[Contribution from the Chemical Laboratory of Harvard University]

THE ADSORPTION OF WATER VAPOR BY CHARCOAL

By Albert Sprague Coolidge

Received December 9, 1926 Published March 9, 1927

Adsorption is generally classed as a "physical" rather than a "chemical" phenomenon. While this distinction has lost its former rigidity, it remains in many cases a useful qualitative guide. Thus, water is distinguished among all known substances by the extreme or anomalous values characteristic of many of its physical properties. It is to be anticipated, therefore, that its adsorption relations will prove in some respects peculiar, and that these peculiarities may throw some light on the general problem of adsorption.

In comparing the adsorption of water vapor with that of other substances, it is clearly desirable to use data obtained with the same adsorbent, and especially with that which has been most thoroughly investigated, charcoal. Comprehensive and satisfactory data for the system: charcoal-water seem not to exist. Investigations have been made by Bachmann,[1] Schmidt and Hinteler,[2] Lowry and Hulett[3] and Gustaver.[4]

These workers operated only at a single temperature, or within a narrow range of temperatures, and did not secure reversible results. In a previous paper[5] the author published data for the adsorption of water on coconut charcoal over an extensive range of temperatures and pressures, which, except for the smallest concentrations (quantities adsorbed), were believed to correspond to true equilibrium conditions. A typical isotherm is displayed in Fig. 1, together with isotherms for other substances upon the same adsorbent. The data are taken from the same paper, except those for ammonia, which have not been published. To facilitate comparison, the isotherms have been "reduced;" that is, the ordinates and abscissas are the logarithms of the ratios which the observed concentrations and pressures bear to the maximum concentrations and pressures, respectively, occurring at saturation at the given temperatures. The pressure ratio is known as relative pressure, since the maximum pressure is equal to the vapor pressure of the pure liquid.

Inspection of Fig. 1 makes clear the existence of two types of isotherms, which seem to be characteristic of non-polar and of polar substances, respectively. To the first class belong benzene, ether, chloroform and carbon disulfide, also sulfur dioxide, as incomplete experiments have shown. Their isotherms are in every part concave toward the axis of

---

[1] Bachmann, *Z. anorg. allgem. Chem.*, **100**, 1 (1917).

[2] Schmidt and Hinteler, *Z. physik. Chem.*, **91**, 103 (1916).

[3] Lowry and Hulett, This Journal, **42**, 1393 (1920).

[4] Gustaver, *Kolloidchem. Beihefte*, **15**, 185 (1922).

[5] Coolidge, This Journal, **46**, 596 (1924).

pressures, a behavior which has been repeatedly described and is regarded as normal. To the second class belong methyl alcohol, ammonia and water. Their isotherms are mostly convex towards the axis of pressures, and only near saturation is the normal behavior shown. The water isotherm evidently occupies an extreme position.

Unfortunately, the data from which the water isotherm is plotted were the least reliable of any, especially at low concentrations, where equilibrium failed to be reached by the methods which had proved effective with other vapors. For a given concentration and temperature, the pressure varied according to the previous history of the system, and was always lower than seemed reasonable. Some of the water appeared to be held combined in an irreversible manner, and could not be completely recovered even at 300°. More adequate knowledge of adsorption equilibrium conditions within this range seemed greatly to be desired, and work was carried forward with this end in view.

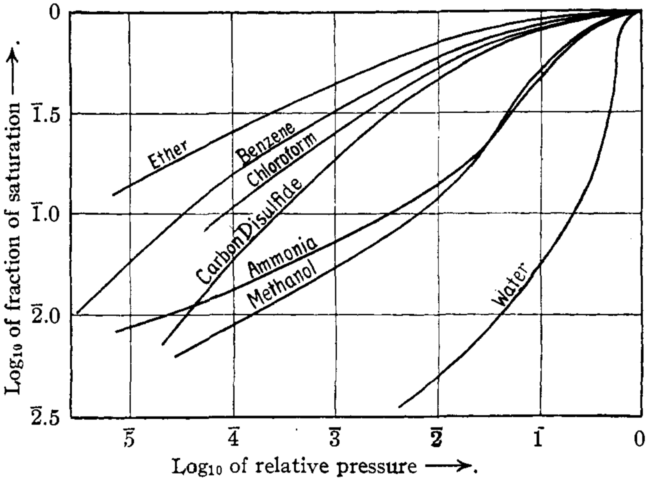

Fig. 1.

