

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Adsorption at High Pressures. I

BY ALBERT SPRAGUE COOLIDGE

Most experiments on adsorption phenomena are performed with the adsorbent in a container which it does not completely fill. Some account must be taken of the effects due to the unadsorbed fluid in the dead space. There seems to be available no general discussion of this point (including thermal effects) applicable over the whole range of existence of the adsorbed substance in the fluid state. It is usually assumed that the "dead" fluid can be either neglected or treated as a perfect gas. A closely related question is the application of buoyancy corrections to spring-balance experiments.¹

The method of applying these corrections is essentially a matter of definition, which may vary according to the purpose in hand. As frequently happens, a purely objective definition, suitable for strict thermodynamic discussion, may prove more precise, but less illuminating, than another into which are permitted to enter certain quantities of an interpretive character, which are not open to exact and unambiguous measurement, but may by various means be estimated. In the case of a highly disperse porous adsorbent, two such interpretive quantities are φ_1 , the "true" or "skeleton" specific volume of the adsorbent, and φ_2 , the specific pore volume or adsorption space.

In making this statement about φ_1 , no disrespect is intended toward the many workers who have attacked the problem of the true density of adsorbents. Their methods all involve special assumptions, and lead to results only approximately in agreement. It is clear that no experiment on the displacement of any fluid by an adsorbent will give the true density unless some assumption is introduced concerning the amount of adsorption which occurs, and a definition resting on such an assumption cannot logically be used to determine adsorption itself. In the author's opinion, highly porous adsorbents approach molecular dispersity, and their "true" density is in principle as elusive as the "true" density of a solute in an ordinary solution.

The pore volume, φ_2 , is still more ambiguous. For a plane adsorbent the conception is meaning-

(1) See, for example, J. W. McBain and G. T. Britton, *THIS JOURNAL*, **52**, 2198 (1930).

less. Porous adsorbents on the other hand show evidence of a fairly constant adsorption space. The amounts of various saturated vapors which they pick up are surprisingly well-defined (if we neglect the transition curvature which appears in the isotherms just below the saturation pressure), and it has been frequently noted² that these amounts correspond quite closely to the quantities of the corresponding liquids which would be required to fill a certain volume, at normal or somewhat elevated pressure. We may take this volume as a measure of φ_2 , ignoring the possibility that a portion of the pore volume is not accessible to adsorbed molecules. An alternative is to place $\varphi_1 + \varphi_2$ equal to the total or block volume, possibly measurable by displacement of mercury. Or, again, φ_1 and φ_2 may be treated as arbitrary parameters, adjustable in order to give the best agreement between experimental and predicted isotherms.

A possible definition, A, places the amount adsorbed just equal to the total amount contained in the pore volume (*i. e.*, all matter under the influence of the adsorption forces). Data reduced on this basis lend themselves to a simple physical interpretation: they correspond to experiments performed with a container which the adsorbent completely fills (a container of volume $\varphi_1 + \varphi_2$). When the actual container is larger, the extra volume is considered as dead space, and a corresponding correction applied. This method is open to the objection that φ_2 is not uniquely known. The classical definition, B, avoids this difficulty by defining the amount adsorbed as the excess material present in the pores over that which would be present under the normal density at the equilibrium pressure. This amounts to including φ_2 as part of the dead space in computing the correction, so that the result is less simple of interpretation; yet it is still subject to the ambiguity inherent in φ_1 . A completely objective definition, C, can be achieved only by including $\varphi_1 + \varphi_2$ in the dead space, and thus placing the amount adsorbed simply equal to the excess fluid present in the container over that which would be

(2) G. C. Schmidt and B. Hinteler, *Z. physik. Chem.*, **91**, 103 (1916), Table 9; M. Polanyi and F. Goldman, *ibid.*, **132**, 321 (1928), Table 17.

present under the same external conditions if the adsorbent were completely absent. The departure from simplicity of interpretation is no more serious than with definition B.

It will be seen that in each case the problem of corrections can be formally reduced to that of calculating, from observations upon a system at volume V , the properties which it would have under identical external conditions except that its volume were reduced to some special value V^0 , with the aid of the assumption that the "dead space" $V' = V - V^0$ contains nothing but pure fluid in its normal state. V^0 is to be chosen equal to $\varphi_1 + \varphi_2$, to φ_1 , or to zero, accordingly as we adopt definition A, B or C. Definitions of thermal quantities, and corresponding corrections to calorimetric experiments, follow from the same principle.

