3. The results of the analytical study are not very satisfactory from the stoichiometric point of view, because side reactions may occur, diphenylbenzidine and diphenylbenzidine green are very slightly soluble, and diphenylbenzidine violet decomposes rapidly, especially at low acidities.

4. The absorption spectra of oxidized diphenylamine and diphenylbenzidine solutions have been determined and found to be identical; the maxima of the curves are very flat, and shift toward the longer wave lengths in stronger acid solutions.

5. The solubility of diphenylbenzidine in water is 0.06 ± 0.005 mg. per liter at 25–50°; and its ionization constant at 25° is of the order of 2×10^{-14}.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES IN INTENSIVE DRYING[1]

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The following is an account of an experimental study of the intensive drying, and therewith "the catalytic" effect of small traces of water, mainly in liquid benzene, which leads to an explanation of the phenomenon observed. Since Baker's work was published in 1922 there has been a constant stream of theoretical explanations of intensive drying, as well as a large number of experimental studies dealing with this strange phenomenon.

It is unnecessary in this paper to give even a synopsis of either the theoretical or the experimental aspects of this problem, inasmuch as quite recently this whole subject has been carefully and most adequately reviewed in book form under the title of "The Effects of Moisture on Chemical and Physical Changes," by J. W. Smith.[3]

Suffice it to say that since Baker's[4] paper data have accumulated which tend to support, and lately some as justly to contest, the view that when the last traces of water are removed from certain liquids, there occur physical changes in the latter that are consistent with the assumption of an association of the molecules in the liquid. The properties investigated have been such as the boiling point, freezing point, density, vapor density, surface tension, latent heat of vaporization and vapor pressure. However,

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[1] Based on a dissertation submitted June, 1929, to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Holder of the Boston Alumnae Fellowship of the American Association of University Women for 1929–1930, when this work was completed.

[3] Longmans, Green and Co., **1929**.

[4] Baker, *J. Chem. Soc.*, **121**, 568 (1922).

from a theoretical and practical consideration of the work of other investigators, it was assumed when this work was begun in 1927 that the vapor pressure of the liquids was the property the least open to misinterpretation and also the most reliable from the standpoint of experimental technique. This work began with the purpose of finding a means of producing liquids exhibiting the intensive drying effect in a shorter time than previously in order that the phenomenon might be more readily investigated.

Experimental Part

The Possibility of Compound Formation with Phosphorus Pentoxide and Benzene.—In the course of the preliminary work, benzene that had been purified by the method used by Hill[5] was found to produce color in pure phosphorus pentoxide when the mixture was stored in the light. The phosphorus pentoxide was prepared by resubliming Baker's pure phosphoric anhydride in a current of pure oxygen according to the method of Finch and Fraser[6] and the product satisfied the requirements of Baker[7] and of Finch and Peto[8] for purity.

Experimental investigation indicated that small traces of impurities in benzene—mainly sulfur compounds such as thiophene and carbon disulfide—are capable of imparting color to phosphorus pentoxide, varying from pale grayish-pink to yellow, when a mixture is stored in the light.

An investigation of the methods more generally used for the purification of benzene rarely revealed attempts to eliminate carbon disulfide which along with thiophene is one of the chief contaminants of commercial benzene.

Rigid purification of benzene either by an extension and combination (1) of the methods of Goldberg[9] and Haller and Michel[10] or (2) of the methods of Goldberg and Victor Meyer[11] which proved to be the more convenient method—gave a product which distilled within 0.01° and failed to impart any color to the phosphorus pentoxide upon heating or after a year's exposure to light.

The increased boiling points reported by Baker were ascribed by Balarew[12] possibly to the formation of compounds with phosphorus pentoxide and benzene. A search of the literature revealed that Giran[13] reported definite, solid, colored compounds insoluble in benzene resulting from the reaction of phosphorus pentoxide and benzene. As stated previously, impure

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[5] Hill, This Journal, **44,** 1168 (1922).

