[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Influence of Intensive Desiccation on the Vapor Pressure of Benzene

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The present article reports the results of studies of benzene and of a few other liquids as dried by various desiccants. Only in the case of purified benzene dried by purified phosphorus pentoxide under dust-free conditions were changes upon desiccation observed. A brief account of the results of earlier portions of this work has appeared elsewhere.[1]

It has been known for over a hundred years that the presence of traces of water may influence the speed, or the occurrence, of chemical reactions. That such traces of water may likewise affect the physical properties of substances is a possibility that has received attention only in more recent times. It is unnecessary here to do more than refer to the earlier work, for an excellent account of most of it has been furnished by J. W. Smith.[2]

Following a private communication in 1910 of the results, published in the next year, obtained by Smith and Menzies[3] for intensively desiccated calomel, H. B. Baker[4] initiated experiments in which a number of different liquids were intensively desiccated by phosphorus pentoxide. After a period of nine years' drying, Baker reported rises in the boiling points of these liquids ranging from 14 to 60°; and rises also in surface tension and in freezing point. These reports were so extraordinary that many critical investigators were attracted into this field of work. Without attempting to enter into detail, it may be stated broadly that the rises in boiling point reported by Baker have been explained away in their four several laboratories by Smits,[5] Smith,[6] Lenher[7] and Cohen with Cohen de Meester[8] in terms of accidental superheating, which occurs also with undried liquids. Failure to observe changes in physical properties as a result of intensive desiccation has been reported by Lenher and Daniels,[9] Briscoe, Peel and Robinson,[10] Rodebush and Michalek,[11] Timmermans,[12] Greer,[13] J. W. Smith,[6] and (although not in the earlier) in the more recent investigations of Smits and his collaborators.[5] The results of Mali[14] and of Manley,[15] on the other hand, are not inconsistent with those of Baker. Upon one matter there appears to be no stated disagreement, namely, that intensive desiccation retards, at least initially, speed of distillation.[5k,16]

In returning to this confused subject after a lapse of over twenty years, we thought it best to confine ourselves in the first place to the study of a reputedly normal type of liquid which could be purified readily, and thus we selected benzene. It was only later that a study of existing literature led us[17] to believe that liquid benzene exhibits evidence of allotropic change in the neighborhood of 40°. Accordingly, we later included in our studies three other liquids, carbon tetrachloride, normal heptane and cyclohexane; but in describing our procedure we shall, for clarity, speak only of benzene. Because of its sensitiveness, we selected vapor pressure as a chief property to study.

Since the experience of others had demonstrated that the conditions of experiment were all-important, we were at pains to devise for the work a glass apparatus which, while very simple, enabled us to meet the following specifications: (a) superheating cannot occur; (b) time at equilibrium can be protracted at will; (c) every portion of the glass can be freed from capillaries; (d) all of the completed apparatus can be strongly

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(1) Menzies and Lacoss, *Proc. Nat. Acad. Sci.*, **19**, 393 (1933).

(2) J. W. Smith, "Effect of Moisture on Chemical and Physical Changes," Longmans, Green and Co., 114 Fifth Ave., New York, N. Y., 1929.

(3) Smith and Menzies, *Z. physik. Chem.*, **76**, 713 (1911).

(4) *Cf.* (a) H. B. Baker and M. Baker, *J. Chem. Soc.*, **101**, 2339 (1912); (b) H. B. Baker, *ibid.*, **121**, 568 (1922); (c) **123**, 1223 (1923); (d) 2902 (1927); (e) 1051 (1928); (f) 1661 (1929).

(5) *Cf.* A. Smits (and collaborators): (a) *Z. physik. Chem.*, **76**, 421 (1911); (b) **100**, 477 (1922); (c) **129**, 33 (1927); (d) *J. Chem. Soc.*, **125**, 1069 (1924); (e) **125**, 2554, 2573 (1924); (f) 2657 (1926); (g) 2399 (1928); (h) 2712, 2724 (1929); (i) *Verhandl. Akad. Wetenschaffen Amsterdam*, **34**, 468 (1931); (j) *Z. physik. Chem.*, **A171**, 445 (1934); (k) **A172**, 1 (1935).

(6) J. W. Smith, (a) *J. Chem. Soc.*, 867 (1927); (b) 788 (1929); (c) 528, 2573 (1931).

(7) S. Lenher, *J. Phys. Chem.*, **33**, 1579 (1929).

(8) E. Cohen and Cohen de Meester, *Verhandl. Akad. Wetenschaffen Amsterdam*, **33**, 1003 (1930).

