A secondary band is in equilibrium with the primary band and on the decrease of one of the bands the other increases in height.

The dissociation constant for the indicators studied was determined by a photometric method.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADSORPTION OF VAPORS BY CHARCOAL

BY ALBERT SPRAGUE COOLIDGE

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In a previous paper[1] in collaboration with Professor A. B. Lamb, have been reported the results of some measurements of the heats of adsorption of the vapors of various liquids on activated coconut charcoal. As stated in that paper, our original object was to study both heats of adsorption and equilibrium pressures, but the measurements of pressure were found to be beset with so many difficulties and uncertainties that it seemed best to postpone this part of the problem until the passing of the war emergency should allow more leisure. Work was resumed in the summer of 1921, and is still in progress; but as the technical difficulties appear to have been overcome and a fair body of reliable data accumulated, it seems desirable to publish the results so far attained without waiting for the completion of the proposed program. Additional results, together with a critical discussion, will be given in a later paper.

Most of the work was done in my laboratory on South Mountain, Pittsfield, Massachusetts, the remainder in the laboratories of Harvard University.

Variables Influencing Results

A charcoal-vapor system is most conveniently treated as consisting of two components and two phases, and accordingly enjoying two degrees of freedom. If p, the pressure, be the dependent variable, the independent variables may be chosen as the temperature, t, and the concentration of the condensed phase, q; that is, the quantity of vapor adsorbed by one gram of gas-free charcoal, the vapor being measured by volume under standard conditions. If the phase rule holds, then the pressure observed when quantities of charcoal and vapor are isolated in a closed system will be completely determined by (*a*) the kind of charcoal used (source, method of activation, etc.); (*b*) the vapor used; (*c*) the concentration of the condensed phase; (*d*) the temperature. Actually, however, other observers have found that the following additional variables have or may have an influence on the result: (*e*) temperature of previous outgassing of charcoal; (*f*) time of outgassing; (*g*) efficiency of outgassing

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[1] Lamb and Coolidge, THIS JOURNAL, 42, 1146 (1920).

pump; (*h*) previous exposure of charcoal to the same or other vapors; (*i*) time elapsed since last change in concentration; (*j*) direction in which experiment is made, that is, whether concentration is being increased (in-curve) or decreased (out-curve). There are, then, at least ten variables whose effects must be studied and controlled, before a single pressure measurement worthy of confidence can be obtained.

The problem will be greatly simplified if we can show that certain of these variables have a negligible influence on the results, at least if they are confined within certain limits. Thus, we might expect to find that (*e*), the temperature of outgassing, would not affect the results, providing that it was sufficiently high to drive out all adsorbed gases, and not high enough to break down the structure of the charcoal. This, however, proves to be not the case. Over the range of temperatures studied, the results obtained vary continuously with the temperature of outgassing, which must therefore be added to our list of fundamental variables. The remaining five influences, fortunately, can be eliminated by suitable choice of conditions. The evidence in support of this statement is as follows.

(*f*), (*g*), (*h*) In every determination of pressure the charcoal was first heated to a definite maximum temperature for at least four hours, at a pressure maintained below 3 mm. by an oil pump. During at least the last hour of the evacuation, a small mercury condensation pump was operated, and was kept in operation thereafter while the charcoal cooled, so that the final pressure was never more than 0.001 mm. But this was only the minimum thoroughness of evacuation. The procedure was frequently varied by prolonging the time (up to 40 hours), by continuous operation of the mercury pump, by using a much larger pump, or by gradually lowering the temperature near the end of the evacuation, as is done in evacuating lamp bulbs. Furthermore, the same sample of charcoal was repeatedly used in successive adsorptions, being given a similar outgassing before each. In the pressures subsequently measured, no discrepancies greater than the errors of experiment could be traced to any of these variations in preliminary treatment, which proves that the minimum evacuation described suffices to eliminate the effects of variables *f*, *g* and *h*. This confirms the results of the previous calorimetric work. In that work, however, it was found that variable *h* becomes important in the case of halogen compounds, exposure to which seemed to produce permanent alteration in the charcoal; this result is likewise confirmed by the present measurements. Accordingly, no sample of charcoal which had been exposed to one of these compounds was used further. Another exception is presumably the case of oxygen. Lowry and Hulett[2] found that the adsorption of this gas is not reversible, and that it can be re-

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[2] Lowry and Hulett, This Journal, 42, 1408 (1920).

covered only at a high temperature in the form of carbon monoxide. For this reason, exposure to air was avoided, once the charcoal had been outgassed, the apparatus being kept continuously under a vacuum. However, brief exposures to air occasionally occurred through accident, and did not produce any observable change in the behavior of the subsequently evacuated charcoal.

(*i*) The time required for establishment of equilibrium is not simple to determine, for the reason that the adsorption occurs in at least two different stages of widely divergent rapidity. Equilibrium between charcoal phase and gas phase (external equilibrium) is quickly reached. If, for example, at any stage in the adsorption process the gas space in connection with the charcoal is suddenly pumped out, upon cutting off the pump the pressure will be found to regain its previous value in a few minutes. (This assumes, of course, that the pressure is so low that the loss of the amount of vapor required to fill the space will not significantly lower the concentration of the charcoal phase. The phenomena here under discussion occur at pressures below, say, 0.1 mm. At higher pressures the processes become more rapid, and the difficulties correspondingly less.) It is not to be supposed, however, that the pressure thus duplicated is the true equilibrium pressure, for if it be measured again after a few hours it will be found to have decreased (supposing that the first measurement was made within a couple of hours of the original admission of the vapor). This decrease continues for several hours, or even days; it is evidently caused by a slow penetration within the charcoal itself (internal equilibrium). If, after this process appears to have ceased, the experiment is still further prolonged, it will sometimes happen that a second increase in pressure sets in, and continues without apparent limit. I am satisfied, however, that this is of only accidental significance, being caused by the presence in the charcoal of traces of gas which are slowly evolved or displaced by the penetration of the more powerfully adsorbed vapor. The evidence is as follows. First, the secondary increase is less marked, the more thorough the preliminary outgassing. Second, if the system be gently pumped, the increase immediately disappears, the pressure falling to the lowest value previously reached, or a little lower, while if the gas so removed be collected, it will be found to be very small in amount. Continued pumping, however, does not reduce the pressure further until much larger amounts of gas have been removed, that is, until the concentration has been materially decreased. Finally, it is easy to test the gas in the system for impurities by compressing a portion over mercury. Immediately after admission, all gas condenses to a liquid at a given pressure; but when a secondary increase in pressure has occurred, condensation is incomplete, proving the presence of volatile impurities which can have come only from the charcoal. Davidheiser and Patrick[3] have recorded exactly parallel phenomena. When a certain amount of ammonia was adsorbed on silica gel containing about 5% of water, the pressure was 287 mm. at 100°, but was observed to increase slowly, reaching 471 mm. in nine days. When the system was cooled with ice, the pressure fell to 4.53 mm. (almost exactly the vapor pressure of water) and, when it was again heated to 100°, rose immediately to 471 mm. The authors connect this phenomenon with the presence of water in the gel, for when the water content of the gel was reduced to 0.3%, no such effect was observed.

The effect of temperature changes is much simpler. External equilibrium is established with no more lag than that attending the complete attainment of the new temperature. Internal equilibrium, if once reached at any temperature, is apparently not disturbed by even wide variations in temperature, provided loss of vapor and consequent change of concentration be prevented. If, however, internal equilibrium has not already been reached, its attainment is very much accelerated by a rise in temperature. This is probably due to several causes. First, the pressure is enormously increased (roughly ten times for each 30° rise), which naturally hastens the diffusion process. Second, the viscosity of the adsorbed vapor may be diminished, if it is in a state resembling the liquid. Third, the displacement of traces of foreign gas must be facilitated, precisely as in outgassing, by increased temperature. Harned[4] has found that such traces exert powerful retarding action on the velocity of adsorption. Whatever may be the explanation, the fact is a most fortunate one, for it enables us to reduce greatly the time required for a determination by annealing the charcoal after admission, escape of vapor being prevented by closing a trap close to the charcoal. The temperature used must be chosen according to the circumstances; it must not be sufficient to decompose the vapor nor to distil it out into the cold parts of the apparatus.

If the equilibrium be disturbed by decreasing instead of increasing the concentration, readjustment seems to be more rapid, and no lag of more than a few minutes was observed. It should be noted, however, that when once a concentration corresponding to a pressure of 0.1 mm. is reached, no further considerable decrease can be produced at the given temperature, even by prolonged pumping with large pumps and wide tubes. Thus, 1 g. of charcoal at 0° and 0.1 mm. holds enough benzene to fill a space of 600 liters at that pressure; when one-quarter of the benzene is removed, the pressure falls to $^1/_{10}$ of the given value, and the charcoal becomes equivalent to a reservoir of 4500 liters' capacity, the rate of exhaust being correspondingly slower. It is, therefore, not possible to determine at what rate internal equilibrium is adjusted after a sudden

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[3] Davidheiser and Patrick, This Journal, **44**, 5 (1922).

[4] Harned, *ibid.*, **42**, 383 (1920).

great decrease in concentration. Such a decrease can readily be produced with the aid of higher temperature, but this also accelerates the rate of adjustment, so that when the original temperature is reëstablished, equilibrium is found to be already complete.

(*j*) Hysteretic lags have sometimes been reported in adsorption work. In the early stages of the present investigation, wide discrepancies between the in-curve and the out-curve were noticed at low pressures, the curves running together at high pressures. It was noticed, however, that in subsequent experiments on the same sample, the out-curves coincided with those of the first experiment, while the in-curves were not reproduced, but tended to coincide with the out-curves. If at any stage before saturation the process of addition was interrupted and a little vapor pumped off, points on the out-curve were immediately obtained. Evidently, then, the out-curve is the true curve, and the in-curve is vitiated by the accumulation in the pressure gage of varying amounts of impurities, either present in the vapor or displaced from the charcoal. The fact that the effect decreases with repetition of the process points to the latter hypothesis. Harned[4] has found precisely similar effects in studying the rate of adsorption. At low concentrations, the rate is at first abnormally slow and irregular; it becomes normal and reproducible only after repeated adsorptions and outgassings. At higher concentrations the effect disappears. When at any stage the system is gently pumped, the impurities are swept out by fresh pure vapor from the charcoal, and correct results are obtained. This is obviously analogous to boiling a liquid whose vapor pressure is to be measured, in order to sweep out the dissolved air.