[6] Finch and Fraser, *J. Chem. Soc.,* 117 (1926).

[7] Baker, *ibid.,* **121,** 569 (1922).

[8] Finch and Peto, *ibid.,* **121,** 693 (1922).

[9] Goldberg, *Z. angew. Chem.,* **4,** 75 (1899).

[10] Haller and Michel, *Bull. soc. chim.,* [3] **15,** 1065 (1896).

[11] Victor Meyer, *Ber.,* **18,** 1489 (1885).

[12] Balarew, *J. prakt. Chem.,* **116,** 57 (1927).

[13] Giran, *Compt. rend.,* **126,** 592 (1898); *ibid.,* **129,** 965 (1899).

benzene did impart similar colorations to pure phosphorus pentoxide, but this present investigation indicated no such compounds as described by Giran with pure benzene and pure phosphorus pentoxide. Moreover, a fused glass apparatus containing a differential mercury manometer such as is described in the following section of this paper revealed no decrease in the vapor pressure of impure benzene dried with phosphorus pentoxide for two years. This would indicate that even if a compound were formed in the impure benzene, it was insoluble as Giran reported, and had no measurable vapor pressure, thus causing no change in the vapor pressure of the benzene.

Experiments with Phosphorus Pentoxide and Fused Glass Apparatus.—In 1926, Smits[14] reported that capillary-free glass hastened the drying of liquids with phosphorus pentoxide. His glass surfaces were fused and then cleaned with chromic acid, washed, steamed and dried. This chromic acid treatment has been shown by other investigators[15] to etch the surface of the glass. In order to preserve the beneficent effects of a fused pyrex glass surface, the apparatus used in the present investigation was first cleaned with chromic acid and, in the usual manner, washed with water and dried. It was then fused by an expert glass blower who melted the glass completely and then shaped it, blowing at all times through a tube of phosphorus pentoxide to avoid the access of water to the apparatus.

The entire apparatus of the circulating and of the static types similar to those used by Smits,[14] was constructed of fused glass and contained a differential mercury manometer to indicate the difference in pressure between the benzene being dried with phosphorus pentoxide on the one side, and a sample of the same normal benzene in a fused glass bulb on the other side. The vessels were filled under moisture-free conditions by the passage of a stream of air dried with phosphorus pentoxide. The liquids were frozen with solid carbon dioxide and ether when the apparatus, evacuated thoroughly by using a mercury diffusion pump in series with a high vacuum oil pump, was sealed off. The manometer was then filled with dry mercury from a reservoir in the apparatus by tilting the latter slightly.

No difference between the vapor pressures on the two sides of the pieces of apparatus has been observed even after three years in one case and twenty-seven months in two other cases. Moreover, in defense of Baker when his work was attacked by Balarew,[12] Smits[16] reported that he could detect no vapor pressure change in some of his pieces of apparatus after two years' drying.

Experiments with Silica Gel and Benzene.—A preliminary experiment

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[14] Smits, *J. Chem. Soc.*, 2655 (1926).

[15] Frazer, Patrick and Smith, *J. Phys. Chem.*, **31**, 897 (1927).

[16] Smits, *Z. physik. Chem.*, **129**, 33 (1927).

using pure, activated silica gel as the drying agent indicated a definite decrease in the vapor pressure of benzene. This drying effect appeared within twenty-four hours and seemed to have reached complete equilibrium after being kept for five days in a thermostat at 25°.

Apparatus of the type shown in Fig. 1 was constructed and joined in ring form. The differential manometer M contained pure mercury which was heated in the manometer with pumping for several hours to remove dissolved air and moisture. The pumps continued while the whole apparatus was heated well with a carbon flame to remove surface moisture and tested for leaks with a spark coil.

