$(V - \sum_{1}^{i} N_i V_i^0)$ measured by Matuyama[13] for the liquid binary cadmium–lead, cadmium–bismuth and lead–bismuth systems and also for the equal-molal mixtures in the liquid ternary cadmium–lead–bismuth and cadmium–lead–tin solutions.

The three entropy surfaces illustrate the fallacy of seizing on relatively simple methods for predicting the thermodynamic behavior of liquid metallic solutions. For example, the virtually ideal entropy of mixing in the three binary systems, lead–bismuth, lead–antimony and lead–tin might lead one to guess that the three ternary cadmium systems should show strikingly similar entropy surfaces. Comparison of the three surfaces is sufficient to demonstrate the inadequacy of such an argument.

Acknowledgments.—The authors wish to express their appreciation to Donald L. Guernsey and Margaret Connors for analyses of the electrolytes and electrodes. They also wish to express their appreciation to the National Research Council for a predoctoral fellowship and to the Atomic Energy Commission for support of the investigation under Contract No. AT-30-GEN-368 (Scope I).

CAMBRIDGE, MASS. RECEIVED DECEMBER 16, 1950

[13] Y. Matuyama, *Science Reports of the Tohoku Imperial University, Japan, Series 1*, **18**, 19 (1929).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

A New Multilayer Isotherm Equation with Reference to Surface Area

BY G. D. HALSEY, JR.

Using the London Law for the dispersion force causing multilayer adsorption and assuming various exponential distributions of sources for the force, coöperative multilayer isotherms are derived. Under certain circumstances these isotherms yield a surface area comparable to the BET area. Under other circumstances they reproduce, and explain deviations and pseudo-agreement with the BET treatment.

Introduction

In an earlier paper[1] it was shown that on a uniform surface adsorption will take place coöperatively, at constant pressure, as soon as the coverage θ reaches ~ 0.02 of its saturation value. Furthermore, it was shown that in the absence of transmitted forces from the surface adsorption will proceed only to the depth of one layer, until the relative pressure p/p_0 reaches unity, and bulk condensation begins. If an energy ΔE_n in excess of the liquefaction energy is transmitted from the surface to the n'th layer the n'th layer condenses at a pressure

$$p/p_0 = \exp\{-\Delta E_n/RT\} \qquad (1)$$

leading to an isotherm composed of a series of steps. If ΔE_n falls off according to the usual inverse power law for dispersion forces, then $\Delta E_n \sim 1/x^r$ where x is the distance from the surface. At large distances from the surface it would seem reasonable to replace x with θ, since they are proportional, leading to the isotherm

$$p/p_0 = \exp\{a/RT\theta^r\} \qquad (2)$$

The derivation implies that x varies continuously with θ, while in actuality x can only be an integral multiple of the molecular diameter. Therefore (2) should be replaced by a step function, which is less than (2) except when θ is integral. However, most real isotherms are smooth, and readily fitted by (2) as it stands, with r varying from ~ 1 to ~ 10. Realizing that surface heterogeneity would tend to "smooth out" the step function, (2) was proposed as a semi-empirical isotherm.

However, as Hill has pointed out,[2] the value of r should be exactly three from the simple London treatment of dispersion forces, and somewhat larger if higher terms are included. The fact that for the simple system nitrogen–anatase $r = 2.67$, lends some support to the approximate validity of (2). Nevertheless it is difficult to explain the small but definite deviation from $r = 3$, which is in the wrong direction and tends to get greater as θ increases.

In what follows we shall show that the agreement achieved with (2) is accidental, and that the empirical value of r in (2) has no simple relation to the power in the expression for London forces.

In addition it should be pointed out that there is no reference to the volume of a monolayer in (2) and thus no indication of surface area. True enough, if $r > \sim 2$, the typical point of inflection and "point B" of the BET theory appears, but the position of this pseudo "point B" is clearly a function of temperature, and can have no reference to any particular degree of coverage in terms of monolayers. In the treatment of discrete layers which follows, this defect will be remedied.

The Isotherm Equation

We have shown previously[1] that the isotherm equation for coöperative adsorption is merely the normalization integral of the distribution function of site-energies $N(\Delta E)$ between the limits $\Delta E = \infty$ and the ΔE of eq. (1)

$$\theta_{(1)} = \int_{-RT\ln p/p_0}^{\infty} N(\Delta E)\mathrm{d}\,\Delta E \qquad (3)$$

The distribution function is normalized so that $\theta_1 = 1$ when p/p_0 reaches the condensation pressure of the bulk liquid adsorbate. We shall make the following assumptions: (1) The source of the van der Waals energy ΔE has its origin one adsorbate diameter below the center of the first layer. (2) ΔE decays with the third power of distance. (3) Regions of equal ΔE are localized into large enough patches so that edge effects can be neglected.

