dioxide with such molecules as hydrogen, due to quadrupole-quadrupole interaction. At low temperatures the contribution of such forces may be appreciable and may lead to a solubility of solid carbon dioxide in compressed hydrogen greater than that calculated on the basis of pure van der Waals forces. To test this hypothesis the solubility of solid carbon dioxide was measured in compressed hydrogen at 190° K and, as a comparison, in compressed helium also at 190° K.

EXPERIMENTAL

APPARATUS.—Solubilities were measured by a static method in which the solid component 2 was allowed to come into equilibrium with the gaseous component 1 and a small sample was then taken from the gas phase and analyzed by low temperature fractionation.

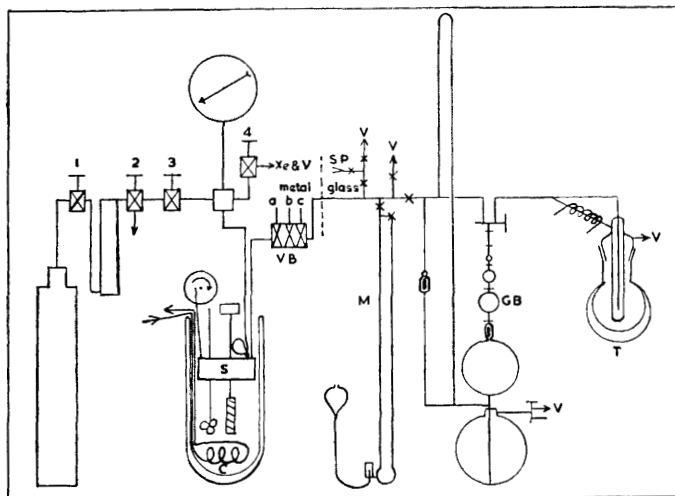


FIG. 1.—Diagram of apparatus.

The essential parts of the apparatus are shown diagrammatically in fig. 1, the remainder consisting of a conventional gas handling system. The saturator S consisted of a brass bomb of about 100 cm³ capacity. It was rocked slowly and the fluid in it was agitated

by a ball-bearing ball running backwards and forwards in an open-ended brass tube along its axis. The space between the brass tube and the wall of the bomb was loosely packed with copper turnings. The sampling outlet of the saturator was connected to the three valve block V.B. and was made of stainless steel capillary (0.032 in. ext. diam., 0.015 in. int. diam.) in order to reduce the dead space. Samples as small as 0.07 cm³ could be taken between the several valves of this block. The other tube to the saturator was made of copper (0.125 in. ext. diam., 0.064 in. int. diam.) and connected it with a Bourdon pressure gauge, with the vacuum line and the xenon storage bulb through the valve 4, and with a gas drier and the cylinder of solvent gas through the fine-control valve 3.

The saturator was immersed in a cryostat consisting of a one-gallon Dewar vessel filled with petroleum ether (30–60° C) and cooled by pumping liquid nitrogen through a 12-ft. copper coil C at a steady rate. The temperature was regulated by an immersion heater controlled by a bimetallic strip regulator acting through an electronic relay. The temperature was measured by a copper-constantan thermocouple connected to a Leeds and Northrop K2 potentiometer. All the controls as well as a stirrer and the leads and suspending wires of the saturator, passed into the cryostat through a lid lined with 1 in. of cork. When both the flow rate of the liquid nitrogen and the voltage on the control heater were properly adjusted the cryostat temperature remained constant to within $\pm 0.05^\circ$ C.

The remainder of the apparatus was made of glass and consisted of the sampling point S.P. at which sampling bulbs of 100 cm³ capacity could be attached, a mercury manometer M, the calibrated gas burette B and the condensing trap T. The Dewar vessel surrounding the trap could be evacuated in order to cool the trap to the temperature of solid nitrogen. One limb of the connection to the trap was heated in order to circulate the contents of the trap by thermal convection. The gas burette was combined with a Toepler pump (500 cm³ bulb) and was calibrated at five points (10.5, 2.3, 0.5, 0.15, 0.06 cm³). Pressures in the gas burette were read by means of a cathetometer to 0.001 cm but owing to capillary corrections were accurate only to ± 0.02 cm. The capillary corrections were large and not accurately reproducible due to contamination of the burette by tap grease. The burette was cleaned from time to time through the barrel of the tap and the capillary corrections were determined repeatedly between analyses.

