[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE]

THE INTERPRETATION OF ADSORPTION ISOTHERMS AND ISOSTERES

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When experiments are made upon the adsorption of vapors by a porous adsorbent, and the quantities found to be adsorbed at a particular temperature are plotted against the logarithms of the relative pressures (observed pressures divided by the vapor pressure of the free liquid at the same temperature), curves of the general scope of Curve 1, Fig. 1, are obtained. Let P be the relative pressure, Q the quantity adsorbed (in any convenient unit of measurement); then the lower portion of the curve will be in approximate agreement with the familiar Freundlich equation, $\log P = a \log Q + b$. At higher values of Q, this relation ceases to hold; the curve becomes nearly straight, shows a rather sudden bend at the point marked "A," and appears to terminate suddenly, having a finite slope, at "B," where $P = 1$, and the system is therefore saturated. However, as I have shown in a previous paper,[1] this sudden termination actually occurs only at temperatures below the freezing point of the liquid. Above this temperature, the isotherms bend upward when the relative pressure is just less than unity, and approach as asymptote the line $\log P = 0$, so that no definite quantity can be said to be adsorbed at saturation. The dashed line near "B," Fig. 1, represents this behavior on an exaggerated scale. This portion of the isotherm is generally ignored. We shall assume that it is due to some secondary effect, and that the isotherm of true adsorption runs as drawn right up to the point of saturation, "B." This assumption is justified partly because no progress can be made without it in studying the phenomena of saturation, and partly because the ultimate capacities of the system, as thus determined for various substances and at different temperatures, show many regularities, and evidently correspond to something real.

There appears to have been put forward no satisfactory interpretation of the characteristic form of the adsorption isotherm, especially of the manner in which it approaches saturation. Most theories start by assuming a particular isotherm as experimentally given, and attempt to derive therefrom all other isotherms. Langmuir's[2] simplest equation gives isotherms showing points of inflection and definite ultimate capacities, but the latter are reached only at infinite pressures. Williams[3] has derived the equation $\log a/c = A_0 - A_1 a$, where a is the amount adsorbed, c the concentration in the gas phase, A_0 and A_1 are constants. For moderate values of a,

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[1] Coolidge, THIS JOURNAL, **46**, 609 (1924).

[2] Langmuir, *ibid.*, **40**, 1361 (1918).

[3] Williams, *Proc. Roy. Soc.* (London), **96A**, 287 (1919).

such that A_1a greatly exceeds log a, this is in agreement with the straight portion already noted, just to the left of "A," Fig. 1. The equation does not claim to hold up to saturation.

It strikes me that the suddenness with which saturation is reached is very surprising. When the vapor-pressure curve of a solid or liquid, plotted against temperature, or that of a solution plotted against concentration, shows a sudden change in slope, the physical chemist looks for the appearance of a new phase. In the case of an adsorption pushed beyond saturation, no one doubts that the excess of vapor introduced condenses to ordinary liquid (except below the freezing point). But it is hard to see how this can be considered a new phase, since it is generally believed that the adsorbed vapor itself, or at least its superficial layers, are already in the form of the liquid, evaporation being hindered by the operation of some force caused by the proximity of the adsorbent. It is not easy to understand why this force should suddenly cease to act. Furthermore, if saturation means the formation of a new phase, it should be possible by careful work to delay its appearance and to produce a supersaturated adsorption (analogous to a supersaturated solution). This I have been able to do[1] below, but not above, the freezing point, which apparently proves that while the solid appears as a new phase, the liquid does not. A possible explanation of the suddenness of saturation, which involves neither of these difficulties, will be suggested in this paper.

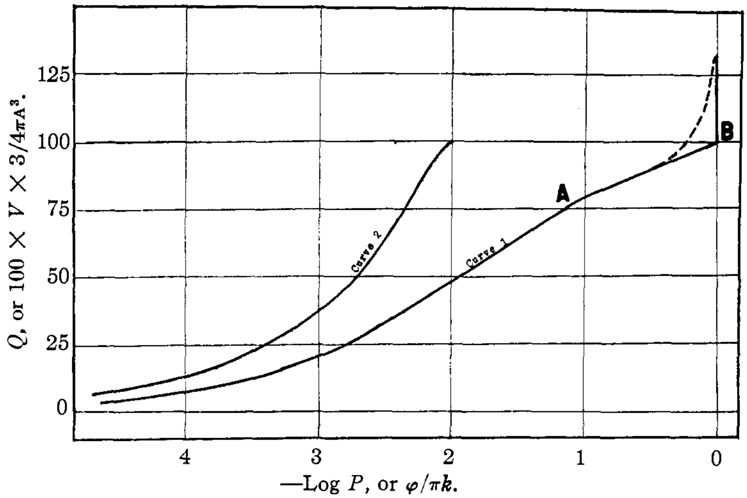

Fig. 1.

The idea that adsorbed vapors condense to something resembling the normal liquid state is based primarily on the experimental fact that the quantities of different vapors necessary to saturate a given adsorbent are nearly the same as those required to produce, when condensed, a fixed volume of normal liquids. This will appear from Table I, taken from my data[1] for activated coconut charcoal. In this table, the second column gives the volume of normal liquid, in cubic centimeters, which would be produced at 0° by the quantity of the indicated vapors which suffices to saturate 1 g. of charcoal at 0°. The third column, which will be needed later, gives the apparent specific volume of a similar charcoal, as measured by Harkins and Ewing with the corresponding liquids; the fourth is the sum of the second and third, and the fifth is the compressibility of the liquid. (This has been taken where possible from 0 to 500 atmospheres at 0°; but in some cases where data were lacking, the value at 20° from 300 to 500 atmospheres has been substituted as being roughly comparable.)

