sample) was used; for the Calvert method the remaining 15 cc. of extract (equivalent to 15 cc. of original sample; 3 times the quantity used for either of the fluorescein reaction tests) was used. The results are shown in Table III.

When freshly prepared all the final solutions obtained by the Andrew and Handy-Hoyt tests showed varying degrees of fluorescence. Even when fresh, by both tests the No. 2 sample showed diethylphthalate by its strong and unmistakable fluorescence and the No. 5 and No. 7 samples in both cases were suspicious. After the tests had stood over night the only samples in either set which showed fluorescence were the No. 2, No. 5 and No. 7 samples. Even in the No. 5 and No. 7 test portions which contained at the most not over 0.5 mg. of diethylphthalate the fluorescence stood out clear and unmistakable and could easily be differentiated from Nos. 1, 3, 4 and 6 even when viewed from a distance.

This series of experiments, II (*b*) (4), has brought out the following facts:

1. A substance which shows a yellowish green fluorescence in alkaline solution is not necessarily fluorescein.

2. Saccharin (or *o*-sulphobenzoic acid or its anhydride), succinic acid, malic acid, and formic acid will condense with resorcinol to give compounds which exhibit marked, though transient, fluorescence in alkaline solution. (According to the experiments of Bischoff and Adkins, diphenic anhydride would also be included in this list of compounds.)

3. Saccharin (or *o*-sulphobenzoic acid or its anhydride) has been found to react in a manner identical with diethylphthalate in the Calvert test. Water-soluble saccharin is, however, practically insoluble in petroleum ether and hence does not interfere when testing the petroleum ether extract of a sample containing saccharin for diethylphthalate.

4. Diethylphthalate detection tests made on the petroleum ether extract of portions of a sweet wine containing, respectively, 0.1% of these substances, *i. e.*, saccharin, succinic acid and malic acid, give entirely negative results provided the final test solutions are allowed to stand over night before the interpretation of the results is made.

5. Either the Andrew or Handy and Hoyt method will differentiate correctly between a sample of sweet wine containing 0.1% succinic acid (which in our experience condenses with resorcinol to give a test solution most nearly like that of true fluorescein) and a sample containing only 0.01% diethylphthalate in addition to 0.1% succinic acid, on test portions of the samples as small as 5 cc.

(To be concluded in next issue. Bibliography will appear at end of the article.)

ADSORPTION OF IODINE FROM ORGANIC SOLVENTS BY RED PHOSPHORUS AND CHARCOAL.*

BY NEIL E. GORDON† AND JOHN C. KRANTZ, JR.

Bancroft,[1] in suggesting a number of interesting research problems through the National Research Council, mentioned the work of Sistini[2] who had found that car-

[1] Bancroft, *J. Ind. Eng. Chem.*, 13, 154, 1921.

[2] Sistini, *Gazz. chim. ital.*, 31, 216, 1871.

bon disulphide was completely stripped of iodine dissolved therein by contact with red phosphorus. The writer suggested that it would be interesting to perform the experiments and plot the curves of adsorption for different temperatures; for it was thought, by Bancroft, that as the density of phosphorus changed with the temperature, at an increased temperature the phosphorus would expose a greater surface and consequently a greater adsorption would result.

These experiments were carried out with six of the organic solvents—benzene, toluene, xylene, carbon tetrachloride, carbon disulphide and chloroform. The usual methods of drying and purifying the solvents were employed; the red phosphorus was of good commercial variety, dried for three hours at 110° C. and sifted through a bolting cloth sieve. At the first consideration, it was thought that Bancroft's suggestion was correct as shown here by the adsorption data and curves for xylene and carbon disulphide. When, however, the adsorption was applied to

Carbon disulphide at 30° and 45° C.

Moles $\frac{x}{m}$ × 10⁻⁴

Moles iodine dissolved in 50 cc. of solvent.

Xylene at 30° and 50° C.