OPERATION.—With the cryostat lowered out of the way, the heavy component was condensed into the saturator by immersing it in liquid air. The cryostat was then put into place and only when it had reached the desired temperature was the solvent gas admitted to the saturator. At least 45 min was allowed for equilibration before a first small sample was taken through the valve block. This gas served to flush out the sampling line and was pumped away before an actual sample was taken into a sample bulb. At low pressures two or three fillings of the valve block between the valves *a* and *c* had to be taken in order to obtain a sample of sufficient size. (100 cm³ at 6 mm was the minimum amount of gas required for one analysis.) In such cases a duplicate sample was taken after about 10 min. At higher pressures a single sample between valves *a* and *b* gave sufficient gas for duplicate analyses.

At the end of a run the gas in the saturator was blown off through two liquid-air traps and a pressure-vacuum pump, the pressure in the manifold never exceeding 200 mm. Only after most of the gas had escaped was the saturator allowed to warm up and was finally heated by immersion in hot water. In this way 80 to 90 % of the xenon used in a run was recovered. This was then pumped, sublimed, and pumped again and finally condensed back into the storage bulb.

For analysis the gas was transferred from the sample bulb to the burette by means of the Toepler pump and its total pressure was measured twice at one of the large volumes of the burette. The gas was then transferred to the trap by raising the mercury in the burette to just below the side arm to the trap. Twenty minutes were allowed for condensation of the heavy component before the trap was pumped on the high vacuum system for 1.5 min. Mixtures containing more than 5 % of the heavy component were pumped for only 1 min in the first instance and the trap was warmed up and cooled in solid nitrogen again for 10 min before it was pumped for another $\frac{1}{2}$ min. This was done to eliminate any of the light component which might have been occluded in the condensed heavy component. Finally the trap was warmed and the heavy component of the mixture measured in the burette in several portions. After filling the evacuated Toepler bulb from the trap three times the next filling would usually give a reading smaller than the experimental error of the first reading.

CALCULATION OF RESULTS.—The pressure readings of the gas burette were corrected for temperature, and the mole fraction calculated from the ratio of the partial pressure of

the heavy component to the total pressure. Corrections for the non-ideal behaviour of the gases were found to be negligible.

In order to calculate the ratio x_2/x_2° the mole fraction x_2° was calculated from the concentration of the saturated vapour of the pure solid (c_2° mole/l.) and the concentration c_1 of the solvent gas at the partial pressure $p_1 = P - p_2^\circ$ by the equation

$$x_2^\circ = \frac{c_2^\circ}{c_1 + c_2^\circ}.$$

The density of saturated xenon vapour was found by graphical interpolation of published values of the vapour pressure,³ and by using the second virial coefficient calculated by the Lennard-Jones (12 : 6) potential to calculate the density corresponding to this pressure.

The molar volume of solid xenon used in calculating the Poynting term (see below) was found by graphical interpolation between the volume at the triple point⁴ (161° K) and an X-ray crystallographic value at 130° K.⁵ It was found to be 36.75 cm³/mole at 150° K and 36.93 cm³/mole at 155° K.

The densities of the solvent gases were read from large-scale density isotherms interpolated between published isotherms by plotting isochores. The sources of these data are given in table 1.

TABLE 1

gas	ϵ/k° K	b° cm ³ /mole	source of ϵ/k° and b°	source of density
Xe	224.5	84.65	<i>a</i>	<i>b</i>
CO ₂	205	85.05	<i>c</i>	<i>d</i>
N ₂	95.05	63.78	<i>e</i>	<i>e</i>
H ₂	29.2	29.76	<i>f</i>	<i>d</i>
He	10.22	21.07	<i>g</i>	<i>h</i>

(a) Beattie, Barriault and Brierly, *J. Chem. Physics*, 1951, **19**, 1222.

