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ever, the use of this theory leaves much to be desired from the logical standpoint. Real progress in the theory of unimolecular reactions requires the evaluation of the specific transition probabilities in the Ramsperger-Rice-Kassel treatment. Until this is done, the theory of uni-

molecular decompositions must remain on a semiquantitative basis.

Statistical Thermodynamics of the Sorption of Vapors by Solids

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The statistical method of treating the sorption of vapors, begun by Fowler and Guggenheim and extended to multilayer sorption by Cassie and Hill, is further generalized to include variable heats of sorption in different layers. It is shown under what conditions multilayer sorption can lead to a linear isotherm and to various modifications of the BET equation. The treatment is also extended to the case of interaction between sorbed molecules in the same layer.

IN a previous paper[1] methods of calculating the free energy and heats of sorption of water vapor by proteins and high polymers were discussed for the cases of linear, Langmuir, and BET[2] sorption isotherms. At first sight it might appear unsound to apply equations derived on the basis of a kinetic picture of equilibrium between gas molecules colliding with and evaporating from a solid surface to the sorption of water by solids such as proteins and high polymers where the water molecules must diffuse through the solid to reach the points of sorption, but when it is realized that Fowler and Guggenheim[3] and Cassie[4] and Hill[5] have derived both the Langmuir monolayer adsorption and the BET multilayer adsorption equations on the basis of statistical reasoning, the theoretical justification for this procedure becomes apparent.

At this point we wish to emphasize that application of the BET equation to the sorption

isotherms of water sorbed by high polymers in no way implies any estimate of a surface. In fact, by a careful study of the statistical derivation it is realized that the BET equation gives as one of its parameters the number of adsorption sites, not the surface. The surface can only be obtained by a further calculation in which a value for the area per site is assumed. Thus the area is a derived quantity. By adsorption we mean adsorption on a free surface, where the gas molecule can collide directly with the adsorbing site, while by sorption we mean the increase of weight of the solid as the result of the penetration and sorption of water vapor within the solid, at sorption sites where there is no free surface. Justification of the application of the BET equation to the sorption of water vapor by high polymers depends upon the existence of a real reversible equilibrium, no hysteresis, upon the negligible contribution of change of volume to the free energy of the sorption process, upon the sorption sites of the polymer remaining fixed in space during sorption (otherwise the process would be that of mixing two liquids), and upon the absence of interaction between sorbed molecules. In a later paper giving new data on the sorption of water by certain experimental polymers we shall discuss the applicability of the

[1] M. Dole and A. D. McLaren, J. Am. Chem. Soc. 69, 651 (1947).
[2] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. 60, 309 (1938).
[3] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (University Press, Cambridge, 1939), p. 426.
[4] A. B. D. Cassie, Trans. Faraday Soc. 41, 450 (1945).
[5] T. L. Hill, J. Chem. Phys. 14, 263 (1946). The treatment of Hill is a correction to and extension of that of Cassie.

BET equation more fully and compare the theory presented here with that of Barrer.[6]

In this paper we extend the statistical treatment to consider cases of varying heats of sorption between layers and of multilayer sorption with interaction between molecules in the same layer. The nomenclature of Fowler and Guggenheim will be used for the most part.

GENERAL STATISTICAL TREATMENT

Let

S_0 = number of sites having no sorbed molecules,
S_1 = number of sites having one sorbed molecule,
S_2 = number of sites having two sorbed molecules, etc.,
N_1 = total number of sorbed molecules in the first layer,
N_2 = total number of sorbed molecules in the second layer, etc.,
N_S = total number of sorption sites,
N = total number of sorbed molecules,
a_1 = internal partition function for sorbed molecules in the first layer,
a_2 = internal partition function for sorbed molecule in the second layer, etc.,
a_L = internal partition function for molecule in the liquid state,
$x = p/p_0$, partial pressure ratio of sorbate in the vapor phase,
Q = total partition function of all sorbed molecules, and
n = total number of layers.