The pressure measurements were made by the same devices previously employed. As a precaution, they were calibrated by observing the known vapor pressures of ice at known temperatures. New methods, however, had to be found for determining the concentrations, or quantities of water vapor adsorbed. The first to be tried was one due to McBain,[6] in which the charcoal, in a suitable container, was suspended from a helical spring balance of fused quartz, the extension of which, as determined by the cathetometer, gave at once and without any corrections the weight of water adsorbed at any given time. The great drawback in this plan was found to lie in the large free space which has to exist in order to give

---

[6] McBain and Bakr, This Journal, **48**, 690 (1926).

the spring room to function freely. While this dead space does not, as in most schemes, give rise to a correction, it makes it difficult to establish in any particular experiment the concentration desired; in particular, it renders impossible the process of annealing, which consists in raising the temperature of the system without permitting the escape of vapor from the charcoal. This is referred to as Method A.

It was found better to place the charcoal in a simple glass cell, and keep the volume of the free space as small as possible, especially when working at pressures so high that the quantity of vapor in the dead space was a significant fraction of the whole. This made possible the direct determination of isosteres, in which the author was especially interested. The total amount of vapor in the system was determined by one of two methods. Small amounts were measured out of a gas buret, steam-jacketed and maintained at 600 mm. pressure. Under these conditions, adsorption of vapor by the buret walls must have been either negligible or constant, for the adsorbed water could always be quantitatively recovered by heating the charcoal and cooling the buret. When the valve was closed and the buret again heated, the pressure and volume were found to be the same as before. Larger amounts of water were determined by being condensed, at the conclusion of the experiment, in a small bulb which could be sealed off and weighed. The volume of the dead space was determined by calibration with hydrogen, the charcoal being at 218°, and the amount of vapor calculated to fill this space under the conditions of each experiment was subtracted from the total amount in the system to give the amount adsorbed. This correction amounted to 25 and 10% for charcoal temperatures of 156° and 100°, respectively, and low concentrations. At high concentrations it was relatively less. For determining the isosteres, the correction was transferred to the pressure; that is, the pressure which the system would have had if all the vapor had been adsorbed was calculated. This could be done with approximate knowledge of the forms of the isotherms. This is referred to as Method B.

During some experiments with sulfur dioxide and the same activated coconut charcoal used in the previous work, made with the spring balance, it was noticed that the weight of the charcoal suffered a permanent increase after each adsorption, which not even prolonged outgassing at 550° would entirely remove. The thought that the gas might be reacting with alkaline ash suggested extracting the charcoal with hydrofluoric acid. Some charcoal was accordingly so treated for several days, after which it was steamed for a month. By this treatment the ash was reduced from 1.7 to 0.4%, and the retention of sulfur dioxide eliminated.

The water isotherms were next determined, and found to exhibit a profound change, which is illustrated in Fig. 2. (In this figure the amounts adsorbed, in milligrams, are plotted against relative pressures.) A,A represent the isotherms of the untreated charcoal at 0° and 100°, the higher curve always corresponding to the lower temperature. B,B are the isotherms of the extracted charcoal. It will be seen that the ultimate capacity of the charcoal was not affected by the treatment, but that the amount adsorbed at relative pressures below 0.3 became very much less. The range over which the pressure is nearly independent of the concentration became much greater. The irreversibility at low concentrations was found to be greatly diminished. The pressures read on falling concentrations still lagged somewhat below those on rising concentrations, but the effect was small, and all the water (within 0.1 mg. per g. of charcoal) came off in a few minutes of pumping at 184°.