In the above discussion, no numerical data have been given to support the conclusions drawn. This is because it would be very difficult and uncertain to investigate any one of the variables at issue until methods had been found for bringing the others under control. When the point of view outlined above had been arrived at after much experimenting, it became possible to devise a technique of working in harmony with it, and to test its adequacy. The technique is as follows. The charcoal is first outgassed as already described. It is then allowed to adsorb a quantity of vapor in excess of that required to produce the highest concentration which it is desired to measure. When sufficient vapor has been adsorbed, and without waiting for equilibrium, the system is annealed by heating to 100° or 200° for a few minutes, without permitting the vapor to escape. It is then cooled to 0°, or to the lowest temperature at which the pressure will be measurable, and maintained at that temperature for about an hour, during which it is gently pumped from time to time, the vapor removed being collected and measured. The pressure is then read. The volume in connection with the charcoal is adjusted to be roughly inversely proportional to the pressure (within the available limits) so that at low pressures any impurities evolved from the charcoal are largely diluted with the pure vapor, whereas at high pressures the amount of vapor required to fill the dead space is not too great to be accurately determined. (This amount, of course, must be subtracted from the amount introduced into the system, in order to get the amount adsorbed.) When a reading has been obtained, the temperature is raised, and after an hour a new reading made at the new temperature; and this is repeated until the pressure approaches the limit of the apparatus. The system is then pumped down to a lower concentration, advantage being taken of the high temperature at which the last reading was made; it is cooled once more, and a new series of readings made on the lower concentration at various temperatures. The following data will serve to illustrate the method and prove its efficiency.

About 1 g. of charcoal was evacuated for four hours at 550°, the mercury pump being operated continuously. It was then iced and allowed to adsorb a little more than 50 cc. of benzene. At the end of an hour and a half, the system was pumped down to 49.9 cc., while still on ice, and the pressure read as a function of the time: in two minutes, 0.0086 mm.; in 15 minutes, 0.0097 mm.; in 30 minutes, 0.0096 mm. External equilibrium had evidently been reached within 15 minutes. In one hour the pressure was 0.0087 mm.; in six hours, 0.0062 mm.; in 15 hours, 0.0051 mm., in 24 hours, 0.0052 mm., and in 39 hours, after a single stroke of the pump, 0.0052 mm. The amount of vapor removed by the stroke of the pump was 0.002 cc., too small an amount to alter the concentration appreciably. The space in connection with the charcoal was 350 cc., approximately. Internal equilibrium had been established in 15 hours. The charcoal was then warmed, first to 40°, then to 100°, for 15 minutes, and again iced. In each case the original pressure was restored within 15 minutes after icing. The temperature was then raised to 218° for ten minutes. One hour after icing, the pressure was only 0.0041 mm., but it is believed that this measurement was affected by some error. The experiment was repeated, and the charcoal kept at 218° for two hours. In one hour after icing the pressure was 0.0104 mm.; evidently, 0.002 cc. of residual gas had been evolved. Two strokes of the pump reduced the pressure to 0.0051 mm., another stroke to 0.0047 mm., and yet another to 0.0046 mm. The heat treatment then appears to have produced a slight additional penetration which two days at ordinary temperature had not sufficed to complete.

The charcoal was then evacuated, and the whole experiment begun over again in exactly the same way. After the icing and pumping, the pressure was 0.0212 mm. Without delay for internal equilibrium to be reached, the charcoal was annealed for ten minutes at 218°. Thirty minutes after icing, the pressure was 0.0050 mm., and a single stroke of the pump reduced this to 0.0047 mm. This shows that internal equilibrium was achieved in ten minutes at the high temperature. In order to see whether equilibrium could be reached from above as well as from below, sufficient benzene was then introduced to bring the pressure up to 0.20 mm. The excess was then pumped out at 100°, the charcoal iced, and the pressure found to be 0.0048 mm.

At still lower pressures, similar effects occur, but more slowly. Thus, a sample of charcoal, after outgassing, was allowed to adsorb a quantity of benzene which it was anticipated (by extrapolating the isosteres; see below) would produce a pressure of 0.0002 mm. at 33°. The system was annealed in the usual way, but the pressure did not go lower than 0.00034 mm., even after two days. It was then heated to about 100°

for 16 hours, cooled to 33°, and the pressure found to be 0.00024 mm. There was not time to check this result by further annealing and waiting, but as it was just about the expected result, it was considered to be within a few per cent. of the true value.[5]

In order to see whether still longer periods of time would lead to any other changes in pressure, two samples of charcoal were outgassed and filled in the standard way, and kept for ten days at 33°. The pressure two hours after the final pumping was 4.30 mm. in one, and 26.6 in the other. No change whatever was noticed throughout this period, except fluctuations of about 1% caused by slight temperature changes.

This seems to prove that the annealing and pumping process establishes permanent equilibrium and prevents trouble from the evolution of residual gases.

As proof that the outgassing was sufficient, the following experiment may be cited.

A sample of charcoal equal in weight to that used in the first experiment quoted, was heated to 550° for 30 minutes on the oil pump (about 3 mm.). It was then evacuated with the condensation pump for an hour at 350°. When 50.2 cc. of benzene was adsorbed and annealed in the usual way, the pressure was 0.0048 mm., in complete agreement with the results with four hours' outgassing. However, it might be supposed that the effects of incomplete outgassing would be more apparent at high temperatures, where the residual gas would be more readily evolved. Accordingly, a sample was kept at 550° for 40 hours, the mercury pumps being run whenever possible, and in the intervals the charcoal was left in communication with a large evacuated space so as to keep down the pressure as much as possible. The pressures read on this sample at 215° and 303° are shown on the benzene isotherms (Fig. 5) in parentheses; it will be seen that they are not materially divergent from those obtained with charcoal outgassed only for the customary four hours.

The effect of varying the temperature of outgassing has not been discussed here, for the reason that it very early became apparent that this was one of the fundamental variables. The purpose of the preceding discussion is to demonstrate that the effects of variations in the last five of the influences listed on pp. 596–7 are of only incidental significance, and can be eliminated by proper choice of conditions. The data given appear to sustain this view. There remain five fundamental variables: kind of charcoal, temperature of outgassing, identity of vapor, temperature and concentration. It has been my purpose to assemble a body of self-consistent data on the equilibrium pressure as a function of these variables, covering as wide a range in each as possible; such a body of data is indispensable to the critical testing of any theory of adsorption. It would be far too laborious to explore the whole field, or rather region of five-dimensional space, covered by the simultaneous variations of all of these variables. It was, therefore, decided to make a thorough study of a somewhat restricted portion of this region, and then to extend the limits of each variable separately, reasoning by analogy as to the effects of simultaneous variations. The range which has been so far encompassed includes two kinds of charcoal (the same used in the earlier work),

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[5] Homfray observed a similar effect at —190°. *Z. Physik. Chem.*, **74**, 156 (1910).

temperatures of outgassing of 350° to 1050°, the vapors of water and eight organic liquids, temperatures from —33° to 305°, and concentrations varying from 0.1 cc. per g. to saturation. The dependent variable, pressure, has been measured between 0.00024 mm. and 1300 mm. With active charcoal outgassed at 550°, experiments were made with all the vapors over a temperature range of 0–305°, or up to the point where decomposition began, and at pressures from 0.01 mm. to 1000 mm. Charcoal and outgassing temperature were varied in the cases of water and benzene, pressures below 0.01 mm. were read in the case of benzene only. Rough measurements were made on benzene at —33°.

Experimental Part

Fig. 1 shows the type of apparatus which has been used.

It is constructed entirely of Pyrex glass (except, of course, the quartz fibers of the gage), without stopcocks or ground joints above the mercury level, so that the vapors can never come in contact with any materials but glass and mercury. With the exception of the quartz fiber gage and its cold trap, all parts are arranged with downward openings, so that mercury cannot collect in embarrassing places. It may be conveniently described in four sections, which are indicated by dashed lines in Fig. 1.

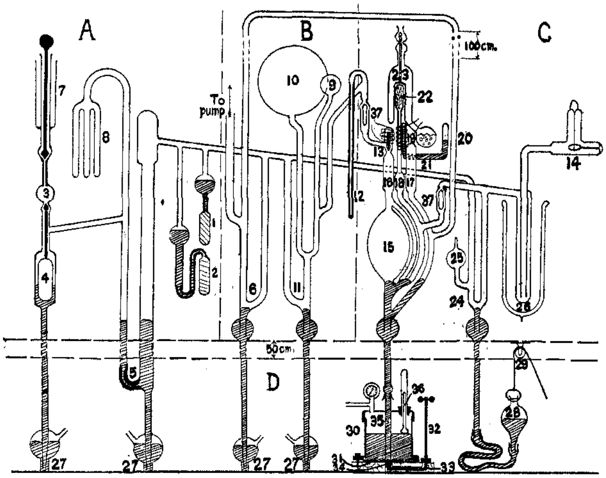

Fig. 1.—Apparatus.