Thus, in the second layer the distribution func-

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[1] G. Halsey, *J. Chem. Phys.*, **16**, 931 (1948).

[2] *Ibid.*, **17**, 590 (1949).

tion N_2 of energy over the sites is the same as in the first layer, if the energies are divided by 2^3.

$$N_2(\Delta E/2^3) = N_1(\Delta E) \tag{4}$$

and

$$\theta_{(2)} = \int_{-RT\ln p/p_0}^{\infty} N_2(\Delta E)\mathrm{d}\,\Delta E = \int_{-RT\ln p/p_0}^{\infty} N_1(2^3\Delta E)\mathrm{d}\,\Delta E = \frac{1}{2^3}\int_{-2^3RT\ln p/p_0}^{\infty} N_1(\Delta E)\mathrm{d}\,\Delta E \tag{5}$$

In general, the coverage in the n'th layer

$$\theta_{(n)} = \frac{1}{n^3}\int_{-n^3RT\ln p/p_0}^{\infty} N_1(\Delta E)\mathrm{d}\,\Delta E \tag{6}$$

All the distribution functions are to be normalized so that when $p/p_0 = 1$, $\theta_n = 1$.

To proceed further, it is necessary to assume a specific form for the distribution function N_1. We shall assume the exponential form

$$N_1 = \frac{1}{\Delta E_m}\exp\{-\Delta E/\Delta E_m\} \tag{7}$$

where ΔE_m, the modulus of the distribution is a constant.

Then, substituting eq. (7) in eq. (6)

$$\theta_{(n)} = (p/p_0)^{n^3RT/\Delta E_m} \tag{8}$$

already normalized to $\theta_n = 1$ at $p/p_0 = 1$. If we write $z = (p/p_0)^{RT/\Delta E_m}$

$$\theta = \sum_{n=1}^{\infty}\theta_{(n)} = \sum_{n=1}^{\infty} z^{n^3} \tag{9}$$

This series converges if $z < 1$, and approaches infinity as p/p_0 reaches the saturation pressure. If we apply the Clausius–Clapeyron equation to (8) for $n = 1$ the excess partial molal heat of adsorption over the energy of liquefaction is

$$-R\frac{\partial \ln p/p_0}{\partial(1/T)} = \Delta E_m \ln \theta_1 \tag{10}$$

Thus at $\theta = 1$, the partial molal heat of adsorption equals the heat of liquefaction, corresponding to the special hypothesis that on the weakest sites $\Delta E = 0$. We shall replace this hypothesis by the more general one that on the weakest sites in the first layer $\Delta E = \Delta E_0$. Then, instead of (6)

$$\theta_{(n)} = \int_{-n^3RT\ln p/p_0 > \Delta E_0}^{\infty} N_1(\Delta E)\mathrm{d}\,\Delta E \bigg/ \int_{\Delta E_0}^{\infty} N_1\,\mathrm{d}\,\Delta E \tag{11}$$

For the exponential distribution (6)

$$\theta_{(n)} = z^{n^3}/\exp\{-\Delta E_0/\Delta E_m\} \tag{12}$$

and

$$\theta = \exp\{+\Delta E_0/\Delta E_m\}\sum_{n=1}^{\infty} z^{n^3} \tag{13}$$

subject to the condition for each term

$$z^{n^3} \leqslant \exp\{-\Delta E_0/\Delta E_m\} \tag{14}$$

When a term in (13) rises above this limiting value, the limit is substituted for the term. That is, $\theta_{(n)}$ cannot exceed unity.

In the discussion which follows, the notation $\theta_{1.0}$ will be used for the case where $\Delta E_0 = 0$, and $\theta_{0.7}$ will be written for $\exp\{-\Delta E_0/\Delta E_m\} = 0.7$, etc.

It is easy to sum eq. (13) numerically because of its rapid convergence. At first sight it might appear that only the first few terms would be of importance, even at reasonably high values of p/p_0. However, because $z = (p/p_0)^{RT/\Delta E_m}$, a larger value of $\Delta E_m/RT$ (that is, a lower temperature) increases the contribution of higher terms in the sum for θ.