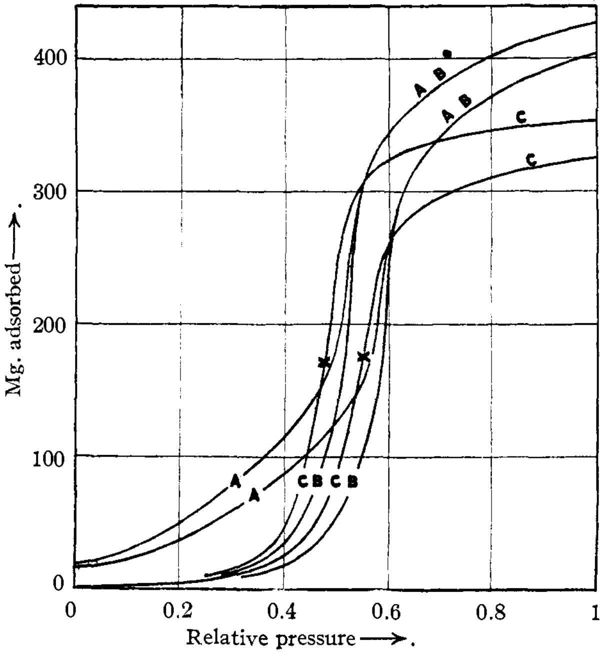

Fig. 2.

Entirely analogous results were obtained with ammonia. A few experiments on benzene showed that the capacity near saturation was again unaffected by the treatment with hydrofluoric acid. At 303° and a concentration of 10 mg. per g. of charcoal, the capacity was decreased by 30%, and at a concentration of 0.3 mg., below which Henry's law holds, the decrease reached 50%. The general form of the isotherm was not changed. No irreversibility of the kind displayed by the inorganic vapors had been noticed, even with the untreated charcoal.

A tentative explanation of these striking phenomena was desired as a basis for further work, and was suggested by the relations illustrated in

Fig. 3. In this figure are displayed (in natural, not logarithmic scale) the reduced isotherms of water on several widely different adsorbents, at ordinary temperatures. The curves for purified coconut and sugar charcoals are from data given below. That for birchwood charcoal is by Lowry and Hulett,[3] that for silica gel is by Anderson,[7] and shows the usual hysteretic loop, drawn shaded. The curve for chabasite is from unpublished observations made in this Laboratory by Mr. J. C. Woodhouse, while those for platinum and glass were determined by McHaffie and Lenher[8] by a method which could not detect the presence of adsorbed films too stable to evaporate except at very low relative pressures. Such films certainly exist on glass; the lower part of the glass isotherm (and perhaps the platinum isotherm also) is, therefore, not trustworthy.

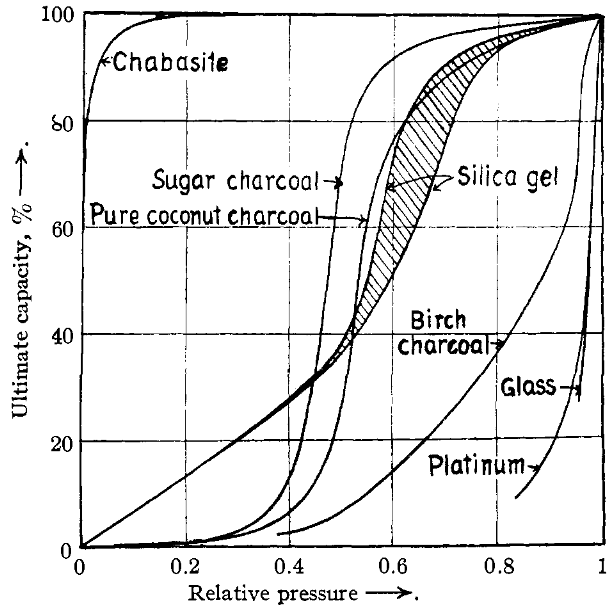

Fig. 3.

Fig. 3 shows that at small concentrations carbon is an exceedingly poor adsorbent for water vapor. None of the charcoals considered adsorbs more than about 1% of its ultimate capacity at a relative pressure of one-third. The inorganic substances, on the other hand, adsorb much better at low concentrations. With ammonia, conditions are similar. Chabasite holds ammonia with extraordinary tenacity, and glass surfaces take up large quantities of the gas, which escapes only at low relative pressures. On the other hand, benzene, an example of an or-

---

[7] Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

[8] McHaffie and Lenher, *J. Chem. Soc.*, **127**, 1559 (1925).

ganic or non-polar substance, is scarcely adsorbed at all by chabasite, and very little by glass, while by charcoal it is so strongly held that half of the ultimate capacity is retained even at a relative pressure of one one-thousandth. This is entirely in accord with our ideas of hydrophilic and hydrophobic substances. Charcoal is a typical hydrophobic substance. It is difficultly wet by water, and in aqueous solution is able to adsorb small concentrations of almost every substance, undoubtedly with corresponding displacement of water; this seems to prove that the direct attraction of carbon for water is exceptionally small.