Table I

Volume and Compressibility Relations

1	2	3	4	5
Hg	(0.000)	1.156	(1.156)	4
H_2O	.424	0.543	0.967	41
CCl_4	.435	..	..	73
$CHCl_3$	.442	.502	.944	70
CS_2	.450	.486	.936	66
CH_3OH	.450	..	..	80
$HCOOC_2H_5$	.454	..	..	..
C_6H_6	.467	.498	.965	67
CH_3COOCH_3	.490	..	..	73
$(C_2H_5)_2O$	.494	.472	.962	107

It is strongly suggested that the adsorbent presents a fixed volume, rather than a fixed surface, where adsorption can occur, and that when this volume is exactly filled the system is saturated, showing the same vapor pressure as the free liquid. The surface layer is to be considered as identical in state with that of the free liquid, and to be under no additional forces. Such forces appear as soon as the amount of liquid present is insufficient to fill the adsorption space. If, in spite of being under these forces, the superficial liquid layer may be assumed to preserve its identity of state with that of the free liquid, then the work which an evaporating molecule has to do against the additional forces producing adsorption may be calculated, according to kinetic theory, by the equation $\varphi = -kT \ln P$, in which φ is the work desired, k the Boltzmann constant, T the absolute temperature, and P, as before, the relative pressure. The assumption seems to me a precarious one, but as it is generally made or implied in the development of theories of this class, we shall retain it unless it proves untenable.

Concerning the nature of the forces against which this work is done, two hypotheses are current. According to one, they are simply the cohesional attraction of neighboring adsorbed molecules, supposed to act with more than normal vigor because of the concavity of the liquid surface. It is well known that the relative pressure over such a surface should be given by the equation $ln\ P = -2\sigma v/rRT$, in which σ is the surface tension, v the molecular volume, and r the mean radius of concavity. If we agree to assume that this effect is the sole cause of adsorption (that is, that none of the superficial molecules experience any direct attraction by the adsorbent), then it is still not possible to predict the form of any isotherm, since we do not know how the radius of concavity should vary with the degree of saturation. But if we make the additional assumption that the angle of contact between liquid and adsorbent is always zero, then we can use a single experimental isotherm as a basis for predicting others. For the radius r should be a function solely of the volume actually occupied by liquid (for a given specimen of adsorbent). The contour of the liquid surface is determined by the condition that its area, plus that of the film covering projecting portions of the adsorbent, must be a minimum consistent with the enclosure of a specified volume; these conditions contain no reference to specific properties of the liquid, or to temperature (except in so far as the adsorbent itself expands, which must be very little). Assuming the liquid to have its normal density, the relationship between radius and volume can be found empirically from a single isotherm, and the theory tested by seeing to what extent points on other isotherms can be predicted. A few examples will show how far from successful it proves.

Consider first my data[4] for activated coconut charcoal, taking benzene, the most carefully studied vapor, as standard. When, at 0°, enough benzene has been adsorbed to fill a space of 0.2 cc. with subcooled liquid at normal density (about half the ultimate capacity), the pressure of the system is 0.0055 mm., so that $-\log P = 3.68$. Taking $\sigma = 32$ and $v = 86.9$, we get $r = 2.89 \times 10^{-8}$ cm. Overlooking the fact that this radius is already of molecular magnitude, let us use it to predict the relative pressure under different conditions, but always with enough vapor adsorbed to fill 0.2 cc. with normal liquid at the temperature in question.

Substance	Benzene	Benzene	Carbon disulfide	Ether	Water
Temperature, °C.	99	150	0	0	0
$-\log P$, calculated	1.82	1.19	2.65	2.51	1.80
$-\log P$, observed	2.74	2.44	2.60	4.0	0.26

It has been supposed that the capillary condensation theory under discussion may hold better in the case of inert adsorbents like silica gel. Suitable data for a test are given by McGavack and Patrick.[5] Interpolating from their Fig. 8, we find for a volume of 0.1 cc. of sulfur dioxide at 0°, that $-\log P = 1.54$, whence, using their data for σ and v, r is found to be 3.16×10^{-8}. On this basis, the calculated relative pressures should, at −80° and at 100°, have the negative logarithms 2.99 and 0.47, instead

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[4] Ref. 1, p. 611.

[5] McGavack and Patrick, THIS JOURNAL, **42**, 946 (1920).

of the observed 1.71 and 1.16, always for 0.1 cc. of liquid sulfur dioxide. As in the system benzene-charcoal, it is evident that the actual temperature coefficient is much less than that demanded by the theory.

Since the relative pressure for equal volumes increase with the temperature, the volumes for equal relative pressures must decrease with rising temperature. In this fact, McGavack and Patrick see confirmation of the capillary condensation theory. Owing to the pull of the concave meniscus, they reason that the liquid must be in a state of negative pressure, under which it will be distended the more, the higher is the temperature and in consequence the compressibility. The volume as calculated from the normal liquid density will, therefore, be smaller than that actually occupied, by an amount increasing with the temperature. The actual volume occupied they believe to be the same at all temperatures, for a given relative pressure. However, this last idea is untenable; the relative pressure for a given volume must have, in general, a temperature coefficient, since it is given by an equation which contains not only r, which is independent of temperature, but also σ, v and T, which vary with the temperature. As we have noticed, the effect of these variations alone, neglecting any changes in compressibility, gives a theoretical change of P with T for constant volume, and therefore of volume for constant P, which greatly exceeds observed values. The correction advocated by McGavack and Patrick would only increase the discrepancy. These authors believe that the ordinary relation between P and r, as given, is not valid for very small values of r. This seems probable, but there is no reason to suppose that the quantities σ v, and T cease to be involved, and therefore to confer a temperature coefficient upon P.

Further objections to the ideas of McGavack and Patrick suggest themselves. The negative pressure ought not to increase with temperature, as they believe, but to decrease, in proportion to σ, since σ measures the direct cause of the negative pressure—the tendency of the surface to contract. Their device of dividing the calculated volumes of liquid by a fractional power of σ, in order to correct for distension, is clearly illogical, for the distension cannot be the same fraction of the volume at all stages of adsorption. At saturation, no distension should occur, and the calculated volumes, without correction, are actually found the same at all temperatures, a fact much stressed by the authors. If the volumes are corrected in the given manner, they will, of course, no longer coincide at saturation.