As a result of these definitions,

$$S_0 = N_S - N_1, \quad S_1 = N_1 - N_2, \quad \text{etc.},$$

$$\sum_{i=1}^{n} N_i = N.$$

The total partition function is given by the equation

$$Q = \frac{N_S!}{\prod_{0}^{n} S_i!} \prod_{i=1}^{n} (a_i)^{N_i}, \tag{1}$$

or

$$Q = \frac{N_S!}{(N_S - N_1)!(N_1 - N_2)! \cdots (N_{n-1} - N_n)! N_n!} \cdot a_1^{N_i} \cdots a_n^{N_n}. \tag{2}$$

[6] R. M. Barrer, Trans. Faraday Soc. **43**, 3 (1947).

The Helmholtz free energy, F, then follows from (2), after approximating the factorials by Stirling's theorem.

$$-\frac{F}{RT} = \ln Q = N_S \ln N_S - (N_S - N_1) \ln(N_S - N_1)$$

$$- \cdots (N_{n-1} - N_n) \ln(N_{n-1} - N_n)$$

$$- N_n \ln N_n + \sum_{i=1}^{n} N_i \ln a_i. \tag{3}$$

For the conditions of equilibrium between the first and second layers, similarly to Hill,[2] we obtain

$$\frac{N_S - N_1}{N_1 - N_2} = \frac{N_1 - N_2}{N_2 - N_3} \cdot \frac{a_2}{a_1}, \tag{4}$$

and for equilibrium between the second and third layers, etc.,

$$\frac{N_1 - N_2}{N_2 - N_3} = \frac{N_2 - N_3}{N_3 - N_4} \cdot \frac{a_3}{a_2}, \quad \text{etc.} \tag{5}$$

In Hill's treatment

$$a_3 = a_2,$$

with a consequent simplification of (5) and similar relationships.

Finding the variation of the free energy with respect to N and setting the result equal to the chemical potential of the pure liquid phase, we deduce that

$$\frac{N_n}{N_{n-1} - N_n} = x \cdot \frac{a_n}{a_L}. \tag{6}$$

Substituting (6) into (4), (5) and similar relations, we find, also similarly to Hill,

$$N_1 - N_2 = (N_S - N_1) x \cdot \frac{a_1}{a_L},$$

$$N_2 - N_3 = (N_S - N_1) \frac{x^2}{a_L^2} \cdot a_1 \cdot a_2,$$

$$\vdots \qquad \vdots$$

$$N_n = (N_S - N_1) \frac{x^n}{a_L^n} a_1 \cdots a_n, \tag{7}$$

except that in Hill's case (the BET model)

$$a_2 = a_3 = \cdots = a_n = a_L.$$

Making use of (7), the generalized sorption equation results for the model used here, that is, localized sorption on definite sites with no interaction between molecules on adjacent sites, namely,

$$\frac{N}{N_S} = \frac{y(a_1 + 2ya_1 \cdot a_2 + 3y^2 a_1 \cdot a_2 \cdot a_3 + \cdots)}{1 + ya_1 + y^2 a_1 \cdot a_2 + y^3 a_1 \cdot a_2 \cdot a_3 + \cdots}, \quad (8)$$

where

$$y = \frac{x}{a_L}.$$

Letting

$$\phi = 1 + ya_1 + y^2 a_1 a_2 + \cdots,$$

it is readily seen that

$$\frac{N}{N_S} = y\frac{\phi'}{\phi}. \quad (9)$$

SPECIAL SOLUTIONS

1. Partition Functions in All Layers Equal

The simplest assumption is that the a_i's are all equal, and are some fraction, k, of the pure liquid-state partition function a_L. For an infinite number of layers the solution is

$$\frac{N}{N_S} = \frac{kx}{1 - kx}, \quad (10)$$

and for a finite number n,

$$\frac{N}{N_S} = kx\frac{[1 - (n+1)(kx)^n + n(kx)^{n+1}]}{(1 - kx)[1 - (kx)^{n+1}]}. \quad (11)$$

In case k is equal to unity, which would be true for an ideal solution, then (10) reduces to

$$N = x, \quad (12)$$

which is Raoult's law (N is the mole fraction of the vapor in the solid).

2. Partition Functions All Equal Beyond the First Layer

If

$$\frac{a_1}{k} = a_2 = a_3 = \cdots = a_n = a_L,$$

the BET equations result.