A summary of the required thermodynamical relations will be useful. We assume that a system containing the fixed quantities of adsorbent M and fluid N (in arbitrary units, but N is conveniently measured in moles) will have a unique P - V - T relationship measurable in the ordinary way, so long as V is not allowed to become smaller than some value which is roughly the block volume of the adsorbent. We need not inquire what actually happens at smaller volumes, for we discuss this domain only in connection with the above-mentioned purely formal device for establishing corrections. The total energy of the system, U , will not be open to experimental determination. But we may determine ΔU , the energy loss on forming the system from its components, by means of an experiment in which we measure the heat evolved minus the work received when the evacuated adsorbent comes to equilibrium with the fluid, in such a way that the pressure of the latter is not changed. We may write

$$U = Mu_a + Nu_f - \Delta U \tag{1}$$

where u_a and u_f are the original specific energies of adsorbent and fluid, at the given T and P . Since the adsorbent cannot exist in the pure state except at zero pressure, we may neglect its compressibility and consider u_a a function of temperature only. Subject to the given restriction on the range of V , we shall find that for a given P and T , ΔU is proportional to M , and is independent of N or V ; and this empirical fact will be incorporated as a fundamental assumption in what follows.

Two new quantities may be defined as follows:

$$\Delta U = M(u_a - \bar{u}_a) = N(u_f - \bar{u}_f) \tag{2}$$

$$U = Nu_f + M\bar{u}_a = Mu_a + N\bar{u}_f \tag{3}$$

\bar{u}_a and \bar{u}_f are essentially the apparent specific or molal energies of adsorbent and fluid in the system, and are functions of P and T ; \bar{u}_f also depends on N/M , but \bar{u}_a is independent of both M and N . Evidently \bar{u}_a may be regarded as the partial specific energy of the adsorbent, $(\partial U / \partial M)_{N, P, T}$, while the partial molal energy of the fluid is simply u_f .

Analogous quantities may be defined in connection with volume or any other extensive property. In the case of volume, we cannot observe v_a and therefore ΔV ; but on the other hand V is directly measurable, and the equation

$$V = Nv_f + M\bar{v}_a \tag{4}$$

serves to give an unambiguous definition of the partial specific volume of the adsorbent in the system as a function of P and T only. Heat effects cannot well be derived in the usual way from a heat function, because the pressure is not constant during the ordinary operations. We may define

$$\Delta Q = \Delta U + NPv_f = N(h_f - \bar{u}_f) \tag{5}$$

(with $h_f = u_f + Pv_f$)

as the heat evolved when N moles of fluid flow into an evacuated bulb containing the adsorbent, things being so arranged that the fluid enters the calorimeter slowly and at the pressure P , and that the final pressure in the bulb is also P . We shall also be interested in the heat evolved when 1 mole of fluid, at pressure P , is transferred to a very large system in which the equilibrium pressure is already P . This quantity we shall call

$$q = h_f - \left(\frac{\partial U}{\partial N}\right)_P = \frac{\partial}{\partial N} \Delta Q - N \frac{\partial h_f}{\partial P} \frac{\partial P}{\partial N} = h_f - \bar{u}_f - N \frac{\partial \bar{u}_f}{\partial P} \frac{\partial P}{\partial N} \tag{6}$$

We shall now introduce the assumption that the process just described is physically indistinguishable from one in which the system is originally chosen so as to include the one mole of fluid and the volume it occupies, and is then compressed through 1 molar volume. (This simply means that when the system is brought into contact with a quantity of pure fluid at the same pressure, nothing of importance will occur.) We then obtain the Clapeyron equation

$$q = v_f(P + \partial U / \partial T) = v_f T (\partial P / \partial T)_V \tag{7}$$

We now imagine the system divided into two parts, of volumes V^0 and V' containing, respec-

tively, N^0 and N' moles of fluid, with all the adsorbent in the first part, and proceed to calculate the properties (designated with 0) of this part taken alone. We find

$$N^0 = N - N' = N - V'/v_t \quad (8)$$

$$\Delta U^0 = \Delta U \quad (9)$$

$$\bar{v}_a^0 = \bar{v}_a \quad (10)$$

$$\bar{v}_t^0 = \bar{v}_t \quad (11)$$

$$\bar{u}_t^0 = \bar{u}_t - N' \Delta U / NN^0 \quad (12)$$

$$\Delta Q^0 = \Delta Q - PV' = \Delta U + N^0 P v_t \quad (13)$$

$$q^0 = v_t T \left(\frac{\partial P}{\partial T} \right)_V = \frac{1}{1 - \frac{\partial u_t}{\partial N} / \frac{\partial N}{\partial N}} \left[q + N' \frac{\partial u_t}{\partial P} \frac{\partial P}{\partial N} - v_t P \frac{\partial N'}{\partial N} \right] \quad (14)$$

$$\text{where } \frac{\partial N'}{\partial N} = - \frac{V'}{v_t^2} \frac{\partial v_t}{\partial P} \frac{\partial P}{\partial N} \quad (15)$$