Clearly the capillary condensation theory cannot claim among its merits any ability even to approximate the facts of experiment. Such approximation might presumably be secured by introducing suitable *ad hoc* assumptions concerning angle of contact, failure of the liquid completely to fill the pores, delay in reaching equilibrium, or the like; but by these means any other theory could be equally well established. It seems to me more reasonable to conclude that the principal cause of adsorption lies not in the surface forces of the liquid itself, but in another class of forces, less influenced by temperature changes and more by the specific nature of the components of the system. This brings us to the second, or adhesion hypothesis, according to which every adsorbed molecule, including those about to evaporate from the liquid surface, is under the direct influence of the adsorbent. The theory has been extensively developed by Polanyi.[6] He assumes that the force upon each adsorbed molecule is specific as to the chemical nature of the molecule, but otherwise depends only upon its position relative to the adsorbent, and neither upon the temperature nor upon the proximity of other adsorbed molecules. The adsorbed liquid obeys its ordinary equation of state; it has its normal density at the surface layer, whether the system is saturated or not, and inferior layers are denser by reason of the compression due to the "weight" of those above. The adsorption space can be considered as the seat of a field of force, the potential of which at each point is the work which the adsorbent does upon a molecule moving to this point from infinity. The surface layer being normal, this potential is to be calculated as before by the equation $\varphi = -k\ T\ ln\ P$, P being now the relative pressure observed when the system has been brought to that degree of saturation which causes the surface of adsorbed liquid to pass through the point in question. Actually there is no method of recognizing particular points in the adsorption space. However, at a given degree of saturation, all points in the liquid surface must have the same potential, which can therefore be considered as a function solely of the volume enclosed between this surface and that of the adsorbent itself. What the nature of this function should be is not predicted by the theory. It can, however, be empirically determined from a single isotherm, the volumes being estimated in the first instance by assuming the normal liquid density. (A better approximation can be made.) The function will evidently have the same form as Curve 1, Fig. 1, with suitable changes of scale. The potential will be found to vanish at a definite volume, with a finite derivative with respect to the volume.

Now, at first sight, this seems impossible. No force is known which acts between two bodies according to such a law that its potential vanishes at a finite distance and with a finite space derivative. All known potentials vanish asymptotically at infinity. If the surface of the adsorbent is nearly plane, the volume of liquid adsorbed should be roughly proportional to the distance separating its surface from the adsorbent, and the potential at its surface should be an asymptotically vanishing function of its volume. But if the adsorbing surface is sharply concave, the volume will itself be a rapidly converging function of the distance, and the ratio of potential to volume may be always finite.

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[6] Polanyi, *Verh. deut. Phys. Ges.*, **18**, 55 (1916).

By way of example, let us calculate the potential as a function of the volume, in the particular case of a spherical cavity of radius A, every molecule within which is attracted by each element $d^2\omega$ of the wall surface with a force d^2F inversely proportional to the cube of the distance. In Fig. 2, M represents the position of the molecule, N is any point of the wall, and S, X, M, L, are distances as indicated. Let the attraction of N for the molecule at M be $d^2F = k\mathrm{S}^{-3}d^2\omega$.

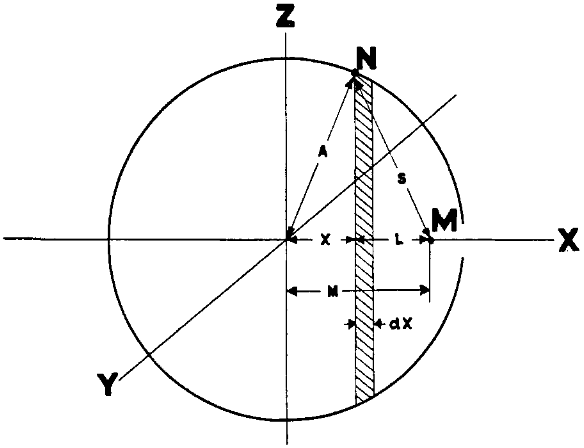

Fig. 2.

Owing to the symmetry of the figure, only the x-component of this force will contribute to the ultimate result. Let this be $d^2F_x = k\mathrm{LS}^{-4}d^2\omega$. In the figure, the shaded band represents an annular element of wall surface, including N, bounded by the intersections of the planes $X = \mathrm{x}$, and $X = \mathrm{x} + \mathrm{dx}$, and possessing the area $\mathrm{d}\omega = 2\pi\mathrm{A}\mathrm{dx}$. Its attraction for the molecule will evidently be $\mathrm{d}F_x = k\mathrm{LS}^{-4}\mathrm{d}\omega = 2\pi\mathrm{A}k\mathrm{LS}^{-4}\mathrm{dx}$.

The potential at M is the sum of the elements of potential contributed by all the annular elements of wall surface, each of which is to be found by integrating the attraction by the distance, from infinity to M. (The molecule is supposed to enter the cavity along the X-axis through narrow channel, too small to prevent treating the wall as a perfect sphere.) For the element $\mathrm{d}\omega$ of potential contributed by the wall element containing N, we find (noting that $\mathrm{S}^2 = \mathrm{L}^2 + \mathrm{A}^2 - \mathrm{X}^2 = \mathrm{M}^2 + \mathrm{A}^2 - 2\mathrm{MX}$):

$$\mathrm{d}\varphi = 2\pi\mathrm{A}k\mathrm{dx}\int_{\infty}^{\mathrm{L}} \frac{\mathrm{L}\,\mathrm{dL}}{(\mathrm{L}^2 + \mathrm{A}^2 - \mathrm{X}^2)^2} = \frac{\pi\mathrm{A}k\mathrm{dx}}{\mathrm{L}^2 + \mathrm{A}^2 - \mathrm{X}^2} = \frac{\pi\mathrm{A}k\mathrm{dx}}{\mathrm{M}^2 + \mathrm{A}^2 - 2\mathrm{MX}}$$

Finally, integrating this with respect to X, from —A to A, we get for the whole potential

$$\varphi = \frac{\pi\mathrm{A}k}{\mathrm{M}}\, ln\, \frac{\mathrm{A} + \mathrm{M}}{\mathrm{A} - \mathrm{M}} = 2\pi k\left(1 + \frac{\mathrm{M}^2}{3\mathrm{A}^2} + \frac{\mathrm{M}^4}{5\mathrm{A}^4} + \dots\dots\right)$$

Now, this is also the potential for all other points whose distance from the center is M. But the locus of these points is a sphere, enclosing between itself and the walls the volume $\frac{4}{3}\pi(\mathrm{A}^3-\mathrm{M}^3)$. We may, therefore, eliminate the parameter M and obtain the potential as a function of the volume. The function has the form of Curve 2, Fig. 1. (For convenience in computation, the potential and volume have been reduced to abstract numbers by dividing out the dimensional constants; the abscissas are $\varphi/\pi k$ and the ordinates are $100 \times V \times {}^3/_{4\pi\mathrm{A}^3}$.) For small adsorption, when $\mathrm{A}-\mathrm{M} << \mathrm{A}$, the volume may be expressed as $V = 4\pi(\mathrm{A}-\mathrm{M})\mathrm{A}^2$, and the potential as $\pi k\ ln\ \frac{2\mathrm{A}}{\mathrm{A}-\mathrm{M}}$. Its negative is therefore a linear function of the logarithm of the volume, in agreement with the Freundlich equation for the isotherm.