Moles $\frac{x}{m}$ × 10⁻⁴

Moles iodine dissolved in 50 cc. of solvent.
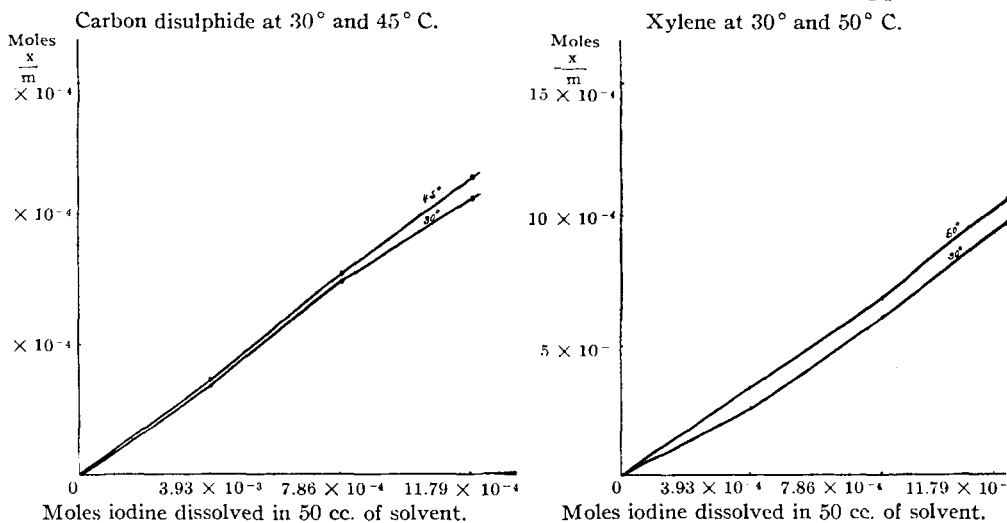
carbon disulphide, the stripping of the iodine as recorded by Sistini could not be duplicated, as in all cases there remained a considerable quantity of iodine in the carbon disulphide after adsorption equilibrium had been established. The inference was that, in all probability, Sistini had present in his adsorption mixture some impurity which caused either chemical reaction or increased adsorption. The most natural foreign substance thought to be present was water. Experiments were performed introducing a small quantity of water (1 cc. to 50 cc. of solvent) in the adsorption mixture and not only with carbon disulphide, but with the other organic solvents, the iodine was completely removed. We believe this to be due to chemical reaction between the iodine and phosphorus in the presence of water, further that the different curves that were obtained for different temperatures were probably due to increased or decreased chemical reaction due to the water unavoidably present in the adsorption mixture.

Bancroft also referred to the work of Davis,[1] who worked along those same lines using different charcoals as adsorbents, as being one of the most outstanding articles published in this work. An examination of the work of Davis showed that

[1] Davis, *J. Am. Chem. Soc.*, 91, 1682, 1907.

this experimenter had drawn the conclusion that there was no relationship between the solubility of iodine in the solvents and the quantity adsorbed. These relationships were expressed as usual in grams; it occurred to the writers to convert these quantities to moles and arrange these molar quantities in the inverse order of their molar solubilities. Three of the solvents used by Davis were selected, in which there was little likelihood of chemical reaction between the solute and solvent, and the following data and curve were obtained:

SOLUBILITY OF IODINE AT 30° C.   MOLES IODINE ADSORBED 30° C. BY CHARCOAL.

1 mole I_2 dissolves in 15.75 moles toluene   Toluene 1.24 $\times$ 10^{-3}
1 mole I_2 dissolves in 18.35 moles benzene   Benzene 1.31 $\times$ 10^{-3}
1 mole I_2 dissolves in 64.20 moles chloroform   Chloroform 1.62 $\times$ 10^{-3}
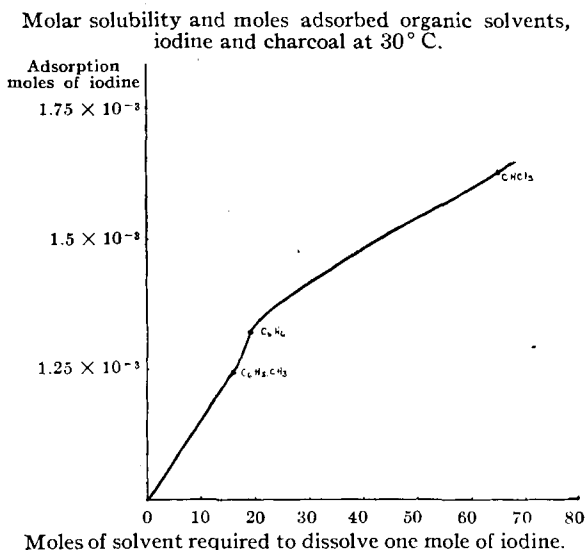
It will be noticed that the adsorption calculated in terms of moles shows an inverse relationship to the solubility of iodine in the organic solvent, when this too is calculated in moles.

This relationship having been established, the writers endeavored to show the same relationship with the data obtained in the phosphorus experiments. An examination of the tabulated results will show that this relationship does not hold in the case of phosphorus, although the results are expressed in moles; this we attribute to chemical reaction due to traces of water.