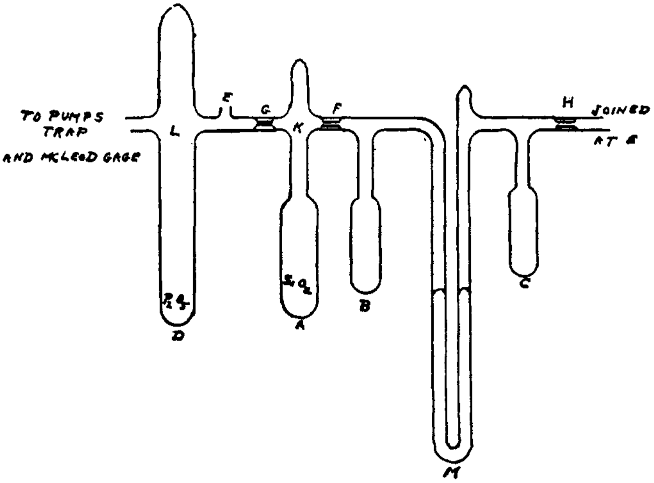

Fig. 1.

After the purified silica gel,[17] activated at 500°, was sealed up in vessel A, tube D was cracked and filled with pure phosphorus pentoxide and benzene, purified by the methods recommended earlier in this paper. Point L was plugged with glass wool to retain the phosphorus pentoxide used for the preliminary drying of the benzene. Tube D was quickly sealed while its contents were frozen with liquid air. The system was then evacuated to 10^{-5} mm. using an oil pump in series with a two-stage mercury diffusion pump. The liquid in D was melted, boiled, frozen with liquid air and opened to the pumps to remove dissolved air. This deaeration was repeated at least three times, or until no further air was removed by the process. The benzene was then distilled from D into vessels B and C simultaneously by immersing them in liquid air and removing the refrigerant from D. The apparatus was then pumped down to 10^{-5} mm. while the silica gel was heated to remove adsorbed liquid. The apparatus was sealed off at H while the pump continued and the silica gel in A was then

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[17] Patrick, Frazer and Rush, *J. Phys. Chem.*, **31**, 1511 (1927).

heated for half an hour with a large air flame which was kept in constant motion to prevent collapse of A. The apparatus was sealed off at G at a pressure of 10^{-5} mm. of mercury. The liquid air was removed from B and C when the silica gel had become cold and the benzene in B was allowed to distil onto the activated silica gel.

This method was used with pure benzene, pure carbon tetrachloride and pure carbon disulfide. With each a decrease in vapor pressure was observed upon drying the liquid with activated silica gel. Out of the nine pieces of apparatus that lasted through the above treatment without breaking, only one failed to manifest a decrease in pressure on the dry side.

Results.—These vapor pressure differences were measured at constant temperatures by means of a cathetometer and were checked to be certain that equilibrium had been attained. The vapor pressure differences observed for one liquid varied somewhat from one apparatus to another, as for example

Liquid	T, °C.	ΔP, mm.
CCl_4	0	3.67
CCl_4	0	3.30

Likewise, the vapor pressure differences varied among the different liquids as is shown by examples in Table I and plotted in Fig. 2. These values were taken at definite points as the temperature of the thermostat was raised from 20 to 50°, and were checked as it was lowered from 50 to 20°.

Table I

Vapor Pressure Data

Liquid (1) Benzene		Liquid (2) Carbon Tetrachloride		Liquid (3) Carbon Disulfide	
T, °C.	ΔP, mm.	T, °C.	ΔP, mm.	T, °C.	ΔP, mm.
−80.0	0.0	−80.0	0.0	−180.0	0.0
0.0	3.13	0.0	3.67	0.0	3.35
5.7	5.07	21.8	6.53	10.5	7.00
11.0	5.92	31.1	6.88	14.8	10.20
20.8	7.54	40.8	7.24	16.4	11.92
25.6	8.40	48.3	7.54	18.9	13.84
27.2	8.83			21.0	15.85
34.7	10.33			23.2	18.46
38.3	11.24				
45.5	12.71				
50.6	13.76				

These differences are all of similar order of magnitude and in the same direction as those reported in the De Liefde dissertation,[18] and there were no differences manifested at −180.0 and −80.0°, showing that the systems were air-free and that the differences were not due to dissolved air or gas.