Therefore, it is not surprising that small amounts of hydrophilic impurities, probably siliceous, should exercise a profound influence upon the adsorption of water by carbon at low concentrations, and should be able to cause a serious irreversible retention. At higher concentrations, where the determining factor is the volume of capillary space available, the effect would not be noticed. On the other hand, in the case of organic vapors, the effects of the impurities would be relatively unimportant at any concentration.

In view of these considerations, the next logical step was to prepare a still purer form of charcoal. Pure cane sugar was recrystallized from conductivity water with the aid of alcohol, and charred in a platinum basin. The charcoal was heated in a vacuum for 24 hours at about 1000°, and then in steam for 90 minutes at about 850°. No accurate means of maintaining or determining the temperatures used were available, and

TABLE I

WATER ISOTHERMS ON SUGAR CHARCOAL (IN ORDER OF DETERMINATION). METHOD A

Concn. (mg. of H_2O per g. of charcoal)	Press., mm. of Hg	Temp., °C.	Concn. (mg. of H_2O per g. of charcoal)	Press., mm. of Hg	Temp., °C.
2.1	120	100	6.1	1.47	0
4.2	200	100	4.6	1.17	0
171.3	3.41	0	2.7	none	0
174.0	3.82	0	174.5	4.56(?)	0
167.2	3.07	0	172.6	3.91	0
161.0	2.71	0	171.8	3.84	0
151.8	2.49	0	179.0	4.58	0
127.5	460	100	176.3	4.23	0
66.0	400	100	169.0	3.41	0
4.5	210	100	162.8	2.82	0
10.2	300	100.5	162.8	760	100
44.7	390	100.5	161.4	750	100
162.3	750	100.5	150.5	580	100
160.0	740	100.5	159.1	670	100
138.8	480	100.5	150.5	560	100
121.5	2.29	0	142.0	500	100
72.3	2.12	0	109.0	430	100
23.0	1.82	0			

different specimens of the charcoal prepared in this way had slightly varying properties as adsorbents. The ultimate capacity was less than half that of an equal weight of coconut charcoal, but there seemed to be no good reason for spending time in an effort to improve the capacity by varying the method of preparation or activation. The ash was unweighable.

The water isotherms of this charcoal at 0° and 100° are tabulated in Table I and shown in Fig. 2, marked C,C. In order to facilitate comparison with those of the extracted charcoal (B,B) the ordinates have been doubled, so that the scale in the left-hand margin gives the number of milligrams adsorbed by 2 g. of this charcoal. It will be observed that there is a general resemblance between the two families of isotherms, but that it is by no means possible to bring them into coincidence by merely changing the scale. In other words, adsorption is not determined solely by the extent of the carbon surface, for if it were, the quantities adsorbed by two different specimens of adsorbent having the same surface would be equal at every pressure.

The behavior of this charcoal at low concentrations was the object of special interest, and was investigated thoroughly. It may be summarized thus. Provided a partial pressure of about 0.1 is at no time exceeded, adsorption is rapid and reversible (within 0.02 mg. per g.) at and above 100°, and Henry's law holds. (See Table II.) Systems in equilibrium at 100° can be cooled isosterically as low as —30°, and show pressures which still obey Henry's law. If much vapor is withdrawn

TABLE II

HENRY'S LAW AT HIGH TEMPERATURES. SUGAR CHARCOAL. METHOD B

Concn. in arbitrary units, approx. 0.075 mg. per g. of charcoal. Probable error, 0.1 unit.