Equation (14) is derived by considering the heat evolved upon the simultaneous admission, at equilibrium pressure, of dN^0 moles of fluid into the volume V^0 and dN' moles into the dead space V' , namely

$$q^0 dN^0 = q^0 dN^0 + v_t P dN' - N' (\partial u_t / \partial P) dP \quad (16)$$

Upon replacing 0 by a,b,c , and setting $V^a = \varphi_1 + \varphi_2$, $V^b = \varphi_1$, $V^c = 0$, we get at once the required correction formulas for the various quantities according to the three possible definitions.

For the amount adsorbed we find

$$N^a = N - (V - \varphi_1 - \varphi_2) / v_t = -(M\bar{v}_a - \varphi_1 - \varphi_2) / v_t \quad (17)$$

$$N^b = N - (V - \varphi_1) / v_t = -(M\bar{v}_a - \varphi_1) / v_t \quad (18)$$

$$N^c = N - V / v_t = -M\bar{v}_a / v_t \quad (19)$$

When the experiments are made with a spring balance, we have

$$w_t N^a = W - M w_a + w_t (\varphi_1 + \varphi_2) / v_t \quad (20)$$

$$w_t N^b = W - M w_a + w_t \varphi_1 / v_t \quad (21)$$

$$w_t N^c = W - M w_a \quad (22)$$

where W is the apparent weight (corrected for buoyancy of container and spring), and w_t and w_a are specific weights.

The definition of thermal quantities is somewhat more involved. By "heat of adsorption" we wish to express the quantity of heat accompanying some isothermal process connected with adsorption, divided by the simultaneous change in quantity adsorbed. Thermal effects due to dead fluid must be corrected for. This correction does not enter the total irreversible adsorption heat, which is simply $\Delta U / N^a$, $\Delta U / N^b$ or $\Delta U / N^c$. Note that the quantity $\Delta U / M$ is available as a uniquely determined function of P and T , without reference to any definition.

The term "reversible integral heat" implies

that during the process of building up the quantity adsorbed, each portion of added fluid must come from a supply at the momentary equilibrium pressure. The required quantity is

$$(1/N^0) \left(\Delta U + \int_0^{N^0} P v_t dN \right) = (1/N^0) \left(\int_0^{N^0} h_t dN - U \right) \quad (23)$$

with N^0 in the initial fraction defined as desired. It is difficult to avoid the conclusion that the upper limit of integration should be N^a . In practice, what is determined is "total adsorption heat," in which the whole quantity of fluid is taken from a supply maintained at the final equilibrium pressure. The distinction vanishes if the heat content of the fluid is independent of pressure; in fact, the heat evolved in an experiment then becomes independent of the pressure at which the fluid enters the calorimeter, provided that it enters slowly and is not precooled by expansion. This can be secured by providing the entrance to the calorimeter with a throttling constriction. In general the quantity desired is $\Delta Q^0 / N^0 = \Delta U / N^0 + P v_t = (1/N^0) (\Delta Q - P V')$ (24) with Q^0 and N^0 defined as desired. Note that in accordance with the accepted definition B, even if the calorimeter is entirely filled with adsorbent, not all the heat evolved is credited to adsorption, but a correction term $P \varphi_2$ has to be subtracted, equal to the heat which would be observed if fluid were allowed to flow into an evacuated calorimeter of volume equal to the pore volume.

When the fluid is added reversibly in small instalments, we obtain the reversible differential adsorption heat, q^a , q^b or q^c . The corrections required in calculating these quantities from thermal experiments on an actual system are given in the right-hand side of eq. (14). q^a has a simple physical meaning—the heat set free in a calorimeter completely filled with adsorbent. q^c can be reduced with the aid of eq. (16) to the form

$$q^c dN^c = q^c dN + (V/v_t) (d u_t + P d v_t) \quad (25)$$

That is, it is the difference between the heat observed in the actual calorimeter and that which would be observed in the same calorimeter in an experiment in which the adsorbent was absent, but all external conditions were the same, this difference then being divided by dN^c as previously defined. This is a purely objective definition. q^b , corresponding to the accepted definition, has neither advantage. It is to be

noted that the differential heats are not the derivatives of the total heats, but differ by a term involving $\partial h_t / \partial P$. The q 's can always be calculated from the correspondingly defined isosteres, by the Clapeyron equation.

