[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

SOLUBILITY V. CRITICAL SOLUTION TEMPERATURES OF WHITE PHOSPHORUS WITH VARIOUS LIQUIDS.

BY JOEL H. HILDEBRAND AND THEO. F. BUEHRER.

Received September 7, 1920.

Introduction.

According to the theory of solubility advanced by one of us, and supported by extensive experimental data, in the previous papers of this series,[1] Raoult's law expresses the maximum solubility to be expected in the case of solutions of relatively non-polar substances, and where no changes arise in the molecular species present. This maximum solubility is shown whenever the substances are of equal internal pressure in the liquid state, while differences in internal pressure give rise to roughly proportional decreases in solubility.

In the case of non-polar liquids sufficiently unlike in internal pressure to form 2 liquid phases, the critical temperature of mixing of the 2 layers may be taken as a measure of their mutual solubility, as has been previously[2] explained. When one liquid forms 2 layers with several others the critical mixing temperatures can serve to compare the deviations from Raoult's law, or the solvent powers of the first liquid for the several others.

But few of the substances in the table of relative internal pressures given in the third paper are far enough apart in their internal pressures to form 2 liquid layers, so that other methods of studying their solutions must be employed. However, white phosphorus, at the bottom of the list, is so different from most of the other substances there given that a number of 2-layer systems are possible. In the third paper the following statement was made: "It is to be expected that, except as relative internal pressures may be altered by changing temperature, there will be a progressive rise in the critical temperatures of mixing of molten phosphorus with another liquid as we ascend the table." The present paper presents the results of experiments made to test this prediction.

Purification of Materials.

As one ascends in the table of internal pressures to substances above carbon disulfide the critical temperatures of mixing with phosphorus become so high as to make desirable the selection of substances of low pressure. The substances chosen for the investigation were carbon disulfide, ethylene bromide, *p*-dibromobenzene, phenanthrene, naphthalene, chlorobenzene and decane.

---

[1] THIS JOURNAL, 38, 1452 (1916); 39, 2297 (1917); 41, 1067 (1919); 42, 2180, (1920). There has recently come to our attention in a paper by P. Walden, *Z. physik, Chem.*, 66, 409 (1909), a partial statement of the same theory as governing the solubility of other liquids in water.

[2] *Ibid.*, 38, pp. 1455-1458. See also paper by Keyes and Hildebrand, *ibid.*, 39, 2126 (1917).

Since carbon disulfide decomposes on standing, especially when exposed to light, it was purified immediately before use. Some carbon disulfide which had stood in contact with lime for several months was shaken with mercury and then with finely pulverized mercuric chloride, which is somewhat soluble in the liquid and which removes the sulfur. Fractional distillation by the aid of a bead column yielded a product which boiled at 46.1°.

The ethylene bromide used was shaken with a solution of sodium carbonate, washed repeatedly with distilled water, left in contact with calcium chloride for 36 hours and fractionally distilled. The portion distilling between 131.5° and 133° was fractionally crystallized. The material used had a melting-point of 9.5° and a boiling-point of 132.6°.

Very pure samples of *p*-dibromobenzene and phenanthrene were used after recrystallization from benzene.

Naphthalene, already of a high degree of purity, was twice sublimed and then recrystallized, the first crystals from the molten liquid being selected.

Chlorobenzene and decane, already very pure, were used without further purification. The high critical temperatures of these substances with phosphorus made accurate determinations impossible, and careful purification was, therefore, without purpose.

The principal impurities likely to be present in phosphorus are arsenic and oxides of phosphorus. Some high grade red phosphorus was used as a source of material. It was boiled with a solution of sodium hydroxide, washed with distilled water, then with alcohol and finally dried *in vacuo* at about 110°. On distillation in the dark or in ruby light this yielded beautiful colorless crystals of active phosphorus. This distillation was carried out in connection with the filling of the tubes with mixtures to be used, as described in the succeeding paragraphs.

Experimental Procedure.

The filling of the tubes with phosphorus and the respective substances whose critical temperatures of mixing with phosphorus were to be determined, was carried out in an apparatus illustrated in Fig. 1, constructed of Pyrex glass. The purified red phosphorus was put into Compartment A, which was then sealed off at H. Wads of glass wool were placed at the ends of both A and B to avoid dusting over during the distillation. The substance whose mixtures with phosphorus were to be investigated was introduced into E, which was then sealed and evacuated to remove dissolved air. When a solid substance was used it was melted during the evacuation.

