

RESULTS

The solubility of *p*-chloriodobenzene 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 Scheffer³ 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.

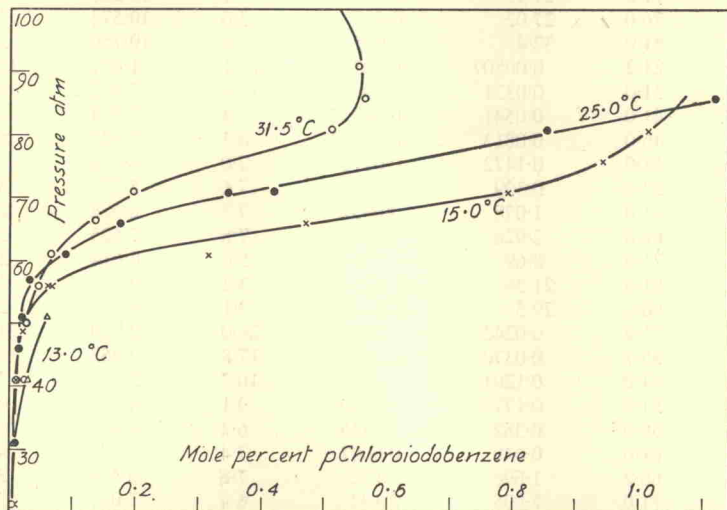


FIG. 2.—Solubility isotherms of the system *p*-chloriodobenzene + ethylene.

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 $\ln(x_2/x_2^\circ)$ 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*-chloriodobenzene and x_2 and $\ln(x_2/x_2^\circ)$ 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 ± 0.1 atm. The volume concentration of ethylene was found from the measured pressure by means of large-scale plot of density isotherms⁴ 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	$\ln(x_2/x_2^\circ)$	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
25.0	81.0	32.4	1.095	2.4	10.756	2.3
	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 $\ln(x_2/x_2^\circ)$ it was necessary to know the saturated vapour pressure of *p*-chloriodobenzene. 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*-chloriodobenzene 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

$$\Delta H_S = 14.67 \text{ kcal/mole } (\pm 1\%).$$

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. counter⁵ surrounding the equilibrium bomb, while the counting efficiency should be much higher with a