duce an entirely self-consistent set of figures. Lowry and Olmstead used the van Laar equation in connection with the observed vapor pressures and coexisting densities of carbon dioxide; but the latter are not wholly consistent with the

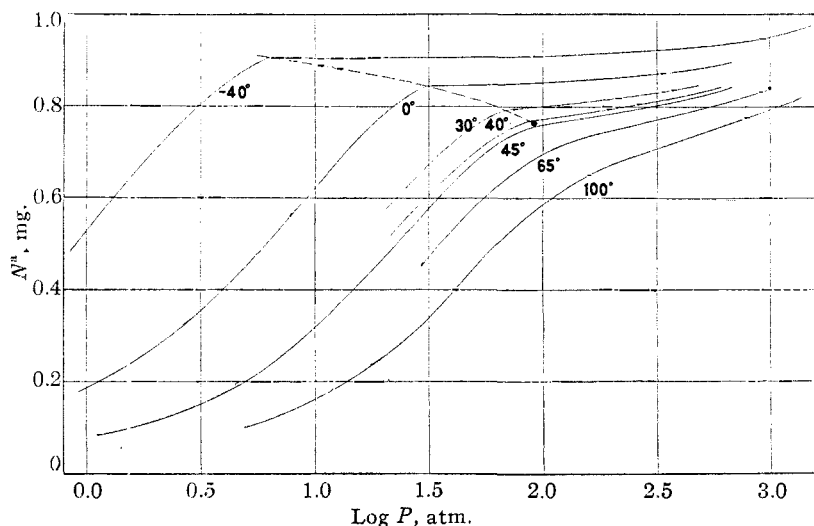


Fig. 1.

former, as is shown by the necessity of introducing an arbitrary correction in the calculated potential ϵ in order to secure the same value for the coexisting phases. We have preferred to secure perfect consistency by using the vapor pressures and coexisting densities given by the equation itself (by finding at each temperature two densities for which the calculated pressures and potentials are the same). The fictive gas is somewhat less volatile than the actual, and has a higher critical temperature; for purposes of illus-

There are not available experimental results (particularly thermal data) over sufficient range to serve as illustrations of the functions and relations which have been discussed. Now, in spite of the *a priori* impropriety of applying bulk equations of state to matter in a state of subdivision approaching the molecular scale, the Polanyi method has proved capable of predicting successfully adsorption isotherms, and can be readily extended to include thermal properties. It therefore seemed worth while to work out by this method the general character which the most important quantities may be expected to display in the region of high pressure, and especially in the critical region. For this purpose we have considered a typical ϵ - ϕ curve for charcoal, and assumed a hypothetical gas which accurately obeys van Laar's equation of state, with the constants adopted for carbon dioxide by Lowry and Olmstead.³ The reason for this choice was that we wished to pro-

tration this is unimportant. Isotherms were first calculated substantially by the method of Lowry and Olmstead, except that it was necessary to use their complete equation

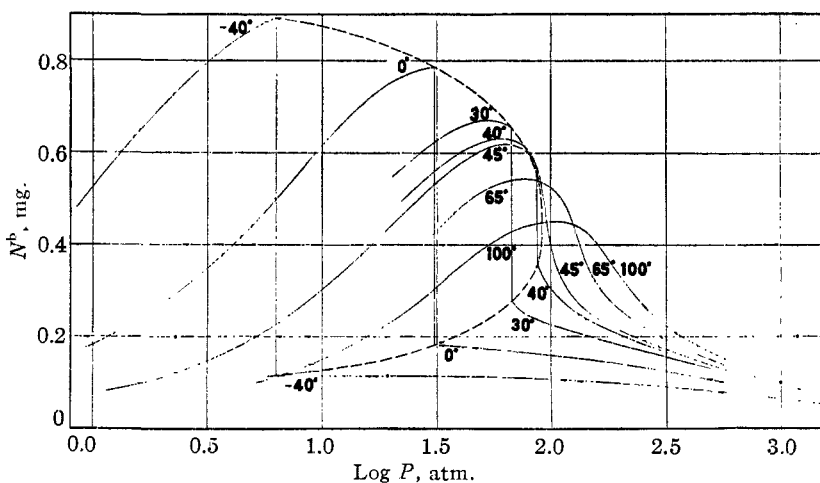


Fig. 2.