Loading Devices. (A).—Air-free water is contained in Bulb 1, confined by mercury in the capillary tube and bulb above it. It is transferred to the apparatus as needed by immersing 1 in a freezing bath up to the capillary. Some of the water is forced up through the mercury as ice forms below. Air-free benzene is contained in Bulb 2, and is obtained by gentle boiling, the vapor bubbling up through the confining mercury. The other liquids are introduced through the air-lock, 3, which is provided with two mercury-sealed glass valves, the upper being worked manually by means of its long stem, while the lower is operated by the movements of the float 4; these are controlled by adjusting the level of the mercury in which the float swims. In use, the upper valve is normally closed and sealed with mercury poured in at the top. When a new liquid is to be introduced, the lower valve is raised into position; the upper valve is loosened, allowing the mercury to run through and seal the lower valve, and then removed. The apparatus is now evacuated through mercury valves 5 and 6. Meanwhile, some liquid is poured in at the top, and caused to fill 3 by warming and cooling. The contents of 3 are now boiled until free from air, as shown by the absence of a bubble in the capillary when the flame is removed and the vapor allowed to condense. A water jacket, 7, is fitted above the lock to prevent loss of vapor in boiling. When all air is removed, Valve 5 is closed, the upper valve of the lock is replaced and sealed, and the lower valve allowed to fall out by lowering 4; 8 is a multiple appendix kept immersed in water in a porous cup, so that its temperature is always slightly lower than that prevailing throughout the rest of the apparatus. Consequently, when Valve 5 is opened to allow some of the vapor of the liquid to expand into the rest of the apparatus, there is no danger that the pressure can rise so high as to permit condensation, and consequent error in measurement.

Vapor-measuring Devices. (B).—The quantity of vapor is measured in the small flask 9 or in this and the large flask 10, according to the position of the mercury in Valve 11. The volume being known, the temperature is fixed by the water-bath surrounding the flasks, and the pressure is measured on the manometer, which will be described later. The quantity of vapor is calculated by assuming the perfect gas laws.

Whatever errors are introduced in this method of measuring the vapors must be largely compensated by the method by which the flasks are calibrated, namely, by direct weighing of the vapor (benzene or carbon tetrachloride) which they deliver under conditions similar to those of the adsorption experiments. Water is measured as a liquid in the capillary buret 12, into which it is condensed for the purpose with the aid of ice applied to the outside. In this case the vapor space is reduced to a minimum.

Pressure-measuring Devices. (C).—Pressures from 0.0001 mm. to 0.05 mm. can be read on the quartz fiber manometer 14. (See note, p. 680.) For pressures from 0.02 mm. to 1 mm. the modified McLeod gage 15 is used. The use and limitations of this gage have already[6] been discussed. (Before the development of the quartz fiber gage. readings as low as 0.001 mm. were regularly made on the McLeod gage. These readings were quite reproducible, but when tested with the quartz gage were found to be seriously in error; by 10% at 0.01 mm., and by 100% at 0.001 mm. Consequently, no readings below 0.02 mm. are here reported, except in one case which will be discussed later.) Briefly, the gage is used by compressing the vapor which originally filled the main chamber into a portion of the calibrated tube 16, whose upper end is closed by the electric valve 13 and mercury-sealed. The ratio of compression varies from 20 to 100, and care is taken that the pressure after compression does not approach the condensing point. The level of mercury in 16 and also in evacuated tube 17 is determined by a micrometer microscope sliding on level ways; this gives the final volume and pressure, from which the original pressure is deduced. The organ also serves as a Töpler pump for manipulating the vapor, the charge being expelled through 13 into the measuring flasks, so that none is lost. Pressures from 1 to 100 mm. are read between 18 and 17, by means of the micrometer microscope. To permit still higher pressures to be read, the mercury is forced into the capillary 19, which is heated electrically or steam-jacketed in order to prevent condensation. The pressure is then read by a meter stick on Arm 20, the level being transferred from 19 by the inverted siphon 21 with evacuated arms. This device compensates errors due to the differences in bore and temperature between 19 and 20. 19 is not hot enough to generate an appreciable pressure of mercury vapor. but when any mercury gets into the charcoal cell 22 serious errors arise, and it becomes

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[6] Coolidge, This Journal, **45**, 1639 (1923).

necessary to pump it out and make a new reading. At high pressures, loss of mercury into other sections of the apparatus is stopped by Valves 37, 37.

The charcoal cell may conveniently be discussed here. It is as small as possible, with a capillary stem, and a glass-wool plug to prevent loss of charcoal, as even a minute grain of charcoal in the McLeod gage would ruin its performance. Experiments on much larger amounts of glass wool demonstrated that its adsorptive power is too small to introduce error; nevertheless, the plug is made as small as possible. The capillary stem was chosen in deliberate violation of the rules of vacuum technique, for the following reason. When the charcoal and the manometer are at different temperatures, their pressures will also be, in general, different. This difference has been assumed to be that given by West,[7] whose formula in the units here employed becomes

$$\frac{dp}{dT} = \frac{p}{2T + 0.33\,(r\sqrt{MT})\,p/\eta + 0.0051\,(r^2M)\,p^2/\eta^2}$$

where T is the absolute temperature, r the radius of the connecting tube, M the molecular weight and η the viscosity of the vapor. As the application of this equation is laborious and uncertain, it seemed wise to extend as far as possible the region over which the simple relation $dp/dT = p/2T$ holds. As inspection of the formula shows, this is accomplished by decreasing r as far as practicable.

Where the outgassing is to be performed at a higher temperature than 550°, a porcelain cell is used, consisting of a tube of about 8mm. bore closed at one end and glazed inside. As charcoal was found to attack the glaze, the tube is lined with a cylinder of platinum foil. In order to keep the charcoal from falling out, and to reduce dead space, a close-fitting silica tube, closed at both ends, is introduced after the charcoal, followed by a wisp of glass wool. A Pyrex capillary is then sealed as close as possible to the end of the filler, care being taken to work the glass well down inside the porcelain in order to get a tight joint with the glaze. This type of cell has proved very satisfactory.

The weight of charcoal used is determined as follows. A supply of charcoal is kept exposed in the balance case (not desiccated), and a standard sample of about 1.1 g. apparent weight is kept under identical conditions. Cells are filled from time to time with amounts equal in apparent weight to that of the standard, whatever that may be under the particular conditions prevailing, and therefore containing the same quantity (about 1 g.) of gas-free charcoal. The true weight is determined from time to time by weighing the evacuated cells (sealed off) and subtracting the weight of the glass. A vacuum correction is made.

The temperature of the charcoal is maintained by a block of ice, hollowed out to fit over the cell, or by a suitable liquid boiling in the jacket 23. The liquids used, with their approximate boiling points at the altitude of South Mountain, are ether, 33°; carbon disulfide, 45°; chloroform, 59°; water, 99°; bromoform, 148°; naphthalene, 216°; benzophenone, 303°. Temperatures are read to 0.1° on small thermometers completely immersed. Small variations caused by barometric fluctuations are corrected for by the aid of the isosteres. The choice of bromoform was not happy, as much trouble has been found with the temperature changing and bromine fumes coming off. However, the last sample purchased seemed much the most stable.

Valve 24 serves to permit the charcoal and quartz gage to be exhausted independently of the rest of the apparatus. This is necessary at the lowest pressures, as the walls of the apparatus must be heated in order to keep down the subsequent evolution of residual gas. It would be impossible to heat the whole apparatus in this way. 25 is a miniature MacLeod gage, which gives useful information concerning the working of the pumps (before 11 or 24 is opened), or the purity of the vapor from the loading

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[7] West, *Proc. Phys. Soc. London,* 31, 278 (1919).

devices, before it is introduced into the flasks. If the vapor is pure, it will condense completely when entrapped in the appendix and compressed. 26 is a cold trap to keep mercury vapor from the quartz gage. It is filled with ice and hydrochloric acid at or below —20°.

Mercury-controlling Devices. (D).—The mercury used in Valves 4, 5, 6, 11 and 24, is controlled by pressure or vacuum applied to Reservoirs 27, 27, or by rubber tube and leveling bulb, as at 28. The bulb is supported by a cord passing over a pulley with helical grooves, 29, such as is used in adjusting the height of shades in large windows; by this means it can be quickly secured in any position. The manometer is fitted with an iron reservoir, 30, the floor of which is covered by a sheet of leather, 31. When it is desired to clamp the mercury at any definite level for reading, Screw 32 is turned down, causing Lever 33 to press Plunger 34 against the leather pad, and tightly close the opening into Riser 35. This diaphragm valve construction eliminates the presence of tight threads, stuffing-boxes, stopcock plugs, etc., all of which may leak or stick under mercury pressure. It also has the advantage that the whole weight of the manometer and the mercury therein is supported directly from the floor in a straight line. 36 is a tell tale float, to give warning when the mercury falls so low in the reservoir that there is danger of air entering 35.

The method of working with the apparatus is as follows. When everything is properly evacuated, 6 and 24 are closed, 15 is filled with mercury up to the zero of the micrometer scale (about the position of the figures "16" in the diagram), 13 is opened (unless water is to be measured), and vapor driven from one of the loading devices into 9 and 10 (or, in the case of water, condensed in 12) 11 is now filled so as to leave communication open between 13 and 9, or 9 and 10, depending on whether a small or a large volume of vapor is to be measured; the pressure is read between 16 and 17. If, however, water is to be measured, 11 is filled so as to close off 9 and 10, 12 is immersed in water at 18°, and the volume occupied by the water read. In either case, the adjustments of 11 and 24 are not altered during the subsequent manipulations, so that the total amount of vapor in the system is determined only once. By manipulating the pump 15 and the temperature of the cell 22, various fractions of this amount can be transferred from flasks (or buret) to cell, or *vice versa;* the quantity in the cell is at all times known by measuring the amount remaining in the flask (or buret), and subtracting this from the amount originally introduced. Thus, each value of q is obtained directly as the difference of two measurements, and no accumulation of errors can occur. An exception is made at very low pressures. Pump 15 will not readily reduce the pressure below 0.001 mm. in the presence of vapors; when a low pressure reading is projected, it therefore becomes necessary to make the final pumping, just before reading, with the condensation pump. This is done by closing 15 partially, and opening 6 and 24 for two or three minutes. The amount of gas so lost is insignificant.

