Thermodynamic Functions of Adsorbed Molecules from Heats of Immersion[1]

By George Jura and Terrell L. Hill

If N_s molecules are adsorbed on a solid of area $\mathcal{A}$, it is of interest[2] to know the entropy and energy per molecule, $s_s = S_s/N_s$ and $E_s = E_s/N_s$, respectively. These functions can be calculated from two adsorption isotherms, measured at neighboring temperatures down to very low pressures, as illustrated in a paper by Hill, Emmett and Joyner.[3] In favorable cases, with careful measurements, this can be an accurate method. On the other hand, in other cases very serious errors in the surface pressure, φ, and hence in s_s and E_s, may arise owing to uncertain extrapolation of the adsorption isotherm to $p = 0$. These errors can be especially serious in systems in which there are first order phase changes in the adsorbed phase: the phase change might be missed or the actual pressure at which it occurs may be uncertain.

An alternative and in general more precise method of obtaining s_s and E_s is to combine a computation of φ from a single adsorption isotherm with heats of immersion or ordinary integral calorimetric heats of adsorption, measured at the same temperature. Harkins and Jura[4] used this method to obtain thermodynamic functions referred to the *solid surface.* We shall point out below the relations between the Harkins–Jura functions and the thermodynamic functions of the adsorbed molecules (*e.g.*, s_s and E_s). Incidentally, if the solid is perturbed by the adsorbed phase, the equations given below are still valid (see IX).

Let U_0 be the heat of immersion (in the liquid adsorbate) of the clean solid adsorbent, carried out in a container of fixed volume, and let U be the heat of immersion of the solid with N_s molecules adsorbed on it. Then it is easy to see that

$$E'_L - E_s = (U_0 - U)/N_s \tag{1}$$

where E'_L is the internal energy of the liquid adsorbate per molecule (in equilibrium with vapor). Also,[2] using Eq. (1)

$$T(s_s - s'_L) = [(U - U_0)/N_s] + (\varphi/\Gamma) - kT \ln x \tag{2}$$
$$x = p/p_0,\ \Gamma = N_s/\mathcal{A}$$

assuming the vapor is a perfect gas and omitting a negligible volume term.

A comparison of the quantities calculated by Harkins and Jura[4] in their Fig. 9 with the present notation gives the following relations between the two sets of functions

$$(\gamma_s - \gamma_{sf})_{HJ} = \varphi \tag{3}$$
$$(\epsilon_s - \epsilon_{sf})_{HJ} = (U_0 - U)/\mathcal{A} = \Gamma(E'_L - E_s) \tag{4}$$

$$-T(s_s - s_{sf})_{HJ} = \Gamma(E'_L - E_s) - \varphi = \Gamma[T(s'_L - s_s) - kT \ln x] \tag{5}$$

Whenever there is *strong* binding of the first layer to the surface, regardless of the details (solid adsorbents with small pores are excepted) and independent of any particular theory, one would expect a minimum in $s_s - s'_L$ at about the completion of a monolayer.[5] This is because a virtually filled monolayer has fewer possible statistical configurations than either an incomplete monolayer or a complete monolayer plus an incomplete second layer. When combined with an estimate of the surface area per molecule in a filled monolayer, the above entropy minimum[6] can be used as a method for surface area determination not dependent on a detailed theory. In the two cases worked out so far[3,7] excellent agreement with the B.E.T. surface area is obtained. Minima in the function $(s_s - s_{sf})_{HJ}$ do not have this simple theoretical relation to surface area, because of Γ and x in Eq. (5).

Alternatively, instead of using heats of immersion, E_s in Eq. (1) (relative to gas or liquid), for use in Eq. (2), may be found from integral calorimetric heats of adsorption,[2] as done by Drain and Morrison.[7]

Finally, we wish to examine the effects of errors in φ of the type mentioned above. For this purpose, we assume that errors in the heat measurements are negligible and that errors in φ arise only from pressures below the pressure region under discussion. Following V, let φ be the true spreading pressure, Φ the incorrect spreading pressure and a the error in Φ

$$\Phi(p,T) = \varphi(p,T) + a(T) \tag{6}$$

Let s_s be the correct entropy obtained from Eqs. (V-86, 93) and s'_s the incorrect entropy found by using Φ instead of φ in these equations. In this latter case, let a_1 be the value of a at T_1 and a_2 at T_2. Then the error in the entropy is (V)

$$s'_s - s_s = \frac{1}{\Gamma}\frac{\Delta a}{\Delta T} \tag{7}$$
$$\Delta a = a_2 - a_1,\ \Delta T = T_2 - T_1$$

On the other hand, using Eq. (2) and an intermediate a and T, the corresponding error is $a/\Gamma T$. If a is of the same order of magnitude as Δa, the error in the heat calculation will thus be smaller in the ratio $\Delta T/T$. However, if the error is systematic (*i.e.*, $\Delta a \cong 0$), the opposite result is possible ($\Delta a/\Delta T < a/T$).

We have also

$$E'_s - E_s = \frac{T}{\Gamma}\left(\frac{\Delta a}{\Delta T} - \frac{a}{T}\right) \tag{8}$$

which corresponds to Equation (7).

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[2] T. L. Hill, *J. Chem. Phys.*, **17**, 520 (1949), hereafter referred to as V; *ibid.*, **18**, 246 (1950), hereafter referred to as IX; *Trans. Faraday Soc.*, **47**, 376 (1951) (in this paper H^σ should be replaced by $\mathcal{H}^\sigma$ in lines 29, 31, 33 and 34, p. 378).

[3] T. L. Hill, P. H. Emmett and L. G. Joyner, This Journal, **73**, 5102 (1951). Errata: Change s_s to $\bar{s}_s$ in Eq. (1), in third line below Eq. (2), third equation, in third line below Eq. (17), and in line 17 of "Results and Discussion." Change H_s to $\bar{H}_s$ in line below Eq. (6), and in Eq. (7). See This Journal **73**, 5933 (1951).

[4] W. D. Harkins and G. Jura, *ibid.*, **66**, 919 (1944).

[5] See, for example, T. L. Hill, *J. Chem. Phys.*, **17**, 772 (1949).

[6] In many cases the differential entropy curve will be available but not the molar integral entropy curve. In this case, if there is a "loop" in the differential entropy,[2,3,7] the surface area can be estimated by assuming that a monolayer is completed at the inflection point in the loop.

[7] L. E. Drain and J. A. Morrison, American Chemical Society Meeting, New York, September, 1951.