

with the theoretical. In contrast to tetrabutylammonium picrate, no concentration dependence of the 60-cycle slope is visible, but there is a systematic decrease of the Wien coefficient with increasing frequency, which becomes more pronounced with decreasing concentration.

As stated in the introduction, the Langevin time constant is of the order of milliseconds for these solutions: at $c = 5 \times 10^{-4}$, $\tau_L = 0.077 \times 10^{-3}$ sec., and at $c = 1 \times 10^{-4}$, $\tau_L = 0.455 \times 10^{-3}$ sec. With decreasing concentration, τ_L increases, almost hyperbolically in the region of the minimum in equivalent conductance. For the higher concentrations and low frequency the ionic distribution has time to adjust itself to the field and we find the normal Wien effect. But when the frequency becomes high and the concentration low, the field-sensitive reaction Ion pair \rightarrow Free ions becomes increasingly less able to follow the field. Consequently the Wien coefficient decreases.

The Langevin time constant also depends on field strength, as Onsager pointed out; for our case, this dependence is a second order effect, because the fields used were far below those corresponding to saturation.

Summary

1. The conductance of tetrabutylammonium bromide in diphenyl ether at 50° has been measured at low voltage over the approximate concentration range 10^{-6} – 10^{-3} normal.

2. Conductances at 60, 600 and 1000 cycles at field strengths up to 20 KV/cm. were measured in the concentration range 0.5 – $5.0 \times 10^{-4} N$.

3. For low frequencies, the Wien effect is in agreement with Onsager's theory; when the Langevin time of relaxation becomes comparable to the period of the impressed field, a dispersion of the Wien effect appears.

SCHENECTADY, N. Y.

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On a Theory of the van der Waals Adsorption of Gases*

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A search of the literature on the van der Waals adsorption of gases reveals that there exist five different types of isotherms. To give an example of each type we may mention the adsorption of oxygen on charcoal at -183° (Type I),¹ nitrogen on iron catalysts at -195° (Type II),² bromine on silica gel at 79° (Type III),³ benzene on ferric oxide gel at 50° (Type IV),⁴ and water vapor on charcoal at 100° (Type V).⁵ The five isotherms in Fig. 1 illustrate these five types; they are imaginary, not real isotherms. Type I is the well-known Langmuir adsorption isotherm, Type II is the S-shaped or sigmoid isotherm, but no names have been attached so far to the three other types. Types II and III are closely related to Types IV and V, only in the former cases the adsorption increases as the vapor pressure p_0 of the adsorbed gas is approached, whereas in the latter cases the maximum adsorption is attained, or almost attained, at some pressure lower than the vapor pressure of the gas.

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(1) Brunauer and Emmett, *THIS JOURNAL*, **59**, 2682 (1937).

(2) Emmett and Brunauer, *ibid.*, **59**, 1553 (1937).

(3) Reyerson and Cameron, *J. Phys. Chem.*, **39**, 181 (1936).

(4) Lambert and Clark, *Proc. Roy. Soc.*, **A123**, 497 (1929).

(5) Coolidge, *THIS JOURNAL*, **49**, 708 (1927).

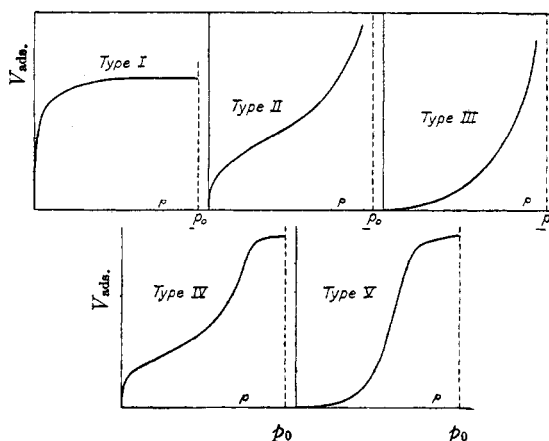


Fig. 1.—The five types of van der Waals adsorption isotherms.

An interpretation of the Type I isotherm was given by Langmuir who in 1915 derived his celebrated isotherm equation for adsorption in a unimolecular layer.⁶ Brunauer, Emmett and Teller⁷ derived an isotherm equation for the multimolecular adsorption of gases that includes both the Langmuir isotherm and the S-shaped isotherm as

(6) Langmuir, *ibid.*, **37**, 1139 (1915).

(7) Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938). This paper henceforth will be referred to as paper I.

special cases, but hitherto no one has derived equations to cover isotherms of the shape designated as Types III, IV, and V.

It is a fact that the isotherm of paper I includes not only Types I and II for which it was derived, but also Type III, as will now be shown; it does not, however, include Types IV and V. To overcome this deficiency a new equation is now evolved to cover all five types, and its application is shown in the interpretation of some experiments in the literature. Finally, a comparison is made between the present theory of van der Waals adsorption and the capillary condensation theory.

I. Interpretation of the Type III Isotherms

In paper I the following isotherm equation was derived for multimolecular adsorption on a free surface

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_0} \quad (\text{A})$$

where v is the volume adsorbed at pressure p and absolute temperature T ; p_0 is the vapor pressure of the gas at temperature T ; v_m is the volume of gas adsorbed when the entire adsorbent surface is covered with a unimolecular layer; and c is approximately equal to $e^{(E_1 - E_L)/RT}$, where E_1 is the heat of adsorption of the gas in the first adsorbed layer, and E_L is the heat of liquefaction of the gas. If one plots the function $p/v(p_0 - p)$ against p/p_0 one obtains a straight line whose slope and intercept give the values of v_m and c .