By way of numerical illustration, the details of the observation and reduction of the 59.5° isotherm of carbon disulfide on active charcoal outgassed at 550° may be given. At the time this observation was made, two apparatus were in use, one for high and one for low pressures; the flasks were smaller (1150 cc.) than those later found desirable, so that in order to saturate the charcoal used (0.992 g.) two fillings were necessary. In Table I, Col. 1 gives the total amount of vapor in the system, Col. 2 the amount remaining in the flask, Col. 3 the volume of the dead space, Col. 4 the quantity of vapor contained therein at the prevailing pressure and temperature, and Col. 5 the amount adsorbed per gram (q), obtained by subtracting 2 and 4 from 1 and dividing by 0.992. Col. 6 gives the logarithm of the amount adsorbed, log q. In Col. 7 the observed pressure is shown, and in Col. 8 the correction for thermal transpiration, obtained by substituting in West's formula the values $T = 300$, $r = 0.2$, $M = 76$, $\eta = 0.00012$, and integrating from 293° to 333° absolute, assuming the quantities given to remain constant over this range. The correction is very small, but at the highest temperature used, 303°, it may become ten times as great. Col. 9 gives the temperature of the experiment, and Col. 10 the correction which must be applied to the logarithm of the pressure at this temperature to reduce to the standard temperature, 59.5°. As will be seen from the isosteres (Fig. 11), this amounts to about 0.02 per degree, and is barely significant. Col. 11 gives the logarithm of the pressure, including corrections 9 and 10. Col. 12 gives the value of log p read from the adjusted curve (see below), and Col. 13 the difference between 11 and 12, which is presumably a measure of the experimental error, barring systematic errors that may have escaped detection. The first four determinations were made on the high-pressure apparatus, the remaining five on the low-pressure apparatus. The last two pressures were read with the McLeod gage.

TABLE I

CALCULATION OF 59.5° ISOTHERM FOR CARBON DISULFIDE

1	2	3 Cc.	4	5	6	7 Mm.	8	9 °C.	10	11	12	13
124.25	12.00	2.45	0.15	113.0	2.053	52	......	59.5	0.000	1.716	1.735	−0.02
225.1	72.3	2.45	1.7	152.4	2.183	637	......	59.6	− .002	2.802	2.815	− .01
225.1	65.8	2.45	2.6	168.0	2.199	955	......	59.4	+ .002	2.982	2.990	− .01
225.1	98.7	2.45	0.3	127.1	2.104	105	......	59.7	− .004	2.017	2.020	.00
114.0	12.1	20	.9	101.8	2.008	34.7	......	59.6	− .002	1.538	1.530	+ .01
114.0	48.6	20	.1	65.8	1.818	6.28	......	59.5	.000	0.798	0.820	− .02
114.0	80.8	20	.0	33.5	1.525	1.25	......	59.7	− .004	0.093	0.090	.00
38.7	23.4	350	.1	15.3	1.185	0.222	......	59.7	− .004	$\bar{1}.341$	$\bar{1}.350$	− .01
17.16	12.43	350	.0	4.56	0.659	0.0203	0.0002	59.7	− .004	$\bar{2}.308$	$\bar{2}.360$	− .05

It will be seen that the probable error, from internal evidence, is about 2%; in view of the great range covered and the rapid change of pressure with concentration, this is considered very satisfactory. At high pressures and temperatures the error may be greater, as the dead space correction (about 2 cc.) becomes as much as 10% of the total amount adsorbed; however, this effect is partly compensated by the less rapid change of pressure with concentration at high temperatures. The last measurement is too low by 10%, obviously because the McLeod gage begins to fail. In the case of benzene, the lowest pressures were read with the quartz fiber gage, which appears to be reliable to 2% as low as 0.001 mm. Owing to possible troubles with residual gas, incomplete equilibrium, etc., it is doubtful whether the adsorption measurements at these low pressures were as trustworthy as the gage itself; but as no new phenomena were manifested in this range, the curves behaving in exactly the same way as at higher pressures, it was felt that it would be hardly profitable to expend more effort on these very laborious low-pressure measurements, since little additional knowledge would be obtained.

It seems best to report the results in the manner adopted by the Editors of the International Critical Tables. The observed values were carefully plotted on large-scale coördinate paper, and families of curves drawn such that all pressures measured at a given temperature should lie on or near a smooth curve (isotherm), while those corresponding to a given concentration should approximate another smooth curve (isostere). From the curves thus adjusted, sufficient points were interpolated to enable the curves to be reconstructed within the accuracy of the experiments; these interpolated points are given in the tables following. The curves themselves are also shown on a reduced scale, in order to make apparent the general character of the relations involved; the observed points are shown plotted on the isotherms, in order to indicate the probable accuracy and the magnitude of the adjustments made. The systems of plotting were chosen so that the loci might be as nearly as possible straight lines. This condition led to the choice of two systems for the isotherms: a semi-logarithmic system (log p against q) for the values of concentration which approach saturation, and a full logarithmic one (log p against log q) for the lower values. The isosteres are naturally best plotted as log p against reciprocal absolute temperature. All three systems are given for most of the substances studied, in the case of adsorption by active charcoal, outgassed at 550°, and free from halogen contamination. Experiments with other outgassing temperatures, or with poisoned charcoal, are shown by characteristic symbols on the isotherm figures, but no curves are drawn, nor are values tabulated, because it seems unwise to accumulate numerical results obtained under other than standard conditions. The fresh, active 550° charcoal has yielded so many consistent results that it may properly be chosen as a standard adsorbent, at least within the scope of this work. In the tables, the variables are given in terms of q and log p, and also in certain other units which find application in adsorption work, namely pressure as fraction of the vapor pressure of the pure liquid at the given temperature (the logarithm of the reciprocal of this fraction is tabulated as log r), and concentration in g. of vapor per 100 g. of charcoal (marked w) and in cc. of liquid per 100 g. of charcoal, supposing the liquid to have its normal density at the given temperature and its own vapor pressure. Since this measure of the concentration changes with the temperature, even when q and w are constant, it has a different value for each point on the isosteres; its values are given in italics directly under each log p —log r. The liquid densities used in calculating these values were taken from the papers of Young on critical phenomena, or from the expansion formulas in Landolt-Börnstein-Roth. They are tabulated at the head of each table (marked δ), together with the logarithm of the vapor pressure of the liquid (log p), and the saturation adsorption concentrations (q_0, w_0, v_0), that is, the concentrations (by volume of vapor, weight, or volume of liquid) at which the adsorption mixture equilibrium pressure becomes equal to the liquid vapor pressure, as read from the adjusted isotherms. Special remarks follow the tables for each substance.

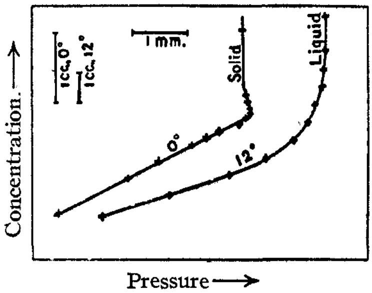

Fig. 2.—Benzene isotherms, enlarged.

In order to calculate the saturation concentration, it is necessary to assume that the isotherm cuts sharply the vertical line representing the vapor pressure of the liquid at the temperature in question, whereas if the adsorbed material is in a state approximating the liquid, one would expect its pressure to run smoothly into that of the liquid, the isotherm curving up near its upper end, and running into the vertical without break. Inspection of the observed points near saturation shows practically no evidence of such an effect. However, the question seemed worthy of more minute study. An apparatus was therefore arranged by means of which the dead space could be enlarged at will to about 200 cc. without disturbing the manometer. A sample of charcoal was outgassed and saturated with benzene at 12°. By enlarging the dead space, the concentration was reduced 3 or 4 cc. below saturation. The dead space was then very gradually decreased, and the manometer read every few seconds in order to determine the precise manner in which the pressure would approach that of the liquid. At first, the pressure increased regularly at the rate given by the slope of the isotherm; later, it began to increase less rapidly, but did not become constant as long as the experiment lasted, each addition of gas producing a smaller but still measurable increase in pressure. This behavior was observed repeatedly. It is shown in Fig. 2 by the curve marked 12° (one run only). In order to satisfy myself that the effect was not due to the accumulation of impurities, I repeated the experiment at 0°. The pressure rose at a uniform rate until it exceeded that of the solid by 0.2 or 0.3 mm.; it then began to fall until it reached a constant value, after which no increase whatever took place, although considerably more gas was added. This behavior also was repeatedly observed; one run is shown in Fig. 2. Since this apparatus was devised merely to find the shape of the isotherm, it was only roughly calibrated, and the absolute values involved were not determined. The cell contained no glass wool. A blank run at 12° without charcoal showed little or no curvature, proving that most of the curvature observed is due to the charcoal itself.

The interpretation of these facts seems to be that the adsorbed material, or at least its outer layer, is truly in the liquid state, *even below the freezing point of the free liquid;* when the adsorbed material is above the freezing point, its pressure runs continuously into that of the free liquid, but the transition region is so restricted that it may ordinarily be neglected, and the saturation value determined by drawing the isotherm straight across the liquid pressure line. It will be seen on the semi-log isotherms that the points thus obtained at different temperatures lie on smooth curves (drawn with dashes). On the other hand, when the adsorbed material is below the freezing point, the adsorption is abruptly terminated by the appearance of the solid as a new phase at a pressure lower than the saturation pressure of the liquid, so that the maximum concentration reached will be lower than one would expect by analogy with the results above the freezing point. These relations are shown in the semi-log benzene isotherm diagram, Fig. 4.

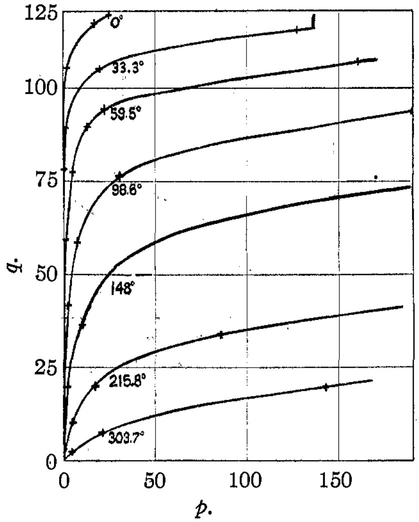

Fig. 3.—Benzene natural isotherms.

