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The solubility of *p*-chloroiodobenzene in compressed ethylene was measured between 13 and 31·5° C and at pressures up to 100 atm using a radioactive tracer technique. The apparatus is described and results are reported. The saturated vapour pressures of *p*-chloroiodobenzene was measured between 30 and 60° C.

A number of methods of measuring equilibria between solids and compressed gases have recently been described [1] and the results have been discussed in terms of molecular interactions in the gas phase.[2] In the present paper, the experimental method used to investigate the system *p*-chloroiodobenzene + ethylene will be described and the results will be given in detail.

The measurements consisted in determining the radioactivity of a gas phase in equilibrium with the solid containing I^{131} as radioactive tracer atoms. By using an empirical calibration, the volume concentration and the mole fraction of the solid dissolved in the gas phase could then be calculated.

EXPERIMENTAL

Equilibrium between the two phases was established in a small dural bomb and a suitably shielded Geiger-Müller counter was placed outside the bomb to measure the radioactivity of the gas phase only. Details of the bomb and counter assembly are shown in fig. 1. The duralum bomb B had a capacity of 11 cm³ and a wall thickness of 1/32 in. It was drilled and turned from a solid bar and was tested to 3000 lb/in² before use. It was connected by a stainless steel collar nut to the rest of the apparatus and was suspended in a stirrup 1 so that it was accurately located and could easily be removed. Inside the bomb was a spiral stirrer 6 which was made of nickel wire and which could be actuated by the solenoid 5. In the bottom of the bomb was a small stainless steel cup which held the solid component. The Geiger-Müller counter 2 was set in a lead block 3 and was further shielded from the solid in the stainless steel cup by the lead block 4. Together with its lead shields, the counter was mounted so that it could be raised or lowered relative to the bomb. The whole assembly was immersed in a 13-gall. oil thermostat which was well stirred and regulated to ± 0·1° C by a toluene regulator.

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The Geiger-Müller counter was of the end window type (G.M. 4) made by General Electric Company, and was connected to a probe unit by a coaxial cable. For temperatures up to 40° C a polythene-insulated cable was satisfactory, but at higher temperatures an air-insulated coaxial cable had to be used for the part of the cable which was immersed in the thermostat oil. The probe unit contained a quenching circuit and a preamplifier, and was mounted close to the G.M. tube. It was in turn connected to a counting ratemeter, the output of which was recorded on a recording ammeter and served to give an instantaneous reading of the counting rate as well as to provide a check on the apparatus while it was not attended. In the actual solubility measurement, some counting rates were so low (approximately 20 counts/min including background) as to make the additional error introduced by the ratemeter undesirable. A scale of hundred was therefore connected in series with the rate-meter and used to record the actual pulses given by the G.M. tube.

Fig. 1.—Equilibrium bomb and counter assembly.

The gas-handling apparatus consisted of a brass storage bomb which could be heated to obtain high pressures, a regulating valve, and a Bourdon pressure gauge which could be read to $\pm$ 0·1 atm. Mounted just above the equilibrium bomb were two shut-off valves by which the bomb could be isolated, one connecting it to the pressure system and the other leading to a vacuum line through which the bomb could be evacuated.

A calibration of observed counting rate in terms of volume concentration of solid in the equilibrium bomb had to be established for every batch of radioactive solid which was prepared.* A standard solution of the solid in a suitable solvent was made up by weighing, placed in the bomb, and its count rate measured. As the counting efficiency of the Geiger-Müller tube was strongly temperature dependent, such a calibration had to be carried out at each temperature of the solubility measurements. A typical value obtained on a freshly prepared sample was 230 counts/min $\equiv$ 1 mg/cm³.
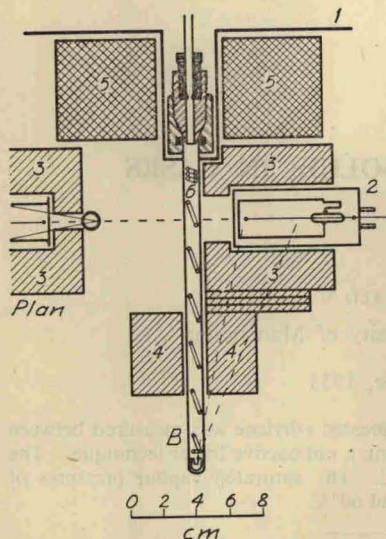
It was found that in spite of the lead shields, a considerable amount of radiation reached the G.M. tubes from the bulk solid contained in the cup at the bottom of the bomb. The count rate due to this radiation was determined at the beginning of each series of solubility measurements by closing the filled cup with a plug of Apiezon Q wax and placing it in the bomb in its usual position. In evaluating the solubility measurements, allowance was made for the decrease of the amount of solid in the cup due to its solution in the gas phase. A typical counting rate due to 100 mg of solid in the cup was 5·72 counts/min. The background counting rate due to cosmic radiation, noise, etc., was determined before each series of measurements and was fairly constant at 10·6 counts/min.