(15), instead of the simplified one (16), because of the high density of the fluid in the free space. This calculation gives N^a provided that ϕ_2 is identified with the maximum ϕ of the ϵ - ϕ curve (in this case 0.708 cc. per gram adsorbent). To get N^b we subtract 0.708 δ , and to get N^c we further subtract 0.472 δ , where δ is the density of the equilibrium fluid, and 0.472 is ϕ_1 upon the

(3) H. H. Lowry and P. S. Olmstead, *J. Phys. Chem.*, **31**, 1601 (1927).

assumption that the adsorbent has the density 2.12. The N 's are here computed in grams per gram of adsorbent. The course of N^a is shown in Fig. 1. Above the critical temperature (42°) the isotherm rises monotonically but at a steadily decreasing rate as the fluid in the pores becomes progressively less compressible, approaching a positive limit at infinite pressure. (The concavity upward which appears at each extremity is due solely to the adoption of a logarithmic pressure scale.) At lower temperatures a discontinuity in slope appears at the saturation pressure,

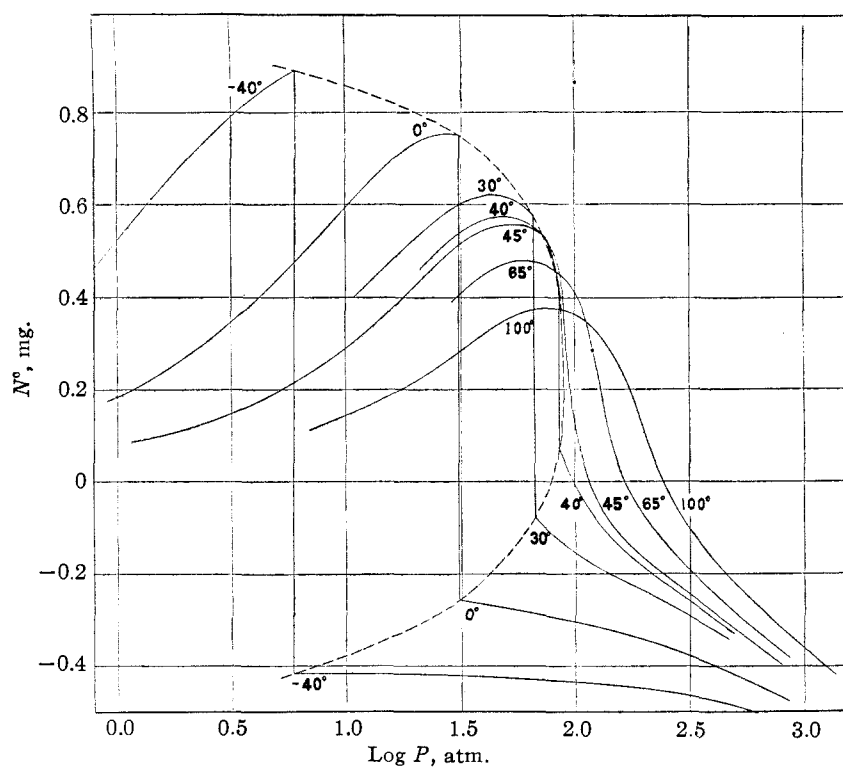


Fig. 3.

and the system is said to be saturated; yet it is possible to force in more fluid, especially if not too far below the critical temperature. The dashed line is the locus of saturated systems, and terminates in the circle marking the critical point.

Figure 2 shows the classical isotherms, N^b . Above the critical temperature, they exhibit maxima, from which they fall rapidly, tending eventually to zero at infinite pressure, when the fluid in the pores can no longer be compressed. (Polanyi⁴ has called attention to this feature.) Below the critical temperature, the saturation

(4) See H. Freundlich, "Colloid and Capillary Chemistry" (Hatfield's translation), Methuen and Co., London, 1926, p. 128, Fig. 27.

line takes a form similar to the familiar "steam-dome." Upon reaching it, each isotherm drops discontinuously from the upper to the lower branch. It is remarkable that the last isotherm below the critical point (40° isotherm) crosses the saturation line below the saturation pressure, and terminates upon it from above, thus anticipating in a way the very rapid fall of the slightly higher isotherms. This produces a very curious overlapping in the critical region.

Figure 3 shows the isotherms of N^c . They are similar to those of N^b except that they become negative at high pressures.

This is not disturbing when we recall the close relation between N^c and \bar{v}_a (eq. (19)). Like any other partial molal or specific volume, \bar{v}_a can be positive or negative, accordingly as repulsive or attractive terms in molecular interaction predominate.

Figures 4, 5 and 6 give the corresponding isosteres (lines of constant N^a , N^b or N^c). The vapor pressure line of the liquid is also included; due to the inadequacy of the assumed equation of state, it is much more strongly curved than that of the real liquid, and this is undoubtedly also true of the isosteres in the same pressure range.