(9) S. Lenher and F. Daniels, *Proc. Nat. Acad. Sci.*, **14**, 607 (1929).

(10) H. V. A. Briscoe, J. B. Peel and P. L. Robinson, *J. Chem. Soc.*, 368 (1929).

(11) W. H. Rodebush and J. C. Michalek, THIS JOURNAL, **51**, 748 (1929).

(12) J. Timmermans, *Bull. soc. chim. belg.*, **38**, 160 (1929).

(13) E. J. Greer, THIS JOURNAL, **52**, 4191 (1930).

(14) S. B. Mali, *Z. anorg. allgem. Chem.*, **149**, 150 (1925).

(15) J. J. Manley, *Phil. Mag.*, **33**, 249 (1932); *Rec. trav. chim.*, **53**, 785 (1934).

(16) *Cf.*, especially, J. W. Smith.[6c]

(17) Menzies and Lacoss, *Proc. Nat. Acad. Sci.*, **18**, 144 (1932). The interesting criticisms of Deinum and of Cohen and his collaborators will be dealt with elsewhere.

heated; (e) no tubes of capillary bore form part of the apparatus; (f) no glass septum need be broken within the dry apparatus; (g) no mercury or stopcocks must be used; (h) the purified phosphorus pentoxide, when this is used, and purified benzene can be redistilled direct into the apparatus; (i) the mass of desiccant used can be many times that of the substance to be dried; (j) the apparatus can be charged under dust-free conditions; (k) desiccation can be carried on at elevated temperatures. While the importance of the other conditions will be appreciated by those who are expert in this field, it should be mentioned that (d) and (j) have been discussed elsewhere[18,19] and that J. W. Smith[6c] attributes failures to the presence of capillary tubes (e) a circumstance bearing on the negative results referred to in footnotes 10 and 12. As to condition (f) Baker, whose earlier work on lack of reaction is not often discredited, remarks[4f] "I have only once seen the want of union between ammonia and hydrogen chloride and never between nitric oxide and oxygen when the broken glass wall was used." The activity of freshly broken glass or quartz surfaces is well recognized today.

General Description of Apparatus and Method.—The apparatus, shown in Fig. 1, was of Pyrex glass and consisted of a simplified isoteniscope[20] with a 2-cc. bulb A, connected to a cylindrical vessel B of about 70-cc. volume, which contained the desiccant. During vapor pressure measurements, B was enveloped in a jacket (not shown in the figure) carrying a thermometer, through which jacket water of controlled temperature near 20° could be circulated, while the bulb A was submerged and agitated in a stirred oil-bath, according to standard isoteniscope technique.[20] The small tubes, shown sealed off, at C, D and E were used for introducing the materials and for currents of dust-free oxygen or nitrogen. The apparatus, whose volume was known, was finally sealed off with a content of many grams of desiccant, about one gram of solidified benzene at -75°, and nitrogen gas at known temperature and pressure, near that of the room.

The temperature at which the vapor pressure of the liquid benzene in A, freed of nitrogen, was equal to that of the nitrogen in B, with its partial pressure of benzene vapor at water-jacket temperature, may conveniently be called the boiling point of the sample, since the pressures were close to one atmosphere. After expulsion of the nitrogen from A by repeated boiling out, the identity of these two pressures, following correct adjustment of the bath temperature, was recognized by the equality of level of the liquid benzene surfaces in the two limbs of the trap F. The boiling point determined in this way shortly after sealing coincided within 0.1° with the known boiling point of the sample as previously ascertained by the customary methods. It has been shown elsewhere[21] that the water content of such benzene is insufficient to give rise to an aqueous pressure which would affect the boiling point of benzene by over 0.1° near 80°.

For purposes of desiccation, the liquid benzene was transferred to B in direct contact with the desiccant. When, after a lapse of weeks or months, it was desired to redetermine the boiling point, the benzene was distilled at room temperature into A, maintained at 0° or colder, a process often requiring over two weeks. When no mention is made of higher temperatures, it should be understood that the desiccation process was permitted to take place at room temperature.

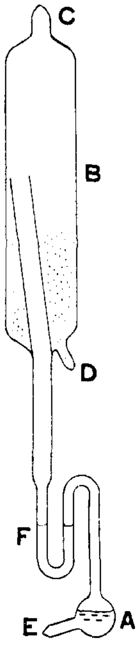

Fig. 1.

