400. *Polymolecular Adsorbed Films. Part II. The General Theory of the Condensation of Vapours on Finely Divided Solids.*

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THE successful interpretation in terms of polarisation of the S-shaped adsorption curves for argon on salt crystals at low temperatures (cf. Part I, this vol., p. 1467) suggests that a similar treatment might be applicable to more complicated systems where the adsorbed molecules possess a permanent dipole. The theory below shows that when dipoles are present results similar to those in Part I are indeed obtained, and that for vapours adsorbed on porous solids the well-known type of curve which is usually explained by capillary condensation may be better interpreted by a thick polarised film, at least over considerable ranges of p/p_s (= pressure/pressure of saturated vapour).

There seems to be a good deal of confusion as to the nature of the adsorbed film of vapours on solids. The treatment in terms of capillary condensation is unsatisfactory, since the size of the pores, calculated from Thomson's equation $\log p_s/p = 2\sigma d/Dp_s r$ (σ = surface tension, d = density of saturated vapour, D = density of liquid, and r = radius of capillaries), is far too small over most of the pressure range, although capillary condensation undoubtedly occurs at pressures near to saturation. Thus when the relative pressure $p/p_s = 0{\cdot}5$, capillaries greater than 15 A. in radius will not hold water in charcoal, and when $p/p_s = 0{\cdot}1$, the largest radius is 4·6 A. (cf. McBain, "The Sorption of Gases and Vapours by Solids"). Thus the capillaries are often of molecular radius, and it is clear that the treatment in terms of meniscus curvature and surface tension then breaks down, and in some cases the molecule could scarcely enter the capillary !

Capillary condensation cannot explain the building up of a thick film on a granular solid, for the curvature of the particles is of the wrong sign for condensation, and places where a film can be built up occur only at the points of contact of the particles. In fact, the capilliary condensation theory stresses the pores in an adsorbent at the expense of the granular surface, and encourages a fallacious comparison of the pores with capillary tubes. The capillary condensation theory cannot be used to calculate the equation to the curve, since the distribution of capillaries is quite unknown, and gives erroneous results, as Coolidge showed (*J. Amer. Chem. Soc.*, 1926, **48**, 1795), when relative pressures for the same volume adsorbed are calculated for a number of adsorbates. The attempt to interpret results by means of a negative pressure on a liquid owing to the meniscus surface (McGavack and Patrick, *ibid.*, 1920, **42**, 946) seems of doubtful value (Coolidge, *loc. cit.*), especially as the expansion occurring on adsorption receives no explanation (cf. Bangham, Fakhoury, and Mohamed, *Proc. Roy. Soc.*, 1934, *A*, **147**, 152). It is true that the adsorption of vapours on solids seems to depend at saturation more on internal volume than on internal surface, since the volumes of different vapours, calculated as liquid, required to saturate an adsorbent are nearly the same. In the filling up of the adsorption space, however, it is probable that only in the last stages is one concerned with capillary condensation. The volumes of liquid adsorbed are not equivalent at values of p/p_s less than unity.

The concept of the thick compressed film has been introduced by Polanyi (*Z. Elektrochem.*, 1920, **26**, 370; 1922, **28**, 110) and by Berényi (*Z. physikal. Chem.*, 1920, **94**, 628; 1923, **105**, 55). Polanyi has more recently modified his theory to include Langmuir's conception of a unimolecular film (Goldmann and Polanyi, *Z. physikal. Chem.*, 1928, **132**, 355), and explains the low-pressure region by islands of adsorbate on the surface. A critical discussion is given by McBain (*op. cit.*).