Concn.	Press., mm.	Ratio	Temp., °C.
1.8	7.6	4.2	100
4.0	17.9	4.5	100
10.1	41	4.1	100
20.6 (?)	72	(3.2)	100
47.7	160	(3.3)[a]	100
23.2	93	4.0	100
10.3	42	4.1	100
4.7	18.4	3.9	100
0.7	19	27	218
1.2	34	28	218
2.5	79	31.5	218
5.0	157	31.5	218
20.7	670	32	218
20.4	620	30.5	218
11.5	360	31	218
5.4	155	29	218
3.0	82	27	218

[a] Concentration exceeds range within which Henry's law holds.

at a low temperature, the pressure tends to be lower than that corresponding to the amount remaining, but after gentle heating (annealing) the pressure rises to its normal value. No experiments were made to determine the existence of a lag in the opposite sense when vapor is added to the cold charcoal. Above partial pressures of about 0.1, Henry's law fails, but in the sense opposite to that generally met in adsorption isotherms; the pressure increases less than proportionally to the concentration, until at a partial pressure of about 0.5 it becomes almost constant. The departure from Henry's law increases as the temperature is diminished from 218° to 20°, as would be expected; surprisingly enough, however, the isotherms for 20, 0 and —30°, are practically indistinguishable (the relative pressure at —30° being calculated with reference to the vapor pressure of water, not ice, at this temperature). No lag appears to exist in this range. However, the curvature of the isotherms is so sharp that accurate interpolation between observed points is impossible, and the precise location of each isotherm and study of possible lag would involve a great many determinations. Since the pressure changes so little with concentration, the irreversible retention of a few milligrams would not be expected to produce much pressure change. When vapor is removed at low temperatures until the system enters the region where Henry's law should hold, lag does appear. In one case, the charcoal was pumped at 0° until no more vapor seemed to come off, and was found to retain 2.7 mg. per gram. However, annealing at 156° was always sufficient to bring the pressure up to the normal value (when the low temperature was again attained).

This behavior is in striking contrast to that of benzene in small concentrations on coconut charcoal. In that case, it was found that the pressure always tended to be higher, rather than lower, than that which was judged by tests of reproducibility and regularity to be the normal value. Lag appeared when vapor was added, but not when it was withdrawn. (This was doubtless due, at least in part, to small traces of vola-

Table III

Water Isotherms and Isosteres on Sugar Charcoal (Determined after Annealing). Method B

Concn., mg. per g.	Pressure, mm., at —30°	0°	20°	61°	100°	156°
0.33	0.0175	0.23	0.76	5.8	20.5	76
1.20	.066	.78	2.85	19.5	74	257
3.39	.125	1.48	5.5	45	173	710
13.14	.16	1.85	7.2	68	330	1500
154[a]	.22	2.77	11.6	120	760	..
159	...	3.20	13.2	142	...	..
167	.28	4.00	16.8	...	...	..
Water	.38	4.58	17.5	156	760	4180.
Ice	.28	4.58	..	...	...	..

[a] Interpolated.

tile impurities.) Annealing caused the pressure to drop to its normal value.

The isotherms in the region under discussion, as determined after annealing, are given in Table III and shown in Fig. 4. The scale of the latter is relative pressure against milligrams per gram, but the charcoal used was a different sample from that on which Curves C,C, Fig. 1, were determined, and had an ultimate capacity about 5% less. It will be noticed that in contrast to the usual arrangement the isotherms for the higher temperatures lie above those for lower temperatures (except below 20°). Considering the form of a single isotherm, this is not surprising. We may

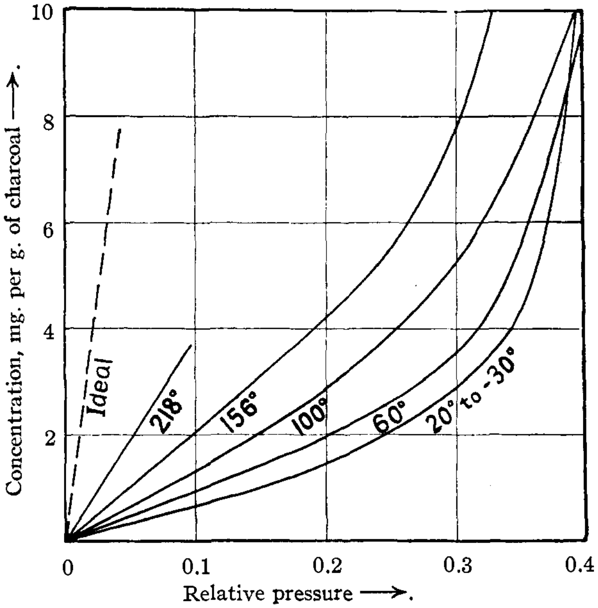

Fig. 4.