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[18] W. C. De Liefde, "Dissertation," Amsterdam, 1927.

Experiments with Liquids Dried with Silica Gel.—In the course of the investigation of these liquids dried with silica gel, attempts were made to study the effect of the replacement of water, the "catalyst," which according to the theory of Smits[19] and Baker[20] is removed by prolonged or intensive drying and causes measurable changes in the molecular complexity of certain substances.

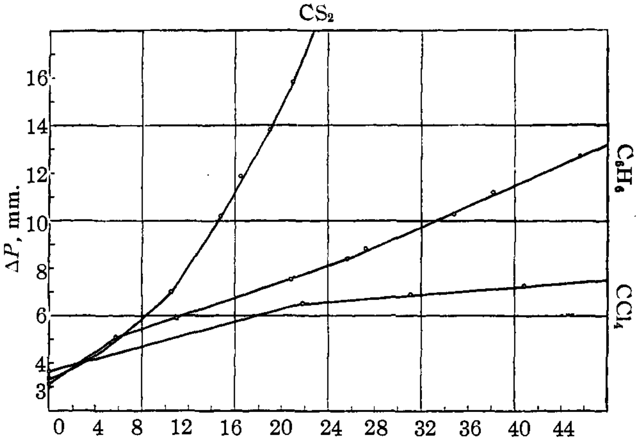

Fig. 2.

In order to effect the addition of moisture to benzene, the silica gel bulb was removed from the dry side of one piece of apparatus which was sealed to a series of bulbs and the pumping system. The mercury manometer had been frozen to act as a seal between the two sides of the apparatus. Silica gel at a saturated vapor tension of 4.5 mm. of water was added to the dry liquid, frozen with liquid air and the system was evacuated. The manometer which should have been level because of the replacement of the "catalyst" showed, however, a pressure difference of roughly 2.5 mm. at room temperature instead of the previous 7 mm. with the dry material alone. After distilling the benzene onto phosphorus pentoxide to remove the moisture and sealing off the silica gel that had been added, the benzene again manifested the previous 7 mm. pressure difference at 20°.

Discussion

The behavior studied in the above experiments in intensive drying indicated no catalytic action, but merely the addition of the partial pressure of water. It strengthened the theory that the difference in vapor pressure was due, not to the catalytic effect of the removal of water from the benzene

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[19] Smits, *Z. physik. Chem.*, **100**, 477 (1922).

[20] Baker, *J. Chem. Soc.*, 949 (1927).

on the dry side, but to the presence of a minute trace of moisture in the benzene on the normal side.

Objections to the above view on the basis of Raoult's law are precluded because that relation demands a large mole fraction of water to produce a partial pressure equal to the pressure differences manifested in this set of investigations where the phenomenon was observed only in liquids in which water is very insoluble, as benzene, carbon tetrachloride and carbon disulfide.

In this work the amount of normal benzene used for comparison with the dried material was very small, varying from one to three grams in the different pieces of apparatus. The solubility of water in benzene at 20° is reported in the "International Critical Tables" as 0.057%. A rough calculation shows that the production at 20° of a partial pressure of 7 mm. of water vapor in one gram of benzene requires only 2.29×10^{-4} g. or 1.27×10^{-5} mole of water. This follows from the relation $P_p/P_s = X/X_s$ where $P_p = 7$ mm., $P_s = 17.363$ mm., the vapor pressure of water, necessary to saturate one gram of benzene at 20°; and $X_s = 0.00057$ g. of water.

However, according to Raoult's law, one gram of benzene requires 9.28×10^{-2} g. or 5.16×10^{-3} mole of water to produce a partial pressure of 7 mm. of water. This concentration of water is 405 times greater than that calculated from the solubility data above.

