

Application of thermodynamics to interfacial phenomena

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Abstract - This paper sets out to identify some of the sources of confusion which have arisen in the past concerning the application of thermodynamics to interfacial phenomena and to indicate their origin and how they can be resolved. Various approaches to the concept of 'surface excess properties' will be outlined and their role in relating observed phenomena to theoretical models will be discussed.

Attention is directed to some of the outstanding problems in the field.

Although there is an extensive literature on the thermodynamics of interfaces, there still seems to be a need to clarify certain aspects. To establish a perspective and to explain the relationship between the approaches used by different authors, it is necessary to restate some well-known results and to indicate how they may be arrived at by alternative routes.

The first objective, as in all classical thermodynamic treatments, is to describe systems involving interfaces in terms of experimentally observable quantities, and then to derive equations which enable one to relate the properties of a system under one set of conditions to those in different circumstances. The equations obtained may be used in several ways. They may enable the thermodynamic consistency of experimental techniques and methods of analysis of data to be checked, or make it possible to derive from one set of experimental data, information on a system which, while in principle observable, may be difficult or inconvenient to obtain by direct experiment. For example, for a liquid/vapour interface it is exceedingly difficult to measure adsorption accurately, but this information can be obtained from surface tension measurements as a function of solution composition. Conversely, for liquid/solid or vapour/solid interfaces, direct measurement of surface tension is generally impossible, but values relative to a standard state can be calculated from readily performed adsorption measurements.

Furthermore, the analysis of experimental data in thermodynamic terms very often presents a picture which is strongly suggestive of a particular molecular dynamic interpretation, and hence leads to the development of statistical mechanical theories which, to a lesser or greater extent, provide an interpretation of the thermodynamic parameters. Thermodynamic relationships again have two roles. For example it is often simpler to derive theoretical equations for adsorption effects from which surface tensions can be derived for comparison with experiment. Secondly they provide a means of checking theories for thermodynamic consistency.

We recall first that in the bulk thermodynamic description of multiphase systems, the system is represented by a subdivision of the space it occupies into volumes, separated by geometrical boundaries, the composition and other intensive variables being uniform within each volume, or phase. This description is entirely adequate provided that the areas of the interphase boundaries do not change, and/or that the fraction of the system within a few molecular diameters of a boundary is negligibly small. When the interfacial area becomes very large (e.g. when one phase is subdivided into regions having linear dimensions less than about 1 μm) interfacial effects play a dominant role as they do for example in the domain of colloid science. In these circumstances bulk thermodynamics becomes invalid and the observed properties are found to depend on the interfacial area. In molecular terms this is because molecules near a boundary are subjected to forces different from those in the interior of a bulk phase, and make different contributions to the thermodynamic properties of the system.

The difference between the behaviour of a system as predicted by bulk thermodynamic arguments, in which the intensive properties of each phase are supposed to remain constant up to the phase boundaries, and the observed behaviour is a measure of the influence of the presence of interfaces: it is thus possible to define 'excess quantities' (which may be positive or negative) which quantify the interfacial contributions to the properties of the system.

The first of these is the surface or interfacial tension which in the framework of continuum thermodynamics is a consequence of the fact that the isotropic hydrostatic pressure in the bulk fluid is perturbed close to an interface and has to be replaced by a stress tensor (Ref.1). The difference between the mechanical properties of an interface calculated on the assumption that the bulk hydrostatic pressures in the bulk phases adjoining the interface remain constant to that interface, and the observed mechanical properties is measured by the surface tension (σ). The position of the interface which satisfies these mechanical conditions is the 'surface of tension'. It follows that the interface perturbs the energy of the system by an amount σA_s where A_s is the area of the interface concerned. Such an interpretation is associated with the so-called 'quasi-thermodynamic' description of a system and in essence can be traced back to Thomas Young (Ref.2).

An alternative phenomenological justification for the inclusion of the σA_s term in energy equations comes from the Laplace equation relating the pressure difference across a curved surface to the surface tension and the curvature of the surface. This may be illustrated by a simple example, presented by Defay and Prigogine (Ref.3). We consider a spherical drop of liquid of radius r , and volume V^ℓ , suspended and in equilibrium with vapour, of volume V^g , (gravity is neglected) contained in a cylinder of total volume V at a pressure p^g . The pressure within the drop, p^ℓ , is given by the Laplace equation. The work done in an infinitesimal compression is then

$$\begin{aligned} dW &= -p^g dV = -p^g (dV^g + dV^\ell) = -p^g dV^g - p^\ell dV^\ell + (p^\ell - p^g) dV^\ell \\ &= -p^g dV^g - p^\ell dV^\ell + (2\sigma \ell_g / r) dV^\ell && \text{(from Laplace's equation)} \\ &= -p^g dV^g - p^\ell dV^\ell + \sigma \ell_g dA \ell_g. \end{aligned} \quad (1)$$