Details of Apparatus and Customary Procedure.—The Pyrex tubing used in constructing the apparatus received the preliminary treatment recommended by Baker.[4d] It was then freed from capillaries according to the method of Smits.[5f] After construction, it was filled with the chromic–nitric acid mixture as used by Baker and allowed to stand for at least twenty-four hours. The acid mixture was then boiled, the apparatus later washed repeatedly with distilled water and finally steamed with ammonia-free water.

For use while charging the empty apparatus we had constantly at hand three filtering and drying trains, each consisting of a calcium chloride drying tower, a 2.5 × 90 cm. tube of closely packed, dried, absorbent cotton and a tube of like size charged with half-inch (1.2-cm.) layers of purified phosphorus pentoxide "plugs," separated by similar layers of ignited asbestos, as described by Baker. In order to dry the apparatus and to destroy dust, each apparatus was heated by burners for about five hours at a temperature only slightly lower than the softening point of the glass in a current of oxygen passed through one of the filtering and drying trains. Except for Nos. 1, 2, 9 and 10, the phosphorus pentoxide desiccant was distilled in a current of oxygen into the apparatus through C from a 3 × 65 cm. Pyrex tube, two-thirds filled with purified pentoxide, heated at about 300° by a tubular resistance oven. Behind this was a filtering and drying train. Similar trains were attached at D and E. Connections were glass seals, except at E where interchangeable unlubricated ground joints were used, whose leakage was always outward. The train attached at E served as a guard tube, and was later replaced by the vessel from which the benzene was distilled into A. After distilling about 10 g. of desiccant into B, the oxygen was replaced by nitrogen gas, the oven turned off and C sealed. About 1 g. of benzene was now distilled into A against a slow counter-current of filtered and dried nitrogen. The benzene was then cooled with the aid of carbon dioxide snow, the gas current stopped and

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(18) H. B. Baker, *Nature*, **125**, 229 (1930).

(19) A. W. C. Menzies, *ibid.*, **125**, 446 (1930).

(20) A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1412 (1910). *Cf.* also Alexander Findlay, "Practical Physical Chemistry," Longmans, Green and Co., 114 Fifth Ave., New York, N. Y., 1931, 5th ed. p. 71. In what follows, familiarity with isoteniscope technique is assumed.

(21) A. W. C. Menzies, *J. Phys. Chem.*, **35**, 1655 (1931).

E sealed. The apparatus was next immersed in water at known temperature and the purifying train at D sealed off, under barometric pressure, thus leaving the apparatus with a known content of nitrogen. A few drops of benzene were now run from A into B, and the apparatus set aside for at least one day. Experiment devised for the purpose demonstrated that this period was longer than sufficient to allow complete saturation of B with benzene vapor at the temperature of the water-jacket. This is further confirmed by the fact that the vapor pressure of the benzene in A, which was now measured and is reported as "original b. p.," agreed, with two understood exceptions, to 0.1° or better with that expected for the pressure computed to obtain in B. In making this comparison, we knew the boiling point of our samples of benzene as previously found by customary methods. In order to compute the equilibrium pressure within the portion of the apparatus above F, we employed the temperature and pressure of nitrogen as observed at the time of sealing. This was corrected to jacket temperature. Furthermore, a correction was necessary by reason of all the nitrogen being now contained in a smaller volume than at sealing, all of it being now above the observed level of benzene condensation, somewhat above F. Below this point benzene and its vapor alone were present. Due allowance was likewise necessary for the presence in B of benzene vapor in equilibrium with the liquid benzene which had been intentionally run into B. Values for this saturation pressure of liquid benzene were taken from the "International Critical Tables."

In connection with the values mentioned in the last sentence, it is perhaps necessary to mention that, when a lowering was found in the vapor pressure of benzene near 80°, the existence of a proportionate lowering should have been allowed for in the vapor pressure of such benzene at jacket temperature, making the contribution of benzene to the total pressure in B somewhat smaller. Since the lowering of pressure observed, due to desiccation, never exceeded 7%, the amount of such a correction, which was intentionally neglected, would never exceed 0.2° in the observed boiling point near 80°, and would, if applied, somewhat increase the rises of boiling point here reported for desiccated benzene rather than diminish them.

Measurement of Temperature.—The temperature of the oil-bath was read to the nearest 0.1° upon the completely immersed thread of an auxiliary thermometer whose readings were compared from time to time with those of a thermometer, whose zero point was occasionally redetermined, certificated to tenths by the Bureau of Standards. For the freezing point of benzene, the readings were controlled similarly by a thermometer certificated by the Reichsanstalt to 0.02°.