Additional evidence that the adsorbed material itself does not freeze is furnished by the facts that the 0° isotherm is exactly in the same relation to the other isotherms as in the case of other vapors which do not freeze, and that the heat of adsorption at 0° shows no anomalies compared with that of other gases. However, it seemed worth while to work at still lower temperatures; so a series of runs was made at about —33.5°, using a jacket of boiling liquid ammonia. No thermometer was available to measure the temperature, but some control could be obtained by saturating the charcoal at the end of each day's work, and observing the pressure of the solid which was formed. It varied considerably, and the other pressures read on the same day were corrected in proportion. The first three points obtained showed about 3 cc.; more adsorbed than was expected. This I supposed was due to a partial freezing and contraction of the adsorbed liquid, which left more room for further adsorption. The charcoal was then warmed to 0° and still showed abnormal adsorption. However, when the charcoal was warmed to 100°, and then cooled to 0°, the pressure rose almost to the expected amount. These points are shown in circles on the semi-log benzene isotherm graph. I was not able to reproduce this phenomenon; twenty or so measurements were made at —33.5° in this immediate neighborhood, and all gave results consistent with the curve (only four of these points are shown), which is in turn entirely consistent with the system of isosteres. (However, it should be mentioned that once, in a previous experiment, ammonia had been used to condense benzene in a sample of charcoal which was to be measured at 0°, and the pressure was found too low at 0°.)

TABLE II

BENZENE ADSORBED ON ACTIVE 550° CHARCOAL

SATURATED

t °C.	δ	Log p	q_0	w_0	v_0
0	0.898	1.42	120.3	41.9	46.7
33.3	.864	2.13	115.8	40.3	46.7
59.5	.834	2.58	112.7	39.3	47.1
60	.834	2.59	.....	....	....
98.6	.790	3.12	108.6	37.8	47.8
150	.729	3.64	.....	....	....

UNSATURATED

		0° log		60° log		150° log		300° log
q	w	p	r	p	r	p	r	p
0.1	0.035	....	....	....	....	....	....	$\bar{2}.94$
0.2	.070	....	....	....	....	....	....	$\bar{1}.25$
0.5	.174	....	....	....	....	....	....	$\bar{1}.70$
1	.348	....	....	....	....	$\bar{3}.59$	6.05	0.05
						0.48		
2	.696	....	....	....	....	$\bar{2}.14$	5.50	0.44
						0.95		
5	1.74	....	....	$\bar{4}.47$	6.12	$\bar{2}.80$	4.84	1.05
				2.085		*2.39*		
10	3.48	....	....	$\bar{3}.26$	5.33	$\bar{1}.46$	4.18	1.56
				4.17		*4.77*		
25	8.70	$\bar{4}.39$	5.03	$\bar{2}.50$	4.09	0.52	3.12	2.38
		9.69		*10.42*		*11.94*		
50	17.4	$\bar{3}.66$	3.76	$\bar{1}.64$	2.95	1.48	2.16	....
		19.4		*20.8*		*23.9*		
75	26.1	$\bar{2}.68$	2.74	0.55	2.04	2.30	1.34	....
		29.1		*31.2*		*35.8*		
100	34.8	$\bar{1}.89$	1.53	1.70	0.89	....	....	....
		37.6		*41.7*				

For the sake of comparison, a typical series of isotherms (benzene) is shown plotted on the natural scale in Fig. 3.

Benzene.—This substance has been most carefully studied. It has proved to be completely stable in contact with charcoal, even at the highest temperature reached, and seems to serve as a type of normal adsorption, the logarithmic isotherms varying gradually and continuously in slope from low temperatures and high concentrations, where p is roughly proportional to the twentieth power of q, down to high temperatures and low concentrations, where p becomes directly proportional to q. Six samples of active charcoal of various sizes, and three entirely independent groups of apparatus have been used in obtaining the points shown in Figs. 4 and 5. Crosses not otherwise marked represent determinations with 550° active charcoal, and solid curves drawn through them give the adjusted isotherms. Points below $q = 5$ are in general not shown on the semi-logarithmic graph, in order to avoid congestion; for the same reason points above $\log q = 2$ are omitted from the log-log graph. Crosses in brackets show pressures read on the McLeod gage, which are too low; they are included only in order to locate approximately the lowest points on the 215.8° isotherm, which were not measured on the quartz gage. Points in parentheses were obtained on the large, thoroughly outgassed

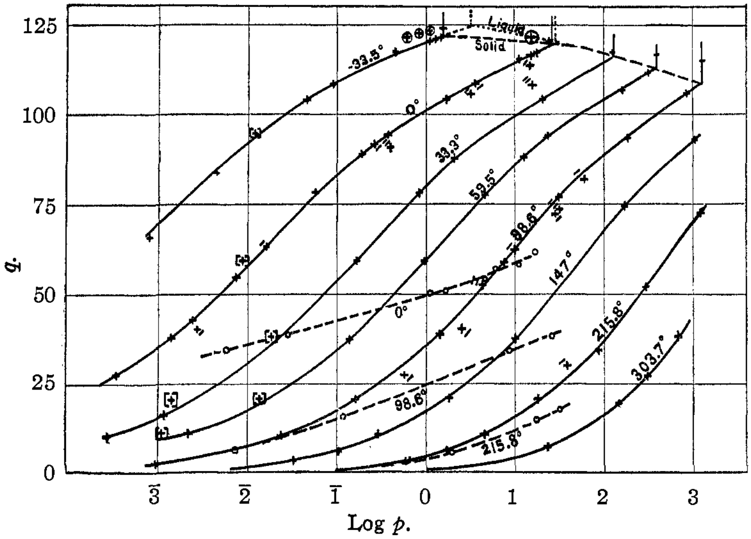

Fig. 4.—Benzene semi-log isotherms.

Outgassed at 350° or 400°,	one bar below cross and to right.
Outgassed at 550°,	plain cross.
Outgassed at 750° or 850°,	one bar above cross and to left.
Outgassed at 1050°,	two bars above cross and to left.
Inactive charcoal,	circle on dashed curve.

sample already mentioned. The vertical lines in the upper right-hand corner of Fig. 4 give the vapor pressure of the liquid or solid; they intersect the isotherms in the saturation points, which are correlated by a dashed line. A few determinations were made on charcoal outgassed at other temperatures. It will be seen that at low concentrations the efficiency of the charcoal improves with the temperature of outgassing, the 350° charcoal showing a higher, and the 850° and 1050° charcoals

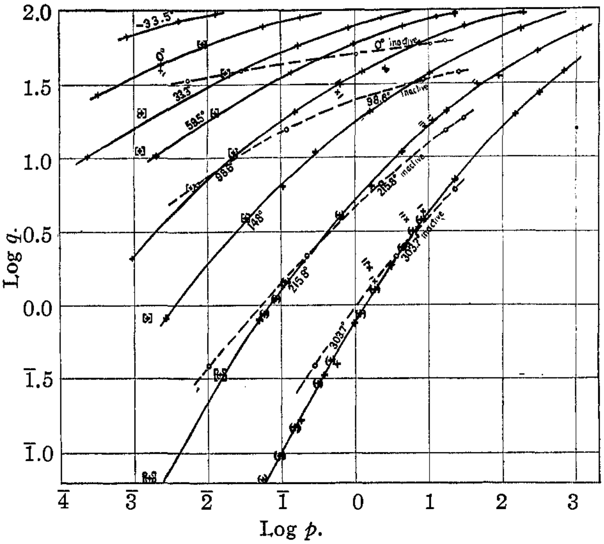

Fig. 5.—Benzene log isotherms.
See notation under Fig. 4.

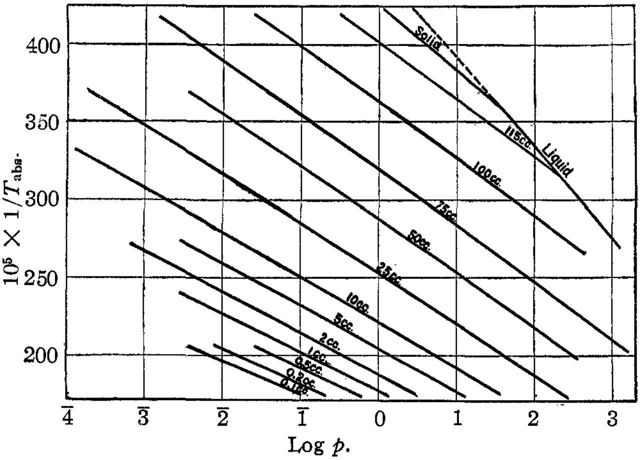

Fig. 6.—Benzene isosteres.

Table III

Ether, Adsorbed on Active 550° Charcoal

Saturated

t °C.	δ	Log p	q_0	w_0	v_s
0	0.738	2.26	109.5	36.2	49.0
33.3	.700	2.87	104.6	34.6	49.4
59.5	.667	3.23	100.7	33.3	49.9
60	.666	3.24	.....	....	....
150	.518	4.12	.....	....	....

Unsaturated

		0° log		60° log		150° log		215.8° log	300° log
q	w	p	r	p	r	p	r	p	p
0.3	0.099	....	....	....	....	....	....	....	$\bar{1}$.56
0.5	.165	....	....	....	....	....	....	....	$\bar{1}$.83
1	.331	....	....	....	....	....	....	$\bar{2}$.55	0.18
2	.662	....	....	....	....	....	....	$\bar{1}$.08	.60
5	1.653	....	....	....	....	$\bar{2}$.78	5.34	....	1.30
						3.19			
10	3.31	....	....	....	....	$\bar{1}$.76	4.36	....	1.92
						6.39			
25	8.27	....	....	$\bar{1}$.15	4.09	1.03	3.09	....	2.77
				12.41		*15.9*			
50	16.53	$\bar{2}$.54	3.72	0.42	2.82	2.13	1.99	....	....
		22.4		*24.8*		*31.9*			
75	24.80	$\bar{1}$.70	2.56	1.52	1.72	....	....	....	....
		33.6		*37.2*					
90	29.75	0.55	1.71	2.43	0.81	....	....	....	....
		40.3		*44.7*					
100	33.1	1.45	0.81	3.18	0.06				
		44.8		*49.6*					

a lower pressure than the 550° standard, for a given q. At high concentrations the relationship is almost exactly reversed; the 350° charcoal is indistinguishable from the standard, while the 850° is slightly, and the 1050° considerably less efficient. Some runs were also made on "inactive" charcoal, represented by circles and dashed lines. It was outgassed at 550°. It is much less efficient at high concentrations, but slightly more efficient at low concentrations.