Although the assumption of an exponential distribution function (7) is a strictly empirical guess, some such assumption is necessary to smooth out the steps that would otherwise be encountered on a uniform surface. Another form for the distribution function would alter the exact shape of the isotherm. The important fact, however, is that the necessary introduction of heterogeneity, which smooths the isotherm for the first few layers, persists into the succeeding layers. The heterogeneity, weakened by distance, nevertheless is of unimpaired influence, because p/p_0 is reaching unity, where an extremely small change in energy influences the isotherm greatly. That is why eq. (2) which is clearly valid for a *uniform* surface at large θ remains invalid when heterogeneity is introduced, even up to $\theta = 10$. The assumption (1) that the origin of ΔE is located in the first layer of the solid, is important, and is common to both (2) and (13). It implies that the adsorbed layer is liquid-like, having the entropy of the liquid, and realizing the full heat of liquefaction.

There are three constants in eq. (13). Since θ is measured in monolayers and thus $\theta = v/v_m$, the volume of a monolayer v_m is an implicit constant, and the equation contains a reference to surface area. ΔE_m the modulus of the distribution function is a scale factor for energy being the energy at which the sites are $1/e$ as numerous as they would be at $\Delta E = 0$, assuming the distribution to be exponential to this limit. Then ΔE_0 is the energy at which the distribution function ceases to hold, below which there are no sites. It has some slight correspondence with the BET energy ΔE_1.

Discussion of the Isotherms: Surface Area.—In Figs. 1–5 the isotherms calculated from eq. (13) are plotted for various values of $\Delta E_0/\Delta E_m$ and $\Delta E_m/RT$. The isotherms $\theta_{1.0}$ for $\Delta E_0 = 0$ show the characteristic "Point B" of the BET treatment when $\Delta E_m > 2RT$, but the position of this point is clearly a function of $\Delta E_m/RT$ and thus of temperature. These pseudo "Point B's," therefore, are unrelated to the saturation of a monolayer, and to surface area. For $\Delta E_m/RT \leqslant RT$ the isotherms are of type III, the surface showing little specific affinity for the adsorbate. The isotherms continue to show pseudo "Point B's" up to $\exp\{-\Delta E_0/\Delta E_m\} = 0.7$.

However, for $\theta_{0.6}$ and $\theta_{0.5}$ the characteristic "Point B," appears, in the sense that the flattest part of the isotherm does not depend on temperature. This behavior is due to the first layer being virtually complete before further layers begin to condense, causing an essentially flat portion to occur in the isotherm at $\theta = 1$. Changes in $\Delta E_m/RT$, and thus temperature merely shift the pressure scale leaving the flat portion at $\theta = 1$ and "Point B" unchanged.

At first glance, an isotherm like $\theta_{0.5}$, $\Delta E_m/RT = 2$, seems to be far from any experimental isotherm, because of the exact flat at $\theta = 1$. However, this exact flatness is a consequence of assuming that

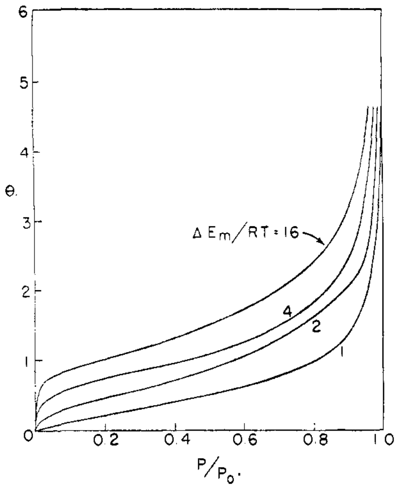

Fig. 1.—The isotherm $\theta_{1.0}$.

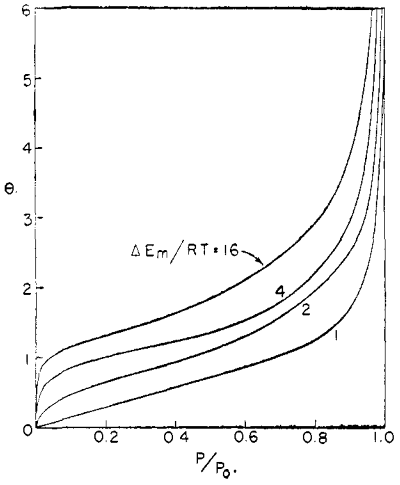

Fig. 2.—The isotherm $\theta_{0.7}$.