(b) Peters and Weil, *Z. physik. Chem. A*, 1930, **148**, 27.

(c) McCormack and Schneider, as quoted by Hirschfelder *et al.* in *Chem. Rev.*, 1949, **44**, 205.

(d) Perry, *Chemical Engineers Handbook* (McGraw-Hill, N.Y., 1950), 3rd ed., p. 205.

(e) Michels, Wouters and De Boer, *Physica*, 1934, **1**, 587.

(f) Michels and Boerboom, *Bull. Soc. Chim. Belg.*, 1953, 120.

(g) De Boer and Michels, *Physica*, 1938, **5**, 955.

(h) Keesom, *Helium* (Elsevier, London, 1942), p. 42.

ERRORS.—The main source of error in the gas analysis was the capillary correction. The standard error of pressure readings was 0.05 % for the total pressures and 0.19 % for the partial pressures, while differences between duplicate analyses showed a standard error in x_2 of 1.36 %. The error of the Bourdon gauge indicating the pressure of the solubility measurement was ± 0.2 atm giving an error in $\ln(x_2/x_2^\circ)$ of ± 0.013 . An independent check of the analytical method is given by a few samples analyzed on a mass spectrograph. These values are marked by asterisks in table 3.

RESULTS

The pressure composition isotherms of the system xenon + nitrogen are shown in fig. 2. Both the shape of these curves and the behaviour of the system during the measurements indicate the formation of a liquid phase rich in Xe at approximately the pressures at which the discontinuities are shown. The upper part of the isotherms thus represents the composition of a vapour phase in equilibrium with a liquid solution of nitrogen in xenon. The general shape of two complete such isotherms is shown in the inset not drawn to scale (cf. part 2⁶). The actual values of the solubility at 155° K are given in table 2. In this and the following tables two concentrations given for one pressure entry indicate the results of duplicate analyses on one gas sample.

The systems xenon + helium and xenon + hydrogen gave no indication of a liquid phase being formed at 155° K in the range of pressures investigated. The results of the solubility measurements are reported in table 3 and 4. The solubility functions (see below) calculated from the measurements on the xenon systems are shown in fig. 3 where the scale of curve I is one-half that of the other two curves.

The solubilities of carbon dioxide in helium and hydrogen were measured at 190° K

and the results are given in table 5 and 6. In fig. 4 the experimental values of the solubility function are compared with calculated values.

FIG. 2.—Solubility isotherms of Xe + N₂.

× 150° K.
○ 155° K.

Inset: extrapolated complete isotherms, not to scale.

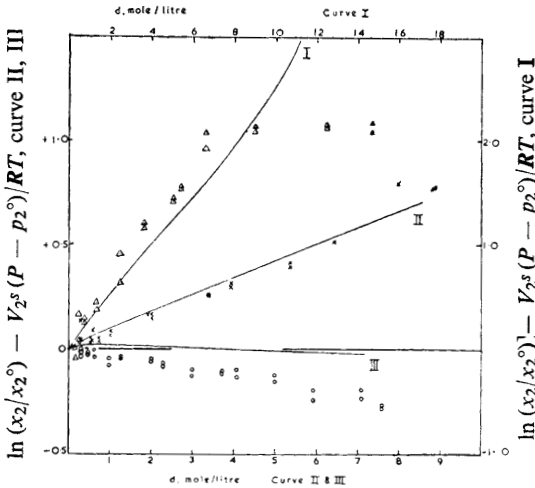
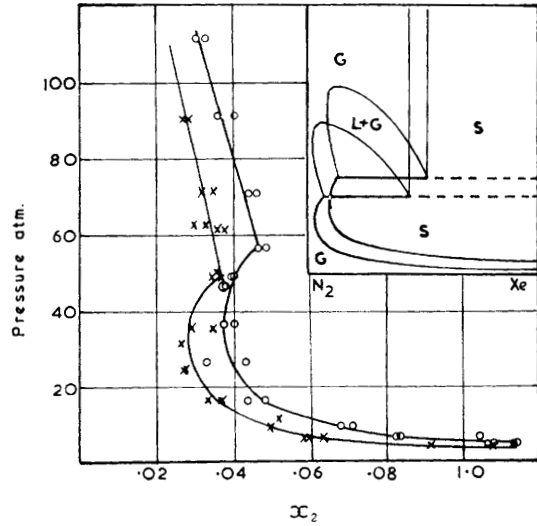


FIG. 3.—Solubility functions of Xe systems, 155° K.

