The Relationship Between the Energy of Adsorption of a Vapor on a Solid and of Immersion of the Solid in a Liquid

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of vaporization of water is 10,480 cal. mole^{-1}. The most convenient method of expressing our results seems to be to give the excess heat of desorption (or adsorption) per mole for each molecular layer, above that for water itself, or $H_{D(n)} - H_{D(\infty)}$.

The values are as follows (Table I) in calories per mole.

TABLE I.

Layer	$H_{D(n)} - H_{D(\infty)}$ or $E_1 - E_L$	Values for exponential decay
1	6550	6550
2	1380	1637
3	450	409
4	80	102
5	40 (?)	26
All above 5	30 (?)	

With our calorimetric equipment the values for the fourth and fifth layers are very inaccurate, but it seems to be certain that the energy is not entirely negligible.

With nitrogen on various non-porous solids at $-195.8°C$, and with water on these solids at 25°C, we commonly obtain films which are from 7 to 10 monolayers thick before saturation is attained, that is, at pressure slightly *below* $p/p_0 = 1$. Since the areas are determined by our absolute method, it is certain that these adsorbed films are highly polymolecular, especially since the nitrogen molecule would have to occupy an area as low as 1.56A^2 to make the film monomolecular, while the lowest area we have ever obtained is 13.7A^2.

The values given in the table suggest that $H_{D(n)} - H_{D(\infty)}$ which is the BET $E_1 - E_L$ undergoes an exponential decay, as indicated by the last column. On this basis the experimental value for the second layer is too low, and for the third, too high, to meet this condition, which suggests an orientation effect in the layers. Unfortunately, the errors in the experimental values are so large that there is no evidence for this point of view.

[1] I. Langmuir, J. Chem. Soc., pp. 520–521 (1940).
[2] S. Brunauer and P. H. Emmett, J. Am. Chem. Soc. 57, 1754 (1935).
[3] P. H. Emmett and S. Brunauer, J. Am. Chem. Soc. 59, 310, 1553 (1937).
[4] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. 60, 309 (1938).
[5] W. D. Harkins and George Jura, J. Chem. Phys. 11, 430 (1943).

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October 19, 1943

THE heat of adsorption of a vapor upon the surface of a solid can in general be calculated more accurately from heats of immersion and condensation than by any direct or indirect experimental adsorption method. It is, therefore, unfortunate that the equations used in the literature to express the relationship between the energies of adsorption and immersion are universally incorrect.

If h is used to designate the increase in the Gibbs heat function per unit area, then

$$h = (\partial H/\partial \Sigma)_{T,P} \quad (\Sigma = \text{total area})$$

may be used as the definition of h. In the following derivation of the correct relationship between the heat of adsorption and the heat of emersion[1] $h_{E(SL)}$ is the heat of emersion of the clean solid from the liquid in erg cm^{-2}; $h_{E(S_fL)}$ is the heat of emersion in erg cm^{-2} of the solid, with n moles of adsorbed vapor per cm^2, to form a clean solid surface; λ is the heat of vaporization in erg mole^{-1}.

Consider a non-porous solid with an area of 1 cm^2 and a negligible volume. The following processes may be imagined to occur:

1. The solid is emersed from n_1 moles of liquid into a vacuum. Here n_1 is assumed to be large in comparison with the n moles considered in the next step.

$$\Delta H = h_{E(SL)}. \quad (1)$$

2. The solid is emersed from n_1 moles of liquid into the vapor of the liquid at the pressure p_1 carrying with it a film of just the correct thickness to give it equilibrium with the vapor *at this pressure*. The amount of liquid removed in this film is n moles.

$$\Delta H = h_{E(S_fL)}. \quad (2)$$

3. Of the n_1 moles of liquid left in (1), evaporate n moles, leaving $(n_1 - n)$ moles, which is the amount of liquid left in 2.

$$\Delta H = n\lambda. \quad (3)$$

Subtract 2 from $1+3$, since this will give the increase in the value of the heat function when the film of n moles is vaporized (desorbed) from the surface of the solid.

$$h_{D(VS_f)} = h_{E(SL)} - h_{E(S_fL)} + n\lambda. \quad (4)$$

Now,

$$h_{E(SL)} = h_S - h_{SL} \quad (5)$$

$$h_{E(S_fL)} = h_{S_f} - h_{SL}. \quad (6)$$

So,

$$h_{D(VS_f)} = h_S - h_{S_f} + n\lambda \quad (7)$$

and since in general

$$h = \gamma - T(\partial \gamma/\partial T)_{p,T}, \quad (8)$$

where γ is the free surface energy per sq. cm

$$h_{D(VS_f)} = \gamma_S - \gamma_{S_f} - T[(\partial \gamma_S/\partial T) - (\partial \gamma/\partial T)]_{p,T} + n\lambda. \quad (9)$$

It has been customary to express the heat of adsorption either in cal. g^{-1} or cal. mole^{-1}. If it is wished to express the heat in cal. g^{-1} the result is

$$H_{D(VS_f)} = H_{E(SL)} - H_{E(S_fL)} + n\lambda, \quad (10)$$

where $H_{E(SL)}$ and $H_{E(S_fL)}$ are the heats of emersion in cal. g^{-1} of adsorbent and n is the number of moles of vapor adsorbed g^{-1}. If it is wished to express the result in cal. mole^{-1} of vapor adsorbed, the equation becomes

$$H_{D(VS_f)} = (1/n)[H_{E(SL)} - H_{E(S_fL)}] + \lambda. \quad (11)$$

Although the equations have been derived for a crystalline material, the results are equally applicable to porous materials.

The relationship that has been used is

$$H_{D(VS_f)} = H_{E(SL)} + n\lambda. \quad (A)$$

This equation was believed to be applicable only when the solid is saturated with the vapor. This formula has even received experimental "proof," which was obtained by using a porous adsorbent. In this case, the pores are filled with adsorbate. This reduces the area of the sample so that the second heat of emersion term becomes effectively zero.

Equation (4) is the fundamental equation for the calculation of the heat of desorption or its negative, the heat of adsorption. This equation is valid for either non-porous or porous solids at any value of p/p_0. In the literature of the subject, the term $-h_{E(S_fL)}$, which may have a considerable magnitude, is always omitted. This makes the equation entirely inapplicable to non-porous solids, and also to porous solids except at $p/p_0 = 1$, where it is *still incorrect*, but gives an approximation to the correct result. The error introduced by the omission of this term may be illustrated by calculations from the data of Razouk.[2] When his sample of charcoal had adsorbed 13.5 percent of that adsorbed at $p/p_0 = 1$, the heat of adsorption (q_a) was 9.9 cal. g^{-1}, while the omission of the term in question gives $q_a = 22.4$ cal. g^{-1}.

[1] W. D. Harkins and H. K. Livingston, J. Chem. Phys. 10, 342 (1942).
[2] R. I. Razouk, J. Phys. Chem. 45, 190 (1941).