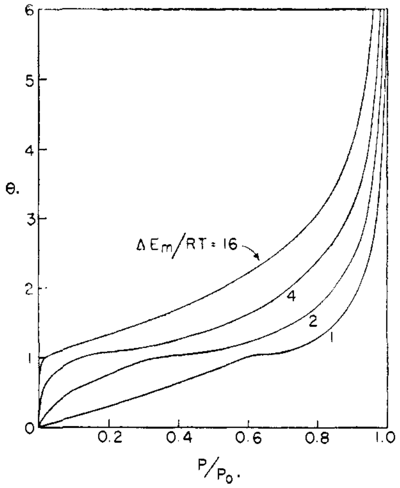

Fig. 3.—The isotherm $\theta_{0.6}$.

the exponential distribution has an exact cut-off at ΔE_0, which is clearly an approximation to the truth rather than the truth itself. Also, the neglect of specific short range forces is most apparent for low values of $\Delta E_m/RT$, it being possible for these forces to completely change the shape of the isotherm below $\theta = 1$. The important point is that the reasonably accurate assumption of an exponential distribution, coupled with the simplest force law, reproduces the observed independence of "Point B" on temperature.

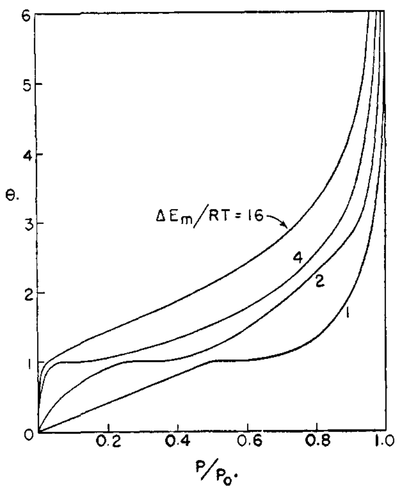

Fig. 4.—The isotherm $\theta_{0.5}$.

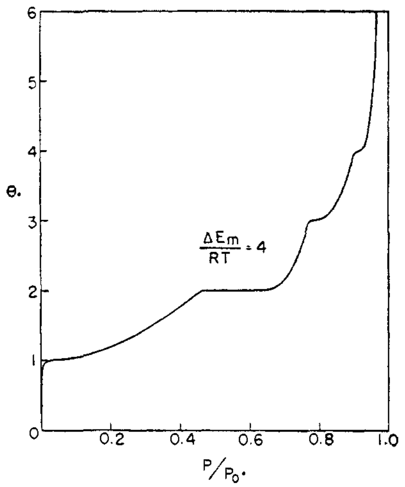

Fig. 5.—The isotherm $\theta_{0.2}$.

In Fig. 6, some BET plots of the isotherms are presented. Since the coverage in monolayers is used in the BET function, a slope of unity indicates agreement between the apparent BET area and the area introduced in the model. For $\Delta E_m/RT = 16$, $\theta_{0.6}$ gives a perfect BET plot, showing that these particular conditions happen to reproduce the BET isotherm exactly. For $\Delta E_m/RT = 4$, $\theta_{0.6}$ reproduces a characteristic failing of the BET equation. The early slope is correct, but at higher p/p_0 there is a marked deviation. For $\Delta E_m/RT = 4$, $\theta_{1.0}$ gives an apparently perfect BET plot, but the slope is markedly different from unity, showing how the BET equation can lead to an incorrect area under certain circumstances.

Visual inspection of $\theta_{0.6}$ $\Delta E/RT = 2$ shows evidence of a saturated monolayer at $\theta = 1$. The BET plot in Fig. 6 is a straight line, but the slope is not unity, showing a conceivable way in which the BET method may err. When the saturation of the first layer is complete at low p/p_0 the initial

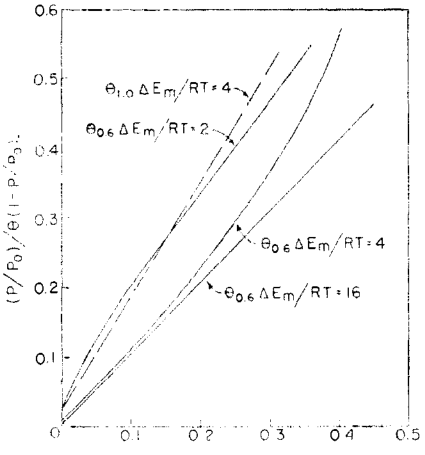

Fig. 6.—BET plots of $\theta_{0.6}$ and $\theta_{1.0}$.

slope of the BET plot will necessarily be correct. At low pressures, the BET function $p/p_0/\theta(1 - p/p_0)$ is approximately $p/p_0/\theta$. If θ is unity and varies slowly, the function in this range is $\sim p/p_0$ which is of course a linear plot of slope unity when plotted against itself.