White phosphorus distilled into B upon heating the tube A to about 300°. To insure uniform temperatures the tube A was enclosed in a block of aluminum which was heated by a Bunsen burner. A small amount of lime was used in B to retain there any traces of oxides of phosphorus. Upon gently heating B the white phosphorus distilled into J when it was later washed down into the tubes D by the other component distilled from E. When the substance in E was liquid, having an appreciable vapor pressure, its vapor was confined to E during the distillation of the phosphorus by means of the device shown at F and G, suggested by Dr. R. F. Newton, of this laboratory. F is a scratched capillary tube and G contains an iron nail enclosed in glass which could be lifted magnetically so as to break the capillary and allow distillation of the liquid from E to J. This arrangement was not used when E contained such a substance as phenanthrene. After a little practise it was found possible to adjust the contents of the tubes D so that they contained the desired proportions of the 2 components, after which, they were sealed off. The entire operation was carried out in ruby light except for the slight illumination from a hand torch. This procedure yielded tubes entirely free from visible signs of red phosphorus and presumably from other impurities as well. The tubes were kept in the dark until used.

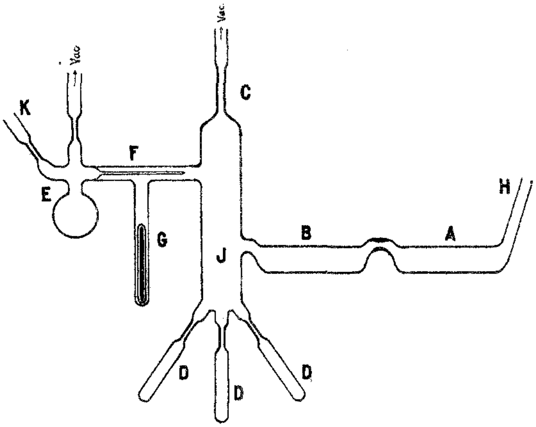

Fig. 1.

In the case of the carbon disulfide mixtures the temperatures of mixing were far below the freezing-point of phosphorus. It was, nevertheless, possible to prevent crystallization of phosphorus in many cases by introducing a trace of alkali, one drop of 3 *N* solution. This alkali probably did not exert a measurable effect upon the observed temperatures, since it is nearly insoluble in both of the other liquid phases present.

Except when carbon disulfide was used the temperatures of mixing were determined in an electrically heated air-bath provided with small windows. The air was vigorously stirred. A ruby lamp was used for the observation. One of the tubes D could be supported in this bath in such a way that it could be rocked in order to stir its contents.

The temperatures were measured by aid of a potentiometer and a 6-junction copper-constantin thermocouple, calibrated by the boiling-points of water and naphthalene and the melting-point of tin. The interpolation table of Adams[1] was found very convenient. Temperatures could be read to 0.1°.

---

[1] This Journal, **36**, 65 (1914).

The mixtures of phosphorus with carbon disulfide were observed in a jacketed brine-bath whose temperature could be closely adjusted. An ordinarily calibrated thermometer was used.

The temperature of mixing was at first roughly fixed, and then determined within narrower limits by decreasing the rate of heating or cooling of the air-bath so as to avoid lag in either the thermocouple or the tube. The disappearance, but more especially the appearance of the cloudiness indicating the presence of 2 liquid phases, was very sharp. The constancy of this temperature upon repeated observation was considered as evidence that the phosphorus did not react with any of the substances with which it was mixed. At higher temperatures, red phosphorus gradually formed, but except for decreasing the fluidity and transparency of the tubes, making observation more difficult, it did not seem to have any marked effect on the critical temperatures.

The composition-temperature curve for the mutual solubility of 2 liquids is always very flat at the top, so that considerable variation in composition is possible without greatly affecting the temperature of mixing. In order to be sure, however, that the composition was not too far removed from the maximum, tubes were prepared containing the substances in various proportions. The composition of the contents was determined by analysis after the observation of its mixing temperature. The method of analysis used for this purpose was oxidation with potassium iodate and titration of the excess iodate with sodium thiosulfate. A preliminary investigation showed that this method was quite accurate for the determination of either white or red phosphorus, and further that none of the other substances present had any effect with the exception of carbon disulfide. When this was used the phosphorus was determined gravimetrically by the phosphate method after oxidation with iodate.

TABLE I.

Naphthalene.

Mol. % P_4	26	49	56	60	74	75	80
Temp. of mixing, ° C.	132.8	201.4	195.5	202.7	201.6	200.2	190.4

Ethylene Bromide.

Mol. % P_4	41	44	47	56	63	81
Temp. of mixing, ° C.	169.6	165.0	163.0	165.5	162.0	151.7

	Phenanthrene.				*p*-Dibromobenzene.				
Mol. % P_4	55	57	73	80	41	49	54	61	70
Temp. of mixing, ° C.	199.2	199.5	199.1	198.0	154.3	159.4	162.0	163.0	159.2

Carbon Disulfide.