The thick-film theory given below differs from Polanyi's in that the attractive forces of the solid are confined to the first layer of adsorbed molecules. The molecules of this first layer are polarised by the surface field, and permanent dipoles are oriented at an angle with the surface normal which depends on temperature. The first layer is built up at low pressures for vapours, according to the ideas of Langmuir. At higher pressures a thick film tends to be built up by the attractive field of the polarised first layer, not by the direct action of the solid. The cohesive forces responsible for the formation of liquids play an important part in the stability of this film, and in general, such condensation to thick liquid films will be possible only for vapours, although the critical temperature of gases may be shifted by the influence of the solid, and the adsorbate exist as a liquid film even above the critical temperature of the bulk gas. With gases sufficiently removed from the critical region unimolecular films will be formed.

As the film gets thicker, meniscuses appear at the points of contact of the particles, but these meniscuses are still quite different from those in the bulk liquid owing to the influence of the solid surface, and the bulk of the adsorbed material lies on a convex surface. Thus a convex surface near to the solid surface may exist in equilibrium with a concave surface at a greater distance from the solid. The concave meniscuses become larger as the pressure approaches saturation, and capillary condensation is responsible for the filling up of the interstices between the solid particles, when the film is so thick that the influence of the solid surface is small.

The reason for the pronounced hysteresis shown by many of the adsorption curves cannot really be settled without more experimental evidence, especially since the phenomenon disappears under some experimental conditions (McGavack and Patrick, *loc. cit.*). In view of the doubtful nature of the pore theory, Zsigmondy's explanation, that when the pores are filling a delay in wetting may occur, is not very convincing. Hysteresis is clearly an effect of secondary importance, perhaps comparable with a delay in boiling. The following is a tentative explanation. When the film is being built up the cohesion of the particles for one another (Bradley, *Trans. Faraday Soc.*, **1936**, **32**, 1088) is not overcome by the incompletely formed liquid film. At pressures nearer saturation, however, a liquid lens is formed between the particles, corresponding with the peptising action of liquids on colloids. Hence, on lowering the pressure, more adsorbate will be held than when the pressure is being raised, at the same pressure, for once the particles have been forced apart they will tend to remain so until the amount of adsorbate is very considerably reduced. Air or other permanent gas favours hysteresis by preventing the formation of a liquid lens (air lens), and on removal of air a liquid lens may form at a point on the adsorption curve if the cohesion of the liquid is sufficient to overcome that of the solid, so that adsorption and desorption curves will coincide as observed by McGavack and Patrick (*loc. cit.*). It is clear that the occurrence of hysteresis will be decided by many factors, *e.g.*, the presence of adsorbed permanent gas, the size and shape of particles, and the surface energies of liquid and solid.

The Theory of the Condensation of Dipolar Vapours.—A simple treatment was given by Bradley (*Phil. Mag.*, **1930**, **10**, 323). Calculations were confined to the dimension at right angles to the surface. The example of a thick dipolar film may be studied as in Part I; some of the symbols used below have slightly different meanings from those in Part I.

A dipole μ in a field F will have energy $\mu F \cos \theta$, where θ is the angle between μ and F (note that, in Part I, μ is the dipole induced in the first layer of molecules). Hence the average value of the moment induced in the direction of the field at temperature T is

$$\begin{aligned} \mu \cos \overline{\theta} &= \mu \frac{\int e^{\mu F \cos \theta / k'T} \cos \theta \,.\, 2\pi \sin \theta \,.\, d\theta}{\int e^{\mu \cos \theta / k'T}\, 2\pi \sin \theta \,.\, d\theta} = \mu(\coth x - 1/x) \\ &= \mu(1 - 1/x + 2e^{-2x}) \text{ for large values of } x \\ \text{or} \quad &= \mu(x/3 - x^3/45) \text{ for small values of } x \end{aligned}$$

where $x = \mu F/k'T$ (see Debye, "Polar Molecules," p. 28) and k' is the gas constant. Taking $\mu = 10^{-18}$ approx., and $F = 5 \times 10^4$ (see Part I), we find that $x =$ approx. 1, so that the function $\coth x - 1/x$ is best represented by $x/3$ for this and smaller values of x, as is seen in the following table :

x.	$1 - 1/x$.	$x/3 - x^3/45$.	$x/3$.	$\coth x - 1/x$.
1	0	0·33	0·33	0·31
2	0·5	0·45	0·67	0·54
3	0·66	0·40	1·0	0·66

Thus, by comparison with the values of F given in Part I, it is clear that the function fortunately does not change its approximate representation over the thick film, where the variation in F is considerable.