If the adsorption takes place in a limited space, so that even at saturation pressure only a limited number of layers can be adsorbed on the adsorbent, one obtains the expression

$$v = \frac{v_m c x}{1 - x} \frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (c - 1)x - cx^{n+1}} \quad (\text{B})$$

where $x = p/p_0$, v_m and c have the same meaning as before, and n is the maximum number of layers of adsorbed gas that can build up on the walls of the capillaries, supposedly of plane parallel sides. Equation (B) reduces to (A) when $n = \infty$; and in the other extreme case when only one adsorbed layer can form on the surface, *i. e.*, when $n = 1$ it reduces to the Langmuir type equation

$$p/v = p_0/cv_m + p/v_m \quad (\text{C})$$

Equation (C) describes a Type I isotherm, and equations (A) and (B) describe Type II isotherms when $c \gg 1$ or $E_1 > E_L$, in other words, when the attractive forces between adsorbed gas and adsorbent are greater than the attractive forces between the molecules of the gas in the liquefied

state. All of the cases treated in paper I belong to this class. It should be noted, however, that when the forces between adsorbent and adsorbate are small—*i. e.*, when $E_1 < E_L$ —then equations (A) and (B) describe Type III isotherms.

Some of the most interesting Type III isotherms available in chemical literature are those of Reyerson and Cameron³ on the adsorption of bromine and iodine on silica gel. Brunauer and Emmett^{1,7} investigated the adsorption of six different gases on two samples of silica gel sent to them by Reyerson. They found that the capillaries in silica gel are relatively large in diameter, n is about 9, so in fitting the curves of Reyerson and Cameron we shall assume as an approximation that $n = \infty$, whereupon the simpler equation (A) can be used. Reyerson and Cameron calculated from the Clapeyron–Clausius equation that the differential heat of adsorption of bromine on silica gel is 7700 calories per mole. This value, however, is the heat of adsorption for the first part of the unimolecular layer covered, so E_1 , the average heat of adsorption for the entire first layer, is most probably smaller than this. The heat of liquefaction of bromine is 7200 calories per mole, so we assumed as a first approximation that $E_1 = E_L$, or $c = 1$. Under this condition it follows from (A) that $v = v_m$ when $p = 0.5 p_0$, and thus the constant v_m is obtained from one of the isotherms. The 79° isotherm gives the value $v_m = 3.62$ millimoles of bromine per gram of silica gel, which corresponds to a specific surface of 470 square meters per gram, using 21.4 Å.² as the area covered by one bromine molecule on the surface. (This area has been calculated from the density of liquid bromine in the manner described in reference 2, page 1558. The density of liquid bromine was taken as 3.06, from the "International Critical Tables," Vol. I, page 102). The average surface area obtained from adsorption isotherms of nitrogen, argon, oxygen, carbon monoxide and carbon dioxide on another sample of the same silica gel^{1,7} was 507 square meters per gram. These five gases yield Type II (S-shaped) isotherms on silica gel, and yet the v_m value shows a remarkable agreement with that obtained from the Type III bromine isotherm. This we consider to be one of the most interesting confirmations of our assumptions.

Having obtained the two constants, $c = 1$ and $v_m = 3.62$ millimoles of bromine per gram of silica gel at 79°, one can proceed to calculate the

isotherms by equation (A). The values of c and v_m at the three other temperatures were calculated as described in reference 7, page 316. Figure 2 gives the results. The four curves are the calculated isotherms; the circles, squares, and triangles are the experimental points of Reyerson and Cameron.⁸ (The empty circles, etc., represent adsorption points, the full circles desorption points.) The isotherm equation not only describes the shapes of the curves, but gives also the temperature dependence, since c and v_m were obtained from only the one isotherm, namely, that at 79°.

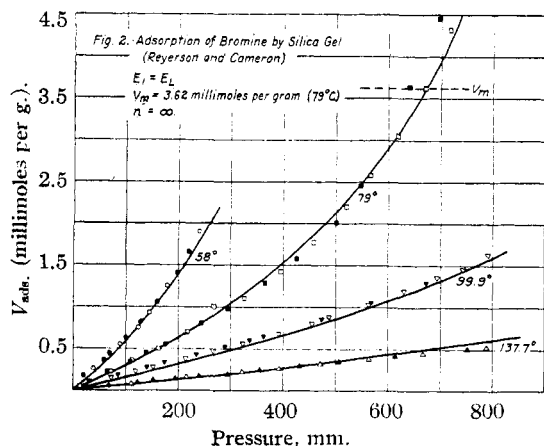


Fig. 2.—Adsorption of bromine by silica gel (Reyerson and Cameron): $E_L = E_L$; $V_m = 3.62$ mmoles. per gram at 79°; $n = \infty$.

The iodine isotherms on silica gel obtained by Reyerson and Cameron are striking because of the very small adsorption values. Here again we assume as an approximation that $n = \infty$, and therefore that equation (A) applies. Using the surface area obtained from the bromine isotherm, and assuming that the packing of the iodine molecules on the surface is the same as in the liquid state, one estimates that $v_m = 2.93$ millimoles of iodine per gram of silica gel. We have seen that for bromine at $p = 0.5 p_0$ the amount adsorbed was just sufficient to cover the surface of the entire silica gel with a unimolecular layer. Not so with iodine: the 178.4° isotherm shows an adsorption of 0.12 millimole per gram at $p = 0.5 p_0$ (330 mm.), which is only one twenty-fourth of the amount necessary to cover the surface with an adsorbed layer of iodine. This indicates that the forces of adsorption are considerably weaker than the forces existing between iodine molecules in the liquid state. Indeed, a value of $E_L - E_1 =$

3500 calories gives a good fit for the 178.4° isotherm, as Fig. 3 shows. One can then proceed to calculate the values of v_m and c at the other temperatures (reference 7, page 316) and obtain the three other isotherms.

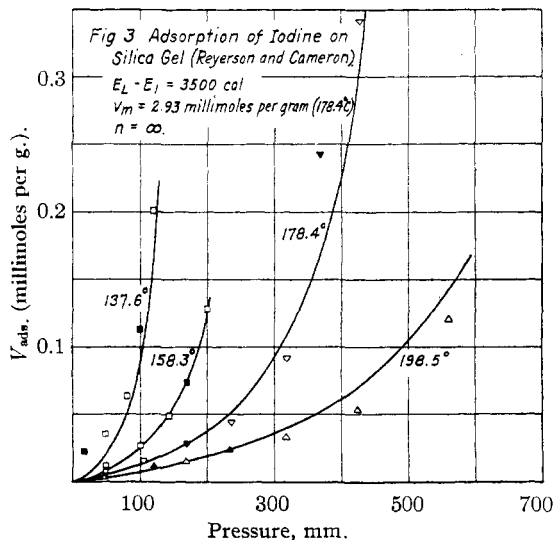


Fig. 3.—Adsorption of iodine on silica gel (Reyerson and Cameron): $E_L - E_1 = 3500$ cal.; $V_m = 2.93$ mmoles. per gram at 178.4°; $n = \infty$.