If

$$a_2 = ka_1 = a_3 = a_4 = \cdots = a_n \neq a_L,$$

and if n is limited to a finite number, we obtain

$$\frac{N}{N_S} = \frac{cx[1 - (n+1)(ckx)^n + n(ckx)^{n+1}]}{[1 - ckx][1 + cx\{1 - k - (ckx)^n\}]}, \quad (13)$$

where $c = a_1/a_L$. When n goes to infinity

$$\frac{N}{N_S} = \frac{xc}{[1 - ckx][1 + cx(1 - k)]}, \quad (14)$$

which becomes identical to the BET equations on setting $k = a_L/a_1$. Equation (14) is closely similar to that deduced by Anderson[7] (Anderson's Eq. (6)) which in our terminology can be written

$$\frac{N}{N_S} = \frac{cxk}{[1 - kx][1 + (c-1)kx]}. \quad (15)$$

When Eqs. (14) and (15) are put into a linear form and solved for N_S and c, it can be seen that in Anderson's case

$$N_S = \frac{1}{Ik + S},$$

where I and S are the intercept at x equal to zero and the slope, respectively, and in our case

$$N_S = \frac{1}{Ick + S}. \quad (16)$$

As the functions plotted are

$$\frac{x}{N(1 - ckx)} \text{ against } x \quad \text{and} \quad \frac{x}{N(1 - kx)} \text{ against } x$$

in the two cases, it is obvious that both Anderson's and our treatment will yield equal values of N_S. However, if the constant c is solved for

$$c = \frac{Ick + S}{I}$$

in our case, and

$$c = \frac{Ik + S}{Ik}$$

[7] R. B. Anderson, J. Am. Chem. Soc. **68**, 686 (1946).

in Anderson's case, it is evident that a difference results. As Anderson derived his equation for a heat of adsorption in the second to the ninth layer different from that in the first layer as well as different from the heat of condensation in the pure liquid, one would not expect his and our equation to be identical (Anderson did not give details of derivation).

It should be noted that our equation reduces to the Langmuir isotherm on setting k equal to zero, whereas Anderson's equation does not.

3. Partition Functions Decreasing Harmonically

Let us make the arbitrary assumption that

$$a_2 = 1/2a_1, \quad a_3 = 1/3a_1, \quad \text{etc.,} \qquad (17)$$

then

$$\phi = 1 + ya_1 + \frac{y^2a_1^2}{2!} + \frac{y^3a_1^3}{3!} + \cdots ,$$

$$= e^{ya_1}$$

and

$$\frac{N}{N_S} = x \cdot \frac{a_1}{a_L} = cx. \qquad (18)$$

This demonstrates that given the proper decrease in the internal partition function with increasing number of sorbed layers, a linear sorption isotherm can be obtained. In the case of the sorption of water by high polymers there are a number of examples of the sorption following a linear relationship with the pressure up to 50 to 60 percent relative humidity. There is no *a priori* reason in these cases why the partition function should not fall to zero in the limit. In fact, the Langmuir isotherm can be obtained from (8) by setting all partition functions except a_1 equal to zero.

MULTILAYER SORPTION WITH INTERACTION

Fowler and Guggenheim[8] have shown how the Langmuir treatment is to be modified if interaction between adjacent molecules forming a number of pairs, N_{ii}, in any layer is taken into account. If the contribution to the internal partition function for such pairs is a_{ii}, then the total partition function for multilayer sorption

becomes

$$Q = \frac{N_S!}{\prod\limits_{i=0}^{n} S_i!} \prod\limits_{i=1}^{n} (a_i)^{N_i}(a_{ii})^{N_{ii}'} \qquad (19)$$

where N_{ii}' is a statistical average number of pairs when N_i molecules are adsorbed. Making the assumption of a completely random arrangement, Fowler and Guggenheim deduce the equation

$$N_{ii}' = \tfrac{1}{2}z\frac{N_i^2}{N_S}, \qquad (20)$$

where z is the number of nearest neighbors in any layer. The contribution of the interaction energy, W, to the total energy can be expressed by the equation,

$$E^{\text{int.}} = \frac{N_i^2}{N_S} \cdot W. \qquad (21)$$

(This follows from the assumption that the excess energy resulting from interaction can be expressed by the factor $N_{ii}[2W/z]$.)