EXPERIMENTAL.

Introduce 1 Gm. of red phosphorus, dried at 110° C., and sifted through a bolting cloth sieve, into a 250-cc. flask. Add 50 cc. of the solvent containing 0.1, 0.2 or 0.3 Gm. of iodine. Place in constant temperature bath and agitate the contents every ten minutes until equilibrium has been established. This is shown by drawing off 10 cc. of the supernatant liquid and titrating the residual iodine with $N/50$ sodium thiosulphate solution at intervals until a constant quantity is found to be present. Then, in an aliquot part of the solvent the residual iodine is again estimated with $N/50$ $Na_2S_2O_3$ solution and by difference the quantity adsorbed can be calculated.

The following table shows the solubilities of iodine at two different temperatures, determined by saturating the solvents with iodine and titrating the iodine in a weighed quantity of the solution with $N/50$ sodium thiosulphate solution.

Molar solubility and moles adsorbed organic solvents, iodine and charcoal at 30° C.

Moles of solvent required to dissolve one mole of iodine.

ADSORPTION OF IODINE BY RED PHOSPHORUS FROM ORGANIC SOLVENTS.

Solvent conc. in 50 cc.	Gm. adsorbed per gram phosphorus.		Moles adsorbed per gram phosphorus.	
	30° C.	50° C.	30° C.	50° C.
Xylene				
0.3	0.2505	0.2696	9.87×10^{-4}	10.6×10^{-4}
0.2	0.1543	0.1776	6.06×10^{-4}	7.01×10^{-4}
0.1	0.0650	0.0845	2.56×10^{-4}	3.33×10^{-4}
Toluene				
0.3	0.2623	0.2669	10.3×10^{-4}	10.5×10^{-4}
0.2	0.1533	0.1830	6.02×10^{-4}	7.21×10^{-4}
0.1	0.0666	0.0783	2.62×10^{-4}	3.08×10^{-4}
Benzene				
0.3	0.2400	0.1883	9.45×10^{-4}	7.4×10^{-4}
0.2	0.1471	0.1305	5.79×10^{-1}	5.12×10^{-4}
0.1	0.0633	0.0691	2.49×10^{-4}	2.72×10^{-4}
Chloroform				
0.3	0.2010	0.1670	7.91×10^{-4}	6.57×10^{-4}
0.2	0.1387	0.1043	5.47×10^{-4}	4.09×10^{-4}
0.1	0.0785	0.06305	3.15×10^{-4}	2.48×10^{-4}
Carbon tetrachloride				
0.3	0.2770	0.2870	10.9×10^{-4}	11.3×10^{-4}
0.2	0.1864	0.1864	7.32×10^{-4}	7.32×10^{-4}
0.1	0.0940	0.0940	3.7×10^{-4}	3.7×10^{-4}
Carbon disulphide		45° C.		45° C.
0.3	0.2672	0.2878	10.5×10^{-4}	11.3×10^{-4}
0.2	0.1852	0.1897	7.28×10^{-4}	7.48×10^{-4}
0.1	0.0884	0.0914	3.48×10^{-4}	3.59×10^{-4}

MOLAR SOLUBILITIES OF IODINE AT 30° C.

1 mole I_2 dissolves in 12.81 moles xylene
1 mole I_2 dissolves in 15.75 moles toluene
1 mole I_2 dissolves in 18.35 moles benzene
1 mole I_2 dissolves in 64.2 moles chloroform
1 mole I_2 dissolves in 78.7 moles carbon tetrachloride
1 mole I_2 dissolves in 15.2 moles carbon disulphide

AT 50° C. EXCEPTING CS_2 AT 45° C.

1 mole I_2 dissolves in 7.87 moles xylene
1 mole I_2 dissolves in 15.7 moles toluene
1 mole I_2 dissolves in 10.94 moles benzene
1 mole I_2 dissolves in 32.45 moles chloroform
1 mole I_2 dissolves in 35.05 moles carbon tetrachloride
1 mole I_2 dissolves in 9.4 moles carbon disulphide

CONCLUSIONS.

1. When the solvent and adsorbent are free from moisture and there is no chemical reaction between the solvent and solute, adsorption and solubility show an inverse relationship when expressed in moles in the case of iodine, charcoal and the organic solvents.

2. Adsorption data, when compared with solubility, has greater significance when expressed in moles rather than in grams, when a non-electrolyte is adsorbed from solution in a molecular state.

3. When adsorption of iodine with red phosphorus is considered, the absence of moisture is essential for correct results.

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