Curves calculated by eqn. (5), points, experimental values.

I, Δ Xe + N₂, scale on right.

II, × Xe + He, scale on left.

III, ○ Xe + He, scale on left.

In tables 2 and 4, P is the pressure in atm at which the solubility was measured, c_1 the concentration in mole/l. of the solvent gas, and x_2 the measured concentration, as mole fraction, of the heavy component in the gas phase.

TABLE 2.—Xe + N₂, 155° K P , atm; c_1 , mole/l.; x_2 , mole fraction

P	C_1	x_2	P	C_1	x_2	P	C_1	x_2
4.74	.303	.108	16.2	1.34	.0473	56.6	6.60	.0462
4.81	.307	.107			.0439			.0482
4.9	.321	.114	26.6	2.47	.0432	70.4	9.01	.0438
4.9	.321	.114			.0330			.0459
6.92	.500	.104	36.6	3.64	.0402	91.3	12.47	.0358
6.92	.500	.0830			.0376			.0404
6.92	.500	.0822	46.1	5.01	.0377	111.6	14.69	.0328
9.5	.731	.0714			.0371			.0305
		.0682	48.9	5.41	.0393			
					.0400			

$$x_2^0 = \frac{1.1194}{c_1 + 1.12}$$

TABLE 3.—Xe + He, 155° K

P, atm; c ₁ , mole/l.; x ₂ , mole fraction								
P	C ₁	x ₂	P	C ₁	x ₂	P	C ₁	x ₂
4.40	.300	.119	16.7	1.266	.0311	81.8	5.91	.0067
4.40	.300	.117			.0308			.0070
4.47	.305	.113 *	26.5	2.01	.0198	99.9	7.09	.0059
4.47	.305	.114			.0200			.0062
4.61	.325	.110	30.1	2.27	.0173	107.5	7.59	.0055
4.61	.325	.111			.0176			.0054
6.58	.467	.0789	30.3	2.28	.0175 *			
6.58	.467	.0784	39.9	3.00	.0130			
8.42	.612	.0605			.0134			
		.0605	49.9	3.72	.0110			
8.42	.612	.0627 *			.0109			
13.2	.987	.0385	54.8	4.06	.0100			
		.0373			.0103			

$$x_2^{\circ} = \frac{0.1599}{c_1 + 0.16}$$

* analyzed by mass spectrograph

TABLE 4.—Xe + H₂, 155° K

P, atm; c ₁ , mole/l.; x ₂ , mole fraction								
P	C ₁	x ₂	P	C ₁	x ₂	P	C ₁	x ₂
4.06	.278	.134	10.19	.744	.0550	52.58	3.93	.0158
4.06	.278	.131	13.79	1.022	.0425			.0160
4.06	.278	.145			.0417	72.04	5.36	.0135
4.47	.317	.118	25.36	1.90	.0260			.0138
4.47	.317	.118	26.65	2.00	.0245			.0133
6.92	.511	.0762			.0246	87.2	6.42	.0152
6.99	.521	.0764	45.03	3.38	.0171	110.9	7.98	.0152
7.87	.565	.0700			.0172			

$$x_2^{\circ} = \frac{.08055}{c_1 + 0.08}$$

TABLE 5.—CO₂ + He, 190° K

P, atm; c ₁ , mole/l.; x ₂ , mole fraction								
P	C ₁	x ₂	P	C ₁	x ₂	P	C ₁	x ₂
4.7	.255	.141	12.36	.734	.0562	45.4	2.77	.0160
		.140	12.36	.734	.0558			.0158
4.7	.255	.148	13.2	.795	.0530	62.3	3.77	.0120
4.7	.255	.139	13.2	.795	.0536			.0119
4.9	.270	.140	21.1	1.29	.0338	83.27	4.97	.00903
5.0	.275	.136			.0341			.00905
5.29	.295	.124	25.1	1.54	.0281	100.5	5.91	.00784
5.29	.295	.124			.0280			.00793
8.8	.515	.0774	41.4	2.54	.0177	142.5	8.21	.00583
8.8	.515	.0796			.0178			.00576