In all the measurements counting was continued until a count of 10,000 was obtained, giving a statistical accuracy of $\pm$ 1 %. All the observed count rates were corrected for radioactive decay by converting to a standard time using the half-life of I^{131} of 8·02 days.

After these preliminary measurements, the bomb was flushed out three times with the solvent gas and then filled to the desired pressure; stirring was commenced and the increase in the count rate followed on the ratemeter. When the count rate appeared to be constant, counting was started with the scale of hundred. The total count of 10,000 was divided into several shorter counts in order accurately to check the constancy of the counting rate. As long as these short counts showed a statistically significant trend, they were rejected. A series of solubility measurements was always carried out at successively higher pressures.

* The p-chloroiodobenzene was prepared on a 0·005-M scale by a Sandmeyer reaction from p-chloroaniline. One millicurie of radioactive iodine was introduced with the potassium iodide in the form of an aqueous solution of sodium iodide.

RESULTS

The solubility of p-chloroiodobenzene in compressed ethylene was measured between 13° and 31·5° C at pressures up to 100 atm.   Fig. 2 shows the molar concentration of the solute plotted against pressure.   Diepen and Scheffer [3] investigated the coexistence curves of this system and found an upper critical temperature for a saturated liquid solution at 12° C and showed that a second liquid phase, richer in solute, is formed at higher temperatures and pressures.   In the present work it was found that a liquid phase was still formed at 13° C and 51 atm, and only at 15° C could a gas solubility isotherm be measured over the whole range of pressure.   At 31·5° C the second liquid phase would be expected to be formed at 71 atm and, although there is no direct evidence for it from the present measurements, this may be the cause of the abnormal shape of the 31·5° C isotherm shown in fig. 2.
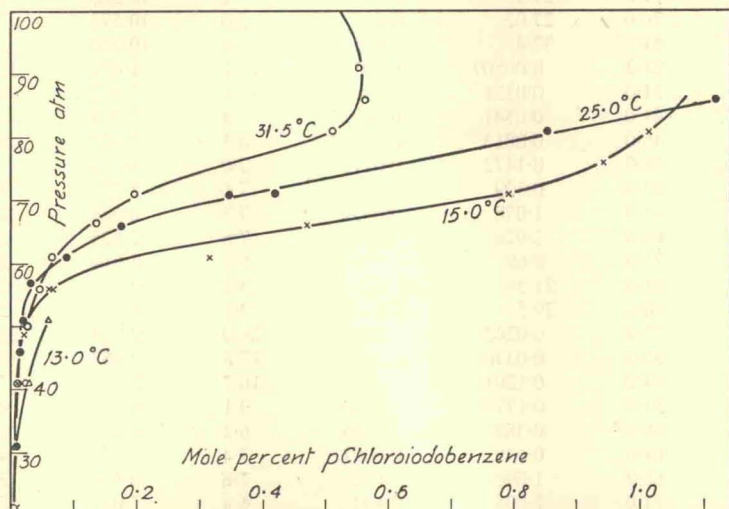

FIG. 2.—Solubility isotherms of the system p-chloroiodobenzene + ethylene.

The solubility isotherms of this system and of other solid + gas systems have been discussed by Ewald, Jepson and Rowlinson.[2]   It was then shown that the function ln $(x_2/x_2°)$ could be expressed in terms of the virial coefficients of the mixed gas phase and could be calculated in first approximation by the theory of corresponding states. In this function x_2 represents the observed solubility expressed as mole fraction, and $x_2°$ the concentration which would be given by the saturated vapour pressure of the solid component.   In the above paper no experimental values were given and these are reported in table 1, where d_2 is the observed volume concentration of p-chloroiodobenzene and x_2 and ln $(x_2/x_2°)$ are shown together with their respective experimental errors.

The experimental error in determining the volume concentration of the solid in the vapour phase was estimated to be $\pm 2·4\%$ of which $1·4\%$ was due to the empirical calibration.   The error in the pressure measurements was $\pm 0·1$ atm.   The volume concentration of ethylene was found from the measured pressure by means of large-scale plot of density isotherms [4] and was assumed to be unaffected by the presence of the solute.

The mole fraction of the solute is given by

$$x_2 = \frac{d_2}{d_2 + (d_1 M_2/M_1)} \approx \frac{d_2 M_1}{d_1 M_2},$$

where d_2 and d_1 are the volume concentrations in the vapour phase of the solute and solvent respectively, and M_2 and M_1 their molecular weights.   The error in d_1 corresponding to an error in the pressure readings of 0·1 atm, will depend on the slope of the density isotherm.   It will be particularly large in the region of high compressibility near the critical region of the gas.   The ratio $x_2/x_2°$ is given by $d_2/d_2°$, where $d_2°$ is the density of the saturated vapour, and hence is independent of the density of the solvent gas and the error in the pressure measurements.