Other relations between potential and volume, of generally similar character, can be obtained by changing the size or shape of the cavity, or the exponent in the law of force. The latter change will destroy the validity of the Freundlich equation as the limiting case. But this is hardly an objection, since at very low concentrations the presence of liquid is doubtful; the fact that the inverse cube law of force does lead to the Freundlich isotherm is probably a coincidence, and cannot be regarded as proof that it is the correct law.

Curves of the class under consideration differ from observed isotherms in one fundamental respect: they terminate abruptly at finite potentials and volumes, instead of reaching zero potential at finite volumes. Physically, this means that the smallest potential which exists anywhere inside a cavity is greater than zero, since all places within the cavity are under the influence of the walls. Thus, for the case just calculated, the minimum potential (at the center of the sphere) is $2\pi k$, and for any relative pressure corresponding to a lower potential, the cavity will remain completely full. If an inverse fourth-power law be assumed for the same cavity, we get

$$\varphi = \frac{4\pi k\mathrm{A}}{3(\mathrm{A}^2-\mathrm{M}^2)} = \frac{4\pi k}{3\mathrm{A}}\left(1 + \frac{\mathrm{M}^2}{\mathrm{A}^2} + \frac{\mathrm{M}^4}{\mathrm{A}^4} + \dots\right)$$

and the minimum value of the potential is $4\pi k/3\mathrm{A}$. Now, an actual adsorbing body should not be supposed to contain cavities of exactly uniform dimensions (with the possible exception of crystalline adsorbents like chabazite). All possible sizes and shapes must be expected to be present. At saturation, they will all be full; as the pressure falls, they will begin to empty successively, each at the moment that the pressure corresponds with its particular minimum potential. The observed isotherm will be a kind of average of the isotherms of all the cavities, and its form will depend upon the manner in which the total volume is distributed among the different kinds of cavities. Since this volume is finite, there must exist a certain volume of single cavity, than which cavities having a greater volume occur much less frequently. As a highly arbitrary, but instructive device, let us suppose that all the cavities are spherical, and so distributed that among the larger cavities their number decreases as the fifth power of their radius, and their combined volume as the square. That is, if dN be the number of cavities having radii between A and $\text{A} + d\text{A}$, then

$$dN = \frac{3n\,d\text{A}}{4\pi \text{A}^5}$$

where n is a constant. Taking the fourth-power law expression for φ, as just given, we find for the *empty* volume of a single cavity corresponding to a given potential, the value

$$V_e = \frac{4}{3}\pi \text{M}^3 = \frac{4\pi \text{A}^3}{3}\left(1 - \frac{4\pi k}{3\varphi \text{A}}\right)^{\frac{3}{2}}$$

The empty volume of all cavities of radius between A and $\text{A} + d\text{A}$ will be $n\left(1 - \frac{4\pi k}{3\varphi \text{A}}\right)^{\frac{3}{2}}\frac{d\text{A}}{\text{A}^2}$, and the total empty volume will be found by integrating this expression from infinity to $\text{A} = 4\pi k/3\varphi$, which is the smallest cavity that will empty at all. The result is $3n\varphi/10\pi k$; in this case, therefore, the isotherm near saturation will be a straight line of finite slope, as observed, continuing to zero potential.

The analysis just presented cannot lay claim to even approximate rigor, since there is no reason to suppose that either the dimensions or the distribution of the cavities in an actual adsorbent are as regular as assumed. However, I believe it is useful as showing that it is not impossible to reconcile the discontinuity observed at saturation, with the hypothesis that the adsorbed vapor is present in the liquid state, without assuming the presence of forces acting as discontinuous functions of the distance. The effect is rather to be ascribed to a discontinuity in the relationship between space available for adsorption, and proximity to the adsorbent surface. The fact that the discontinuity at saturation is not absolutely sudden, may perhaps be explained as due to the action of the outside, plane or convex, surface of the granules of adsorbent. The isotherm of such a surface should show no saturation, but should approach asymptotically the vapor-pressure line of the liquid, as indicated by the dashed line in Fig. 1. But the outside surface is so small in comparison with the interior, that its contribution to the whole isotherm would be recognizable, if at all, only as a correction term. There is some evidence that this correction term becomes more important when the convex surface is increased by powdering the adsorbent. Thus, Gustaver[7] and Williams[8] report more transition curvature at saturation than my curves display. Gustaver worked with powdered charcoal; Williams does not give the state of his charcoal. On the other hand, Lowry and Hulett[9] reduced their charcoal to 0.001 mm. without producing transition curvature.

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

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

[9] Lowry and Hulett, THIS JOURNAL, **42**, 1411 (1920).

It remains to discuss the effects of temperature on adsorption. This is most conveniently studied by plotting isosteres, or vapor-pressure curves of systems of constant composition. If log p (actual, not relative pressure) is plotted against reciprocal temperature, almost perfectly straight lines are obtained. If the equation of Clausius and Clapeyron is applicable, the negative slope of these lines is proportional to the heat of adsorption. I can see no reason to doubt the validity of this principle. The fact that the condensed phase is capable of varying its composition is no obstacle, for the Clausius-Clapeyron equation unquestionably applies to solutions which are thermodynamically indistinguishable from adsorptions. Nevertheless, doubt and confusion appear to exist, whether and under what condition the principle may be extended to adsorption systems, and a brief discussion seems relevant.

Freundlich[10] states that it is applicable in case the heat of adsorption is measured under such circumstances that the amount adsorbed is practically unchanged. Williams[11] points out the difficulty in conceiving a "heat of adsorption" when nothing is adsorbed. The heat required to elevate the temperature of the system, while the pressure is so adjusted as to prevent any change in composition, is evidently merely a specific heat. In the same paper, "following Donnan in an unpublished paper," Williams advances the idea that the Clausius-Clapeyron equation should hold for heats measured isothermally and under equilibrium pressure, provided the adsorbent does not change its surface during the adsorption. In comparing the heat measurements of Titoff[12] with the heats calculated from the same experimenter's isotherms, he finds the former systematically greater. A part of the discrepancy, Williams believes, is due to the fact that the gas entered Titoff's calorimeter at greater than equilibrium pressure. A residual discrepancy appears to him as proof that the charcoal surface increases during adsorption, evolving a quantity of heat not taken account of by the Clausius-Clapeyron equation. This increase is conceived as strictly reversible, and the energy change involved must be added.