The various thermal quantities can be readily computed by a natural extension of the Polanyi method. In accordance with the basic postulates, we assume that the total energy of any adsorption system can be found by adding: first, the internal energy of the adsorbent (a constant which may be arbitrarily set equal to zero); second, the internal energy of the adsorbed fluid as given by its normal equation of state under the conditions assumed to prevail within the adsorption space; and, finally, the mutual potential energy of adsorbent and fluid, as given by the product of adsorption potential times density in each element of volume. Let u_f and f_f be the total and free molal energies of the fluid at any pressure or

density δ (not necessarily, as before, the equilibrium pressure). Then elementary considerations show that at each place in the adsorption space, the adsorption potential ϵ is equal to $f_t - f_t^f$, where f_t^f is the value of f_t in the free space. The total potential energy is therefore $-\int d\phi \delta (f_t - f_t^f)$. The total internal energy of the fluid is $\int d\phi \delta u_t$. For the total energy of the system we have

$$U = \int d\phi \delta (u_t - f_t) + f_t^0 N_a \quad (23)$$

This can be evaluated exactly as Polanyi evaluates $N_a = \int d\phi \delta$, by combining the funda-

The equation of state assumed is

$$Pv = [1 + b_g/(v - b_0)]RT - a/v \quad (25)$$

where a , b_g and b_0 are functions of the temperature, either analytic or empirical. Expressing their temperature derivatives with primes, we find

$$u_t = RT^2[(b'_g b_0 - b_g b'_0)/b_0^2 \ln(v - b_0/v) - b_g b'_0/b_0(v - b_0)] - (a - a'T)/v \quad (26)$$

(The energy of the very dilute gas at the given temperature is arbitrarily taken as zero.) h_t is found by adding Pv as given by the equation of

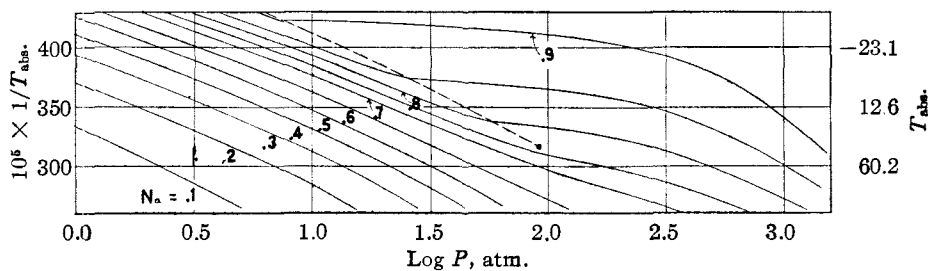


Fig. 4.

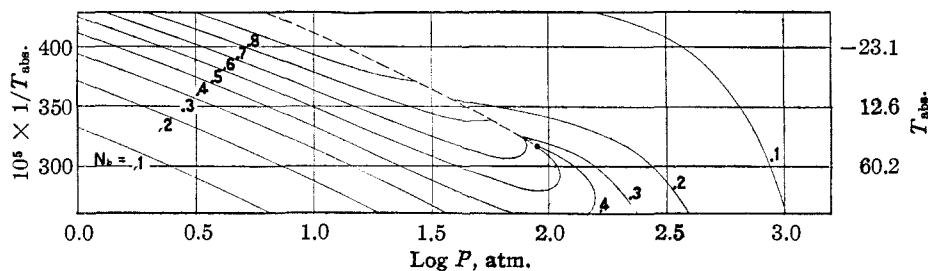


Fig. 5.

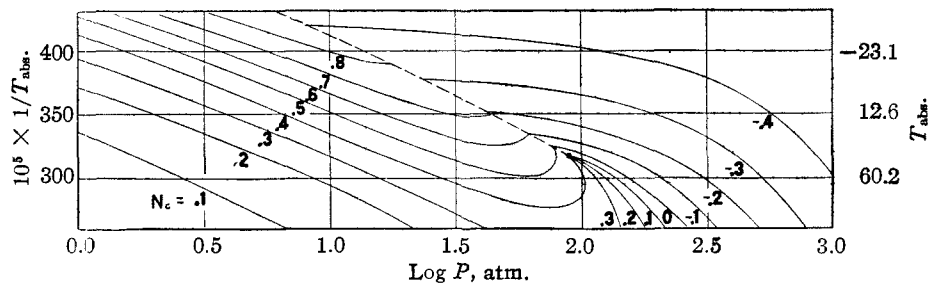


Fig. 6.

mental ϵ - ϕ curve with one showing $\delta(u_t - f_t)$ as a function of ϵ , the latter being characteristic of the fluid alone. (Since u_t contains an undefined constant, the value of U so computed will contain an arbitrary term proportional to N_a , but this will fall out when we compute differences like ΔU .)

