

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 cm<sup>3</sup> 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  $\pm 0.05^\circ\text{C}$ .

The remainder of the apparatus was made of glass and consisted of the sampling point S.P. at which sampling bulbs of 100 cm<sup>3</sup> 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 cm<sup>3</sup> bulb) and was calibrated at five points (10.5, 2.3, 0.5, 0.15, 0.06 cm<sup>3</sup>). 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  $\pm 0.02$  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 cm<sup>3</sup> 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  $x_2/x_2^\circ$  the mole fraction  $x_2^\circ$  was calculated from the concentration of the saturated vapour of the pure solid ( $c_2^\circ$  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,<sup>3</sup> 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 point<sup>4</sup> (161° K) and an X-ray crystallographic value at 130° K.<sup>5</sup> It was found to be 36.75 cm<sup>3</sup>/mole at 150° K and 36.93 cm<sup>3</sup>/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	$\epsilon/k^\circ \text{K}$	$b^\circ \text{cm}^3/\text{mole}$	source of $\epsilon/k^\circ$ and $b^\circ$	source of density
Xe	224.5	84.65	a	b
CO <sub>2</sub>	205	85.05	c	d
N <sub>2</sub>	95.05	63.78	e	e
H <sub>2</sub>	29.2	29.76	f	d
He	10.22	21.07	g	h

(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  $\pm 0.2$  atm giving an error in  $\ln(x_2/x_2^\circ)$  of  $\pm 0.013$ . 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 2<sup>6</sup>). 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