As before, it will be supposed that the first layer comes under the influence of the solid and is polarised. A propagation of polarisation occurs throughout the thick film, so that if F_m is the field at the m^{th} layer, the total induced dipole in the direction of the surface normal is given by

$$\mu_m = \alpha F_m + \mu^2 F_m/(3k'T) = k_2 F_m, \text{ where } k_2 = \alpha + \mu^2/(3k'T) \quad . \quad . \quad (1)$$

Similarly, $\mu_{m-1} = k_2 F_{m-1}$, etc.; α is the polarisability and μ the permanent dipole moment. It will be taken, as before, that the bulk of the adsorption occurs on similar lattice points, which will be valid for most adsorbents.

The analysis is very similar to that given in Part I, but is best made in terms of the F's rather than the μ's. If there are only m layers, we have

$$\begin{aligned} F_m &= k_1\mu_{m-1} \\ F_{m-1} &= k_1(\mu_{m-2} + \mu_m) \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ F_1 &= F + k_1\mu_2 \end{aligned}$$

where F is the surface field of the solid. Hence

$$\begin{aligned} F_m &= k_1k_2F_{m-1} \\ F_{m-1} &= k_1k_2(F_{m-2} + F_m) \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ F_1 &= F + k_1k_2F_2 \end{aligned}$$

By using the analogous results in Part I, and putting $k_1k_2 = k$, it follows that

$F_m = Fk[k/(1 - k^2)]^{m-2}\,(1 - k^2)/(1 - 2k^2)$ and $F_q = F[k/(1 - k^2)]^{q-1}(1 - k^2)/(1 - 2k^2)$

for $q = 1$ to $m - 1$. The energy of the qth layer per g.-mol., forces of cohesion and the lateral repulsion of dipoles being neglected for the present, is given by

$$\tfrac{1}{2}N\alpha F_q^{\,2} + N\mu^2F_q^{\,2}/(3k'T) = NF_q^{\,2}[\alpha/2 + \mu^2/(3k'T)]$$

where N is Avogadro's number. Hence, as before,

$$E_m - E_{m-1} = NF^2[\alpha/2 + \mu^2/(3k'T)](3 - k^2)k^{2m-2}/[(1 - 2k^2)^2(1 - k^2)^{2m-6}] + E'_0 \quad . \quad (2)$$

where E'_0 allows for cohesive forces.

The allowance for the interaction of dipoles in one sheet must be considered more exactly than in Part I, where the effect was very small. When permanent dipoles are present the interaction is, of course, governed by the temperature. As a first approximation, however, we may consider the values of μ_q induced by the field normal to the surface, and calculate the interaction of these vertical components on the basis of a hexagonal surface packing. If a_1 is the distance apart of the molecules which are arranged on a hexagonal packing, then the approximate value of the energy of repulsion of the oriented dipoles in the mth layer is $4{\cdot}8\mu_m^{\,2}N/a_1^{\,3} = 4{\cdot}8NF^2k^{2m-2}[\alpha + \mu^2/(3k'T)]^2/[a_1^{\,3}(1 - k^2)^{2m-6}(1 - 2k^2)^2]$. It follows that, with sufficient accuracy

$$\begin{aligned} E_m - E_{m-1} = NF^2[\alpha/2 + \mu^2/(3k'T) - 4{\cdot}8k_2^{\,2}/\{a_1^{\,3}(3 - k^2)\}] \times \\ (3 - k^2)k^{2m-2}/[(1 - 2k^2)^2(1 - k^2)^{2m-6}] + E'_0 \quad . \quad . \quad (3) \end{aligned}$$

In Part I, owing to the small value of the induced dipole moment, the correction is very small and $3 - k^2$ was taken as of the order unity.