Since we have found that $E_1 = E_L$ for bromine on silica gel, and $E_1 < E_L$ for iodine, we might suspect that $E_1 > E_L$ for chlorine on silica gel. This means that instead of Type III isotherms one would expect the more customary Type II isotherms. The experiments of Reyerson and Wishart⁸ show that this is actually the case. Since they worked with small p/p_0 values (their experiments extend up to $p/p_0 = 0.096$), their isotherms represent the lower region of Type II curves, the region that is concave toward the pressure axis. They were not able to fit their curves with a simple Langmuir equation probably because the heat of adsorption varied strongly over the surface.

If $E_1 \ll E_L$, then no appreciable adsorption takes place until the pressure reaches a value close to p_0 , the saturation pressure. Such very curious shaped isotherms were obtained by McHaffie and Lenher,⁹ who found that no appreciable adsorption of water on glass took place until p/p_0 became greater than 0.7. Even more exaggerated results were obtained by Frazer, Patrick and Smith,¹⁰ for they have found that within their

(8) Reyerson and Wishart, *J. Phys. Chem.*, **41**, 943 (1937).

(9) McHaffie and Lenher, *J. Chem. Soc.*, **127**, 1559 (1925).

(10) Frazer, Patrick and Smith, *J. Phys. Chem.*, **31**, 897 (1927).

experimental error of a few molecular layers no appreciable adsorption of toluene took place on virgin glass. The interpretation of their results very close to saturation becomes extremely difficult, since it depends very strongly on the exact value of the vapor pressure. In terms of our theory these two papers give very interesting examples of adsorption phenomena where the forces of adhesion (*e. g.*, between glass and toluene) are very small compared with the forces of cohesion (between toluene and toluene).

Finally mention should be made of some adsorption measurements of Keesom and Schmidt^{11,12} on helium and neon at temperatures close to their boiling points. In spite of the fact that the adsorption took place on free glass surfaces and not in narrow capillaries, a unimolecular adsorbed layer was not exceeded even close to saturation. The concave form of the isotherms shows that, as should be expected, the forces of attraction between the adsorbent and the adsorbed molecules are greater than the forces between the adsorbed molecules themselves, so that an explanation of the sort given for the experiments of McHaffie and Lenher, and of Frazer, Patrick, and Smith, does not apply here. The experiments, however, might be explained by assuming that the heat of adsorption in the second layer is smaller than the heat of liquefaction. This may possibly be due to a configuration of atoms in the first layer imposed upon the adsorbed atoms by the surface structure of glass and differing more strongly than in other cases from the structure of a unimolecular liquid layer.

II. Derivation of a More General Isotherm Equation that Includes All of the Five Isotherm Types as Special Cases

As was stated earlier, equations (A) and (B) include the first three types of isotherms, but not the last two. Types IV and V suggest that the complete or almost complete filling of the pores and capillaries of the adsorbent occurs at a pressure lower than the vapor pressure of the gas—indeed, sometimes at a considerably lower pressure. This lowering of the vapor pressure indicates that as the pressure of the gas is increased some additional forces appear that make the heat of adsorption or energy of binding in some higher layer to be greater than E_L , the heat of liquefaction

(11) Keesom and Schmidt, *Proc. Acad. Sci. Amsterdam*, **36**, 825 (1933).

(12) Keesom and Schmidt, *ibid.*, **36**, 832 (1933).

of the gas. This must necessarily be so, since the *last adsorbed layer in a capillary is attracted on both sides*, and therefore its heat of evaporation must be greater than that of any other layer (with the possible exception of the first layer where the adsorptive forces are very different). We shall denote this *additional* energy of evaporation by Q , whereupon the rate of evaporation of the adsorbed gas from the last layer will not be $ke^{-E_L/RT}$, but $ke^{-(E_L + Q)/RT}$. When the last layer is adsorbed, not only the heat of liquefaction will be liberated, but in addition also twice the surface energy is set free, since two surfaces disappear. Thus if the last adsorbed layer fits in exactly and without strain, Q will be equal to $2\sigma S$, where σ is the surface tension, and S is the surface area covered by one mole of the liquefied gas spread out into a unimolecular layer. The value of S will naturally depend on the assumed type of packing. If the fit of the last layer is not exact, Q will be smaller.

The derivation of the adsorption isotherm equation is similar to the derivation of equation (B) in paper I. Let $s_0, s_1, s_2, \dots, s_i, \dots$ represent the surface area that is covered by only 0, 1, 2, \dots, i, \dots layers of adsorbed molecules. When equilibrium is established the principle of microscopic reversibility demands that all of the following evaporation-condensation equilibria be true:

$$\begin{aligned} a p s_0 &= b s_1 e^{-E_1/RT} \\ a p s_1 &= b s_2 e^{-E_L/RT} \\ a p s_2 &= b s_3 e^{-E_L/RT} \\ &\vdots \\ &\vdots \\ a p s_{n-2} &= b s_{n-1} e^{-E_L/RT} \\ a p s_{n-1} &= b s_n e^{-(E_L + Q)/RT} \end{aligned}$$

where p is the pressure, E_1 is the heat of adsorption in the first layer, E_L is the heat of liquefaction of the gas, $E_L + Q$ is the heat of adsorption in the last layer, and a and b are constants. The approximations used are the same as in paper I. It should be noted that E_L is not the heat of adsorption of an isolated molecule of the i -th layer condensing on top of the $(i - 1)$ -st layer, but rather the average energy liberated in the building up of the i -th layer. Thus the average interaction of the molecules in the i -th layer is roughly taken into account.