Mol. % P_4	6	34	43	50	59	74
Temp. of mixing, ° C.	—7.8	—6.7	—5.9	—6.4	—6.4	—6.6

Results.

Table I summarizes the experimental observations. Each temperature recorded represents the mean of from 6 to 10 observations upon the individual tubes. These observations seldom differed among themselves by more than 0.4°. The figures indicating composition have been rounded off to whole numbers, as the effect of composition upon temperature of mixing is small in the region investigated.

The values in Table I were plotted and a smooth curve was drawn through each set of points in order to obtain the critical temperatures shown in Table II. Temperatures are there given only to whole degrees, as any greater accuracy would doubtless be illusory.

TABLE II.

	Crit. temp. of mixing. ° C.	Rel. internal pressures at 20°.		
		$\gamma/V^{1/3}$.	$(5200 + 30t_2)/V$.	$a/v^2.10^6$.
Decane	> 390	3.8	53	2.5
Chlorobenzene	264	7.1	90	4.9
Naphthalene	202	7.8	96	5.2
Phenanthrene	200	....	98	5.7
p-Dibromobenzene	163	7.9	98	6.0
Ethylene bromide	165	8.7	106	5.5
Carbon disulfide	—6.5	8.7	109	6.1
Phosphorus	....	12.4	199	13.7

The figure for chlorobenzene represents observations upon one tube only, others having burst. From the manner of disappearance of the phases, however, it was evident that the proportions were such as to yield the maximum temperature. Some red phosphorus was formed, but this seems to be so insoluble as to exert little effect.

The value for decane likewise represents a single observation. It was evident from the high interfacial surface tension that the system at 300°, where red phosphorus was rapidly forming, was still far below the critical temperature.

In addition to the figures given in the table a determination was made using anthracene, but without the careful precautions to avoid oxidation or other impurity. This gave a value of about 198°.

An attempt was also made to observe a critical temperature using bromoform. It was impossible, however, to avoid crystallization of the bromoform in the neighborhood of 0°, before separation of 2 liquid phases.

Discussion.

In Table II are given, in addition to the critical temperatures of mixing with phosphorus, the relative values of internal pressures taken from the third paper of this series. It will be seen that the prediction quoted earlier in this paper is well fulfilled by the facts. The slight reversal in the case of *p*-dibromobenzene and ethylene bromide is insignificant in view of the extrapolation involved in the figures for the former because of its high melting-point. Even this may be accounted for by a reversal of position at higher temperatures, for the value of $\gamma/V^{1/3}$ at 100° becomes 6.0 for ethylene bromide and 6.2 for *p*-dibromobenzene.

The only surprise is the great difference between the critical temperatures for ethylene bromide and carbon disulfide mixtures. Until a more quantitative treatment is given we will not attempt to account for this difference.

Summary.

Critical temperatures of mixing of liquid phosphorus with other substances have been determined as follows, decane, >300; chlorobenzene, 264; naphthalene, 202; phenanthrene, 200; *p*-dibromobenzene, 163; carbon disulfide, —6.5. These figures confirm predictions made in a previous paper.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY.]

A METHOD OF MEASURING LOW VAPOR PRESSURES, WITH ITS APPLICATION TO THE CASE OF TRINITRO-TOLUENE.

BY ALAN W. C. MENZIES.

Received September 7, 1920.

The method most in favor for the measurement of rather low vapor pressures is perhaps the gas-current saturation method. Against this method may be urged its cumbrousness; the trouble of maintaining constant temperatures far from room temperature over prolonged periods of time; the need of the assumption of a normal molecular weight for the vapor in question; and other objections,[1] varying in seriousness with circumstances. It is, therefore, perhaps of interest to note that a single McLeod gage can be very simply utilized in measuring low vapor pressures, yielding readings for different temperatures as fast as a bath can be adjusted to each new temperature. The present paper indicates how such measurements may be carried out.

Outline of the Method.—Elsewhere,[2] the writer has described a method for measuring vapor pressures involving the use of 2 McLeod gages, one of which actually contained the vapor in question. In the present case, in which one gage only is used, none of the vapor enters the gage.

The apparatus consists of a McLeod gage, immersed in a large vessel of stirred water to secure constancy of temperature, and connected by capillary glass tubing with a bulb, preferably cylindrical, which can be completely submerged in a bath or surrounded by a jacket to give it the temperatures desired. The bulb, which may be of glass, porcelain, platinum or other material, should have as large a volume as convenient relative to that of the gage. This simple system is connected through a mercury seal to a source of dry inert gas and to a vacuum pump. The system

---

[1] Cf. Menzies, THIS JOURNAL, 42, 978 (1920).

[2] *Ibid.*, **41**, 1783 (1919).