Measurement of Pressure.—Our barometric readings were controlled by the mercurial gage described by West and Menzies.[22] Isoteniscope readings were good to better than 1 mm. of head of confining liquid in trap F, which corresponds to a pressure of mercury very much less than 1 mm.

Refractive Index.—This was measured by a Pulfrich instrument, described elsewhere,[23] with temperature control within 0.1°.

Materials. Phosphorus Pentoxide.—Sterling C. P. grade was distilled in an atmosphere of oxygen, according to the method of Finch and Frazer[24] and stored in glass-stoppered bottles under a sealed bell jar containing phosphorus pentoxide. No specimen of the distilled pentoxide gave a positive test for the lower oxide of phosphorus by the silver nitrate test [25] or the mercuric chloride test.[26] Later samples were tested also, with negative results, by the permanganate test of Smith.[6c] When used, this purified pentoxide was, in all but two cases, redistilled into the apparatus in a current of oxygen.

Benzene.—Three different samples of purified benzene were used, all of which behaved similarly in respect to desiccation. Sample 1 was prepared from Merck C. P. crystallizable grade. The fraction of this distilling between 80.0 and 80.2° at 760 mm. was shaken with successive portions of concentrated sulfuric acid, washed with distilled water, with dilute sodium hydroxide and again with water. This gave no test for thiophene with isatin. After drying over calcium chloride on a shaker, it was poured off, distilled, and refluxed with successive portions of sodium wire until the sodium remained bright. It was then frozen out four times, about one-fifth being discarded each time. The third and fourth crystallizations took place at 5.48°, with air present and at atmospheric pressure. After refluxing again over sodium, the benzene distilled at a constant temperature of 80.1° at 758 mm. The refractive index for the D lines of sodium was 1.50138 at 20°. This sample was used in experiments 1, 2 and 6 to 12, inclusive.

Sample 2. This had the same origin and treatment as sample 1, except that the final drying was by purified phosphorus pentoxide. The boiling point and refractive index were the same. This sample was used in experiments 3, 4 and 5.

Sample 3. This was prepared from Kahlbaum "brown label" benzoic acid by distillation with lime.[27] It was treated similarly to sample 1, but was frozen out only thrice, as the second and third crystallizations both took place at 5.49°. It was finally refluxed over three successive portions of sodium wire. The refractive index for the D lines of sodium was 1.50140 at 20°. This sample was used in experiments 13–18, inclusive, and in the six experiments with desiccants other than phosphorus pentoxide.

Carbon Tetrachloride.—Merck reagent grade was refluxed for fifteen hours while a slow stream of chlorine gas passed through the liquid. It was then washed successively with sodium hydroxide solution, concentrated sulfuric acid and distilled water. After drying under reflux with phosphorus pentoxide for thirty hours, the complete sample distilled at 76.7° under 760 mm.

***n*-Heptane.**—A sample secured from Ethyl Gasoline Corporation was fractionally distilled using a three-foot (91-cm.) still head of the Vigreux type. Four-fifths distilled at 98.3° and this was washed successively with con-

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[22] W. A. West and A. W. C. Menzies, *J. Phys. Chem.*, **33**, 1881 (1929).

[23] Smyth and Stoops, THIS JOURNAL, **50**, 1883 (1928).

[24] Finch and Frazer, *J. Chem. Soc.*, 118 (1926).

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

[26] H. Whitaker, *ibid.*, **127**, 2219 (1925).

[27] *Cf.* E. Mitscherlich, *Ann.*, **9**, 39 (1934).

centrated sulfuric acid, sodium hydroxide solution and distilled water, and dried by refluxing over phosphorus pentoxide for thirty hours. It distilled constantly at 98.3° under 760 mm.

Cyclohexane.—One liter of Eastman Kodak Co. cyclohexane was recrystallized six times with rejection of the liquid portions until one-tenth remained. After refluxing over phosphorus pentoxide the liquid showed a constant f. p. in air of 6.4° and a b. p. of 80.7° at 760 mm.

Details of Individual Experiments.—The first eighteen experiments were made with purified benzene, using phosphorus pentoxide as desiccant. In twelve of the fourteen of these in which the most rigorously purified desiccant was used, changes in vapor pressure were observed after various periods of desiccation. For brevity these changes are interpreted as changes in b. p. and so noted in degrees on the ordinate axis in Fig. 2, against weeks of desiccation on the axis of abscissas. The original boiling points varied according to the conditions under which each apparatus was sealed, and all except No. 2 fell within 2.4° of 82.8°. Experiment 2 was sealed when the glass was warm, and had an original b. p. of 70.3°. In the case of the first five numbered experiments, the temperature and pressure within the apparatus were not measured at the moment of sealing as was done in all the later experiments. When it is stated that an experiment was discontinued, this signifies that the apparatus met with some fatal accident.