The work done on the system can then be split into three terms, two arising from volume changes of the bulk phases, and the third from the change in interfacial area. A more complex case is that of a liquid confined by rigid solid walls (Ref.4). Making use of Gauss' equation for the effect of a shift of the ℓ/v interface on the ℓ/v , v/s and s/ℓ interfacial areas the contributions of the surface area changes to the energy of the system are shown to be of the form $\sigma \times$ (area). These arguments are to be preferred over the more conventional justification for the inclusion of a surface term which requires one to carry out 'thought-experiments' with surface pistons; only in the special case of the Langmuir trough do these have a real meaning.

In even more general terms one may start by asserting that it is self-evident that the independent variables describing a system must include the interfacial area, and define σ as the intensive factor conjugate with the area.

A thermodynamic approach requires us also to be able to describe the material state of the system containing interfaces. Again we consider the effect of the interfaces on the material composition by comparing the content of different substances calculated as though the interfaces had no effect, i.e. assuming constant bulk compositions (c_i^α, c_i^β) up to the boundary between phases α and β , with the amounts of these substances actually present in the system (n_i). These differences are called 'surface excess amounts' (n_i^σ)

$$\begin{aligned} n_i^\sigma &= n_i - n_i^\alpha - n_i^\beta \\ &= n_i - c_i^\alpha V^\alpha - c_i^\beta V^\beta. \end{aligned} \quad (2)$$

where V^α and V^β are the volumes of the two phases. A difficulty arises, however, because while the phrase 'up to the phase boundary' sounds innocuous, it turns out that in real physical systems the values to be ascribed to the surface excess amounts are extremely sensitive to the location chosen for the surface defining the interface and hence to the values of V^α and V^β . For the above definition to have any operational meaning it would be necessary to locate this dividing surface with an experimentally unattainable precision. As is well known this problem was first addressed by Gibbs (Ref.5), although over a century later his method of solution, employing a so-called Gibbs dividing surface (G.D.S.) is still widely misunderstood, and in the opinion of some, the cause of major difficulties. It is said to have 'bedevilled the student' and been a 'source of endless confusion' (Ref.6); and by others to imply an impossible physical situation.

We shall first consider briefly the Gibbs method, and then two alternative approaches which do not appeal directly to the concept of a dividing surface.

For simplicity we consider a plane interface of area A_s , and consider $\Gamma_i = n_i^\sigma / A_s$, the *surface excess concentration* or *areal surface excess*. (Ref.7). The dividing surface is placed a distance z from an arbitrary plane which is parallel to the physical surface. It is readily seen that the change in the value of Γ_i if the dividing surface is moved by a

distance δz in the direction of the α -phase is given by

$$\delta\Gamma_i = (c_i^\alpha - c_i^\beta)\delta z. = \Delta c_i \delta z. \quad (3)$$

Graphs of Γ_1 and Γ_2 as a function of the chosen position z of the G.D.S. therefore have the form shown in Figure 1.

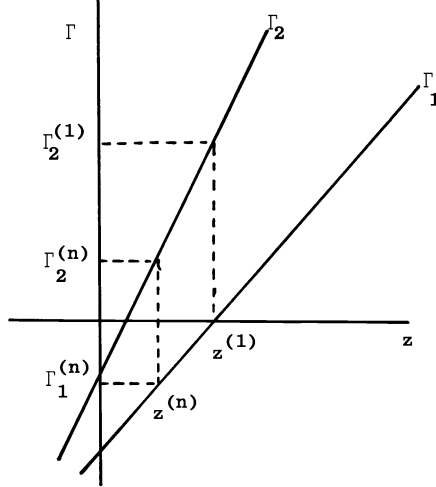


Figure 1

The problem is to define a procedure for locating the G.D.S. which can be directly related to experimental quantities and provide an unambiguous description of the material state of the system. One way of doing this is to locate the G.D.S. at $z^{(1)}$ at which $\Gamma_1 = 0$. The value of Γ_i at $z^{(1)}$ is then called the *relative adsorption of i with respect to component 1*, $\Gamma_i^{(1)}$. Simple geometry then shows that if we do not know where to locate the G.D.S., but make an arbitrary choice then we can still calculate $\Gamma_2^{(1)}$ through the equation:

$$\Gamma_i^{(1)} = \Gamma_i - \Gamma_1 \frac{\Delta c_i}{\Delta c_1}, \quad (4)$$

where Γ_i and Γ_1 are defined with respect to the same but arbitrarily chosen G.D.S. It is perhaps this dual interpretation of $\Gamma_i^{(1)}$ which sometimes causes confusion.