regard an "ideal adsorption," after the analogy of the "ideal solution," as one in which Henry's law holds throughout the entire range. The isotherms would be straight lines connecting the origin with the point of saturation. The beginning of such a line is shown dashed on Fig. 2. Because the actual isotherms lie below this line in this region, we should expect them to move toward it as the rising temperature causes the adsorption to become more nearly ideal. In the same way, since the isotherms at high concentrations lie above the ideal isotherm, we should expect them to move down with rising temperature. This they invariably do, even when allowance is made for the temperature coefficient of the saturation point itself. At some intermediate point, the real and ideal isotherms must cross. This point is marked X on the 0° and 100° isotherms in Fig. 2. It will be seen to occur on the two isotherms at almost exactly the same concentration, but this is probably a mere coincidence. Neither the relative pressure nor the percentage of saturation is the same for the two points, nor do points representing equal percentage of saturation have the same relative pressure. The temperature coefficient of the relative pressure, for constant concentration, remains positive for some distance below the points X, so that in this region the behavior becomes less ideal with rising temperature. While the behavior of ideal solutions can be predicted theoretically with the aid of simple assumptions which in many cases are nearly fulfilled, this is not true of ideal adsorptions, and the analogy cannot be expected to bear any great weight of reasoning.

These relations become very interesting when we consider their bearing on the energy changes involved. The "net heat of adsorption" or heat of transfer from free liquid to adsorption may be obtained by substituting the relative for the absolute pressure in the Clapeyron equation.[9] The distance between two isotherms, measured along a line of constant concentration, evidently indicates the sign and magnitude of the net heat. More accurate values may be obtained from the slopes of the isosteres as directly determined, but the qualitative relations are more easily apprehended from the isotherms. The net heat is zero when the relative pressure is the same at different temperatures, which is true for low concentrations between —30° and 20°. Above 20° it is negative, decreasing rapidly as the temperature rises. This would seem to be the first case in which the total heat of adsorption has been found to be less than the heat of vaporization. At higher concentrations the net heat is positive but very small; it increases slightly as saturation is approached. This is again the reverse of the usual case. The heat of adsorption almost always decreases with rising concentration. Williams,[10] however, found a minimum in the heat of adsorption of sulfur dioxide.

Fig. 5 shows the isosteres, logarithm of pressure (not relative pressure) being plotted against reciprocal temperature. The vapor pressures of water and ice are also included. The slopes of the lines are directly proportional to the heats of adsorption, evaporation or sublimation, and the difference in slope between an isostere and the water curve gives the net heat of adsorption at the given temperature. The relations discussed above can be easily verified, and others deduced. The isosteres are parallel below concentrations of about 1 mg., at distances corresponding to Henry's law. (Attempts were made to get isosteres as low as 0.1 mg., but the results were irregular, probably because of adsorption troubles from the glass, not surprising in view of the fact that only 1 mg. of water vapor was contained in a total volume of about 300 cc. Duplicate isosteres at about

---

[9] Coolidge, THIS JOURNAL, **48**, 1808 (1926).

[10] Williams, *Proc. Roy. Soc. Edinburgh*, **37**, 161 (1917).

0.3 mg. were parallel to those at about 1 mg., and it seems unlikely that if Henry's law holds over this interval it should break down at lower concentrations.) The lower isosteres are markedly convex upward (negative temperature coefficient of heat of adsorption), while the upper ones are nearly straight. Here is still another anomaly, for most substances give straight isosteres at low concentrations, and convex ones near saturation.

Interesting relations are disclosed near the triple point. The highest isostere shown has a slope greater than the water line, but less than the ice line, so that it is terminated at each end by one or the other of these lines. This means that an adsorption nearly saturated at 0° becomes saturated with respect to water when warmed, and with respect to ice when cooled. The capacity of charcoal for water has, therefore, a maximum (aside from metastable states) at 0°. The heat of transfer from ice to charcoal is negative at all concentrations. In the case of benzene, it is always positive.