Experiments 1 and 2.—The desiccant was introduced not by distillation, as in the case of all other experiments except Nos. 9 and 10, but by inserting Baker "plugs" of pentoxide through C against a countercurrent of purified nitrogen; and in these four experiments also the benzene was distilled in through C instead of through E, which was absent from the apparatus. Experiment 1 showed no change in b. p. even after thirty-two weeks of desiccation at room temperature, after which it was discontinued. In the light of later findings, this negative result may be attributed to poor initial technique and the possible admission of dust. Experiment 2 showed the positive results indicated on Fig. 2. After thirty-two weeks of desiccation, when the b. p. had risen 2.2°, the benzene in A was heated near 68° for four hours out of contact with the desiccant. On again taking the b. p. it was found that this had reverted to the original normal value. The same type of result was observed in experiments 13 and 15, but not in experiment 4 where the desiccation had been more drastic. Discontinued.

Experiment 3 showed a b. p. rise of 0.6° in thirteen weeks, after which it was discontinued.

Experiment 4 has a fuller history than is shown on Fig. 2. After thirty-two weeks' desiccation, in order to test whether the temperature at which the benzene was kept prior to a determination had an influence upon the b. p., now raised by 1.7°, the benzene, then in bulb A, was maintained for seven days at 16° and then for one month at 40°. Neither treatment influenced the b. p., which remained 1.7° high. Following this, the desiccation at room temperature was continued until the total time of desiccation reached eighty-two weeks, with a b. p. rise of 2.2°. At this point, experiments were made to test whether the b. p. could be made to revert to the normal value, as in experiments 2, 13 and 15. The apparatus was heated for ten days at 120° with the benzene *in contact with the desiccant*, then for eight days at 120°, four days at 135° and nine days at 150° with the benzene in bulb A. The b. p. was taken after each period of heating, after first distilling the benzene to the bulb A, maintained at 15° while B was maintained at 80°. To minimize the possibility of the apparatus being burst by internal pressure during heating, it was placed within a steel tube, containing ordinary benzene, closed with a cap and gas-tight gasket. This "bomb" was heated in a long cylindrical resistance heater designed for the purpose, of which that end was kept slightly cooler in which it was desired that the liquid should remain. In no case did the b. p. change as a result of any one of these heating processes, remaining constant at 2.2° above the original b. p. The efficiency of phosphorus pentoxide as a desiccant at 90° has been discussed elsewhere.[28] The apparatus was then set aside to continue desiccation at room temperature until the total period of desiccation reached one hundred and ten weeks, after which the b. p. was still 2.2° high.

At this point a test for fractionation was made. Normally the liquid whose b. p. is measured by our method consists of about four-fifths of the volume of benzene originally in A, since one-fifth of this is distilled off to furnish a confining liquid in the trap F. The vapor pressure is controlled by the larger surface of agitated liquid in A. The liquid in the trap was now poured into B, and a measurement made upon the remaining three-fifths contained in A during the measurement. This procedure was repeated twice, so that at the last measurement only one-fifth of the original benzene remained in A. All four measurements gave identical results 2.2° higher than the original b. p. Such measurements would doubtless fail to detect fractionation of two mixed liquids differing in b. p. by even several degrees. Discontinued.

Experiment 5 gave the results shown on Fig. 2, with a progressive rise to +1.5° after one hundred and ten weeks. At this stage the tip of C was opened intentionally, offering a hole of about 4-mm. diameter for connection with the atmosphere of the room. Eighteen minutes after opening the b. p. had fallen to 0.5°, after two hours to 0.3° and after five hours from opening to 0.0° above the normal value 80.1° at 760 mm. which was that finally reached.

Experiment 6.—The desiccation was first carried out by placing the apparatus in a thermostatically controlled oven at 90°, with A a few degrees hotter. As shown in Fig. 2, the found b. p.'s were 0.0, −0.1, −0.1 and −0.1° lower than the original value after four, seven, twelve and sixteen weeks, respectively. The desiccation was thereafter carried out at room temperature as usual, whereupon the b. p. rose 0.2° in twenty weeks and reached a value 0.2° above normal after a total period of desiccation of one hundred and twelve weeks.

Experiment 7.—This was discontinued after thirteen weeks, with a b. p. rise of 0.6°.