In this reasoning I am unable to concur. No condition is involved in the proof of the Clausius-Clapeyron equation which is not admirably met by a charcoal-vapor system, as the following analysis will show. Let us postulate a thermodynamic system the state of which is completely defined when two variables, which may be chosen as pressure and temperature, are given. Then, for any reversible infinitesimal displacement the increase in the energy of the system will be $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V$, where $\mathrm{d}S$ is the entropy increase and p is the external pressure. At the same time, any kind of internal change, including a change of surface, may occur.

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[10] Freundlich "Kapillarchemie," 3rd ed., p. 181.

[11] Williams, *Proc. Roy. Soc. Edinburgh*, **38**, 23 (1918).

[12] Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

Such changes must be reversible, since otherwise, the system as a whole, would not behave reversibly. They cannot perform any outside work, for if they did, this work would have to take the form of a reaction against some outside generalized force, and the system would be found to be sensitive to changes in this force in addition to pressure and temperature. They are, therefore, of no thermodynamic significance.

By well-known methods we obtain from the last equation the relation

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial q}{\partial V}\right)_T$$

in which ∂q is the heat absorbed. This is certainly applicable to the special case of a system consisting of definite masses of charcoal and vapor, the total volume being just greater than that of the charcoal alone, so that the composition of the whole system is essentially that of the adsorption phase. Such a system is found to be completely definable in terms of temperature and pressure. $\left(\frac{\partial p}{\partial T}\right)_V$ is evidently the slope of the isostere, for constancy of volume implies constancy in concentration of the adsorption phase. On the other hand, if the volume changes isothermally, vapor will be desorbed in quantity sufficient to fill the new space (the volume change of the adsorption phase during this process may be neglected), and the accompanying heat absorbed will be the heat of adsorption per mole (λ) times the concentration (moles per cc.) of the vapor at the given pressure, which may be taken as equal to p/RT. We therefore obtain the equation

$$\frac{\partial p}{\partial T}\text{ (isosteric)} = p\lambda/RT^2, \text{ or}$$

$$\lambda = RT^2\frac{\partial \ln p}{\partial T} = -R\frac{\partial \ln p}{\partial(1/T)}$$

We conclude that the isosteres should agree with the measured heats in accordance with the usual equation, and that a departure, due to possible changes of adsorbent surface, is no more possible than is a departure, in the case of liquids, due to the various internal processes (ionization, solvation, polymerization, etc.) which may be supposed to take place in them.

To return to the first cause suggested by Williams as partly responsible for the observed discrepancies, it must be admitted that heats of adsorption are not measured reversibly. The gas enters the calorimeter at an unknown pressure, higher than that of equilibrium. Now, the heat of adsorption in the sense defined is the "external" heat; it contains not only the total energy difference between the initial and the final states, but an additional term taking account of the work done by everything outside the calorimeter upon everything within. Since the total energy of a perfect gas is independent of its pressure, the internal energy change during adsorption will not depend upon the initial pressure of the gas, provided that the temperature at which it enters the calorimeter is properly controlled. As for the outside work term, each element of gas dn may be thought of as having the pressure p' at the instant it enters the calorimeter; the work done by the environment will be $p'\mathrm{d}V = p'\dfrac{\mathrm{d}V}{\mathrm{d}n}\mathrm{d}n = RT\,\mathrm{d}n$; and the total work will be simply RTn, whatever may have been the pressure. The observed heat, therefore, will not differ from the true λ.

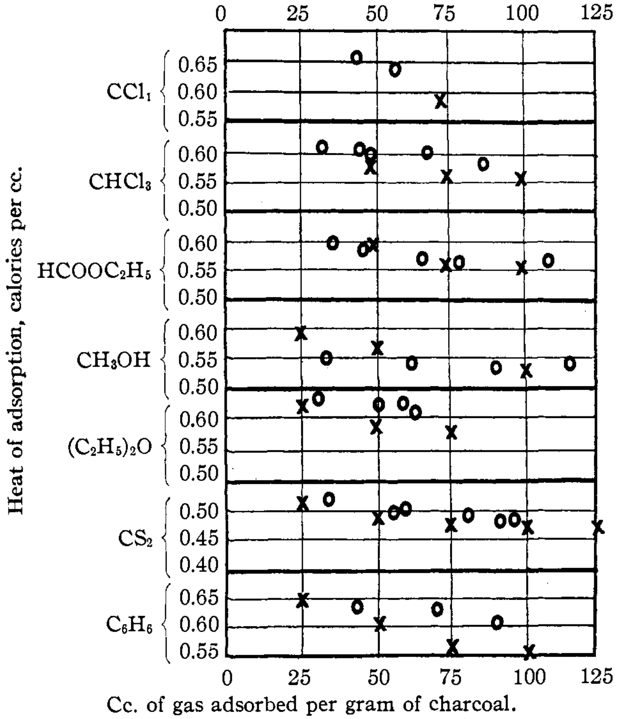

Fig. 3.

It appears, then, that both of the arguments of Williams are thermodynamically unsound, and that the explanation of the excess of measured over calculated heats must be found elsewhere. If things were so arranged that the gas entered the calorimeter with high velocity, its kinetic energy would of course reappear as heat. Calculation shows that with the usual forms of apparatus this effect is negligible. Can the whole difference be laid to experimental error? I think not. The isosteres plotted from my data[4] for organic vapors on charcoal are so regular and extend over so great a range, that it is hard to believe that their slopes are far from correct. In a previous paper[13] in collaboration with A. B. Lamb, I gave direct thermal measurements for many of the same systems, which showed no internal

[13] Lamb and Coolidge, This Journal, **42**, 1146 (1920).

evidence of being as much as one per cent. in error. Fig. 3 shows to what extent the two sets of data are in agreement. Circles show directly measured heats, at average concentrations indicated by the scale of abscissas. Crosses show heats read from the slopes of the isosteres for the indicated concentrations. It will be seen that, as in the data of Titoff, the observed heats generally exceed the calculated, although by a smaller amount. Now, the charcoal used for thermal measurements had been outgassed at 350°, while that used in determining the isotherms had been raised to 550°. This can, however, hardly be the cause of the difference; experiments with benzene and water vapors on differently treated charcoals showed that while the isosteres were slightly shifted, their slopes were unchanged. A more plausible explanation is as follows.