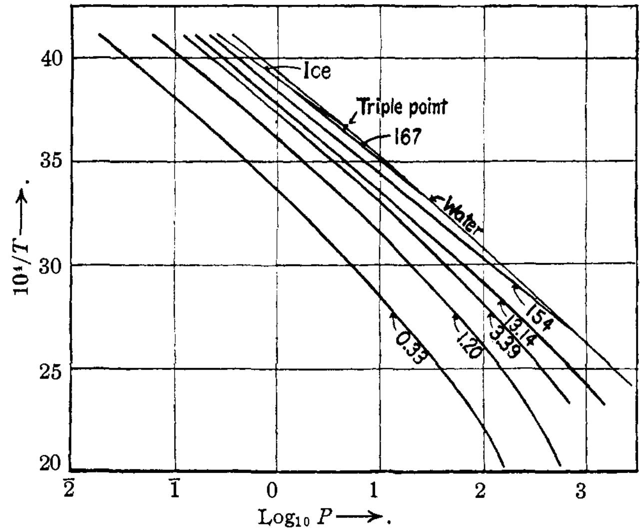

Fig. 5.

Within the range of validity of Henry's law, the molal heat and energy of adsorption are independent of the concentration, and may for many purposes be treated thermodynamically as analogous to the molal heat and energy of evaporation of a volatile pure solid. The heat is given by the familiar equation $\lambda = -R\, \mathrm{d}\, lnP/\mathrm{d}\,(1/T)$, it being understood that the differentiation is performed at constant concentration. The corresponding energy change is found by subtracting RT, the work done upon the system during the reversible adsorption of a mole of gas by a large quantity of adsorbent. The following numerical values, in calories per mole, were calculated from the average slopes of the two lowest isosteres, between each two temperatures of observation, and referrred to the mean of these temperatures.

Temperature, °C.	−15	10	40	80	128	187
Heat, cal.	11,100	10,000	9300	8300	7200	5200
Energy, cal.	10,600	9,400	8700	7600	6400	4300

The decrease in the energy with rising concentration is evidently due to the fact that the specific heat of adsorbed water exceeds that of water vapor (more strictly speaking, the heat capacity of the charcoal-water system exceeds that of the separate components). We cannot very well discuss C_p for adsorption systems, for if the temperature is changed and the pressure kept constant, gas will be desorbed, and the heat absorbed, although perfectly definite and susceptible of thermodynamic treatment in the same way as any other C_p, will from a kinetic point of view be not a specific heat at all, but a latent heat of change of state. In order to have a quantity which can be treated by rigorous thermodynamic methods, and which shall at the same time represent from the kinetic viewpoint the rate at which the system takes up energy when its temperature is changed at constant concentration, we may define C_{vx} as the specific heat of an adsorption system confined within a rigid envelope enclosing only a negligible volume in excess of that occupied by the solid adsorbent. Under all ordinary conditions, the quantity of gas occupying the free space will be negligible, and no significant fraction of the energy absorbed with rising temperature will be used up by evaporating gas molecules. (For example, if 10 g. of charcoal is confined in a volume not more than 2 cc. greater than that occupied by the carbon itself together with the pores, which are considered to be part of the adsorbent in the sense that the gas which occupies them is considered to be adsorbed, then at no temperature below 100° will the amount of water vapor in the free space exceed 1% of the amount adsorbed, and heating at constant volume will be sensibly identical with heating at constant concentration.)