Experiment 8.—The earlier history of this is shown on Fig. 2, with a final rise of 1.3° after one hundred and fourteen weeks. This apparatus was now opened to the atmosphere, as was Expt. 5, but with a larger aperture to permit access of the air of the laboratory. The b. p. re-

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[28] Lacoss and Menzies, THIS JOURNAL, **59**, 2471 (1937).

verted to normal progressively with time, being 1.0, 0.5 and 0.0° high after eight, nineteen and forty minutes from time of opening, respectively.

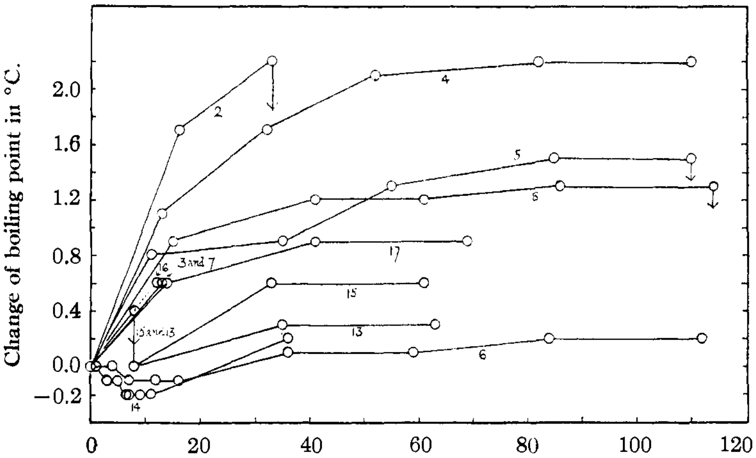

Fig. 2.—Changes with time of boiling point of benzene upon desiccation.

Experiments 9 and 10 were made using unpurified phosphorus pentoxide as desiccant. Obviously, this could not fairly be introduced by distillation and the same method was therefore used as in expts. 1 and 2. Experiment 9 showed b. p. values 0.0, −0.1, −0.1, −0.1 and −0.1° low after fourteen, twenty-nine, fifty-three, ninety-two and one hundred and twenty weeks, respectively. During the second drying period the pentoxide became tinted yellow. Experiment 10 showed no change in b. p. after fourteen, twenty-nine, fifty-three and eighty-one weeks.

Experiments 11 and 12.—In charging these, the dust filters were omitted intentionally. These are the two "understood exceptions," mentioned above, in which the original b. p.'s were found 1.1 and 1.2°, respectively, lower than the computed values. This was due to a faulty technique which heated unduly the glass of the apparatus during sealing. No change of b. p. was found in No. 11 after desiccation periods of eleven, seventeen, thirty-one, fifty-six and eighty-four weeks, nor in No. 12 after eighty-four weeks.

Experiment 13.—The b. p. rose 0.4° after eight weeks of desiccation. The liquid benzene, all in A, was now maintained at 75–78° for twenty-four hours after which the b. p. was found with the original value, confirming similar results with Nos. 2 and 15. Continued desiccation at room temperature produced the rise of 0.3° shown in Fig. 2.

TABLE I

Successive periods of heating, days	Temp. of heating, °C.	B. p. fall, °C.
8	105	0.0
12	105	− .1
12	105	− .1
13	105	− .2
4*	105	− .2
14	120	− .2
14	120	− .2

Experiment 14.—The desiccation was first carried out at elevated temperatures as in No. 6, but with the "bomb" method of heating as used in No. 4. Temperature distribution was arranged so that the liquid benzene was in B during each successive period of heating except that noted by an asterisk in Table I, in which case the liquid was in A. Following these successive periods of heating, desiccation was continued at room temperature in the usual manner, with a final rise of 0.2° above the original value now found after the thirty-sixth week, as shown in Fig. 2. Discontinued.

Experiment 15.—After seven weeks of desiccation, the b. p. rise was 0.4°. After heating the liquid benzene exactly as in expt. 13, the b. p. reverted to the original value, not at all in one day, partially in two days and completely in three days. Further desiccation for a period of twenty-five weeks caused a rise of 0.6° which was maintained till the fifty-fourth week from sealing after which the experiment was discontinued.

Experiment 16 showed a b. p. rise of 0.6° following twelve weeks of desiccation, after which it was discontinued.

Experiment 17 showed a progressive b. p. rise to 0.9° after sixty-nine weeks, as indicated in Fig. 2.

Experiment 18 was prepared and desiccated by our best technique but showed no change after fourteen, thirty-nine and sixty-seven weeks. Our technique is much less likely to have been faulty than in the case of expt. 1, which gave a like negative result but over only thirty-two weeks.