In measuring heats, no special precautions were taken to exclude traces of air. It is known that such traces greatly retard the establishment of equilibrium during the first stages of adsorption, and become less influential as saturation is approached. The ultimate capacity reached is hardly affected. Now, if the first portion of gas is added in the presence of impurities, less heat might be evolved during an hour, say, than if the same amount of pure gas had been used. But when the charcoal is ultimately saturated, the total evolution of heat should be the same, and therefore that observed during the later stages might be greater than normal in the presence of impurities, since it would contain a portion of the heat properly belonging to the first stages, whose appearance had been delayed by the inhibiting effects of the impurities. A discrepancy between observed and theoretical heats, if caused by such conditions, would be negative at low concentrations, zero at some intermediate point, and positive near saturation. Isotherms for low concentrations at 0° cannot be obtained, and comparisons are limited to the later stages of adsorption. Inspection of Fig. 3 shows a marked tendency for the discrepancies to increase with rising concentration, and a rough extrapolation suggests that they might indeed change sign at lower concentrations.

Whatever may be the cause of the discrepancies, the agreement is sufficiently close for a first approximation. Both heat and pressure measurements are evidently entitled to be accepted as free from gross errors, and as furnishing additional confirmation (if any were needed) of the validity of the equation of Clausius and Clapeyron. Furthermore, the slight dependence of the heat of adsorption upon temperature (as evidenced by the straightness of the isosteres) is powerful support for the view stated above, that adsorption does not much depend upon anything with so great a temperature coefficient as surface tension.

The origin of the heat evolved on adsorption has been the subject of discussion. In the paper already cited[13] Professor Lamb and I advanced the idea that it can be regarded as consisting of two parts: first, the ordinary latent heat of condensation of gas to liquid, and second, the heat due to the further action of the adsorbent upon the liquid. The second part, which we termed "net heat of adsorption," alone interested us. A little thermodynamics shows that it bears to the temperature coefficient of the relative pressure, the same relation that the total heat bears to that of the absolute pressure; thus, if l be the net heat, then[14]

$$l = -R\frac{d\ ln\ P}{\mathrm{d}(1/T)} = -R\left(\frac{\mathrm{d}\ ln\ p}{\mathrm{d}(1/T)} - \frac{\mathrm{d}\ ln\ p_0}{\mathrm{d}(1/T)}\right)$$

where p_m is the vapor pressure of the liquid. Graphically, it is given by the difference in slope between the isostere and the vapor-pressure line of the pure liquid, plotted on the same scale. We found that it is nearly the same in magnitude for different liquids, when referred to equal bulk of liquid, and that the residual differences can apparently be correlated with differences in the total heats of compression which equal volumes of these liquids would evolve when put under a pressure of 37,000 atmospheres, as calculated from the expansion coefficients. Assuming that the attractive forces give rise to a unilateral pressure in the liquid film which causes volume and heat changes equal to those which would be produced by an equal hydrostatic pressure, we came to the conclusion that such high pressures actually exist, and that the net heat of adsorption is merely a heat of compression.

There is apparent confirmation of the high-pressure theory in the work of Harkins and Ewing.[15] They find that the apparent density of certain active charcoals, as determined by immersion in liquids, increases with the compressibility of the liquid used, as though the liquid were highly compressed in the pores. This observation is confirmed by my values for the amounts of different liquids required to saturate my charcoal, and therefore presumably just filling its pores. When reduced to volumes of liquid at normal density, these amounts increase with the compressibility of the liquid, suggesting that the real density of the adsorbed liquid is that corresponding to a high pressure. In so far as the charcoal used by Harkins and Ewing is comparable to mine, the sum of their values for apparent specific volume of charcoal, and of mine for apparent volume adsorbed at saturation, should be constant. How far this is the case will appear from Table I.

However, there are grave obstacles, both theoretical and experimental in nature, which must be overcome before these ideas can be accepted as satisfactory. To consider first the former, we must note that heat of compression, in the thermodynamic sense, is heat evolved when a fluid is compressed by some external agency. It is impossible to apply thermodynamic reasoning to compression caused by internal forces without en-

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[14] This equation was derived by Kirchhoff for the case of solutions, in *Pogg. Ann.*, **104** (1856), Ges. Abh. 492.

[15] Harkins and Ewing, THIS JOURNAL, **43**, 1787 (1921).

countering the kind of difficulty which has just been discussed in connection with the theory of Williams. Furthermore, the heat of compression is by no means a measure of the work done by the compressing force, but represents only the difference between the work so performed and the energy retained by the fluid in potential form; it may be positive, negative, or zero. In the case of a liquid attracted to an adsorbing surface, the only outside agency acting upon any given layer of the liquid is the "weight" of the superior layers. That such a "weight" effect exists is apparently indicated by the following experiment, which is typical of the behavior of inorganic liquids, which I am now studying.

> To the empty charcoal add a quantity of vapor much less than that necessary to saturate it, and observe the pressure at constant temperature, say 100°. Equilibrium seems to be reached within a few minutes, but if the experiment is prolonged for 20 or 30 hours, a lower pressure will result. Now empty the charcoal and add a much greater quantity of vapor, which will necessitate the use of a lower temperature. Let it settle for a few hours, and then return to 100° and allow the vapor in excess of the amount first used to escape. The pressure will be found to be much lower than even the lowest pressure observed in the first experiment, although the time elapsed has been less. Evidently, the presence of the excess of vapor has accelerated the penetration of the first instalment, presumably by exercising a pressure or "weight" upon it.

If we think of the liquid as being added in successive instalments to the previously bare adsorbing surface, the weight of each instalment, and the consequent increase in pressure upon all previous instalments, will diminish as we get further from the surface, and will vanish when we reach saturation. Now, when a quantity of liquid is compressed, the heat evolved will be proportional to its specific heat of compression, its volume, and the increase in pressure attained. Since no liquid is originally present, the addition of the first instalment can compress nothing and produce no heat of compression. Subsequent instalments will find increasing quantities of liquid available to be compressed, and will, therefore, cause the evolution of increasing quantities of heat of compression, until the point is reached at which the decrease in weight of the successive instalments overbalances the increase in volume of liquid susceptible of compression. If the net heat of adsorption is truly a heat of compression, it should be zero at zero concentration, and rise to a maximum at some higher concentration. Actually, it has its greatest value at zero concentration, and falls continuously with rising concentration; but at saturation it still has a finite value. It must, therefore, contain an additional term, besides heat of compression.