The experimental determination of $\Gamma_i^{(1)}$ follows immediately by writing eqn. (1) for component i and 1 , and taking these with a third equation $V = v^\alpha + v^\beta$. By elimination of v^α and v^β from these three equations, and rearranging we obtain

$$\begin{aligned} n_i^{\sigma(1)} &= A_s \Gamma_i^{(1)} = A_s \left[\Gamma_i - \Gamma_1 \frac{\Delta c_i}{\Delta c_1} \right] = \left[\left(n_i - n_1 \frac{\Delta c_i}{\Delta c_1} \right) - \left(c_i^\alpha - c_1^\alpha \frac{\Delta c_i}{\Delta c_1} \right) v \right] \\ &= \left[(n_i - c_i^\alpha v) - (n_1 - c_1^\alpha v) \frac{\Delta c_i}{\Delta c_1} \right]. \end{aligned} \quad (5)$$

All quantities on the right hand side are directly measurable so that $n_i^{(1)}$ and $\Gamma_i^{(1)}$ are experimental quantities, provided A_s is known, independent of the choice of G.D.S.¹

Figure 1 suggests an alternative definition convenient when a binary system is considered. We may then choose the G.D.S. at $z^{(n)}$ such that $\Gamma_2^{(n)} = -\Gamma_1^{(n)}$.^{*} Alternatively, if Γ_1 and Γ_2 are defined with respect to an arbitrary G.D.S.

$$\Gamma_2^{(n)} = \Gamma_2 - \Gamma_1 \frac{\Delta c_2}{\Delta c_1}, \quad (6)$$

* More generally we choose $\sum_i \Gamma_i = 0$

where $\Gamma = \Gamma_1 + \Gamma_2$ and $\Delta c = (c_1^\alpha c_2^\alpha) - (c_1^\beta c_2^\beta)$. $\Gamma_2^{(n)}$ is called the *reduced adsorption of component 2*.

The equation for $n_1^{\sigma(n)}$ in terms of experimental quantities is then

$$n_1^{\sigma(n)} = A_s \Gamma_i^{(n)} = (n_i - c_i^\alpha V) - (n - c^\alpha V) \frac{\Delta c_2}{\Delta c} . \quad (7)$$

Since the experimental measurement of $n_1^{\sigma(1)}$ and $n_1^{\sigma(n)}$ involves no mention of a dividing surface, it is relevant to ask whether the formal definitions of these quantities need to involve such surfaces. Before discussing this point we go a little further in developing the thermodynamics.

Other surface excess quantities are defined in an analogous way e.g.

$$U^\sigma = U - \overset{\circ}{u}^\alpha V^\alpha - \overset{\circ}{u}^\beta V^\beta , \quad (8)$$

where $\overset{\circ}{u}^\alpha$ and $\overset{\circ}{u}^\beta$ are the energy densities in the bulk phases. Thus starting from the basic equation for the whole system.

$$dU = TdS - pdV + \sigma dA_s + \sum_{i=1}^c \mu_i dn_i , \quad (9)$$

and subtracting the corresponding equations for the bulk phases we have (remembering that $v = v^\alpha + v^\beta$)*

$$dU^\sigma = dH^\sigma = TdS^\sigma + \sigma dA_a + \sum_{i=1}^c \mu_i dn_i^\sigma . \quad (10)$$

U^σ of course depends on the choice of the position of the G.D.S. Following the conventional procedure of defining a Gibbs energy of the surface

$$G^\sigma = H^\sigma - TS^\sigma \quad (11)$$

and integrating the resulting differential, dG^σ , at constant intensive quantities leads to

$$G^\sigma = \sigma A_s + \sum_{i=1}^c \mu_i n_i^\sigma \quad (12)$$

which on division by A_s gives

$$\hat{g}^\sigma = \sigma + \sum_{i=1}^c \mu_i \Gamma_i . \quad (13)$$

Since σ is a physical quantity, while Γ_i depends on the choice of the G.D.S., \hat{g}^σ must also depend on this choice.