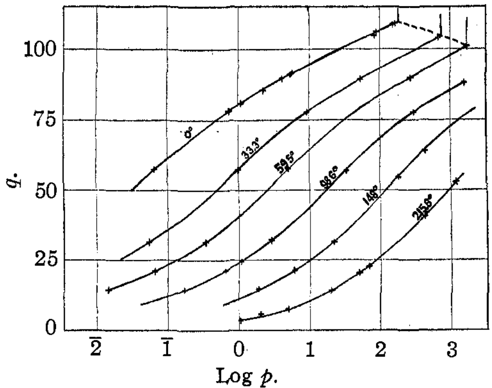

Fig. 7.—Ether semi-log isotherms.

Ether.—This substance behaves in a general way similarly to benzene. It is less readily adsorbed at high concentrations, but below about 2 cc. this relationship is reversed, as will be seen by superposing the ether and benzene isosteres. The slope of the logarithmic isotherms does not change so regularly as with benzene, but seems to remain constant over a considerable range within which, consequently, the Freundlich equation holds. Incipient decomposition was manifested at 303°, the pressure increasing slowly without seeming to approach a definite limit; for this

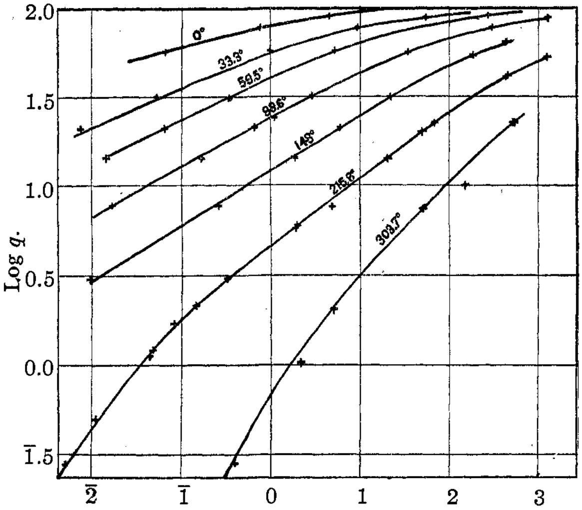

Fig. 8.—Ether log isotherms.

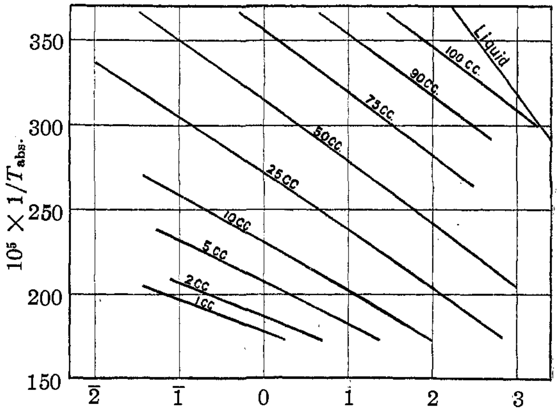

Fig. 9.—Ether isosteres.

reason, the 303.7° isotherm is not as satisfactory as the others. In the final series of accepted experiments, the effect of varying the temperature of outgassing was not tried; some of the preliminary experiments indicated that it would be of the same sign and magnitude as that later found with benzene; that is, that with increasing temperature of outgassing, the adsorption would be more complete at low concentrations and less complete at high concentrations.

TABLE IV

CARBON DISULFIDE, ADSORBED ON ACTIVE 550° CHARCOAL

SATURATED

t °C.	δ	Log p	$q°$	$m°$	$n°$
0°	1.290	2.11	171.1	58.1	45.0
33.3	1.241	2.68	164.6	56.0	45.1
59.5	1.198	3.06	160.0	54.4	45.4
60	1.197	3.07	.....	....	....
98.6	1.128	3.50	.....	....	....
150	.....	3.96	.....	....	....

UNSATURATED

	w	0° log p	0° r	60° log p	60° r	150° log p	150° r	300° log p
5	1.7	....	....	$\bar{2}.45$	4.62	0.19	3.77	1.83
				1.42		*1.63*		
10	3.4	....	....	$\bar{1}.01$	4.06	0.70	3.26	2.31
				2.84		*3.26*		
25	8.5	$\bar{2}.12$	3.99	$\bar{1}.82$	3.25	1.42	2.34	2.92
		6.59		*7.10*		*8.15*		
50	17.0	$\bar{2}.92$	3.19	0.52	2.55	2.06	1.90	....
		13.2		*14.2*		*16.3*		
75	25.5	$\bar{1}.48$	2.63	1.02	2.05	2.48	1.48	....
		19.7		*21.3*		*24.4*		
100	34.0	$\bar{1}.98$	2.13	1.50	1.57	2.91	1.05	....
		26.3		*28.4*		*32.6*		
125	42.5	0.46	1.65	1.98	1.09	....	....	....
		32.9		*35.5*				
150	51.0	1.27	0.84	2.76	0.31	....	....	....
		39.5		*42.6*				

TABLE V

METHANOL, ADSORBED ON ACTIVE 550° CHARCOAL

SATURATED

°C.	δ	Log p	$q_0°$	$w_0°$	$v_0°$
0	0.811	1.47	255.5	36.5	45.0
33.3	.780	2.28	244.5	35.0	44.9
50	.765	2.61	.....	....	....
59.5	.755	2.79	236.0	33.7	44.6
100	.714	3.42	.....	....	....
150	.649	4.01	.....	....	....

UNSATURATED

		0°		50°		100°		150°	
		log		log		log		log	
q	w	p	r	p	r	p	r	p	r
5	0.71	....	....	....	....	$\bar{1}$.04	4.38	0.41	3.60
						1.00		*1.10*	
10	1.43	....	....	$\bar{2}$.66	3.95	0.10	3.32	1.20	2.81
				1.87		*2.00*		*2.20*	
20	2.86	$\bar{2}$.20	3.27	$\bar{1}$.89	2.72	1.08	2.34	1.95	2.06
		3.53		*3.74*		*4.00*		*4.40*	
30	4.29	$\bar{2}$.78	2.69	0.40	2.21	1.52	1.90	2.33	1.68
		5.29		*5.61*		*6.00*		*6.60*	
50	7.15	$\bar{1}$.30	2.17	0.87	1.74	1.93	1.49	2.72	1.29
		8.82		*9.35*		*10.00*		*11.00*	
100	14.3	$\bar{1}$.87	1.60	1.33	1.28	2.35	1.07	3.10	0.91
		17.6		*18.7*		*20.0*		*22.0*	
150	21.4	0.25	1.22	1.68	0.93	2.67	0.75	....	....
		26.4		*28.1*		*30.0*			
200	28.6	0.67	0.80	2.09	0.52	....	....	....	....
		35.3		*37.4*					

Carbon Disulfide.—The behavior was in general similar to that of ether. There was slight decomposition at 303°. No experiments were performed on other than standard charcoal.

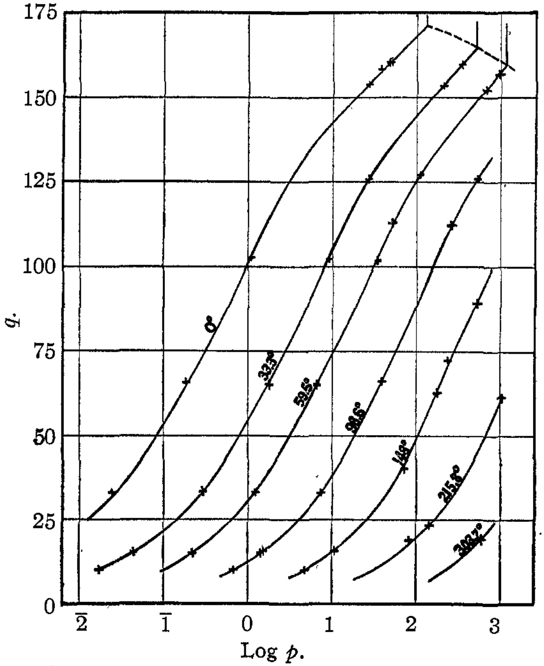

Fig. 10.—Carbon disulfide semi-log isotherms.

Methanol.—Because of rapid decomposition, it was impossible to work with this vapor above 148°. Only five isotherms are therefore shown. For the same reason, it was impossible to pump down to such low concentration as in the case of water, benzene and ether. The logarithmic isotherms are concave upwards, instead of convex, and show no indication of approaching a slope of unity, that is, a condition where p is proportional to q. This behavior is still more noticeable in the case of water vapor. The breaks near the upper ends of the isotherms are caused by a small discrepancy between the readings obtained on the high-pressure apparatus and those made on the low-pressure apparatus. The difference

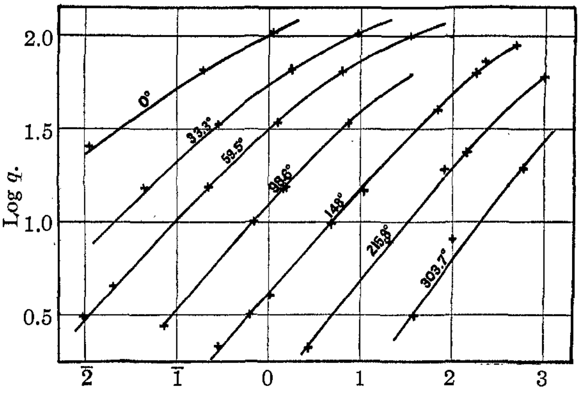

Fig. 11.—Carbon disulfide, log isotherms.