Impure Benzene.—Two experiments were made with this technique using Merck reagent grade benzene without purification, with negative results after nineteen weeks. These are being continued.

Other Desiccants.—With purified benzene, desiccation experiments were run using ignited barium oxide and ignited magnesium perchlorate, respectively, as desiccants, three experiments with each desiccant. These showed no vapor pressure change after sixteen and nineteen weeks, respectively, and are being continued.

Other Liquids.—Using purified dust-free phosphorus pentoxide as desiccant and our perfected technique, nine experiments were made with carbon tetrachloride, normal heptane and cyclohexane, respectively, three experiments with each liquid. After periods of desiccation from twenty-one to twenty-six weeks all results were negative. These experiments are being continued.

Conclusions

In this section the reference numerals in parentheses refer to the serially numbered experiments described in the text above.

A. When purified benzene was dried with ordinary phosphorus pentoxide no change in its vapor pressure was observed (9, 10).

B. When purified benzene was dried with

purified phosphorus pentoxide but without precaution to exclude dust, no change in its vapor pressure was observed (**11**, 12).

C. When reagent grade benzene, not further purified, was desiccated using the technique of D no change in its vapor pressure was observed.

D. When purified benzene was dried with purified phosphorus pentoxide with precaution to exclude or destroy dust, its vapor pressure near 80° was (a) lowered markedly if the drying process had been carried on at room temperatures; and (b) raised slightly if the drying process had been carried on at 90 or 105° (a, – 2, 3, 4, 5, 7, 8, 13, 15, 16, 17; b, – 6, 14).

E. In two cases, no change was observed during the period of our observation under the conditions of D(a), a result attributable, for example, to accidental dust, which likewise is sufficient to explain the negative results obtained by others in desiccation experiments with benzene (1, 18).

F. Interpreted in terms of change of b. p. near atmospheric pressure, desiccation of purified benzene under our conditions at room temperature for two months caused a rise of over 0.4°, for four months of about 0.7°; while the maximum rise observed, practically stationary after twenty months, was 2.2° (2, 3, 4, 5, 7, 8, 16, 17; 2, 4).

G. If the benzene had a history of previous desiccation, the rate of rise was slower and the final value lower (6, 13, 14, 15).

H. Using a somewhat inadequate method, we found no evidence of fractionation even in a sample of benzene whose b. p. had been raised 2.2° by desiccation (4).

I. When ordinary undried air was admitted slowly by diffusion to benzene whose vapor pressure had been reduced by desiccation to an abnormally low value, the vapor pressure gradually reverted again to the normal value (5, 8).

J. Reversion to normal vapor pressure could be produced without opening the sealed apparatus. Two samples (13, 15) whose b. p.'s had been raised 0.4° by two months of desiccation at room temperatures exhibited complete reversion upon heating near 77° out of contact with the desiccant; while a third sample (2), whose b. p. had been raised 2.2° by eight months of desiccation likewise reverted upon heating similarly near 68°.

K. Contrary to the results under J, a sample (4) of benzene contained in an apparatus which, with its contents, had been subjected to still more rigorous desiccation, failed to revert. This had a b. p. raised 2.2° following twenty months of desiccation, and had been further heated for ten days at 120° in contact with the desiccant, without resulting change in b. p. It showed no change after heating, out of contact with the desiccant, for successive periods of eighteen, four and nine days at 120, 135 and 150°, respectively.

L. Desiccation by barium oxide and by magnesium perchlorate, respectively, was found without influence, in the time allowed, upon the vapor pressure of benzene (three experiments in each case).

M. The vapor pressures of purified carbon tetrachloride, *n*-heptane and cyclohexane, respectively, were not influenced, in the time allowed, in our desiccation experiments with purified dust-free phosphorus pentoxide (three experiments in each case).

Discussion

We shall here confine ourselves to indicating how certain criticisms of these experimental results may be met.

a. The possibility that a permanent gas is liberated within the apparatus, perhaps from desorption from the large surface of the pentoxide, so as to increase with time the pressure under which the boiling points were measured was tested by special experiments, with negative results, whose details are not here described because they appeared unnecessary in view of the reversion to normal b. p. found in Expts. 2, 13 and 15.

b. The possibility that the chamber B was not saturated with benzene vapor at the jacket temperature at the time of the measurement of initial b. p. and that the total pressure in B consequently increased with time is negatived by the agreement of the original boiling points as measured and as calculated from the pressure computed on the assumption of saturation. In addition, the time requisite for such saturation was found by special experiment designed for the purpose to be much less than that allowed.