We visualize the adsorption as taking place in a capillary consisting of two plane parallel walls. The maximum number of layers that can fit into this capillary is assumed to be $2n - 1$. We can

obtain the total volume of gas adsorbed by summing up the volume of gas adsorbed on each surface element of *one wall* of the capillary and multiplying the result by two. The only exception is the volume adsorbed on the surface element s_n , which appears only once since it is common to both walls of the capillary. The summation, in a manner similar to that given in paper I, gives the equation

$$v = \frac{v_m c x}{1 - x} \frac{1 + (1/2ng - n)x^{n-1} - (ng - n + 1)x^n + 1/2ngx^{n+1}}{1 + (c - 1)x + (1/2cg - c)x^n - 1/2cgx^{n+1}} \tag{D}$$

where $g = e^{Q/RT}$, and all the other terms have the same meaning as in paper I. The equation describes a Type IV or V isotherm, depending on the value of c ; for $c \gg 1$ one obtains a Type IV isotherm; for $c < 1$, Type V. Equation (D) has been derived for an odd number $(2n - 1)$ of layers fitting into the capillary. An analogous equation can be derived for an even number $(2n)$ of layers, and this latter equation reduces to equation (B) if $g = 1$.

In the derivation of equation (D) it is assumed that whatever happens on one of the walls of the capillary the same thing happens on a corresponding spot of the opposite wall, so that the layers building up on the two walls of the capillary always meet *in the middle*. This may be a fair approximation, but obviously the actual situation must be that when on a surface element of one of the walls one layer is adsorbed, there is a certain probability that on the opposite wall on a corresponding surface element there are zero, one, two, three, or more layers adsorbed. Consequently the last adsorbed layer may form not only in the middle of the capillary, but in any other part. The following derivation takes care of this situation.

We visualize the capillary again as two plane parallel walls between which the adsorption is taking place. By imaginary partitions we subdivide the capillary into a large number of narrow prisms, as Fig. 4 shows, and assume that the gas is adsorbed on the base and the top of the prisms. After equilibrium is established there will be prisms whose bases and tops are both free of adsorbed gas, other prisms with one adsorbed layer on the bases and none on the tops, still others with one adsorbed layer on the tops and none on the bases, one adsorbed layer on each, etc. We

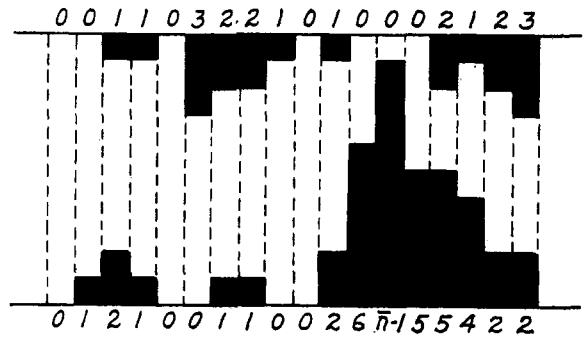


Fig. 4.—Multimolecular adsorption in a capillary.

shall call the corresponding surface areas s_{00} , s_{01} , s_{10} , s_{11} , s_{02} , . . . , s_{ij} , . . . , where s_{ij} denotes the sum of the areas of the bases and tops of all the elementary prisms that have i adsorbed layers at one end and j at the other. The total surface area of both sides of the capillary is then

$$(1) \quad A = s_{00} + s_{01} + s_{10} + s_{11} + s_{02} + s_{20} + s_{12} + s_{21} + s_{22} + \dots$$

and the volume adsorbed at equilibrium is

$$(2) \quad v = 1/2v_0[s_{01} + s_{10} + 2s_{11} + 2s_{02} + 2s_{20} + 3s_{12} + 3s_{21} + 4s_{22} + \dots + (i + j)s_{ij} + \dots]$$

where v_0 is the volume of gas adsorbed on one square centimeter of surface when it is covered with a complete unimolecular layer. It follows that

$$(3) \quad \frac{v}{Av_0} = \frac{v}{v_m} = \frac{\sum(i + j)s_{ij}}{2\sum s_{ij}} \quad \begin{matrix} i + j = 0, 1, 2, \dots, \bar{n} \\ i, j = 0, 1, 2, \dots, \bar{n} \text{ independently} \end{matrix}$$

The principle of microscopic reversibility demands that when equilibrium is established the following evaporation–condensation equilibria hold true

$$(4a) \quad ap_{s_{00}} = be^{-E_1/RT} s_{01}$$

Writing

$$x = \frac{a}{b} p e^{E_L/RT}$$

and

$$c = e^{(E_1 - E_L)/RT}$$

we obtain

$$(4) \quad cx_{s_{00}} = s_{01} = s_{10}$$

Furthermore

$$(5) \quad s_{11} = cx_{s_{01}} = c^2x^2s_{00}$$

and $x_{s_{01}} = s_{02}$, or

$$(6) \quad cx^2s_{00} = s_{02} = s_{20}$$

One can derive by similar argument the equilibrium adsorption relations between any two surface elements. Thus $x_{s_{11}} = s_{21}$, and, therefore

$$(7) \quad c^2x^3s_{00} = s_{21} = s_{12}$$

and again $xs_{21} = s_{22}$, or

$$(8) \quad c^2x^4s_{00} = s_{22}, \text{ etc.}$$

From the foregoing equations one obtains the rule

$$s_{ij} = c^kx^i + i s_{00}$$

wherein k will be 1 when either i or $j = 0$, and 2 if both i and $j \neq 0$.