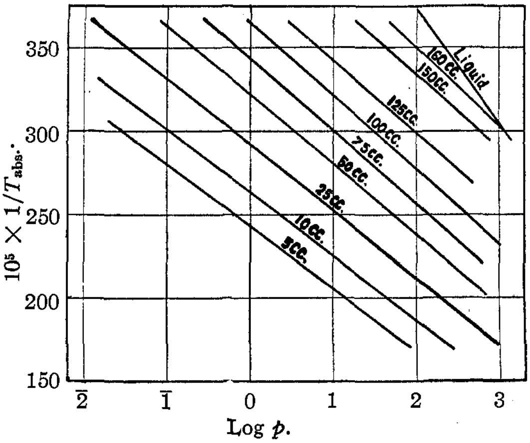

Fig. 12.—Carbon disulfide isosteres.

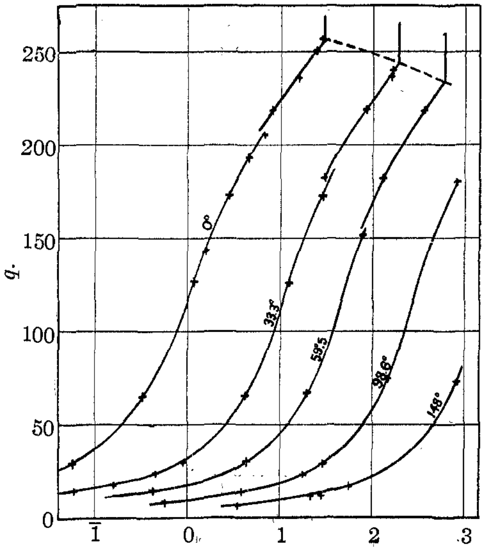

Fig. 13.—Methanol semi-log isotherms.

amounts to 3% in q, and it did not seem worth while to repeat the work in order to find the error. (In no other case was there a difference amount-

TABLE VI

CHLOROFORM, ADSORBED ON FRESH ACTIVE 550° CHARCOAL

SATURATED

t °C.	δ	Log p	q_0°	w_0°	v_0°
0	1.526	1.78	126.7	67.4	44.2
44.8	1.439	2.65	122.5	65.2	45.3
50	1.429	2.73	...	...	...
100	1.300	3.38	...	...	...

UNSATURATED

q	w	0° log p	0° r	50° log p	50° r	100° log p	100° r
10	5.32	...	...	...	...	$\bar{1}$.08	4.30
						4.09	
25	13.31	...	...	$\bar{2}$.95	3.78	0.16	3.22
				9.31		*10.23*	
50	26.62	$\bar{2}$.36	3.42	$\bar{1}$.94	2.79	1.06	2.32
		17.44		*18.62*		*20.46*	
75	39.9	$\bar{1}$.16	2.62	0.72	2.01	1.81	1.57
		26.15		*27.92*		*30.7*	
100	53.2	0.14	1.64	1.66	1.07	2.72	0.66
		34.86		*37.25*		*40.9*	

ing to 1% between readings on different apparatus.) Each isostere above q = 100 is calculated entirely from one or the other set of isotherms, so as to avoid errors in slope.

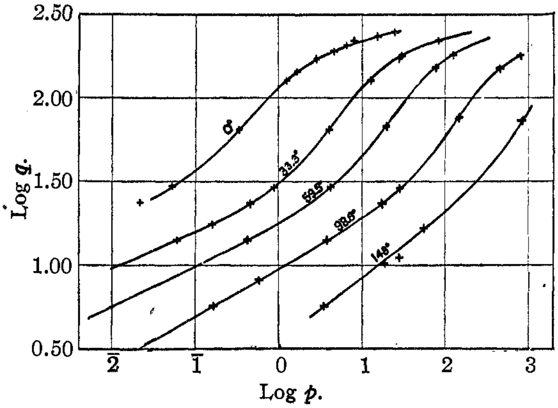

Fig. 14.—Methanol log isotherms.

Chloroform.—The substance decomposed rapidly above 99°, depositing white sublimate in the tubes. Low concentrations, therefore, could not

TABLE VII

CARBON TETRACHLORIDE, ADSORBED ON FRESH ACTIVE 550° CHARCOAL

SATURATED

t °C.	δ	Log p	q_0°	w_0°	v_0°
0	1.631	1.52	103.5	71.0	43.5
44.7	1.546	2.40	96.8	66.4	43.0
50	1.535	2.50	...	...	...
100	1.435	3.17	...	...	...

UNSATURATED

		0° log		50° log		100° log	
q	w	p	r	p	r	p	r
30	20.6	...	...	$\bar{2}$.77	3.73	0.04	3.13
				13.4		*14.3*	
50	34.3	...	...	$\bar{1}$.66	2.84	0.86	2.31
				22.3		*23.9*	
75	51.4	$\bar{1}$.13	2.39	0.76	1.74	1.92	1.25
		31.5		*33.5*		*35.8*	
90	61.7	0.25	1.27	1.78	0.72	...	...
		37.8		*40.2*			

be obtained, and logarithmic isotherms were not plotted, since the range covered is shown best on the semi-log scale. The curves and points thereon represent results on fresh samples of charcoal; points in parentheses show subsequent runs on the same samples, after intermediate outgassing. The impairment of the efficiency of the adsorbent is marked, and seems to be about the same at all temperatures and pressures.

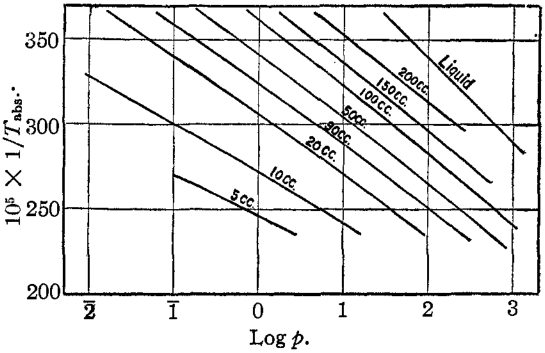

Fig. 15.—Methanol isosteres.

Carbon Tetrachloride.—The behavior is very similar to that of chloroform, and the same remarks apply. The crossing of the isotherms at about $q = 75$ is very interesting.

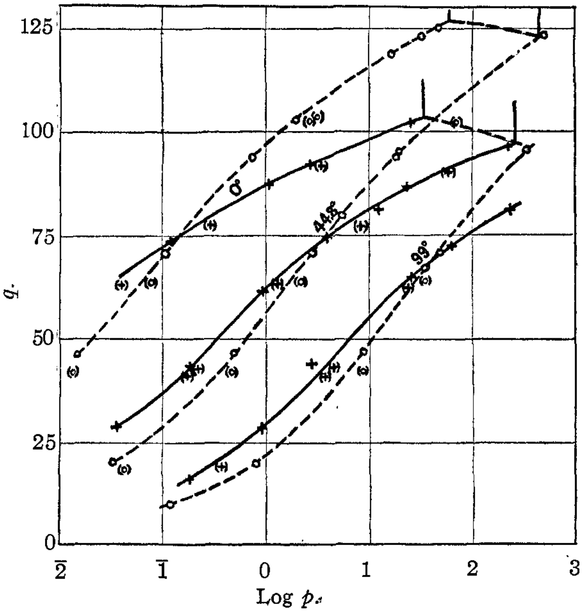

Fig. 16.—Semi-log isotherms. Chloroform, – – – – –; carbon tetrachloride, ———.

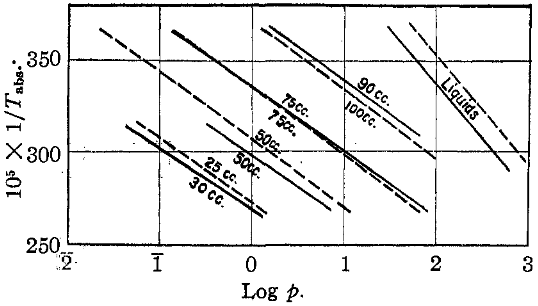

Fig. 17.—Isosteres. Chloroform, - - - - -; carbon tetrachloride, ———.

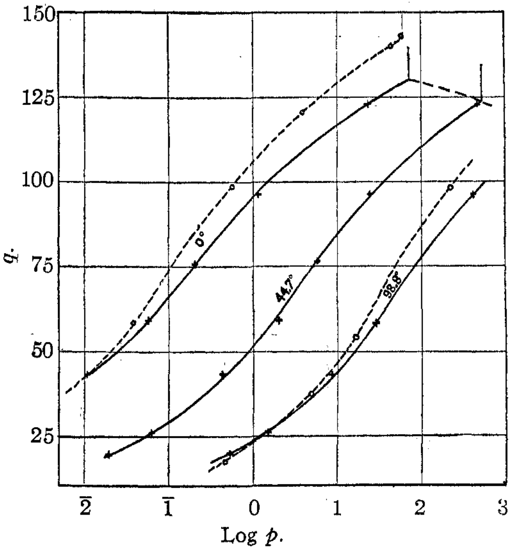

Fig. 18.—Semi-log isotherms. Ethyl formate, ———: methyl acetate, - - - - -.

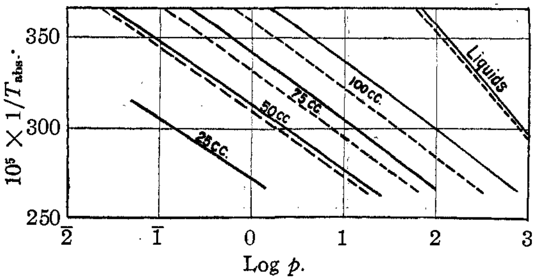

Fig. 19.—Isosteres. Ethyl formate, ———; methyl acetate, - - - - -.

TABLE VIII

ETHYL FORMATE, ADSORBED ON ACTIVE 550° CHARCOAL

SATURATED

t °C.	δ	Log p	$q_0°$	$w_0°$	$v_0°$
0	0.947	1.86	130.0	43.0	45.4
44.8	.889	2.73	123.5	40.8	45.9
50	.882	2.81	...	...	...
100	.811	3.47	...	...	...

UNSATURATED

		0°		50°		100°	
q	w	log p	r	log p	r	log p	r
25	8.26	...	...	$\bar{2}.75$	4.06	0.14	3.33
				9.36		*10.2*	
50	16.5	$\bar{2}.46$	3.40	0.08	2.73	1.24	2.23
		17.4		*18.7*		*20.4*	
75	24.8	$\bar{1}.32$	2.54	0.86	1.95	1.94	1.53
		26.2		*28.1*		*30.6*	
100	33.0	0.20	1.66	1.72	1.09	2.80	0.67
		34.9		*37.4*		*40.7*	

Methyl Acetate and Ethyl Formate.—Both substances decomposed above 99°.