For the present computation, the internal energy of the fluid can be found by applying to the equation of state the well-known formula

$$(\partial u/\partial v)_T = T(\partial P/\partial T)_V - P \quad (24)$$

state. f_t is the negative of ϵ as given by Lowry and Olmstead's eq. (16) without the last term.

Figures 7 and 8 show several thermal quantities as thus calculated, at 0° , plotted against the amount adsorbed. Definition A is used in all cases. It will be noticed that U is a nearly linear function of N . At saturation, the slope increases somewhat. At lower temperatures this change of slope is more pronounced. It is due to the fact that when a new portion of fluid is added

to a system below saturation, it goes almost entirely into a region of lower potential ϵ than that previously occupied. When, at saturation, the available space is all filled, any further fluid forced in will be distributed (under strong compression) throughout the whole space, including regions of high potential ϵ so that the potential

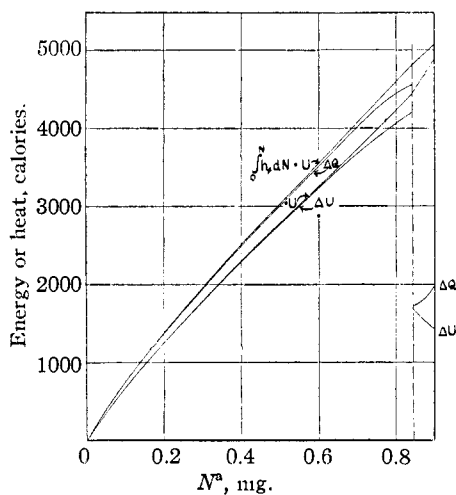


Fig. 7.

energy increases more rapidly (in absolute magnitude). The internal energy of the fluid is also less at high compression, the work of compression being more than compensated by the heat of compression thrown out. The marked curvature in q and ΔQ near saturation is due to the violent fluctuations of the quantity Pv_f in this region. The break in q at saturation is less than one would at first expect. Remembering that $q = h_f - \partial U/\partial N$, we see that this is because the break in $\partial U/\partial N$ nearly cancels that in h_f (the latter break being just the heat of vaporization). At 30° the calculation even shows a slight increase in q at saturation.

The approximate constancy of q now gives a clear explanation of the characteristic form of the isosteres with definition A, Fig. 4. The slope of these isosteres is determined by the Clapeyron equation, which can be written

$$\partial \ln P/\partial(1/T) = -q/\alpha \quad \alpha = Pv_f/T \quad (27)$$

Since q is nearly constant, the slope will be essentially proportional to the ratio α . Now, this ratio is constant and equal to R in the range of low pressures. It falls off somewhat just before saturation occurs, drops discontinuously to a very small value upon condensation of the vapor, and then rises rapidly without limit as the pres-

sure is further increased. This behavior is faithfully reproduced by the slopes with which the isosteric lines cross the 0° horizontal at the various pressures. Indeed, substantially the same values of q may be taken from these slopes (which merely means that the calculations have been correctly performed). This stands in marked contrast with the case of the vapor pressure curve of a liquid, which is very nearly a straight line. In this case, the falling off in the volume change is practically balanced by the diminution in the latent heat, until very near the critical point.

According to Polanyi, q should take a very simple form at low temperatures, where the vapor is dilute and the liquid practically incompressible

$$q = \epsilon + \lambda$$

where ϵ is the potential in the adsorption space at the level where the meniscus is supposed to form, and λ is the latent heat of evaporation. At higher temperatures, q will be greater, owing to the compressibility of the liquid, but will approach $\epsilon + \lambda$ at low values of N . In order to show this, a graph of $\epsilon + \lambda$ is included in Fig. 8. For temperatures above the critical, Polanyi gives two

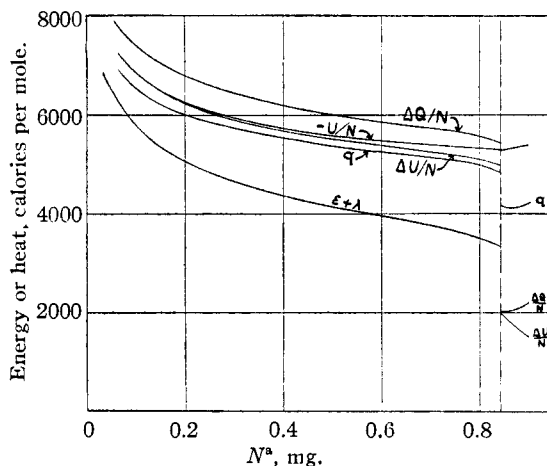


Fig. 8.