There is one important thing to remember, however, and that is the added energy of adsorption in the last layer. Whenever we deal

$$v = v_m \left\{ \frac{x}{1-x} + \frac{2(c-1)x + 2(c-1)^2x^2 + (\bar{n}c^2 + \bar{n}h - 2\bar{n}c - \bar{n}^2c^2)x^{\bar{n}} + (2c + \bar{n}^2c^2 + 2\bar{n}c - 2c^2 - \bar{n}c^2 - 2h - 2\bar{n}h)x^{\bar{n}+1} + (\bar{n}h + 2h)x^{\bar{n}+2}}{2[1 + 2(c-1)x + (c-1)^2x^2 + (c^2 + h - 2c - \bar{n}c^2)x^{\bar{n}} + (\bar{n}c^2 + 2c - 2c^2 - 2h)x^{\bar{n}+1} + hx^{\bar{n}+2}]} \right\} \quad (E)$$

with a surface element for which $i + j = \bar{n}$ (the prism completely full), then the heat of evaporation is not E_L , but $E_L + Q$. For example

$$(9a) \quad ap_{s_{\bar{n}-3,2}} = be^{-(E_L+Q)/RT} s_{\bar{n}-3,2}$$

from which it follows that

$$(9) \quad s_{\bar{n}-3,2} = c^2gx^{\bar{n}}s_{00}$$

where $g = e^{Q/RT}$, as before. It should be noted that in the present derivation it is assumed that there is room for \bar{n} layers of molecules between the walls of the capillary. Since the \bar{n} layers never fit exactly into the capillary, there are therefore $\bar{n} + 1$ possibilities for $i + j = \bar{n}$. Two of these ($i = \bar{n}, j = 0$, and $i = 0, j = \bar{n}$) correspond to gaps left between the walls of the capillary and the last adsorbed layer, and the remaining $\bar{n} - 1$ possibilities correspond to gaps left between the adsorbed layers. One should use therefore two different values of Q , but for the sake of simplification we use only one.

We are now ready to sum up the surface elements s_{ij} to obtain the surface area A . We shall collect the terms involving c first.

$$(10) \quad s_{00} + s_{01} + s_{10} + s_{02} + s_{20} + \dots + s_{0\bar{n}} + s_{\bar{n}0} = s_{00}(1 + 2cx + 2cx^2 + 2cx^3 + \dots + 2cgx^{\bar{n}}) = s_{00}(1 + 2cx\eta + 2cgx^{\bar{n}})$$

where

$$\eta = 1 + x + x^2 + \dots + x^{\bar{n}-2} = (1 - x^{\bar{n}-1})/(1 - x).$$

Next we sum up the surface elements involving c^2 . These are

$$(11) \quad s_{11} + s_{21} + s_{12} + s_{22} + s_{31} + \dots + s_{\bar{n}-1,1} + s_{1,\bar{n}-1} = s_{00}\{c^2x^2[1 + 2x + 3x^2 + 4x^3 + 5x^4 + \dots + (\bar{n}-2)x^{\bar{n}-3}] + (\bar{n}-1)c^2gx^{\bar{n}}\} = s_{00}\left\{c^2x^2\frac{d\eta}{dx} + (\bar{n}-1)c^2gx^{\bar{n}}\right\}$$

since the quantity in the square brackets is $d\eta/dx$. Adding now the two we obtain

$$(12) \quad A = s_{00}\left\{1 + 2cx\eta + c^2x^2\frac{d\eta}{dx} + (\bar{n}c^2 - c^2 + 2c)gx^{\bar{n}}\right\}$$

It has been shown in paper I that

$$(13) \quad \sum_{i+j=0}^{\bar{n}} (i+j)s_{ij} = x\frac{dA}{dx}$$

whence it follows from (3) that

$$(14) \quad v = \frac{v_mx}{2} \frac{dA}{Adx}$$

This is our new isotherm equation. Written in terms of x it appears as

where $h = (\bar{n}c^2 - c^2 + 2c)g$. In order to fit Type IV and V isotherms by means of this equation we may offer the following suggestions. For small values of x , or p/p_0 , the \bar{n} -th and higher powers of x can be neglected and equation (E) reduces to equation (A). From a straight line plot one can obtain the constants v_m and c . To obtain the constants \bar{n} and h one may use the following approximation formula in place of equation (E)

$$(15) \quad v = v_m \left\{ \frac{\bar{n}}{2} - \frac{(\bar{n}-2)x^{\bar{n}} - \bar{n}x^{\bar{n}-1} + \bar{n}x - (\bar{n}-2)c^2}{2(1-x)^3x^{\bar{n}-2}} \cdot \frac{c^2}{h} \right\}$$

Equation (15) is valid in the neighborhood of $x = 1$, for $h \gg c^2$ and $c \gg 1$. For the purpose of evaluation of the constants it is useful to put this equation in the form of a power series

$$(16) \quad v = v_m \left\{ \frac{\bar{n}}{2} - \frac{\bar{n}(\bar{n}-1)(\bar{n}-2)}{12} \left[1 + \frac{1}{2}(\bar{n}-1)(1-x) + \frac{1}{4.5}(\bar{n}+1)(3\bar{n}-4)(1-x)^2 + \frac{1}{3.4.5}(\bar{n}+1)(\bar{n}+2)(2\bar{n}-3)(1-x)^3 + \dots \right] \frac{c^2}{h} \right\}$$

To illustrate the usefulness of equation (E) we fitted some Type IV isotherms of Lambert and Clark⁴ with the results seen in Fig. 5. They represent the adsorption of benzene on ferric oxide gel at 40, 50, and 60°. The experimental isotherms show very strong hysteresis on desorption; the points given in the figure are all adsorption points. Using the constants $v_m = 0.081$ g. of benzene per gram of gel, $c = 27$ ($E_1 - E_L = 2190$ cal.), $h = 47,400$ ($Q = 1690$ calories), and $\bar{n} = 6$, we obtained the curve in the middle of the figure (the 50° isotherm). Then using the same values of $v_m, \bar{n}, E_1 - E_L$, and Q we calculated the two other isotherms at 40 and 60°. It will be noted that the temperature dependence of the isotherms is

satisfactory. That one cannot expect a perfect fit from equation (E) becomes clear if we remember the following facts.