It is not difficult to see what this term must be. When a quantity of liquid "falls" upon a bare adsorbent surface, much potential energy is set free, since the liquid during its approach must be acted on by powerful forces. This energy will be converted into heat, and if the process is isothermal it will be quantitatively transmitted to its surroundings (in addition to that due to the work done by the atmosphere), except that a small portion may be retained if the heat capacity of the system is increased by the process. However, if some liquid is already present, a part of the work done by the adsorbent upon the new liquid will be used in compressing the old, and the heat of compression evolved thereby will not in general be equivalent to the work absorbed. We may expect, therefore, that the observed net heat of adsorption will be closely equal to the work done by the attraction of the adsorbent, only during the initial stages of the adsorption. On the other hand, at saturation the work done (the potential, referred to a mole instead of a single molecule) vanishes, and the net heat of adsorption (heat of wetting) may be regarded as solely heat of compression. This appears paradoxical, for it is hard to see how there could be any compression change at saturation. The difficulty is of the same character as that concerned with the discontinuity in the slope of the isotherm at saturation. If we agree that the potential has a finite derivative at saturation, the proposition may be demonstrated as follows.

Let N_0 be the total number of moles of a given vapor which can be adsorbed by a particular adsorbent at a definite temperature, and let ρ be the reciprocal of the molecular volume of the corresponding liquid at the same temperature and no pressure. Let the molar potential be such a function of the volume not filled by adsorbed liquid, that near saturation $d\varphi/dv = K$. When the system is saturated, v is zero, and the potential and the hydrostatic pressure will vanish at the surface of the liquid. At a certain slightly lower surface, the potential will have a value different from zero, namely, $\Delta\varphi = K\Delta v$, Δv being the volume enclosed between the two surfaces; at the same surface the hydrostatic pressure, due to the weight of the intermediate liquid, will have the value $\Delta p = \rho K\Delta v$. Now suppose the intermediate liquid removed; the amount removed will be $\Delta N = \rho\Delta v$. Since the pressure due to this layer is now removed, the remaining liquid will expand by the amount $V_0\beta\rho K\Delta v$, where V_0 is the total volume of adsorbed liquid (supposed large in comparison to Δv), and β is its mean compressibility in the adsorbed condition. The space left empty will be $(1-\rho K\beta V_0)\Delta v$, and a new surface will form at a depth corresponding to the potential $(1-\rho K\beta V_0)K\Delta v$. Recalling the relation between potential and relative pressure, we find for the latter under these conditions, $-RT\ ln\ P = (1-\rho K\beta V_0)K\Delta v$.

Let us now warm the system, without permitting vapor to escape, until it becomes saturated. Let ΔT be the necessary increase in temperature; then, since the new relative pressure is unity, we may write for its mean temperature coefficient over the particular range,

$$\frac{d\ ln\ P}{dT} = \frac{ln\ 1 - (-\ ln\ P)}{\Delta T} = K\,\frac{1 - \rho K\beta V_0}{RT}\,\frac{\Delta v}{\Delta T}$$

But the reason that the system has become saturated is that the adsorbed liquid has expanded so as to fill the whole adsorption space. If α be its mean coefficient of expansion, this means that $V_0\alpha\Delta T = (1-\rho K\beta V_0)\Delta V$. Eliminating ΔT between these equations, we find $\mathrm{d}\,ln\,P/\mathrm{d}T = V_0\alpha K/RT$. Therefore, by the analogy to the Clausius-Clapeyron equation, the net heat of adsorption in the immediate vicinity of saturation is $V_0\alpha KT$.

To prove that this is identical with heat of compression, let us return the system to its second, unsaturated state at the original temperature and calculate what heat of compression would be evolved from the liquid present, upon replacing the liquid originally removed. By a well-known thermodynamic relation, the heat of compression of a portion of fluid is proportional to its volume, temperature, and expansion coefficient. Multiplying these quantities by the value of Δp already obtained, we find for the desired heat the expression $V_0\alpha T\rho K\Delta v$. Dividing by ΔN, we obtain for the molar heat $V_0\alpha KT$, a quantity identically equal to the net heat of adsorption just calculated. Here, then, is the explanation of the puzzling fact that the heat required to evaporate a liquid from a saturated adsorbent is greater than from the pure liquid, although the vapor pressures and, therefore, presumably the forces which have to be overcome by escaping molecules, are identical. The additional heat is absorbed by the expansion of the remaining liquid when released from the weight of that which evaporates.

Turning to the experimental field, we find many facts which seem to be inconsistent with the high-pressure theory. The original argument from net heats of adsorption was based on comparisons between different liquids measured at their normal densities. But if they are under high pressure, the quantities chosen for comparison should be those which under high pressure occupy the same volume. This change will alter the results.

The pressure existing in the adsorbed layer, according to Polanyi's theory, is much less than that required to account for the whole heat as heat of compression. It rarely exceeds 5000 atmospheres. The capillary condensation theory denies the existence of any pressure at saturation.

I have previously shown[1] that adsorbed benzene does not freeze, even below its freezing point. If it were in the form of ordinary liquid under pressure, it would freeze at ordinary temperatures.

The most interesting evidence, however, because most closely related to that of Harkins and Ewing, is that obtained by comparing the saturating quantities of the same liquid at different temperatures, rather than of different liquids at the same temperature. McGavack and Patrick's work on silica gel agrees with mine on charcoal in showing that if the decreasing capacity of the adsorbent with rising temperature is due simply to the expansion and overflowing of the adsorbed liquid, then this expansion is about the same as that of the free liquid, and is much greater than that of the liquid under 37,000 atmospheres' pressure. In Table II, the column marked "adsorbed" gives the ratio of the amounts of different vapors adsorbed at the lowest and highest temperatures at which I was able to reach saturation, and the column marked "free" gives the ratios of normal liquid densities at the same temperatures. There is some tendency for the "adsorbed" expansion to be less than the "free," but inspection of Bridgman's[16] work shows that in no case would this correspond to a pressure as high as 500 atmospheres.