TABLE 1.—SOLUBILITY ISOTHERMS. p-CHLOROIODOBENZENE $+$ ETHYLENE

temp. °C	press, atm	d_2 g/l.	x_2 mole %	% error	ln $(x_2/x_2°)$	error $\times 10^2$
13·0	31·0	0·0103	0·00242	—	2·868	—
	41·0	0·167	0·0258	—	5·655	—
	51·0	0·588	0·0566	—	6·913	—
15·0	21·0	0·0174	0·00692	27·4	3·226	22·9
	41·0	0·0486	0·00776	14·7	4·254	10·3
	48·8	0·1603	0·0178	13·1	5·447	3·6
	56·0	1·060	0·0622	10·9	7·336	3·1
	61·0	7·52	0·311	4·9	9·295	2·5
	66·0	12·29	0·466	3·3	9·786	2·6
	71·0	21·95	0·788	3·1	10·366	2·8
	76·0	27·02	0·937	3·0	10·574	2·8
	81·0	32·4	1·095	2·4	10·756	2·3
25·0	21·2	0·00807	0·00338	29·1	1·631	32·9
	31·0	0·0321	0·00838	12·9	3·012	9·2
	41·0	0·0541	0·00955	8·4	3·534	5·8
	46·0	0·0813	0·01193	8·3	3·942	5·1
	51·0	0·1472	0·0179	7·0	4·536	3·6
	57·0	0·309	0·0292	7·6	5·277	3·8
	61·0	1·078	0·0852	7·3	6·528	2·9
	66·0	2·928	0·174	7·8	7·525	2·6
	71·0	8·69	0·416	5·0	8·614	2·4
	81·0	21·36	0·850	3·3	9·513	2·6
	86·0	29·5	1·117	3·1	9·813	2·9
31·5	31·0	0·0242	0·00673	26·0	2·229	21·5
	35·7	0·0370	0·00867	17·8	2·653	13·8
	41·0	0·1201	0·0227	10·7	3·829	7·5
	51·0	0·1772	0·0240	9·1	4·219	6·7
	56·0	0·382	0·0436	6·4	4·988	3·7
	61·0	0·640	0·0607	7·4	5·504	4·1
	66·2	1·696	0·132	7·6	6·478	3·6
	71·0	2·995	0·192	6·4	7·047	3·4
	81·0	10·70	0·506	4·6	8·320	3·2
	85·7	12·82	0·557	3·9	8·501	3·3
	91·0	13·38	0·549	3·7	8·544	3·5
	101·0	13·5	0·511	3·6	8·627	3·2

VAPOUR PRESSURE MEASUREMENTS.—In order to calculate the function ln $(x_2/x_2°)$ it was necessary to know the saturated vapour pressure of p-chloroiodobenzene. Ideally this could be measured by the tracer method directly but the apparatus was found to be too insensitive (see below). A butyl-phthalate manometer was therefore used to measure the pressure of air required to balance the vapour pressure of the solid. A glass Bourdon gauge was used to confine the solid and served as a zero indicator. The apparatus was checked by measuring the vapour pressure of ice at 0° C and at $-$ 0·1° C and single readings gave results agreeing within 1 % with published values.

The vapour pressure of p-chloroiodobenzene was measured between 30 and 50° C and was found to be given by

$$\log_{10} p \text{ (mm Hg)} = 9·819 - (3·20 \times 10^3/T)$$

within the experimental error of $\pm$ 1 %. This corresponds to a heat of sublimation of

$$\Delta H_S = 14·67 \text{ kcal/mole } (\pm 1 \text{ %}).$$

CONCLUSION.—Although the method of measuring the solubility of a solid in a compressed gas which has been described provides data capable of qualitative theoretical interpretation,[2] it does not yield the highly accurate results which would be desirable for a more detailed study of the problem. There are, however, several possibilities of refining the method. The counting geometry could be improved six- to eight-fold by using a torroidal G.M. counter [5] surrounding the equilibrium bomb, while the counting efficiency should be much higher with a

scintillation-type counter. The latter would have the added advantage of extending the temperature range of the measurements beyond the limited working range of G.M. tubes. Further improvement in the sensitivity of the method could be obtained by using greater concentrations of the tracer atom, but this could be done only in a laboratory equipped to handle large amounts of radioactive material.

With these refinements, it should be possible to measure the radioactivity of the saturated vapour directly. The ratio $x_2/x_2°$ would then be given by the ratio of the counting rates observed with and without the solvent gas present, thus eliminating the error introduced by the empirical calibration.

[1] *Faraday Soc. Discussions*, 1953, **15.**
[2] Ewald, Jepson and Rowlinson, *Faraday Soc. Discussions*, 1953, **15**, 238.
[3] Diepen and Scheffer, *J. Amer. Chem. Soc.*, 1948, **70**, 4081, 4085.
[4] Michels and Gelderman, *Physica*, 1942, **9**, 967.
[5] Ensell and Chatterjee, *Rev. Sci. Instr.*, 1951 **22**, 700.