The analysis in Part I gives, as before,

$$\log_{10}p_s/p_a = K_1K_3^{\,a} + K_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where

$$\begin{aligned} K_1 = NF^2[\alpha/2 + \mu^2/(3k'T) - 4{\cdot}8k_2^{\,2}/\{a_1^{\,3}(3 - k^2)\}] \times \\ (3 - k^2)(1 - k^2)^6/[2{\cdot}303RTk^2(1 - 2k^2)^2] \quad . \quad . \quad (5) \end{aligned}$$

$$K_3 = [k/(1 - k^2)]^{2m/a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and a is the weight adsorbed.

K_1 and K_4 are temperature-dependent; note that T is now absorbed into the denominator of K_1. The term K_4 allows for the fact that we cannot put $E'_0 = H_0$, the heat of evaporation of the bulk liquid, since in the latter there is an oriented surface film of dipoles, and E'_0 refers only to non-dipolar forces. If K_4 were zero, equation (4) would give the correct value of a for $p = p_s$ ($K_3 < 1$), so that the equation as it stands cannot apply for values of the pressure very near the saturation value. This follows in any case, however, for in this region capillary condensation occurs. Moreover, equation (4) does not give the initial point $p = 0$, $a = 0$, but in practice the constants are such that $a = 0$ at very small values of p/p_s.

One method of solving equation (4) from the experimental figures is to find what value of the constant K_4 in the expression $\log_{10}[\log_{10}p_s/p_a - K_4]$ gives a linear plot with a; K_3 and K_1 can then be determined from the slope of the straight line and the intercept on the log axis for the value $a = 0$. Another useful method, which can be improved by a subsequent linear plot, consists in taking three values of a such that $a_3 = 3a$, $a_2 = 2a$. If $K_3{}^a = x$, then

$$\log p_s/p_a = K_1x + K_4,\ \log p_s/p_{a_2} = K_1x^2 + K_4, \text{ and } \log p_s/p_{a_3} = K_1x^3 + K_4,$$

giving three equations which can be solved for x, K_1, and K_4. Clearly

$$\log (p_{a_3}/p_{a_2})/\log (p_{a_2}/p_a) = (x^2 - x^3)/(x - x^2) = x$$
$$K_1 = \log (p_{a_2}/p_a)/(x - x^2)$$
$$\log K_3 = \log x/a$$

The following tables show that equation (4) can be applied to many cases of the adsorption of vapours up to fairly large values of p/p_s. In most cases, except for the region near to saturation, the errors are of the order of a few %. The constants are derived from the experimental curves in the manner described. The theoretical derivation of the constants from equations (5) and (6) must await a more detailed knowledge of the particulate derivation surface, surface spacing, and surface field.

Water on copper oxide at 25° (Bray and Draper, *Proc. Nat. Acad. Sci.*, 1926, **12**, 297).

$$p_s = 23\cdot83 \text{ mm.};\ \log_{10}(p_s/p) = 4\cdot898 \times 0\cdot8902^a + 0\cdot0762.$$

p (mm.)	0·25	2·6	5·1	10·1	12·9	17·0	18·7	19·7
a, mg. per g. of CuO, obs.	9	14	19	25	27	36	45	56
a, mg. per g. of CuO, calc.	8·1	14·7	18·2	24·2	27·7	25·5	44·3	56·7

Ethyl chloride on charcoal at — 15·3° (Goldmann and Polanyi, *Z. physikal. Chem.*, 1928, **132**, 321).