It is important to stress that σ is not equal to the surface Gibbs energy per unit area (areal Gibbs energy), except in the special case of a one component system when, choosing the G.D.S. such that $\Gamma_1 = 0$, $\sigma = g^{\sigma(1)}$, the relative areal Gibbs energy. Following the same mathematical procedure as that used to derive the Gibbs-Duhem equation for bulk systems, we obtain its surface analogue, the *Gibbs adsorption equation*:

$$d\sigma = - \hat{s}^\sigma dT - \sum_{i=1}^c \Gamma_i d\mu_i , \quad (14)$$

where $\hat{s}^\sigma = S^\sigma/A_s$, or at constant temperature,

$$d\sigma = - \sum_{i=1}^c \Gamma_i d\mu_i , \quad (15)$$

* Since no volume term appears in eqn. (10) there is no distinction between surface energy and surface enthalpy, nor between the Helmholtz and Gibbs surface free energies.

the *Gibbs adsorption isotherm*. If the surface is in equilibrium with both bulk phases, the $d\mu_i$'s are not all independent but must satisfy the bulk Gibbs - Duhem equations for the adjacent phases. When this condition is imposed it follows that

$$d\sigma = - \sum_{i=2}^c \Gamma_i^{(1)} d\mu_i, \quad (16)$$

where $\Gamma_i^{(1)}$ is now the relative adsorption of i with respect to 1. Alternatively we could have obtained (16) more simply from (15) by deciding to choose the G.D.S. such that $\Gamma_1 = 0$ and so reducing the number of independent variables by one.

The Gibbs adsorption isotherm in the form of eqn. (16) is the fundamental equation from which all surface thermodynamic properties can be derived.

Let us now examine alternative approaches which do not involve direct mention of a dividing surface (Ref. 8), limiting the discussion, for simplicity, to a binary system.

The Gibbs-Duhem equation for the whole system is

$$SdT - Vdp + A_s d\sigma + n_1 d\mu_1 + n_2 d\mu_2 = 0, \quad (17)$$

where n_1 and n_2 are the total amounts of components 1 and 2, while, for the individual phases the Gibbs-Duhem equations can be written in the intensive forms, by dividing through by V^α and V^β respectively,

$$\frac{s^\alpha}{s} dT - dp + c_1^\alpha d\mu_1 + c_2^\alpha d\mu_2 = 0, \quad (18)$$

$$\frac{s^\beta}{s} dT - dp + c_1^\beta d\mu_1 + c_2^\beta d\mu_2 = 0, \quad (19)$$

where $\frac{s^\alpha}{s}$, $\frac{s^\beta}{s}$, are the entropy densities in the bulk phases and c_1^α etc. are the bulk concentrations.

We consider isothermal conditions, multiply eqn. (18) by x , eqn. (19) by y and subtract them from eqn. (17) giving

$$-(V-x-y)dp + A_s d\sigma + (n_1 - xc_1^\alpha - yc_1^\beta) d\mu_1 + (n_2 - xc_2^\alpha - yc_2^\beta) d\mu_2 = 0. \quad (20)$$

Here x and y are introduced as arbitrary multipliers. However, if we choose x and y to satisfy the conditions

$$x + y = V \quad (21)$$

and $(n_1 - xc_1^\alpha - yc_1^\beta) = 0 \quad (22)$

then

$$A_s d\sigma = - (n_2 - xc_2^\alpha - yc_2^\beta) d\mu_2. \quad (23)$$

If eqn. (21) and (22) are solved for x and y and the results inserted in equation (23) we obtain

$$A_s d\sigma = - \left[(n_2 - c_2^\alpha V) - (n_1 - c_1^\alpha V) \frac{\Delta c_2}{\Delta c_1} \right] d\mu_2. \quad (24)$$

The term in square brackets is seen immediately to be $n_2^{\sigma(1)}$ as defined in eqn. (5). We thus rederive eqn. (16). Although x and y are initially arbitrary, eqn. (21) requires them to subdivide the total volume into two regions in just the same way as implied by a dividing surface, while the condition (22) further restricts the volume subdivision to be that which (cf. eqn. (1)) makes the adsorption of component 1 zero. While some authors (Ref. 9) have preferred to use this method, it would appear that the concept of a dividing surface is introduced implicitly rather than explicitly.

The reduced adsorption is obtained by the same procedure except that condition (22) is replaced by

$$x(c_1^\alpha + c_2^\alpha) + y(c_1^\beta + c_2^\beta) = n_1 + n_2, \quad (25)$$

which is just the condition that x and y be chosen so that the total adsorption is zero.