TABLE II

EXPANSION OF FREE AND ADSORBED LIQUIDS

Substance	Temp. range, °C.	Adsorbed	Free
Benzene	33–99	1.065	1.09
Ether	0–60	1.09	1.11
Carbon disulfide	0–60	1.07	1.08
Methanol	0–60	1.08	1.07
Water	0–99	1.05	1.04

The case of water is particularly instructive. The expansion of adsorbed water proceeds regularly from 0° to 100°, with no suggestion of a change of sign.

To sum up, then, comparisons between volumes of different liquids adsorbed at one temperature appear to support the high-pressure theory, while those between volumes of one liquid at different temperatures point to the no-pressure or capillary condensation theory. While each of these generalizations has been separately recognized by various authors, the antagonism between them seems to have escaped notice. In order to reconcile the facts, it is necessary to abandon either the idea that all liquids fill the same space, or the idea that every portion of the adsorbed vapor is in a state identical with that of its massive liquid under some particular pressure. I prefer the second alternative for the following reasons.

The properties of a liquid are determined by the forces acting between its molecules. In order to exhibit normal properties, any portion must be surrounded to a distance at least equal to the radius of action of intermolecular forces, by an envelope of similar molecules of the same concentration as exists in the massive liquid. Now I have already given my reasons for believing that every adsorbed molecule (except those at the surface when saturation is reached) is near enough to some portion of the absorbent to be under its direct influence. Unless we are to make the unlikely assumption that the forces between adsorbent and adsorbed molecules have a much greater range than those between adsorbed molecules themselves, this cannot occur unless the adsorbed molecules sacrifice some of their enveloping similar molecules. In other words, the adsorbent should alter the behavior of the adsorbed liquid not only directly by its own attraction, but also indirectly by displacing and removing the attraction of very intimate portions of it. This amounts to dilution, and we are therefore brought

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[16] Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 1 (1913).

back to Homfray's[17] original point of view, from which an adsorption system appears so intimately mixed as to constitute a single phase—a solution. (Her thermodynamic treatment, however, is erroneous and misleading.) The lowering of the vapor pressure and freezing point, and the suppression of the anomaly in the expansion of water, are in complete accord with this view. Solutions of this class are peculiar in that one component is unable to diffuse, so that the concentration is not uniform throughout, but has all possible values. If the adsorbent be considered the solute, then the concentration will be zero at the surface at saturation, and the surface layer of liquid will be in every way normal; in every other portion, the properties of the liquid will be more or less modified, according to laws which will not be more simple than those applying to ordinary concentrated solutions.

This conclusion will make necessary a revision of the ideas expressed in the first part of this paper, but will not vitiate their general validity. The Polanyi theory must be modified, since we can no longer grant its fundamental assumption that the liquid obeys its normal equation of state. In particular, the method of calculating the potential from the relative pressure will not do. The true potential will, however, approach the apparent potential thus calculated, as the system approaches saturation and the surface layer becomes normal. The reasoning advanced to explain the finite volume derivative of the true potential at saturation will still serve to make intelligible the corresponding finite, but different, derivative of the apparent potential, and therefore of the observed isotherm. The interpretations of heat of wetting as heat of compression, need not be altered, since no assumption was made concerning the state of the liquid save that the surface layer is normal at saturation.

It remains to find an explanation of the fact that observed net heats of adsorption do run parallel to heats of compression—that is, to expansion coefficients. The latter are approximately inverse measures of the work which has to be done in separating molecules of different liquids. We have just seen that such separation probably occurs during adsorption. The necessary work must be subtracted from the direct work done by adsorbent on the individual adsorbed molecules, in calculating the total energy change or the net heat, which would, therefore, tend to decrease, as observed, with decreasing expansion coefficient. This is well illustrated by the case of water, with its very low expansion coefficient, high surface tension, etc. The net heat of adsorption of water, calculated from the isosteres under such conditions as to be comparable with those previously given (1 cc. of liquid on 10 g. of charcoal, as in Col. 5, Table VIII of the Lamb and Coolidge article[18]) is only about 22 calories, while the average for the organic liquids was 88 calories. Mercury is not adsorbed at all. This is presumably not

[17] Homfray, *Z. physik. Chem.*, **74**, 129 (1910).

[18] Ref. 13, p. 1164.

because there is no attraction between carbon and mercury atoms, but because this attraction is insufficient to separate the mercury atoms from each other. Similar considerations might be invoked to explain the differences in the adsorbabilities of other liquids. Portions of the adsorption volume might be supposed to be accessible only to single molecules of liquids like ether, which are easily able to detach themselves from their fellows. Speculations of this nature would best be postponed until data are at hand covering, for a single adsorbent, liquids with a wider range of properties. On the accumulation of such data I am actively engaged.

Summary

Adsorption isotherms are observed to exhibit changes of slope at saturation so sharp as to suggest the appearance of a new phase. This interpretation is at variance with most theories of adsorption, and another is to be desired.

The "capillary condensation" theory is examined and found quite inadequate to account for the facts except with the aid of *ad hoc* assumptions. In particular, it predicts temperature coefficients much greater than those observed. It must, therefore, be supposed that all adsorbed molecules are directly attracted by the adsorbent.

The conditions are discussed under which the action of forces which are continuous functions of the distance can nevertheless give rise to potentials which are discontinuous functions of the volume occupied by the adsorbed gas, thus explaining the observed breaks in the isotherms at saturation.

The relation between heats of adsorption and slopes of the isosteres is discussed. Published objections to the application of the equation of Clausius and Clapeyron are examined and found invalid. The equation is tested by experimental data, and found to be satisfied within a few per cent.; an explanation of the residual discrepancy is offered.

The origin of the heat of adsorption is discussed. It is concluded that the earlier conception of this heat as heat of compression, is in general erroneous, but may be correct for a saturated system. For unsaturated systems, the heat is to be considered as principally representing the work done by the attraction of the adsorbent, plus the ordinary latent heat of condensation.

The evidence for and against the existence of a high pressure due to adsorption is examined. The evidence is found incapable of being reconciled with the idea that the adsorbed liquid obeys its ordinary equation of state. It is concluded that the liquid must be thought of as fundamentally altered in state, as in the case of ordinary solutions. The advantages of treating adsorption as a special kind of solution are discussed.

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