c. It might plausibly be said that, owing to the recognized slowness of vaporization of desiccated liquids, the time allowed for vapor pressure equilibrium was inadequate, and the b. p. as measured consequently too low. This suggestion was made by Smith and Menzies[3] in discussing their results with calomel. In the present instance, this possibility was negatived by the results of many experiments continued for an hour, and, in a test case, for many hours. If the criticism were here valid, the liquid must be supposed to occupy perhaps ten minutes in developing about 95% of its equilibrium vapor pressure and thereupon to reach a state stationary for hours.

d. The possibility of superheating cannot come in question with our method of work.

e. The likelihood of phosphorus pentoxide reacting with benzene to produce a soluble impurity of lower volatility than benzene[29] is negatived by the results of expts. 1, 9, 10, 11, 12 and 18 which, over many weeks, showed no elevation of boiling point; of expts. 2, 13 and 15 whose boiling points reverted to normal upon heating; and of expts. 5 and 8 which reverted to normal b. p. upon opening to the atmosphere.

Summary

When purified benzene was desiccated with purified phosphorus pentoxide with precautions to exclude or destroy dust, its vapor pressure, near 80°, was (a) lowered markedly if the drying process had been carried on at room temperature, and (b) raised slightly if the drying process had been carried on at 90 or 105°. Without opening the sealed apparatus, the vapor pressure could be caused to revert to the normal value by heating the liquid in the apparatus out of contact with the desiccant, provided that the desiccation had not been too rigorous. Upon allowing access of ordinary air, vapor pressures likewise reverted to normal value.

No change was found under like conditions in the vapor pressure of benzene if the materials used were not both purified and also dust free, nor when barium oxide or magnesium perchlorate were used as desiccants.

Carbon tetrachloride, normal heptane and cyclohexane all failed to show any change in vapor pressure upon desiccation under the same conditions that had given positive results in the case of benzene.

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[29] *Cf.* D. Balareff, *J. prakt. Chem.*, **116**, 57 (1927).

[CONTRIBUTION FROM THE U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY AND SOILS]

The Use of Low Temperature van der Waals Adsorption Isotherms in Determining the Surface Areas of Various Adsorbents

BY STEPHEN BRUNAUER AND PAUL H. EMMETT

In a number of previous publications[1-3] we proposed a method by which one can evaluate the surface area of iron synthetic ammonia catalysts from adsorption isotherms determined at or near the boiling points of the gases adsorbed. In the present paper we are reporting the results obtained in applying the method to other catalysts, catalyst supports, and various finely divided materials.

Experimental

The apparatus, experimental procedure and the nature of the constant temperature baths have all been described previously.[2,3,4] The "dead space" around the adsorbents was measured with helium. The measured gas volumes were all corrected for the deviations from the perfect gas laws, the percentage deviations used being the same as in a previous paper.[3]

Included in the present work are isotherms for the adsorption of argon and nitrogen at −195.8°; nitrogen, argon, carbon monoxide, and oxygen at −183°; carbon dioxide at −78°; normal butane and sulfur dioxide at 0°. The preparation and purification of all of these gases except sulfur dioxide have been described already.[2,3] Tank sulfur dioxide from the Baker Chemical Company was dried over Dehydrite and used without further purification after it had been shown to contain less than 0.02% inert gases and no sulfur trioxide.

The eighteen adsorbents used in the work described in the present paper are numbers 13 to 30 inclusive in Table III. Similar experiments on soils and soil colloids have been reported in another paper.[5]

One of the two copper catalysts was prepared by Mr. J. F. Shultz of this Laboratory by melting electrolytic copper in an oxy-hydrogen flame in the presence of excess oxygen, crushing the resulting copper oxide to approximate mesh size, and reducing it in hydrogen at 200°. The other copper catalyst was obtained by reducing a commercial copper oxide (Eimer and Amend C. P. cupric oxide) at 200°. Each reduction was started at 200° but was so exothermic as to proceed rapidly after the removal of the furnace. Before each adsorption run the copper catalysts were reduced in hydrogen for one hour at 300° and then evacuated for an hour at the same temperature.

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[1] Brunauer and Emmett, THIS JOURNAL, **57**, 1754 (1935).

[2] Emmett and Brunauer, *ibid.*, **59**, 310 (1937).

[3] Emmett and Brunauer, *ibid.*, **59**, 1553 (1937).

[4] Emmett and Brunauer, *ibid.*, **56**, 35 (1934).

[5] Emmett, Brunauer and Love, *Soil Science* (to be published).