The most general phenomenological approach is that presented by Wagner (Ref. 9). We start from the fundamental eqn. (9) and set up a characteristic function

$$G^{(1)} = H - TS - \sum_{i=2}^c \mu_i dn_i \quad (26)$$

so that

$$dG^{(1)} = -SdT + Vdp + \sigma dA_s + \mu_1 dn_1 - \sum_{i=2}^c n_i d\mu_i \quad (27)$$

Cross-differentiation with respect to A_s and μ_i then gives

$$\left[\frac{\partial^2 G^{(1)}}{\partial A_s \partial \mu_i} \right]_{T, P, n_1, \mu_{j \neq 1, i}} = \left[\frac{\partial \sigma}{\partial \mu_i} \right]_{T, P, n_1, \mu_{j \neq 1, i}} = - \left[\frac{\partial n_i}{\partial A_s} \right]_{T, P, n_1, \mu_{j \neq 1, i}} \quad (28)$$

The last term is therefore the amount of component i which has to be added to the system to maintain the intensive state of the system constant when, keeping n_1 and $\mu_{j \neq i}$ constant, the area is increased by dA_s . The Gibbs adsorption isotherm then appears immediately in the form:

$$d\sigma = - \sum_{i=2}^c \left[\frac{\partial n_i}{\partial A_s} \right]_{\text{int}, n_1, \mu_{j \neq 1, i}} d\mu_i \quad (29)$$

where the subscript int means that the intensive variables are constant.

An alternative definition of the relative adsorption is therefore:

$$n_i^{\sigma(1)} = \left[\frac{\partial n_i}{\partial A_s} \right]_{\text{int}, n_1, \mu_{j \neq 1, i}} \quad (30)$$

Here the concept of a dividing surface appears to be completely absent.

The application of the above definition may be illustrated in the case of adsorption at the solid/liquid interface. If we choose the surface of the solid as G.D.S., then provided the solid is impermeable to all components of the liquid, $\Delta c_i = c_i^l$ and eqn. (7) reduces to

$$n_i^{\sigma(n)} = n_2 - n^{\sigma} \frac{c_2^l}{c_1^l + c_2^l} = n_2 - n^{\sigma} x_2^l \quad (31)$$

We note that the total volume V disappears from this expression.

If the experiment is conducted by taking an amount n° of solution of initial mole fraction x_2° , then $n_2 = n^{\circ} x_2^{\circ}$ and

$$n_2^{\sigma(n)} = n^{\circ} \Delta x_2^l \quad (32)$$

where $\Delta x_2^l = x_2^{\circ} - x_2^l$, the change in mole fraction when the solution is contacted with the solid and adsorption equilibrium set up. Alternatively, applying the same procedure to eqn. (5) one obtains

$$n_i^{\sigma(1)} = n^{\circ} \Delta x_2^l / x_1^l = n_2^{\sigma(n)} / x_1^l \quad (33)$$

The operational application of equation (30) involves an experiment in which, after contacting the solution with the solid, x_2^l is returned to its initial value x_2° by the addition of an amount Δn_2 of component 2: i.e. the initial intensive state is re-established after the surface area has increased by A_s .

$$\text{Now} \quad n_2 = n^{\circ} x_2^{\circ} + \Delta n_2; \quad n = n^{\circ} + \Delta n_2 \quad (34)$$

$$\begin{aligned} \text{and} \quad n_2^{\sigma(n)} &= n^{\circ} x_2^{\circ} + \Delta n_2 - (n^{\circ} + \Delta n_2) x_2^{\circ} \\ &= \Delta n_2 (1 - x_2^{\circ}) \\ &= \Delta n_2 x_1^{\circ} \end{aligned} \quad (35)$$

$$\text{Thus } n_2^{\sigma(1)} = n_2^{\sigma(n)} / x_1^o = \Delta n_2 \quad (36)$$

$$\Gamma_2^{(1)} = \frac{\Delta n_2}{A_s} \quad (37)$$

and $\Gamma_2^{(1)}$ is seen to equal the amount of component 2 which has to be added for unit increase in surface area to re-establish the original mole fraction. We note that the total volume of the system is not involved, nor is it necessary to know the initial amount of solution, n .