$$x_2^{\circ} = \frac{0.1700}{c_1 + 0.17}$$

TABLE 6.—CO₂ + H₂, 190° K

P atm; c ₁ , mole/l.; x ₂ , mole fraction								
P	C ₁	x ₂	P	C ₁	x ₂	P	C ₁	x ₂
5.32	.298	.128	27.3	1.69	.0288	76.5	4.60	.0137
5.32	.298	.128			.0289			.0134
5.6	.317	.131	36.3	2.24	.0238	99.7	5.90	.0117
5.6	.317	.123	43.9	2.70	.0203	101.0	5.98	.0116
10.2	.610	.0697			.0202			.0117
10.2	.610	.0693	60.6	3.69	.0169	111.6	6.55	.0110
15.6	.957	.0484			.0160			.0115
		.0478						

$$x_2^{\circ} = \frac{.0856}{c_1 + .086}$$

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

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

If the equation of state of the mixed gas phase is

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

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

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

On introducing the transformations

$$\begin{aligned} \beta_m &= RT B_m, \\ \gamma_m &= RT (C_m - B_m^2), \end{aligned} \quad (4)$$

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

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

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

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

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 are 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

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{\frac{1}{2}},$$

$$b_{12}^\circ = \frac{1}{2}(b_{11}^\circ) + \frac{1}{2}(b_{22}^\circ), \quad (6)$$

and those of the third mixed virial coefficients by

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

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

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.

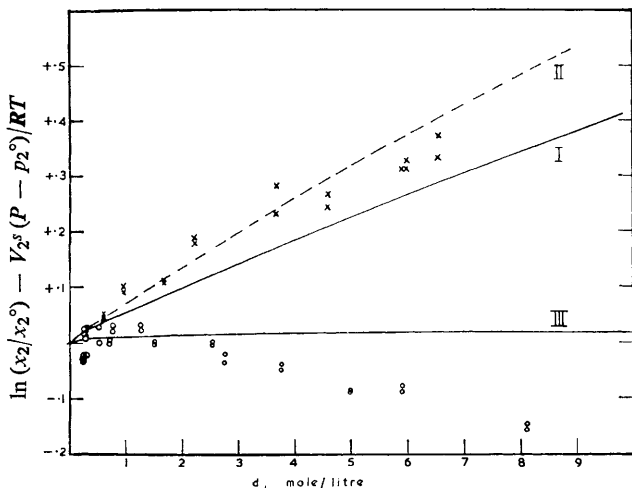


FIG. 4.—Solubility functions of CO_2 systems, 190°K .
 Curves calculated by eqn. (5), points, experimental values.

- I, $\text{CO}_2 + \text{H}_2$, using parameters of table 1.
 II, $\text{CO}_2 + \text{H}_2$, using parameters of ref. (10).
 III, $\text{CO}_2 + \text{He}$.

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 $\ln(x_2/x_2^\circ)$ to four significant figures.

The Poynting term $V_2^s(P - p_2^0)/RT$ expresses the general effect of pressure on the vapour pressure of a solid and in comparing the solvent action of different gases it is therefore desirable to subtract this from $\ln(x_2/x_2^0)$. It was shown in part 1 that $\ln(x_2/x_2^0)$ in first approximation was a linear function of density and in fig. 4 and 5 we have therefore plotted the solubility function $\ln(x_2/x_2^0) - V_2^s(P - p_2^0)/RT$ against the density of the solvent gas. The curves were calculated by eqn. (5) while the points were calculated from the measured solubilities.