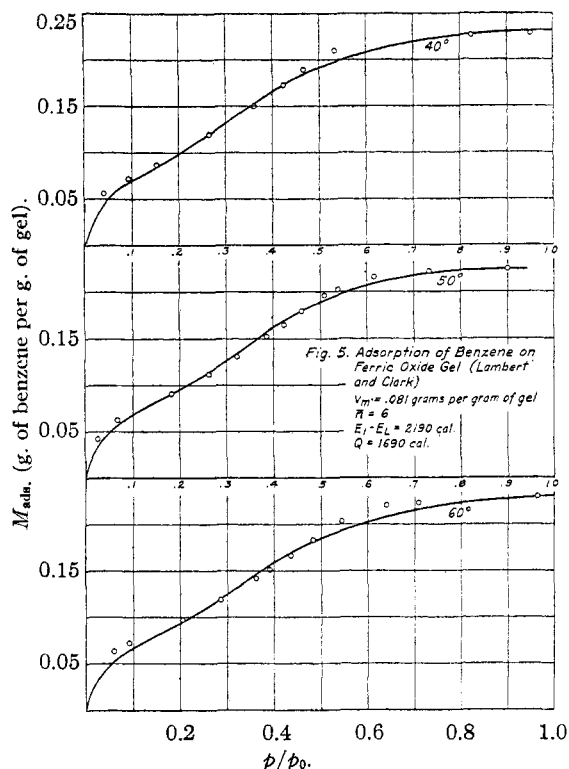


Fig. 5.—Adsorption of benzene on ferric oxide gel (Lambert and Clark): $V_m = 0.081$ g. per g. of gel; $n = 6$; $E_1 - E_L = 2190$ cal.; $Q = 1690$ cal.

(1) In the derivation of the equation we assumed that the capillaries of the adsorbent have a uniform size, whereas actually adsorbents probably have capillaries of differing sizes. Thus in our idealized case we derived an expression for an imaginary *average* sized capillary.

(2) We assumed that the walls of the capillary are parallel, whereas actually the walls may often be convergent (V-shaped pores). To take care of this factor one would need a fifth constant, the angle θ , which would make the equation extremely complicated.

(3) We assumed that the adsorption takes place in capillaries open on the sides. If we deal with completely enclosed capillaries, then the adsorption in each consecutive layer will be less and less, and the maximum adsorption that can take place in each layer will not be a constant v_m , but will be a function of \bar{n} .

Equations (D) and (E) also can be used to clear up some apparent discrepancies between

values of surface area obtained from adsorption isotherms of different gases on the same surface. Some investigators have reported Type I and Type II isotherms on the same adsorbent with different gases. These isotherms at first sight seem incompatible with each other in terms of the present theory. Thus Schlüter¹³ found that carbon disulfide on powdered glass gave S-shaped isotherms, but pentane on powdered glass gave Langmuir type isotherms. An inspection of the curves indicates that the surface of the adsorbent evaluated by means of pentane is about four times as large as that obtained from the carbon disulfide adsorption, while n seems to be 1 for pentane, but at least 6 for carbon disulfide. Naturally, since Schlüter measured the adsorptions on two different samples of the same adsorbent, he ought to have gotten approximately equal surface values and also n values that are compatible with each other. Thus there is an anomaly here that requires clarification. Similar results were obtained by Pidgeon,¹⁴ who found that benzene gave a Type I isotherm on active silica, while water and ethyl alcohol gave Type II isotherms on the same adsorbent.

Figure 6 suggests a reconciliation of this apparent discrepancy. It represents six isotherms of two imaginary gases A and B, on the same adsorbent. For the sake of simplicity the isotherms were calculated by means of equation (D). Gas A consists of smaller molecules than gas B, so that when the capillaries are completely full they can hold one and a half times as many A as B molecules ($n = 6$ and 4, respectively). It is assumed that the forces of adsorption for the two gases in the first adsorbed layer are not very

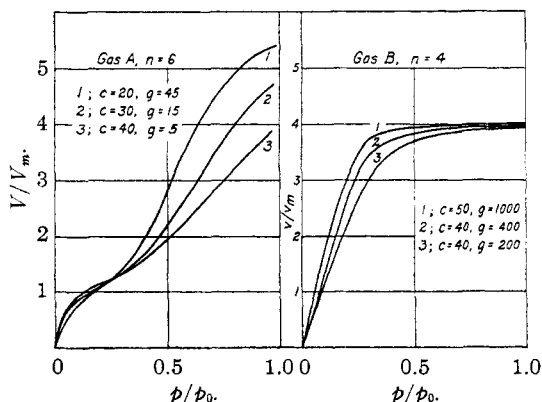


Fig. 6.—Some extreme cases of Type IV isotherms.

(13) Schlüter, *Z. physik. Chem.*, **A153**, 68 (1931).

(14) Pidgeon, *Can. J. Research*, **12**, 41 (1935).

different, *i. e.*, c is about the same for both, but that the additional adsorption forces appearing in the last layer are very different, rather small for A, but quite strong for B ($g = 5$ to 45 for the former, 200 to 1000 for the latter). Superficial inspection of the three isotherms for gas B would suggest that they are Type I isotherms, in which at saturation only one layer is adsorbed. If one would calculate the surface of the adsorbent from these pseudo-Langmuir type isotherms and compare it with the surface of the same adsorbent calculated from the isotherms of gas A, one would find that B gives four times as large a surface value as A does. Furthermore, the n value for A would come out to be 6, while the apparent n value for B is 1. Naturally the solution of the difficulty is that the isotherms of gas B are not Type I, but Type IV isotherms, which appear to be Langmuir type because of the large values of the constant g . The three isotherms of gas A illustrate how a Type IV isotherm goes gradually over into a Type II isotherm as the values of g get smaller.

The results of Schlüter and Pidgeon can thus be relatively easily reconciled in terms of the present theory. On the other hand, some isotherms of Coolidge¹⁵ cannot be explained in the same manner. The two isotherms shown in Fig. 7 were made on two different samples of identically prepared charcoal, therefore the constants obtained from them should be consistent with each other.

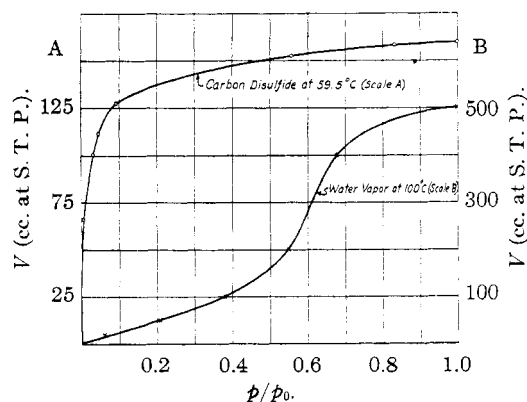


Fig. 7.—Adsorption of vapors by charcoal (Coolidge).