The free energy of the adsorbed material and other relations follow immediately from (19)

$$\frac{F}{RT} = -N_S \ln N_S + (N_S - N_1) \ln(N_S - N_1)$$

$$+ (N_1 - N_2) \ln(N_1 - N_2) + \cdots$$

$$+ N_n \ln N_n - \sum_{i=1}^{n} N_i \ln a_i$$

$$- \sum_{i=1}^{n} \frac{N_i^2}{N_S} \cdot \frac{z}{2} \ln a_{ii}, \qquad (22)$$

$$\frac{N_S - N_1}{N_1 - N_2} = \frac{N_1 - N_2}{N_2 - N_3} \frac{a_2}{a_1} \cdot \frac{a_{22}^{N_2 z/N_S}}{a_{11}^{N_1 z/N_S}}, \qquad (23)$$

$$\frac{N_S - N_1}{N_1 - N_2} = \frac{N_{n-1} - N_n}{N_n} \frac{a_n}{a_1} \left[\frac{a_{nn}^{N_n}}{a_{11}^{N_1}}\right]^{z/N_S}, \qquad (24)$$

$$\frac{N_n}{N_{n-1} - N_n} = x\frac{a_n}{a_L} a_{nn}^{N_n \cdot (z/N_S)}, \qquad (25)$$

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[8] See reference 3, p. 429.

and, finally,

$$\frac{N}{N_S}=\frac{x\cdot\dfrac{a_1}{a_L}a_{11}{}^{N_1\cdot(z/N_S)}+2\left[\dfrac{x}{a_L}\right]^2 a_1\cdot a_{11}{}^{N_1\cdot(z/N_S)}\cdot a_2\cdot a_{22}{}^{N_2\cdot(z/N_S)}+\cdots}{1+x\dfrac{a_1}{a_L}a_{11}{}^{N_1\cdot(z/N_S)}+\left(\dfrac{x}{a_L}\right)^2 a_1\cdot a_{11}{}^{N_1\cdot(z/N_S)}\cdot a_2\cdot a_{22}{}^{N_2\cdot(z/N_S)}+\cdots}. \tag{26}$$

Fowler and Guggenheim[8] point out that the assumption of interaction leads at certain values of the temperature to the splitting of the adsorbed layer into two phases. Hill[5,9] suggests that in the case of multilayer sorption this region of instability, corresponding to a sudden jump in the value of N/N_S, is to be conceived physically as capillary condensation, and he concludes that the multilayer adsorption and capillary condensation points of view are therefore really not in conflict.

In the case of the sorption of water vapor by solids, the present author prefers to consider the sudden increase in N/N_S at constant vapor pressure as analogous to compound formation such as occurs in the hydration of crystals when the percentage of water in the solid (water of hydration) rises from a low to a high value without change of vapor pressure. Such hydration may occur occasionally with very little change in the x-ray diagram of the solid.[10]

Let us consider the application of Eq. (26) to the phenomena of hydration of crystals. When a higher and lower hydrated form of the crystal are simultaneously in equilibrium with a certain vapor pressure of water, then the percentage of water in the crystal will rise without change in the chemical potential, μ, of the water, or

$$\frac{\partial \mu}{\partial N}=0. \tag{27}$$

It is interesting to find the value of N_n corre-

sponding to condition (27). Letting $N_n{}^0$ represent this value, we obtain

$$N_n{}^0=\frac{1+x\dfrac{a_n}{a_L}a_{nn}{}^{N_n\cdot(z/N_S)}}{q}, \tag{28}$$

where

$$q=\frac{z}{N_S}\ln a_{nn}.$$

Differentiating $N_n{}^0$ with respect to x, we find

$$\frac{\partial N_n{}^0}{\partial x}=\frac{a_n\cdot a_{nn}{}^{N_n\cdot(z/N_S)}}{q\cdot a_L\left[1-x\dfrac{a_n}{a_L}a_{nn}{}^{N_n\cdot(z/N_S)}\right]}, \tag{29}$$