Moreover, upon analysis of Fig. 2, the curves for carbon disulfide, benzene and carbon tetrachloride seem very definitely to represent the vapor pressure of solutions of water in those liquids. The three curves show that the vapor pressure deviations from the normal are within a close range at 0°. From this point they converged and diverge again according to the extent of saturation and the change in solubility of water in the liquid with increasing temperature. The curve for benzene with its abrupt change in slope at the melting point of benzene is an excellent illustration of the increasing solubility of water in benzene with temperature.

An explanation of the mode of access of the minute quantities of water required to produce the effects may lie in any of several factors. However, it cannot have come from the benzene, which was dried with phosphorus pentoxide and distilled from it. The moisture may have come from the activated silica gel when it was heated before vessel C of Fig. 1 was sealed off, or from the glass during the sealing process.

In either case, the liquid air with which vessel C and its normal contents were frozen is a very powerful dehydrating agent and might easily have condensed a trace of moisture before it reached the pumps. Another source, despite the preheating described, is the deeper seated moisture in the walls of vessel C. This possibility is compatible with the conditions and observations of this investigation, since the vapor pressure difference was not always immediately apparent. It is supported by the investigation of Baker,[21] who by using sodium amalgam in a glass bottle dried at 150° found that bubbles of hydrogen began to appear after two days and concluded that "since these did not appear within twelve hours, their formation could not be ascribed to surface water," but to the deeper seated moisture.

The gradual emerging of the deeper seated moisture may possibly account for some of the vapor pressure differences observed in intensive drying experiments by other investigators. An experiment in which pure, dry air-free benzene was distilled from phosphorus pentoxide onto pure silica gel—originally saturated with water—which had been pumped down to 10^{-4} mm. pressure, showed that the benzene can displace some of the water adsorbed in the gel, for within six hours a steady pressure of 1 mm. was manifest in one case and 1.4 mm. in another case.

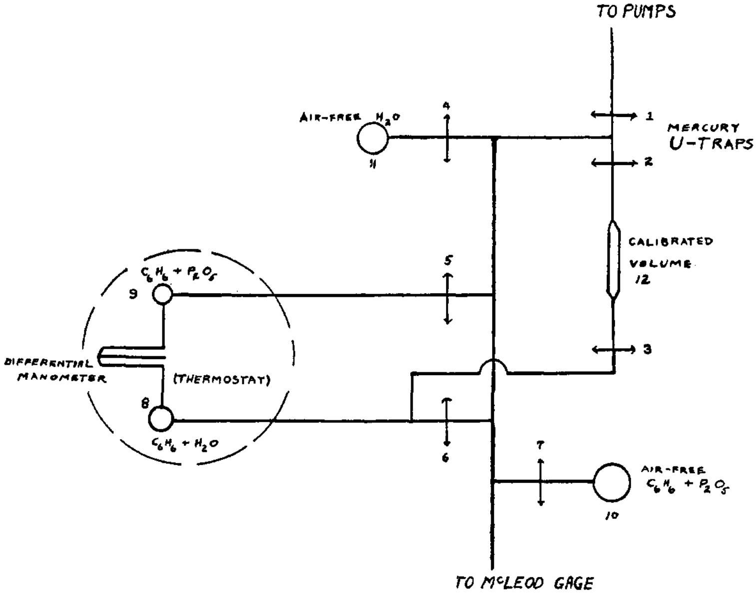

Fig. 3.

Experiments with Solutions of Water in Benzene.—As a confirmation of the calculations and experiments with silica gel and in an effort to test the theory that the vapor pressure changes observed were due to the presence of minute traces of moisture in the normal liquid instead of to intensive drying effects in the dried material, an apparatus was constructed to measure the change of vapor pressure of benzene with the addition of known amounts of water.