TABLE IX

METHYL ACETATE, ADSORBED ON ACTIVE 550° CHARCOAL

SATURATED

t °C.	δ	Log p	$q_0°$	$w_0°$	$v_0°$
0	0.958	1.79	142.5	47.0	49.0
100	.822	3.44	...	...	...

UNSATURATED

		0°		100°	
q	w	log p	r	log p	r
25	8.26	...	...	0.18	3.26
				10.0	
50	16.5	$\bar{2}.36$	3.43	1.15	2.29
		17.2		*20.1*	
75	24.8	$\bar{1}.06$	2.73	1.75	1.69
		25.8		*30.2*	
100	33.0	$\bar{1}.80$	1.99	2.43	1.01
		34.5		*40.2*	
125	41.3	0.80	0.99	...	...
		43.1			

Water.—The adsorption of water vapor is evidently very peculiar. The logarithmic isotherms are even more strongly concave upwards than those of methanol. Below log q = 1, they cease to be reproducible, under the conditions of these experiments. The two branches of each isotherm shown were obtained in two experiments. In the first, the charcoal was thoroughly saturated with water by working it for several days at high concentrations; it was then pumped down and gave the upper branch of each curve. In the second experiment, the concentration did not exceed 3 cc. at any time; evidently the water was not driven in so thoroughly, for at any given temperature and pressure more water could be recovered from the charcoal than in the first experiment. In both cases, however, there appears to be a lower limit to the concentration, the pressure sud-

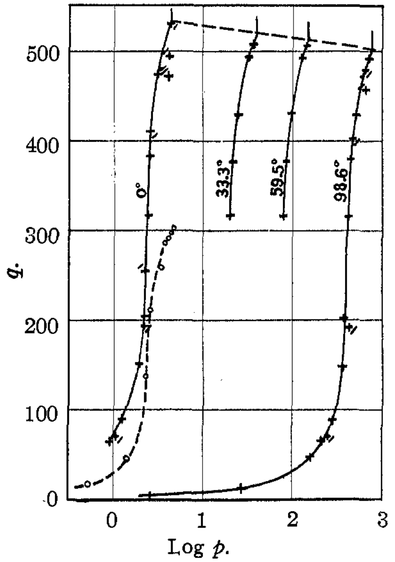

Fig. 20.—Water semi-log isotherms.

Outgassed at 350° or 400°,	one bar below cross and to right.
Outgassed at 550°,	plain cross.
Outgassed at 750° or 850°,	one bar above cross and to left.
Outgassed at 1050°,	two bars above across and to left.
Inactive charcoal,	circle on dashed curve.

Table X

Water, Adsorbed on Active 550° Charcoal

Saturated

t °C.	δ	Log p	q_0°	w_0°	v_0°
0	1.000	0.66	528	42.4	42.4
33.5	.995	1.59	517	41.5	41.7
50	.988	1.97	...	...	...
59.5	.983	2.16	511	41.1	41.8
98.6	.959	2.86	501	40.3	42.0
100	.959	2.88	...	...	...
150	.918	3.55	...	...	...
300	.70	4.81	...	...	...

UNSATURATED

		0° log		50° log		100° log		150° log		300° log	
q	w	p	r	p	r	p	r	p	r	p	r
10	0.80	$\bar{2}.00$	2.66	$\bar{1}.90$	2.07	1.03	1.85	1.80	1.75	3.14	1.67
		0.80		*0.81*		*0.83*		*0.87*		*1.14*	
20	1.61	$\bar{1}.16$	1.50	0.70	1.27	1.66	1.22	2.34	1.21	...	...
		1.61		*1.63*		*1.68*		*1.75*			
50	4.02	$\bar{1}.89$	0.77	...	...	2.20	0.68	...	...	...	....
		4.02				*4.19*					
100	8.04	0.14	0.52	...	...	2.46	0.42	...	...	...	...
		8.04				*8.38*					
200	16.1	0.37	0.29	...	...	2.62	0.26	...	...	...	...
		16.1				*16.8*					
400	32.2	0.43	0.23	1.74	0.23	2.71	0.17	...	...	...	...
		32.2		*32.6*		*33.6*					
500	40.2	0.57	0.09	1.92	0.05	2.88	0.00	...	...	...	...
		40.2		*40.7*		*41.9*					

denly dropping off while a small but easily measurable amount of water still remains unaccounted for, and presumably is present in the charcoal. It is conceivable, of course, that the water has disappeared in some other way, as by adsorption in the apparatus. This seems very unlikely, however, for in the second of the experiments just referred to, more than ten times the amount of charcoal was used, as compared with the first.

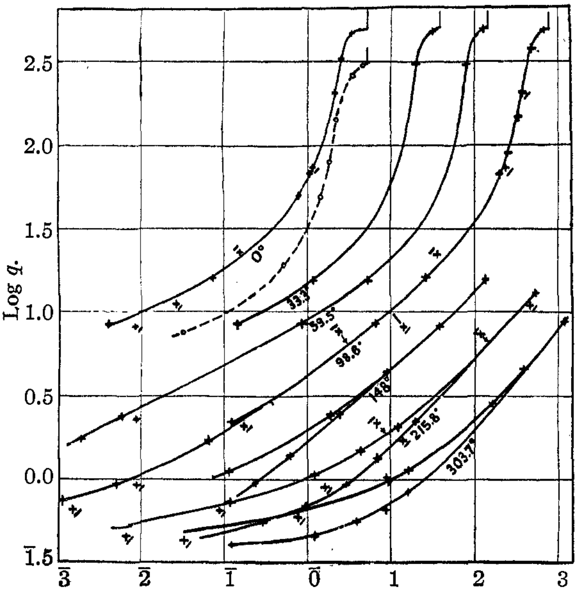

Fig. 21.—Water log isotherms.
See notation under Fig. 20.

Any error inherent in the apparatus should therefore be reduced to less than $^1/_{10}$ of its previous value, when referred to 1 g. of charcoal; but the loss of water is reduced only by 30%, and must therefore be due to a true retention by the charcoal. Isosteres below $q = 5$ are not calculated.

Most of the low pressures shown were measured with the McLeod gage, and have little absolute significance. Relatively, however, they serve to show the effects of variations in the temperature of outgassing; as was found with benzene, increasing this temperature leads to continuous improvement in adsorption at low concentrations, while at high concentrations no effect is observed up to 550°, and at 750° and above, the efficiency decreases. A run was made at 0° on inactive charcoal outgassed at 550°. Contrary to the experiment with benzene, this curve runs throughout parallel to the standard isotherm. Other inactive isotherms (not shown) showed a similar behavor.

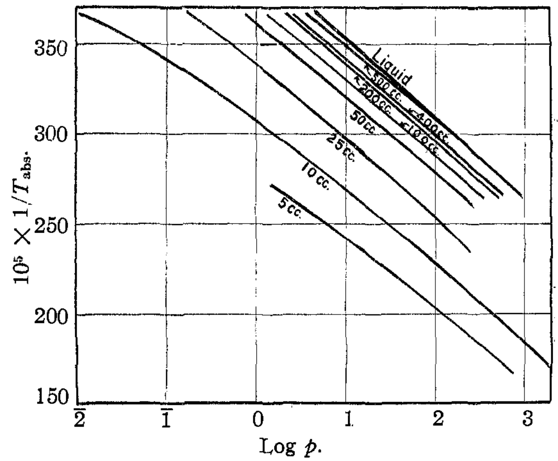

Fig. 22.—Water isosteres.

Additional experimental data, together with an attempted analysis and interpretation of the results, will be forthcoming in a later paper.

Summary

1. The conditions are discussed under which reliable adsorption measurements can be made. The charcoal must be outgassed at a definite maximum temperature, the system annealed at a moderately raised temperature after admission of the vapor, and readings taken during the pumping out of the vapor.

2. A standard adsorbent is defined, and the adsorption of nine vapors determined over a range of temperatures from 0° to 300° (where possible), and of pressures from 0.0002 mm. to 1000 mm.

3. Variations in the adsorbent are investigated in the cases of water and benzene.

4. Additional evidence is found that the adsorbed material exists as a liquid, even below the freezing point of the free liquid.

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[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, No. 88]

THE SPECTROPHOTOMETRIC DETERMINATION OF HYDROGEN-ION CONCENTRATIONS AND OF THE APPARENT DISSOCIATION CONSTANTS OF INDICATORS. I. THE METHODS

BY WALTER C. HOLMES

RECEIVED NOVEMBER 30, 1923

The degree of transformation of any indicator within the range of its utility is dependent upon the hydrogen-ion concentration of its solution. It may be measured with relative accuracy with the aid of the spectrophotometer and given numerical expression in terms of definite spectrophotometric ratios.

In the instance of an indicator which is colored in only one of its forms the suitable ratio (R_1) for defining the degree of transition at any point within the zone of color change is that of the intensity of the absorption at that point to that of an equal quantity of indicator under conditions insuring maximum intensity. With indicators which exhibit the essential behavior of monobasic acids (or bases), and with which complete transformation may be obtained, the numerical value of R_1 is that of the percentage color transformation. It may be determined by means of comparative absorption measurements carried out at a single wave length selected at or near the maximum of the absorption band of the colored form.

With two-color indicators it is possible to employ either or both of two ratios of this type, or to adopt a second type of ratio (R_2), that of the intensities of absorption at two wave lengths selected at or near the respective maxima of the two absorption bands in question. A ratio of this latter type affords a maximum degree of alteration per unit change in indicator transformation, since both the increase in one absorption form and the simultaneous decrease in the other contribute to that end. Its employment may prove further advantageous in other respects. Its value is unaffected by minor variation in the concentration of the indicator and the accuracy with which it may be determined, accordingly, is not impaired by any failure to insure complete uniformity in the quantity of indicator employed.