equations, (35) and (36), the exact meaning of which is not quite clear, but which apparently intend to express what we have called

$$-U = \int d\phi \delta(\epsilon - u_f)$$

with u_f calculated from the van der Waals equation. This, of course, differs from q in being a total, not a differential, quantity, and in omitting the work term. Lowry and Olmstead also put forward an expression (19) for the "heat of adsorption," which in the present nomenclature

becomes $1/N^a \int_0^{\phi_{\max.}} \epsilon \delta d\phi$. This is clearly inadequate, as it omits the contribution from the internal energy change of the fluid in passing from the free to the adsorbed (compressed) state, which will (below the critical point) include the heat of vaporization.

Summary

The phenomenology and thermodynamic theory of adsorption systems are generalized and made applicable to the entire range of conditions within which the adsorbed substance normally exists as

a fluid. Special attention is devoted to the corrections required when experiments are performed at high pressures. The conclusion is reached that several different methods of defining adsorption (all equivalent at low pressures) can advantageously be adopted, according to the purpose in hand. The consequences of adopting each of these definitions are followed in some detail, and illustrated, in the absence of suitable experimental material, by computations based upon the Polanyi theory.

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Adsorption at High Pressures. II

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Introduction

In order to provide experimental material illustrating the application of the ideas developed in the previous paper, we undertook to investigate the adsorption equilibrium between charcoal and several gases over a range of temperature and pressure extending both lower and higher than their critical regions. By working up to 100° and 100 atmospheres, we could accomplish this with carbon dioxide (critical point 31°, 73 atm.), nitrous oxide (c. p. 36.5°, 72 atm.) and silicon tetrafluoride (c. p. -1.5°, 50 atm.).

Materials and Apparatus

The charcoal used was a steam-activated coconut charcoal obtained from the National Carbon Company. The particles passed a 10- but not a 20-mesh sieve. In order to provide a basis for estimating the "skeleton" volume and the "pore" volume, we determined the apparent density by simple displacement (with boiling to expel gases) in several liquids, with the following results:

Liquid	Density	Specific volume
Mercury	0.629	1.590
Benzene	2.06	0.485
Ether	2.12	.472
(Graphite)	(2.25)	(.444)

We also determined an adsorption isotherm with benzene vapor at 20° as follows.

Pressure, mm.	13.5	20.5	39.5	50.0	70.5	74.0
Cc. ads. per g.	181.4	196.6	208.8	215.5	231.8	234.5

Upon extrapolating the isotherm to the saturation pressure of liquid benzene, we obtain 236 cc. of benzene vapor (measured at N. T. P.) as the maximum taken up by one gram of our charcoal.

The carbon dioxide was the last half of the contents of a commercial cylinder, and was used without special treatment to remove impurities, as the coincidence of adsorption and desorption points on a given isotherm seemed to prove that no significant amounts of foreign substances were present. The silicon tetrafluoride was prepared substantially by the method described by Booth and Germann,¹ in which the gas is generated by strongly heating barium fluosilicate, passed through a carbon dioxide cold trap and through glass wool and phosphorus pentoxide to remove water and hydrofluoric acid, and purified by distillation. Before use, each sample was condensed with liquid air and pumped. The density of the gas was carefully determined in a balloon, two runs giving 4.674 and 4.675 g. per liter at N. T. P. Nitrous oxide was taken from a cylinder. The density of the gas drawn from the top of the cylinder in the ordinary way was found too low; but when the cylinder was inverted the evaporated liquid possessed a normal density of 1.976, corresponding to 99.7% pure nitrous oxide, which was considered satisfactory.

The measurements were carried out with a quartz spring balance, from which the glass bucket containing the charcoal depended by a long platinum wire. The whole was housed in a nickel-silver tube, closed at the bottom, of sufficient length so that the upper part, enclosing the spring, did not change perceptibly in temperature during the necessary heating and cooling of the charcoal below. The movements of the spring were followed with a cathetometer through windows of plate glass, set with Wood's metal into a square steel block, which served as a union into which were screwed the lower and upper parts of the nickel-silver tube, as well as the connections to pump, gage and gas supply. Pressures up to 5 atmospheres were read on a mercury column. Above 5 atm. a dead-weight gage was at first used. Later, a large Bourdon gage was obtained, and by occasional comparison with the dead-weight gage was found satisfactory as to accuracy

(1) Booth and Germann, *J. Phys. Chem.*, **21**, 81 (1917).