The water vapor curve appears to be a Type V isotherm, and indeed one can fit it satisfactorily with the help of equation (D) using the value $n = 9$. On the other hand, the shape of the carbon disulfide isotherm is of the Langmuir type, indicating unimolecular adsorption. If one would

(15) Coolidge, *THIS JOURNAL*, **46**, 596 (1924).

calculate the surface of the charcoal from the two different isotherms, one would find a discrepancy that is about five-fold. A possible explanation is that the surface of the charcoal and the size of the capillaries are both influenced by the adsorbed molecules. The large surface of charcoal shows that the material is very finely divided. It may be that under the action of water these fine particles coagulate into coarser ones presenting a smaller surface and a larger pore diameter, whereas under the influence of carbon disulfide they remain finely divided with narrow pores between them. This would explain why water gives Type V, while carbon disulfide gives Type I isotherms on charcoal.

We wish to suggest also an alternative explanation. It is possible that both the water vapor and the carbon disulfide isotherms represent unimolecular adsorption. The carbon disulfide curve is just a customary Langmuir type isotherm. The shape of the water vapor isotherm shows that at low p/p_0 values very little adsorption takes place owing to the small force of interaction between the carbon atoms of the surface and the water molecules. However, as soon as some adsorption has taken place, further adsorption proceeds more easily because of the large dipole attraction between the water molecules themselves. Thus eventually a sharp rise in adsorption takes place, until the capillary is filled. If this second explanation is the correct one, then the water vapor curve is not a true Type V isotherm and one is not justified in using equations (D) or (E) to fit it. Apart from the adsorption of water vapor on charcoal we know of no other adsorption curves that have even the qualitative shape of a Type V isotherm.

III. Comparison with the Capillary Condensation Theory

For the purpose of comparing the present theory with the capillary condensation theory, let us imagine that the adsorbent consists of capillaries bounded by two plane parallel walls and that all capillaries have the thickness D . Then condensation in the capillaries will take place according to the Kelvin equation at the pressure.

$$p_k = p_0 e^{-2\sigma V/DRT}$$

where p_0 , σ , and V are the vapor pressure, surface tension and molecular volume of the liquefied gas at temperature T . Below p_k no adsorption takes place, except possibly that of a unimolecular layer, while above p_k the capillaries are filled up com-

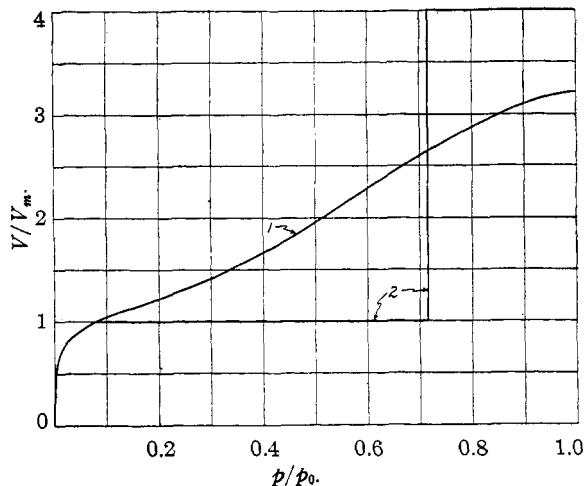


Fig. 8.—Comparison between the present theory and the capillary condensation theory: $n = 8$; $c = 150$ ($E_1 - E_L = 757$ cal.); $g = 17.17$ ($Q = 440$ cal.).

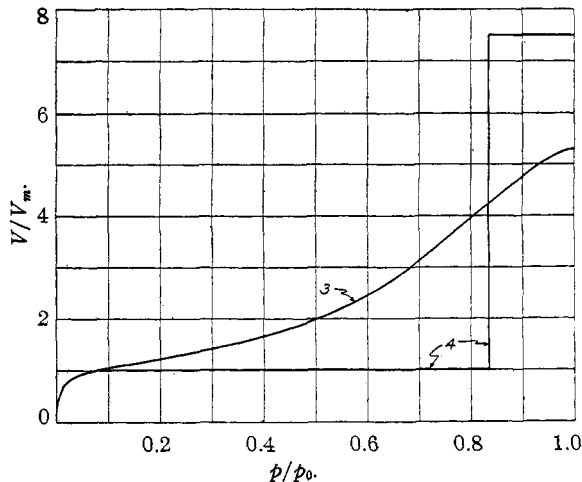


Fig. 9.—Comparison between the present theory and the capillary condensation theory: $n = 15$; $c = 150$ ($E_1 - E_L = 757$ cal.); $g = 17.17$ ($Q = 440$ cal.).

pletely. In the present theory multimolecular adsorption sets in below p_k , and the capillaries are not filled up completely even above p_k . The reason for this difference is that in the present theory the fluctuations are taken into account by considering in detail empty, partly full, and full capillaries. In the capillary condensation theory, on the other hand, only the probabilities of empty and full capillaries are compared, and it is assumed that the state with the greater probability is realized even in the pressure ranges where detailed calculation shows that the probability of partially full capillaries is much greater. Experimentally the sharp rise in adsorption demanded by the capillary condensation theory has never been found. This was explained by assuming a continuously varying distribution of the capillaries. The present theory gives rise to smooth curves, even if the size of the capillary in the adsorbent is uniform.

In Figs. 8 and 9 curves 1 and 3 show two adsorption isotherms calculated on the basis of the present theory, while curves 2 and 4 give the isotherms according to the capillary condensation theory. The constants of the four curves are those of nitrogen at 76°K.; c is taken to be 150, and \bar{n} is 8 for Fig. 8 and 15 for Fig. 9. It is assumed that in the first case 8, and in the second case 15 layers of molecules would fill the capillaries exactly (without leaving any gap), consequently Q is equal to $2\sigma S$, as discussed in the previous section. On the basis of cubic close packing $S = 3^{1/2} N^{1/3} V^{2/3} / 2^{2/3}$, where N is Avogadro's number.

