THE SOLUBILITY OF SOLIDS IN GASES

PART 2

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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 cm^3 and a wall thickness of 1/32 in. It was drilled and turned from a solid bar and was tested to 3000 lb/in^2 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 $\pm$ 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 ratemeter and used to record the actual pulses given by the G.M. tube.

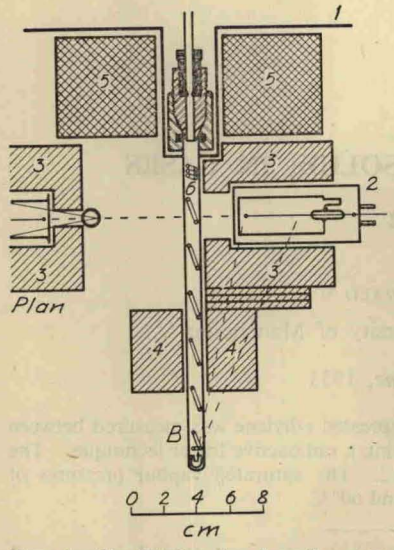

FIG. 1.—Equilibrium bomb and counter assembly.

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/cm^3.

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.