Statistical Mechanics of Adsorption. VII. Thermodynamic Functions for the B.E.T. Theory

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As an application of the thermodynamic methods discussed in an earlier paper, thermodynamic functions are calculated from the B.E.T. statistical model.

I. INTRODUCTION

THE thermodynamic methods given in an earlier paper[1] can be used to calculate thermodynamic functions from experimental isotherm data. In particular, the free energy of the adsorbate, assuming an inert adsorbent,[1] can be broken down into the entropy and heat content of the adsorbate. When an appreciable number of suitable experimental systems have been treated in this way, the results should be very useful in testing theories of adsorption. In anticipation of this, we summarize here for future reference the thermodynamic functions calculated from the statistical B.E.T. theory.[2,3] The B.E.T. theory is the only real theory of physical adsorption in tractable form at the present time. It is well known that the theory fails in general, on comparing theoretical and experimental isotherms, outside the range $0.05 < p/p_0 < 0.35$. Since the adsorption isotherm gives, essentially, the Gibbs free energy of the adsorbate, it follows that thermodynamic functions calculated from the B.E.T. theory outside the above range will generally disagree with experimental functions. Inside the range, in view of the crudeness of the B.E.T. model, it is rather to be expected that, although the Gibbs free energy may be correct, the division of the free energy into heat content and entropy terms will be predicted incorrectly by the theory. This remains to be seen.

In general, only statistical mechanical theories are useful in the above connection, as kinetic (e.g., the original B.E.T. theory[2]) or thermodynamic theories do not give the dependence of crucial parameters on temperature and on detailed molecular properties. Ultimately, the adsorbate will have to be treated as essentially a liquid perturbed by the surface.

II. THE B.E.T. MODEL

We follow reference 3 closely (and therefore omit details), except for a few obvious changes in notation. The adsorption isotherm is, writing $x = p/p_0$,

$$\theta = N_S/B = cx/(1-x)(1-x+cx) = N_S/\alpha\mathcal{A} = \Gamma/\alpha, \quad (1)$$

where $\mathcal{A}$ is the surface area, Γ the surface concentration, and

$$c = (j_S/j_L) \exp[(\epsilon_1 - \epsilon_L)/kT]. \quad (2)$$

The quantities j_L and ϵ_L refer to the liquid state[4] (L') in which liquid is in equilibrium with gas at vapor pressure p_0.

We restrict the generality of the following treatment in this way: We assume ϵ_1, ϵ_L, and α are independent of temperature.

From standard statistical formulas relating E_s and A_s to the partition function Q_s, we find

$$E_S = [1-x][-\epsilon_1 + kT^2(\partial \ln j_S/\partial T)]$$
$$+ x[-\epsilon_L + kT^2(\partial \ln j_L/\partial T)], \quad (3)$$

FIG. 1. Heat content and internal energy per molecule of adsorbate relative to the liquid state (L') as zero.

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[1] Terrell L. Hill, J. Chem. Phys. **17**, 520 (1949).
[2] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).
[3] T. L. Hill, J. Chem. Phys. **14**, 263 (1946).
[4] T. L. Hill, J. Chem. Phys. **15**, 767 (1947), Eq. (21). We might point out here that in writing Eq. (13) of reference 3 the approximation was made (but not mentioned) of writing $\mu_L = A_L/N_L$ (i.e., the term PV_L/N_L was ignored). Of course, this is ordinarily an excellent approximation. An equivalent assumption was made in obtaining Eq. (10) from Eq. (9) of that paper. The same approximation has also been used elsewhere in this series.
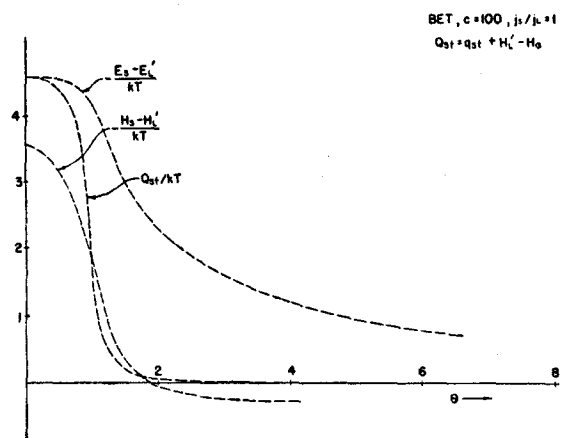
FIG. 2. Heat content, internal energy, and isosteric heat per molecule of adsorbate relative to the liquid state (L') as zero.