Now let us suppose the fixed volume to be connected, by means of a valve, with a cylinder and piston of infinitesimal volume, in the sense that the amount of gas required to fill it is negligible with respect to the total amount adsorbed. We can then imagine the following cyclical process, in which we are interested only in the total energy changes. First, the piston is withdrawn isothermally, allowing dn moles of vapor to be desorbed. The energy of the system is increased by Udn, where U is the energy (or internal heat) of adsorption. The heat capacity of the system at constant volume has become $C_{vx} + (C_v - \bar{c}_v)\text{d}n$, where C_v is the molal heat of the vapor, and $\bar{c}_v$ is the "partial molal heat capacity at constant volume" of the adsorbed vapor. The valve being closed, the system is next heated at constant volume, taking in the energy $[C_{vx} + (C_v - \bar{c}_v)\mathrm{d}n]\mathrm{d}T$. As a result, the pressure in the adsorption chamber rises above that in the cylinder. The piston is therefore advanced isothermally until the two pressures are equal, but this step introduces no energy change, since the vapor is at a pressure so low that it may be regarded as a perfect gas. The valve is now opened and the vapor returned to the adsorbent at constant temperature, causing a net loss of energy $[U + \mathrm{d}U]\mathrm{d}n$. Finally, the system is cooled to the original temperature at constant volume, the heat removed being $C_{vx}\mathrm{d}T$. Hence, by the first law, $C_v - \bar{c}_v = \mathrm{d}U/\mathrm{d}T$ or, adding R to both sides, $C_p - \bar{c}_v = \mathrm{d}\lambda/\mathrm{d}T$.

Since λ is itself found by differentiating the observed pressures with respect to temperature, the values of $\bar{c}_v$ found by applying this equation will depend on second differences, and will not be very accurate. The average value of $\mathrm{d}\lambda/\mathrm{d}T$ is —30 between —15° and 80°, and —29 between 80° and 187°. Taking C_p as 8.5, we find for the most probable value of $\bar{c}_v$ 38 cal. per mole, or 2.1 cal. per gram, an astonishingly high value. However, it is in accord with modern theories of the electrical origin of intermolecular forces, that in the case of a substance whose molecules are dipoles, the forces should decrease with rising temperature, which is thermodynamically equivalent to just such differences in specific heat as have been discussed.

Before it is attempted to develop a theoretical treatment of the peculiarities in the isotherms of polar substances, it will be wise to wait until experiments have shown how far the exceptional behavior of water is shared by other similar bodies. However, it may be tentatively supposed that the abnormally small increase in pressure as a function of concentration is connected with the polymerization or association which is characteristic of polar liquids, especially water. Water vapor is not associated, and the same must be true of adsorbed water as long as Henry's law holds. The initial adsorption of water should then correspond to that of the vapor of a normal liquid; but a normal liquid whose vapor had kinetic constants of similar magnitude to those of water vapor, would be expected to show a much lower boiling point than water, and consequently be less readily adsorbed than the vapor of a normal liquid having a boiling point close to that of water. The abnormally high boiling point of water is believed to be due to association. Since the condition of adsorbed water near saturation is undoubtedly quite similar to the liquid state, it is reasonable to suppose that association will be present at saturation, causing the pressure to be much less than would hold for a normal liquid. As the isotherm is traced upwards from very low concentrations, the pressure will begin to fall below that demanded by Henry's law as soon as association begins to occur.

Another factor tending to draw the upper portions of the isotherm toward the axis of concentrations is the very small molecular volume of water, permitting an unusually large number of water molecules (calculated as H_2O) to be adsorbed at saturation, where the amount of all substances adsorbed is in the first approximation determined by their molecular volumes.

Summary

1. The characteristic adsorption isotherms of non-polar and polar substances are shown to be very different, the former being always concave, the latter partially convex, toward the axis of pressures.

2. Attempts are described to secure reproducible measurements of the adsorption of water vapor by charcoal at low concentrations. Success depends upon the use of a very pure form of carbon. The adsorption of water by pure carbon is very small, and is greatly increased by traces of inorganic impurities.

3. Adsorption equilibrium between water and pure charcoal is studied and found to present many unusual relations. Henry's law holds at all temperatures investigated below a relative pressure of one-tenth; above this the pressure increases less than proportionally to the concentration. For a given high concentration, the relative pressure increases with rising temperature; for a given low concentration, however, the relative pressure is constant between —30° and 20° and decreases at higher temperatures. The adsorption of water vapor reaches a maximum at the triple point.

4. Thermal quantities are calculated from the equilibrium data. The heat of adsorption at ordinary temperatures is nearly constant and nearly equal to the latent heat of evaporation of liquid water. It increases slightly as the concentration increases. At higher temperatures it is much smaller at low concentrations, and increases more rapidly with rising concentration. The partial molal heat capacity of adsorbed water at low concentrations is 38 cal. per mole.

5. It is suggested that the characteristic form of the isotherms of polar substances may be caused by molecular association.