$$p_s = 243 \text{ mm.};\ \log_{10}(p_s/p) = 14\cdot72 \times 0\cdot9164^{a/1\cdot6} - 10\cdot89.$$

p (mm.) ...	0·12	0·57	1·4	3·0	5·5	12·0	17·8	26·3	35·6	58·4	105·7	131·1
a (g.), obs.	0·874	1·455	1·922	2·417	2·845	3·458	3·782	4·098	4·329	4·657	4·848	4·907
a, calc.	0·66	1·57	2·11	2·57	2·96	3·46	3·72	3·98	4·20	4·51	4·93	5·14

Ethyl ether on charcoal at 20° (Kubelka, *Kolloid-Z.*, 1931, **55**, 129; 1932, **58**, 189).

$$p_s = 438 \text{ mm.};\ \log_{10}(p_s/p) = 5\cdot887 \times 0\cdot755^{a/70} - 2\cdot356.$$

p (mm.)	10·7	30·2	92	164	311	429
a (c.c. per l. of C), obs.	90	129	171	192	213	223
a (c.c. per l. of C), calc.	97·3	128·5	165·1	186·0	212·7	227·1

Sulphur dioxide on silica at — 34·4° (McGavack and Patrick, *loc. cit.*).

$$p_s = 279 \text{ mm.};\ \log_{10}(p_s/p) = 3\cdot39 \times 0\cdot2828^{a/100} + 0\cdot1132.$$

p (mm.)	4·22	13·85	29·02	50·07	73·45	116·62
a (c.c. per g. SiO_2), obs.	53·31	81·50	108·18	137·17	162·60	192·06
a (c.c. per g. SiO_2), calc.	54·2	82·8	107·2	132·7	157·4	201·5

Although numerical agreement alone does not prove the above theory, since the adsorption curves may be fitted to many different equations, it should be noticed that equation (4) has a theoretical basis which is reasonable in the light of our conception of molecular forces. There is no need to give the thickness of the oriented film extravagant values. Indeed, the work of Bastow and Bowden (*Proc. Roy. Soc.*, 1931, *A*, **134**, 404) shows that the extended rigid structure supposed to exist in liquid films by Hardy from experiments on adhesion (*Phil. Trans.*, 1932, *A*, **230**, 1) may be explained by extraneous effects such as dust. Later work of Bastow and Bowden (*Proc. Roy. Soc.*, 1935, *A*, **151**, 220) gives no evidence from viscous flow in a thin film of a rigid structure of oriented molecules of *thickness greater than* 10^{-5} cm., and evidence which has been advanced for such an influence of the solid wall on the liquid, extending over 1500—50,000 A., is probably incorrect. However, the work of Bastow and Bowden does not invalidate the existence of an oriented film of thickness less than 1000 A., especially when it is remembered that the orientation dies away as we approach the outer surface of the film. The following simple calculation shows that with small particles a large fraction of the adsorption space can be occupied by films of thickness less than 1000 A. Consider as an ideal case n particles of radius r in 1 c.c. Then $4\pi r^3 n/3 = 0{\cdot}74$, so that the free space is 0·26 c.c. The introduction of a film of outer radius r_1 would fill the free space to the extent that (film shell)/(former free space) = $4\pi(r_1^3 - r^3)n/0{\cdot}26 = (r_1^3 - r^3)0{\cdot}74/(0{\cdot}26r^3)$ approximately. If $r = 10^{-5}$ and the thickness of the film is 100 A. then approximately 80% of the adsorption space can be occupied by such a film; when $r = 5 \times 10^{-5}$, then the film thickness must be 500 A. to give the same result.

SUMMARY.

The equation $\log (p_s/p) = K_1K_3^a + K_4$, where p and p_s are the pressure and saturation pressure respectively, a is the weight adsorbed, and K_1, K_3, and K_4 are constants, has been deduced for the adsorption of dipolar vapours on finely divided solids. Agreement is obtained with published experimental data over a wide range of p/p_s, except at high pressures, when capillary condensation occurs. The formation of liquid meniscuses is discussed.

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