where $E_S = E_S/N_S$ (we use small capital letters throughout to represent extensive properties per molecule—see reference 1), and for the spreading pressure φ,

$$\varphi/\alpha kT = \ln[B/(B-X)] = \ln[(1-x+cx)/(1-x)], \quad (4)$$

which is a well-known result (X is the equilibrium number of molecules in the first layer). Then[5]

$$H_S = E_S + (\varphi/\Gamma) = E_S + [(1-x)(1-x+cx)/cx]kT \\ \times \ln[(1-x+cx)/(1-x)]. \quad (5)$$

For the liquid in the state L',

$$E_{L'} = kT^2(\partial \ln j_L/\partial T) - \epsilon_L \cong H_{L'}. \quad (6)$$

Then

$$E_S - E_{L'} = (1-x)[(-\epsilon_1 + kT^2(\partial \ln j_S/\partial T)) \\ -(-\epsilon_L + kT^2(\partial \ln j_L/\partial T))], \quad (7)$$

$$H_S - H_{L'} = E_S - E_{L'} + [(1-x)(1-x+cx)/cx]kT \\ \times \ln[(1-x+cx)/(1-x)]. \quad (8)$$

We assume the gas phase is a perfect gas. Then

$$E_G = (3/2)kT + kT^2(\partial \ln j_G/\partial T), \quad (9)$$
$$H_G = E_G + kT, \quad (10)$$

where j_G is the internal partition function. The (equilibrium) values for ΔE, ΔH, and ΔS of adsorption are then easily found. For example,

$$H_S - H_G = T[S_S - S_G(p)] \quad (11)$$

$$= E_S + (\varphi/\Gamma) - (5/2)kT - kT^2(\partial \ln j_G/\partial T). \quad (12)$$

From the definition[1] of the differential heat of adsorption,

$$q_d = E_G - E_S - N_S(\partial E_S/\partial N_S)_{\mathbb{Q}, T} \\ = E_G - E_S - N_S(\partial E_S/\partial x)_T(\partial x/\partial N_S)_{\mathbb{Q}, T} \quad (13)$$

$$= E_G - E_S + [-\epsilon_1 + \epsilon_L + kT^2(\partial \ln j_S/j_L/\partial T)] \\ \times [x(1-x)(1-x+cx)/(1+x^2(c-1))]. \quad (14)$$

The isosteric heat q_{st} is given by[1] $q_{st} = q_d + kT = H_G - \bar{H}_S$, where $\bar{H}_S = (\partial H/\partial N_s)_{P, T, \mathbb{Q}}$ and $H = E + PV$ refers to the complete two-component phase adsorbent-adsorbate as in solution thermodynamics.

The above relations have been used to check thermodynamic equations such as[1]

$$H_G - \bar{H}_S = q_{st} = H_G - H_S + (T/\Gamma)(\partial \varphi/\partial T)_\Gamma, \quad (15)$$