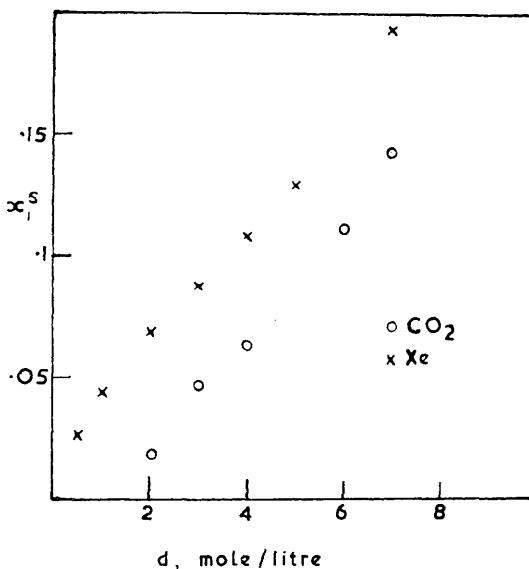


FIG. 5.—Estimated concentration of He in solid phase.
I, \circ Xe + He, 155° K. II, \times CO₂ + He, 190° K.

For the systems Xe + N₂ and Xe + H₂ the solubilities seem to be fairly well represented by eqn. (5) using the interaction parameters calculated by eqn. (6) and (7). The differences between the calculated and experimental values are just outside the experimental error and may be due partly to the uncertainty in the interaction parameters of the pure component. For hydrogen particularly there is some doubt as to how far quantum effects should be considered in the interactions in the mixed gas phase. The parameters shown in table 1 and used in the calculations are classical.

For the system Xe + He the calculated values are very much higher than the experimental values and it seems likely that some effect other than gas phase interaction enters in this system; here again, quantum effects are likely to introduce complications and may particularly affect the validity of eqn. (6) and (7). However, the very large difference in size between xenon and helium atoms and the lattice parameters of solid Xe suggest the possibility of He entering the interstitial spaces of Xe crystals without greatly distorting the crystal lattice and therefore readily forming a solid solution.

It is possible to allow for the formation of a solid solution in the calculation of $\ln(x_2/x_2^0)$ by introducing a factor $RT \ln a_2^s$ on the right-hand side of (5),⁹ where a_2^s is the activity of component 2 in the solid phase. Making the plausible assumption that $a_2^s = x_2^s$, the mole fraction of 2 in the solid phase, it is possible to calculate this concentration from the difference between the experimental and calculated values of $\ln(x_2/x_2^0) - V_2^s(P - p_2^0)/RT$. The result of such a calculation for the system Xe + He is shown as curve 1 in fig. 5.

The calculated and experimental values of the solubility functions of the systems $\text{CO}_2 + \text{H}_2$ and $\text{CO}_2 + \text{He}$ are shown in fig. 4. The curve I was calculated for the $\text{CO}_2 + \text{H}_2$ system using the parameters given in table 1 and by eqn. (6) and (7). As expected the curve lies considerably below the experimental values indicating a gas phase interaction greater than the van der Waals interaction considered in the calculations. Since these measurements were made values of the $\text{CO}_2 + \text{H}_2$ interaction parameters derived from volume changes on mixing have been reported.¹⁰ The value thus found was $\epsilon_{12}/\kappa = 89.39^\circ \text{K}$ whereas the parameters of table 1 and eqn. (6) give $\epsilon_{12}/\kappa = 77.39^\circ \text{K}$. Curve II in fig. 4 was calculated by eqn. (5) using the experimental value of ϵ_{12}/κ and shows very satisfactory agreement with the values derived from measured solubilities.

The system $\text{CO}_2 + \text{He}$ (curve II, fig. 4) shows the same effect as the $\text{Xe} + \text{He}$ system. As the crystal lattice of solid CO_2 is very similar to that of Xe , conditions may again be favourable for the formation of a solid solution and a comparison of this system with the $\text{CO}_2 + \text{H}_2$ system is therefore not possible. The concentration of He in the solid solution which would account for the difference between the calculated and experimental values of $\ln(x_2/x_2^\circ)$ was estimated as for the $\text{Xe} + \text{He}$ system and is shown as curve II in fig. 5.

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