In the calculation of curves 1 and 3 of Figs. 8 and 9 we used a modification of equation (E), in the re-

spect that h was set equal to $c^2 g$ rather than $(\bar{n}c^2 - c^2 + 2c)g$. This was necessary because in the derivation of equation (E) it was assumed that the \bar{n} layers do not fill the capillary exactly, and therefore there are $\bar{n} + 1$ different ways of leaving a gap if \bar{n} layers are adsorbed. If, however, \bar{n} layers fill the capillary exactly, \bar{n} adsorbed layers will have the statistical weight 1. The summation carried out in the same manner as before leads to an equation identical in form with (E), but with $h = c^2 g$.

As the curves show, capillary condensation occurs at pressures at which the walls of the capillaries are covered with a unimolecular adsorbed layer and the rest of the capillary is roughly half full. Thus for $\bar{n} = 8$, capillary condensation would occur at a pressure where v/v_m is about 2.5, and for $\bar{n} = 15$, about 4.25. A further peculiarity of the curves is that the limiting value of v/v_m at the saturation pressure is not $1/2\bar{n}$, which would correspond to completely filled capillaries, but less. Actually the value of $1/2\bar{n}$ is closely approached only if the value of g is high and that of \bar{n} is low. For sufficiently high values of \bar{n} only $\bar{n}/3$ layers will be adsorbed near saturation.¹⁶

(16) This can be shown in the following way. Near saturation the factor x^{i+j} will be independent of $i + j$, the number of layers adsorbed, and the weight factor for the adsorption of a total of ν layers on the two opposite walls ($i + j = \nu$) will be $\nu + 1$. For the average number of layers adsorbed near saturation we have therefore.

$$\frac{\sum_{\nu=1}^{\bar{n}} \nu(\nu + 1)}{\sum_{\nu=1}^{\bar{n}} (\nu + 1)} \cong 2\bar{n}/3$$

for large values of \bar{n} . On one wall we find therefore an average of $\bar{n}/3$ layers.

In Fig. 9 this limiting value is nearly approached for $\bar{n} = 15$. Here in addition to the unimolecular layer one-third of the remaining 13 layers is adsorbed at saturation, giving a total of $v/v_m = 5.33$. That large capillaries according to the present theory are not completely filled up even near p_0 is probably due to the crude manner in which the fluctuations were calculated. We expect that one would get completely full capillaries at p_0 if the interaction of each molecule with its neighbors were to be taken into account in detail. For smaller capillaries with not too small g values the present theory predicts that the capillaries are practically full at p_0 and the above difficulty does not arise.

We believe that the present theory has two advantages over the capillary condensation theory. In the first place it is a unified theory that includes unimolecular adsorption, multimolecular adsorption on free surfaces, and the enhanced adsorption that takes place in capillaries; whereas the capillary condensation theory only deals with the last of these three phenomena. In the second place the present theory supplies an isotherm equation that can describe all the

five different types of van der Waals adsorption isotherms and can be tested by experiment. The Kelvin equation, on the other hand, is not an isotherm equation; at best it allows only the calculation of one isotherm from another. A modified form of the capillary condensation theory, proposed by Patrick and McGavack,¹⁷ although successful in many cases in fitting experimental data, is purely an empirical equation.

Summary

The isotherm equation derived in a previous paper for the multimolecular van der Waals adsorption of gases has been extended to cover two additional cases: (1) when the heat of adsorption in the first layer is smaller than the heat of liquefaction, (2) when the capillaries of the adsorbent are completely filled, the heat of adsorption in the last layer is greater than the heat of liquefaction. The new equation covers all the five types of adsorption isotherms found in the literature. Comparison is made with experimental data and with the capillary condensation theory.

(17) McGavack and Patrick, *THIS JOURNAL*, **42**, 946 (1920).

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Chemisorptions of Gases on Iron Synthetic Ammonia Catalysts¹

BY STEPHEN BRUNAUER AND P. H. EMMETT²

Introduction

In several previous publications we reported the occurrence of chemisorptions³ of carbon dioxide, oxygen, carbon monoxide,^{4,5,6} hydrogen,^{6,7} and nitrogen⁸ on various promoted and unpromoted iron catalysts, and described a method^{5,6} whereby the chemisorptions of carbon monoxide and carbon dioxide in connection with low temperature van der Waals adsorption measurements⁹

can be utilized to determine the fraction of the surface covered by the aluminum oxide and the alkali promoter in singly and doubly promoted catalysts. The present experiments were undertaken to study further the concentration and distribution of the promoters on the surfaces of catalysts, to ascertain the nature of the binding of the chemisorbed gas to the surface, and in general to obtain additional information about the nature of the catalyst surface and the mechanism of promoter action.

Experimental

Most of the chemisorption experiments were performed on three iron synthetic ammonia catalysts: unpromoted catalyst 973 (containing 0.15% Al₂O₃ as impurity), singly promoted catalyst 954 (containing 10.2% Al₂O₃), and doubly promoted catalyst 931 (containing 1.59% K₂O and 1.3% Al₂O₃). Whenever in this paper we refer to the three catalyst types, or to the pure iron, singly promoted, or

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(3) By "chemisorption" we refer to adsorptions that involve forces that are greater than those active in physical adsorption or in condensation, and approach in magnitude the forces active in chemical reactions (see reference 9). In this sense the term includes "activated adsorption" as well as chemical adsorptions that proceed so rapidly that no activation energies can be measured.

(4) Brunauer and Emmett, *THIS JOURNAL*, **57**, 1754 (1935).

(5) Emmett and Brunauer, *ibid.*, **59**, 310 (1937).

(6) Emmett and Brunauer, *ibid.*, **59**, 1553 (1937).

(7) Emmett and Harkness, *ibid.*, **57**, 1631 (1935).

(8) Emmett and Brunauer, *ibid.*, **56**, 35 (1934).

(9) Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).