If saturation of the first layer is not complete at low p/p_0, then the BET method may or may not succeed, as is evident from the examination of the various isotherms here.

Behavior in the Multilayer Region.—If eq. (2) is put in the doubly logarithmic form, all the isotherms here, from $\theta_{0.2}$ to θ_1 give effectively straight lines, above $\theta = 1$, with layer-by-layer fluctuations increasing as ΔE_0 increases (Fig. 7). The slope r is constant at 2.45–2.55 with no indication of changing to three below $\theta = 10$. The effect of $\Delta E_m/RT$ is merely that of a constant added to the doubly logarithmic pressure scale. (A change of the van der Waals force law constant to four changes r to 3.3.)

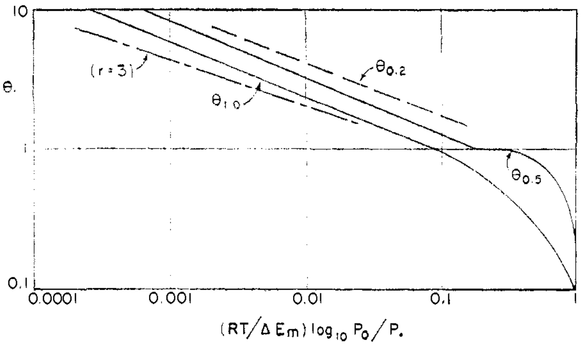

Fig. 7.—The isotherms plotted according to eq. 2. The periodic variations of $\theta_{0.2}$ are smoothed out in the broken line. A line of slope 3 is shown for comparison.

Aside from the scale factor for θ there is thus only one isotherm eq. (2) associated with $r = 2.5$. Since this scale factor can equally well be affected by surface area or a change in ΔE_0 or ΔE_m, there is no possibility of evaluating surface area from the plot in Fig. 7. Only when this plot breaks down, near $\theta = 1$, is it possible to make an unambiguous assignment of area on the basis of a temperature independent "Point B," whose existence must be demonstrated.

Acknowledgments.—I wish to thank Dr. P. H. Emmett and Dr. T. L. Hill for valuable discussions.

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[Contribution from Oak Ridge National Laboratory, Chemical Technology Division and Medical Division of the Oak Ridge Institute of Nuclear Studies]

Preparation of Gallium Citrate by Ion Exchange

By R. E. Blanco and J. D. Perkinson, Jr.

A general method is presented for the preparation of organic salts of gallium by ion exchange using experiments with citric acid as a guide. Gallium citrate was prepared by the elution of gallium from Dowex 50 resin (Nalcite HCR) with 0.5 *M* sodium citrate at *p*H 3.0. A solution 0.14 *M* in sodium citrate and 0.15 *M* in sodium chloride at *p*H 3.0 also proved to be an efficient elutriant. The highest mole ratio of gallium to citrate obtained was 0.24. Elution with sodium citrate at *p*H's 4, 7 and 8 proved to be inefficient for a mass transfer system as the result of hydrolysis and precipitation of gallium in the resin. Equilibrium studies of the distribution of gallium between Dowex 50 resin and sodium citrate in the *p*H range 2–7.5 showed the gallium citrate complex to be very strong at *p*H's 3.0 through 7.5.

Introduction

The preparation of the organic salts of gallium is of biochemical interest since it was shown by H. C. Dudley in distribution studies that gallium tends to concentrate in the skeletal tissue.[1] Thus the injection of radioactive gallium (half life 14.3 h.) might prove to be a treatment for bone cancer or a diagnostic aid in locating early bone cancer. Dudley has prepared radioactive gallium citrate by dissolution of irradiated gallium nitrate in hydrochloric and citric acids, and subsequent neutralization to a *p*H of about 7.0 with sodium hydroxide.

This communication reports the results of a study made to determine a general method for the production of the organic salts of gallium by ion exchange using experiments with citric acid as a guide. Ion exchange offers several advantages: (1) ease of remote control operation when handling radioactivity; (2) elimination of all anion impurities; (3) the possibility that in non-equilibrium systems, a different hydrolyzed form of gallium would be produced than in the case of straight neutralization. This effect could only be determined by distribution studies in animals.

A disadvantage of the ion exchange method, in the case of citric acid, is the low mole ratio of

(1) H. C. Dudley and M. D. Levine, Naval Medical Research Institute, Project NM 011013, No. 3, 13 January 1949.