A diagram of the apparatus is shown in Fig. 3. The previous experiments had indicated the need of an absolute as well as a differential manometer which resulted in a three branched instrument, as shown, carefully

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[21] Baker, *J. Chem. Soc.*, 1663 (1929).

filled *in vacuo* with pure, redistilled, dry, air-free mercury. The air-free water and the air-free dry benzene were prepared by intermittent boiling and pumping the liquids until the residual air pressure could not be measured with the pressure gage. The mercury U-traps (1) through (7) were filled with pure mercury which was boiled out in the trap to remove moisture and air.

The glass was cleaned with chromic acid and washed with distilled water before use and the apparatus was carefully heated all over before being used for the experiment.

The pumping system consisted of a high-vacuum oil pump in series with a two-stage mercury diffusion pump.

The thermostat was constructed elevator style so that the tank could be raised and lowered when large temperature changes were necessary. It was set at 20.89° and with continuous cooling, intermittent heating and rapid stirring was regulated to 0.005°—never more than 0.01°—by a mercoid relay and a metastatic regulator. The thermostat was always kept at least 2.5° cooler than the room in order to prevent condensation outside of the bath.

The volume of vessel (8) was etched in increments of about 1 cc. and was calibrated by weighing water; and calibrated volume (12) was determined directly as 65.578 cc. by use of a gas buret.

Rigidly purified benzene, dried with phosphorus pentoxide was used as the liquid to be studied.

Manipulation and Results.—After the system had been dried out and evacuated to 10^{-5} mm. of mercury, the benzene in storage vessel (10) was frozen with ice and benzene was distilled into vessel (9), containing phosphorus pentoxide, and vessel (8) which were immersed in ice and salt. The vessels were then closed off with mercury traps and the remainder of the system was evacuated to 10^{-5} mm. A preliminary determination of the vapor pressures of the benzene in (8) and (9) at 20.89° showed both to be equal to 7.88 cm., so there was no moisture present at the beginning. Vessel (8) contained 25.635 cc. of pure benzene at 20°.

Water was then added in small quantities, representing about one-tenth of the saturation value, to the benzene in (8) by closing trap (1) and opening the calibrated volume (12) to the air-free water stored in (11) at 25°. After closing the traps and measuring the pressure and temperature of the known volume of water vapor in (12), trap (3) was opened and the water vapor was condensed in (8) which was frozen with a mixture of carbon dioxide and ether. The room temperature during this operation was always 25° or above. Trap (3) was closed and the remainder of the system was evacuated after each addition of water vapor.

The total volume between (8) and traps (3) and (6) was determined from the relation $P_1/P_2 = V_2/V_1$ at 24.2° by condensing water vapor of known pressure and volume (12) into empty vessel (8) by the method described in the preceding paragraph. The volume of liquid benzene was subtracted from this value and the difference was 116.2 cc., the volume of vapor in equilibrium with the liquid. By use of the relation $PV = nRT$ the amount of water present in the vapor and that dissolved in the liquid benzene in the successive solutions was calculated. Equilibrium was attained very slowly.

Results

Table II

Experimental Data

Volume of benzene, 25.635 cc.; volume of vapor, 116.2 cc.; average temperature of vapor, = 22°.

	Total mole H_2O added	Partial press. of H_2O in mm. at 20.89°	Mole H_2O in vapor	Mole H_2O in benzene
1	8.77×10^{-5}	1.87	1.17×10^{-5}	7.60×10^{-5}
2	1.75×10^{-4}	3.88	2.43×10^{-5}	1.51×10^{-4}
3	2.6×10^{-4}	5.52	3.45×10^{-5}	2.25×10^{-4}
4 & 5	4.27×10^{-4}	9.62	6.1×10^{-5}	3.66×10^{-4}
6 & 7	6.03×10^{-4}	13.22	1.01×10^{-4}	5.02×10^{-4}
8 & 9	7.78×10^{-4}	16.79	1.05×10^{-4}	6.73×10^{-4}
	Extrapolation	18.33		$7.15 \pm 0.05 \times 10^{-4}$

By extrapolation to 18.33 mm., the vapor pressure of water at 20.89°, the curve shown in Fig. 4 indicates that 7.15×10^{-4} mole of water is required to saturate 25.635 cc. of benzene. When this saturation value is interpreted in grams, the figure reduces to 0.00057 g. of water per gram of benzene, or 0.057%, which checks the value given in the "International Critical Tables."