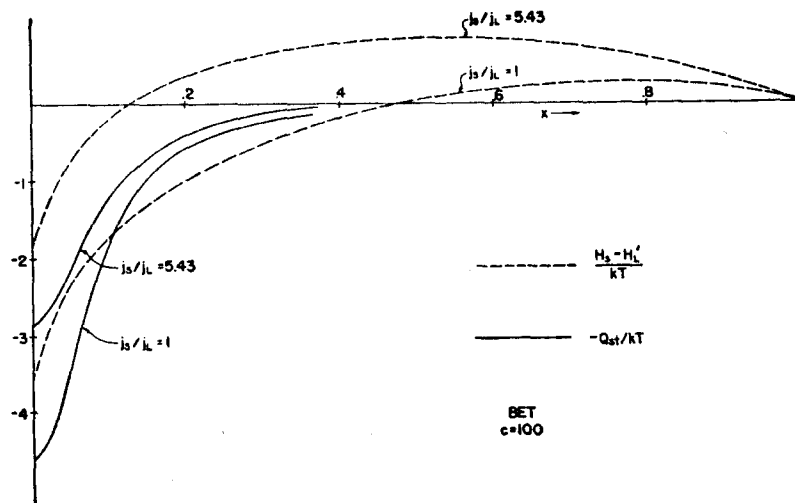$$(\partial \ln p/\partial T)_\varphi = (H_G - H_S)/kT^2, \text{ etc.} \quad (16)$$

Special Case

In order to make numerical calculations, specific choices must be made for j_S, j_L, and j_G. We consider the following simple special case:[3]

$$j_L = (kT/h\nu_L)^3 e, \quad (17)$$

$$j_S = (kT/h\nu_S)^3, \quad (18)$$

$$(\partial \ln j_G/\partial T) = 0. \quad (19)$$

FIG. 3. Effect of j_S/j_L value on heat of adsorption for $c = 100$.

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[5] In $H_s = E_s + \varphi\mathbb{Q} + PV_s$[1] and similar equations, the (negligible) term PV_s is not provided by the B.E.T. model in its usual form. See references 3 and 4.
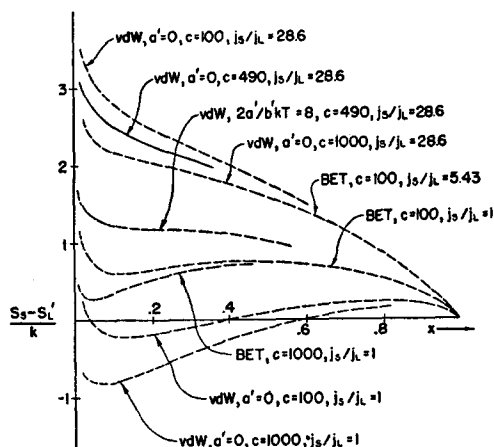
FIG. 4. Entropy per molecule of adsorbate relative to the liquid state (L') as zero. vdW refers to a van der Waals first layer. The curves labeled (1) vdW, $a'=0$, $c=1000$, $j_S/j_L=28.6$, and (2) B.E.T., $c=100$, $j_S/j_L=5.43$ happen virtually to coincide. We have used the equation $T(S_S-S_L') = H_S - H_L' - kT \ln x$ in calculating these curves.

where ν_S and ν_L are independent of T. We then find, for example,

$$(E_S - E_L')/kT = -((\epsilon_1 - \epsilon_L)/kT)(1-x), \qquad (20)$$

$$(H_S - H_L')/kT = -[(\epsilon_1 - \epsilon_L)/kT][1-x] \\ +[(1-x)(1-x+cx)/cx] \\ \times \ln[(1-x+cx)/(1-x)], \quad (21)$$

$$H_G - \bar{H}_S = q_{st} = (1-x)\epsilon_1 + x\epsilon_L - \tfrac{1}{2}kT \\ -[(\epsilon_1 - \epsilon_L)x(1-x)(1-x+cx)/ \\ (1+x^2(c-1))]. \quad (22)$$

It is convenient to define** an "isosteric" equivalent of $H_L' - H_S$, Q_{st}:

$$Q_{st} \equiv q_{st} - (H_G - H_L') = H'_L - \bar{H}_S \qquad (23)$$

$$= [(\epsilon_1 - \epsilon_L)/kT][(1-x)^2/(1+x^2(c-1))]. \quad (24)$$

It will be noticed that $Q_{st} \geqslant 0$ for all x if $\epsilon_1 > \epsilon_L$.