so that for $\partial N_n{}^0/\partial x$ to be equal to infinity as it must in the case of formation of hydrates at constant vapor pressure,

$$x\cdot\frac{a_n}{a_L}a_{nn}{}^{N_n\cdot(z/N_S)}=1. \tag{30}$$

Hence

$$N_n{}^0=\frac{2}{q}. \tag{31}$$

For the layer immediately under the outer layer we obtain, on rearranging (25),

$$N_{n-1}=N_n\frac{\left[1+x\dfrac{a_n}{a_L}a_{nn}{}^{N_n\cdot(z/N_S)}\right]}{x\cdot\dfrac{a_n}{a_L}a_{nn}{}^{N_n\cdot(z/N_S)}},$$

which for $N_n=N_n{}^0$ becomes

$$N_{n-1}=2N_n{}^0.$$

If $N_n{}^0$ equals $1/2N_S$, which it will at the critical

[9] In a paper in press Dr. Hill has gone considerably deeper into the mathematics of the unstable region than he did in the paper quoted in reference (5). We are greatly indebted to him for the opportunity of seeing his paper in advance of publication.

[10] See, for example, the interesting paper by W. O. Milligan and H. B. Weiser, J. Phys. Chem. **41**, 1029 (1937), where x-ray diffraction patterns are given for a number of hydrated zeolites. In their case they heated the hydrated crystals at constant vapor pressure and observed a stepwise decrease in the percentage of water in the crystal.

temperature when

$$W = -2kT$$

or

$$q = \frac{4}{N_S},$$

then

$$N_{n-1} = N_S.$$

In other words, the sorption in the next layer below the outer layer is complete when the top layer is half-covered, as would be expected when the hydration of a crystal proceeds in steps. It would appear, then, that the physical fact which distinguishes between sorption of the types represented by the Langmuir, BET, or other equations and hydrate formation is the interaction energy between the sorbed molecules.

When the sorbed molecules are so far apart that no or insufficient interaction energy exists, no region of increase of water sorbed at constant vapor pressure can exist, no separation of the solid into two phases will occur; on the other hand, a gradual increase of the amount sorbed with increase of vapor pressure will be observed.

Application of the equations contained in this paper to new data on the sorption of water by certain high polymers will be carried out at a later date. The work given here is part of a general program of study of the thermodynamics of high polymers for which grants have been gratefully received from the du Pont Corporation, the Research Corporation,[11] the Richardson Company, and the Visking Corporation.

[11] Frederick Gardner Cottrell grant.

Rotation-Vibration Spectra of Diatomic and Simple Polyatomic Molecules with Long Absorbing Paths.

I. The Spectrum of Fluoroform (CHF₃) from 2.4μ to 0.7μ

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The spectrum of fluoroform has been investigated under high resolution (21-ft. grating) in the photographic infra-red with an absorbing path of up to 60 meters, obtained by multiple reflection according to the method of J. U. White. In addition, with the same path length the spectrum from 1.2 to 2.4μ was obtained under low resolution with a photoelectric infra-red spectrometer. A large number of overtone and combination bands, 47 in all, were found. Two parallel bands in the photographic region were well resolved and analyzed, yielding, for the moment of inertia about an axis perpendicular to the symmetry axis,

$$I_B{}^{[0]} = 81.08 \times 10^{-40} \text{ g cm}^2$$

From this value, assuming tetrahedral angles and a C−H distance as in methane, the C−F distance in fluoroform is found to be 1.329A, a value that is appreciably lower than that found in methyl fluoride, 1.380A. A provisional vibrational assignment of all the bands is given.

A. INTRODUCTION

THE investigation of the rotation-vibration spectra of diatomic and polyatomic molecules in the photographic infra-red by means of large diffraction gratings makes possible a determination of molecular constants (moments of inertia, internuclear distances, etc.) of very high

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precision. Indeed it was only during the last year that this precision has been surpassed by the data obtained from microwave-absorption spectra. The microwave technique is applicable only to a certain group of molecules and to certain molecular constants. Therefore, it remains imperative to continue the study of photographic infra-red spectra. It appears that there are still a number of diatomic and simple poly-