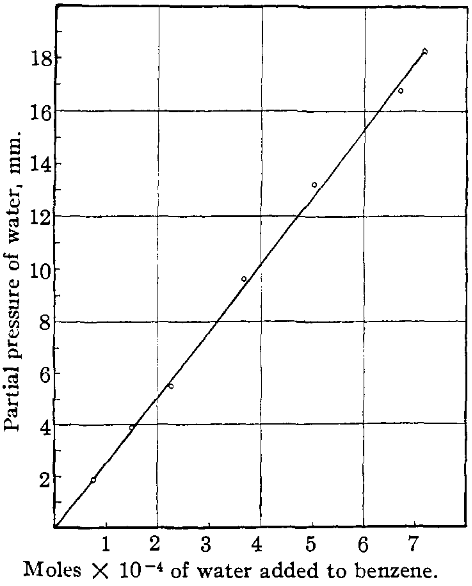

Fig. 4.

From the experimental data presented in Table II and in Fig. 4, it is evident that the solution of water in benzene follows Henry's law rigidly but not Raoult's law. However, the results for benzene at the saturation value and below may be expressed by the equation

$$P = \frac{x}{x_{\text{satd.}}} P_{\text{satd.}} \text{ at constant temperature}$$

where x is mole fraction of water present and $x_{\text{satd.}}$ is mole fraction of water required to saturate the benzene. The average deviation of the observed pressures from this relation is 0.19 mm. pressure or 2.28% of the calculated value.

It seems reasonable to expect that this relation would be fundamental for solutions of water in carbon tetrachloride and carbon disulfide, or for solutions of any two other mutually very insoluble liquids.

In conclusion, the author wishes to express her sincere appreciation to Dr. W. A. Patrick, under whose guidance this problem was completed, and to Dr. J. C. W. Frazer, who in conjunction with Dr. Patrick suggested and coöperated in the investigation.

Summary

1. Benzene free from impurities does not impart color to pure phosphorus pentoxide nor does it form such addition compounds with phosphorus as were described by Giran.

2. Methods have been found that produce benzene free from the usual sulfur compounds of which carbon disulfide has been found to be as undesirable as thiophene, though it is more commonly ignored than the latter.

3. Benzene that has been dried with phosphorus pentoxide in a fused glass apparatus for three years has not shown any change in vapor pressure with respect to the normal liquid in the same apparatus.

4. Within twenty-four hours, benzene, carbon tetrachloride and carbon disulfide dried with activated silica gel manifested vapor pressure differences or decreases, as compared with the normal liquids, that were finally comparable in magnitude and direction with those reported by other investigators in the field of intensive drying.

5. Experimental evidence has been submitted and discussed to support the theory that the vapor pressure decreases or differences from the normal may be explained by assuming the presence of minute traces of water vapor in the normal liquid rather than any catalytic effect due to the removal of water from the dried liquid.

6. Calculations from solubility data show that only 0.000229 g. of water is required to produce a partial pressure of 7 mm. of water in one gram of benzene at 20°. This value deviates from Raoult's law, which requires 405 times more water than is actually effective.

7. The partial pressures of solutions of water in benzene at 20.89° have been measured and plotted. Extrapolation of the curve gives a value of the solubility of water in benzene at 20° which checks that given in "International Critical Tables."

8. The relation of the partial pressures to mole fractions in solutions of water in benzene may be expressed by the equation $P = (x/x_{\text{satd.}})P_{\text{satd.}}$.

BALTIMORE, MARYLAND