One can show, incidentally, that for $j_S/j_L = 1$ the minimum in the entropy curve (Fig. 4) occurs at $\theta \to 1$ and $x \to 1/c^{\frac{1}{2}}$ as $c \to \infty$.

III. MOBILE FIRST ADSORBED LAYER

For comparison, we give here equations for the special case equivalent to Eqs. (17)–(19) when the first layer

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** In a recent paper which had not come to the author's attention when the present paper was submitted, Gregg and Jacobs [Trans. Faraday Soc. **44**, 574 (1948)] obtain an equation equivalent to Eq. (24). Also, Davis and De Witt [J. Am. Chem. Soc. **70**, 1139 (1948)] give an expression for a quantity ΔE_R ($= Q_{st}$)

obeys a two-dimensional van der Waals equation[6] (put $jj_n = kT/h\nu_n$ in Part III of reference 6). One finds by the same methods as above, using Eqs. (17) and (19),

$$\varphi/\alpha kT = [\theta(1-x)/(1-\theta(1-x))] \\ -(\beta/2)\theta^2(1-x)^2 \\ = \ln[Cx(1-\theta+\theta x)/\theta(1-x)^2], \quad (25)$$

$$(E_S - E_L')/kT = -(1-x)[[(\epsilon_1 - \epsilon_L)/kT]+1 \\ +(\beta/2)\theta(1-x)], \quad (26)$$

$$(H_S - H_L')/kT = -(1-x)[[(\epsilon_1 - \epsilon_L)/kT]+\beta\theta(1-x) \\ -[\theta(1-x)/(1-\theta(1-x))]], \quad (27)$$

where $\alpha = 1/b'$ and $\beta = 2a'/b'kT$.

IV. DISCUSSION

Curves calculated for the above special cases are given in Figs. 1–4. Figure 1 gives H_S and E_S for the B.E.T. model and $j_S/j_L = 1$. The abscissa is also the $c=1$ curve for E_S. Figure 2 gives more details for $c=100$. The functions given are plotted against θ instead of x in this figure. The expected effect on the heat content and isosteric heat of changing j_S/j_L (keeping c constant; see Eq. (2)) is shown in Fig. 3. The significance of the value $j_S/j_L = 5.43$ is discussed below.

Figure 4 gives the entropy of the adsorbate for a number of cases. The lowest pair of curves may be considered as reference curves for a van der Waals first layer; the next lowest pair serve as references for the B.E.T. (localized) model. The relative position (localized *versus* mobile) of these two pairs of curves can be analyzed but has little physical significance because the choice $j_S/j_L = 1$ for both is unrealistic. Using the methods of an earlier paper[7] we have estimated, as an example, that for argon on potassium chloride at 90°K j_S/j_L (mobile) = 28.6 and j_S/j_L (localized) = 5.43. The effect on the reference curves of changing $j_S/j_L = 1$ to these values can be observed in Fig. 4. The entropy increases with increasing j_S/j_L.[8] The mobile model now has a higher entropy than the localized model. The van der Waals curve for $a'=0$, $C=490$, and $j_S/j_L = 28.6$ has not been calculated but must fall between the two neighboring curves in Fig. 4. The anticipated effect of attraction between the molecules may be seen by comparing this curve with the curve labeled $2a'/b'kT = 8$.

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which a little algebra shows is also equivalent to Eq. (24). Incidentally, there is a typographical error in their Eq. (6). The denominator is supposed to read $[(1-\theta)^2 + (4\theta/c)]^{\frac{1}{2}}$.

[6] Terrell L. Hill, J. Chem. Phys. **14**, 441 (1946).
[7] Terrell L. Hill, J. Chem. Phys. **16**, 181 (1948).
[8] However, j_S/j_L is not a pure entropy factor. In general it contributes to both energy (Eq. (7)) and entropy.