A further interesting point arises in the case of liquid/solid systems. It has been argued that for a c -component liquid mixture in contact with a solid, the system should be regarded as a $(c+1)$ -component system. Then, in general, if an arbitrary choice of G.D.S. is made, there will, formally, be a surface excess, or deficit, (Γ_s) of solid. In particular, for the choice of a surface which makes Γ_1 , zero, Γ_s will not be zero. The difficulty is readily overcome by choosing by G.D.S. which makes $\Gamma_s = 0$ i.e. the surface of the solid.

$$\text{Then } d\sigma = - \sum_{i=1}^c \Gamma_i^{(n)} d\mu_i \quad (38)$$

However, from the Gibbs-Duhem equation

$$d\mu_i = - \frac{1}{x_1} \sum_{i=2}^c x_i d\mu_i$$

so that

$$d\sigma = - \sum_{i=2}^c \left[\Gamma_i^{(n)} - \frac{x_i}{x_1} \Gamma_1^{(n)} \right] d\mu_i = - \sum_{i=2}^c \Gamma_i^{(1)} d\mu_i \quad (39)$$

Whether we regard the system as a c -component system under the influence of an external field, or a $(c+1)$ -component system including the solid, the same result is obtained.

In the following attention will be limited to the liquid/solid interface. The objective of experimental studies should be to establish, via measurements of $\Gamma_i^{(n)}$ or $\Gamma_i^{(1)}$, and integration of equation (16), the function $\sigma(x_1, T)$,

$$\sigma - \sigma_2^* = \int_{x_2=1}^x \frac{\Gamma_2^{(n)}}{x_1 x_2 \gamma_2} d(x_2 \gamma_2) \quad (40)$$

where σ_2^* is the value of σ for solid in contact with pure component 2 and γ_2 is the activity coefficient of 2 in the solution. When this has been done it is then possible to obtain the corresponding enthalpy and entropy functions. Defining surface enthalpies and entropies through the equation

$$\hat{g}^{\sigma(n)} = \hat{h}^{\sigma(n)} - T \hat{s}^{\sigma(n)} = \sigma + \sum_{i=1}^c \Gamma_i^{(n)} \quad (41)$$

one obtains

$$\left[\frac{\partial(\sigma/T)}{\partial(1/T)} \right]_{x_2}^{\ell} = \hat{h}^{\sigma(n)} - \Gamma_2^{(n)} (h_2^{\ell} - h_1^{\ell}) \quad (42)$$

where h_2^{ℓ} and h_1^{ℓ} are the partial molar enthalpies in the bulk liquid.

It may then be shown (Ref. 11) that the right hand side is the enthalpy of immersion of unit area of solid in a volume of mixture large enough for the resulting change in concentration to be negligible:

$$\left[\frac{\partial(\sigma/T)}{\partial(1/T)} \right]_{x_2}^{\ell} = \Delta_w \hat{h} = \hat{h}^{\sigma(n)} - \Gamma_2^{(n)} (h_2^{\ell} - h_1^{\ell}) \quad (43)$$

Here again $\hat{h}^{\sigma(n)}$ is seen to depend on the standard states chosen for the enthalpies. Similarly, the entropy of immersion is given by:

$$\left(\frac{\partial \sigma}{\partial T} \right)_{x_2}^{\ell} = \Delta_w \hat{s} = \hat{s}^{\sigma(n)} - \Gamma_2^{(n)} (s_2^{\ell} - s_1^{\ell}) = \sigma + T \Delta_w \hat{h} \quad (44)$$

Although $\Delta_w \hat{h}$ is a directly measurable experimental quantity, only differences in σ are accessible via equation (40). Comparison of enthalpies of immersion derived from calorimetric measurements and adsorption measurements must therefore be made through the equations

$$\left[\frac{\partial(\sigma_2^* - \sigma)/T}{\partial(1/T)} \right]_{x_2} = \Delta_w \hat{h}_2^* - \Delta_w \hat{h} \quad (45)$$

or

$$\left[\frac{\partial(\sigma_2^* - \sigma_1^*)/T}{\partial(1/T)} \right] = \Delta_w \hat{h}_2^* - \Delta_w \hat{h}_1^* \quad (46)$$

The latter equation may be used if enthalpies of immersion are available only for the pure liquids.

Finally having established the relationship between experimental quantities, the question remains of the theoretical interpretation of the quantities so derived.

At present only relatively simple theoretical models are available. The ultimate objective will be to be able to calculate the profile of local composition of the liquid phase as a function distance from the solid surface. If this can be established as a function of temperature then the above thermodynamic equations will allow theoretical estimates to be made of the surface excess quantities $(\sigma - \sigma_2^*) \Delta_w \hat{h}$, $\Delta_w \hat{s}$ for comparison with experiment. However, it is more usual, and often more reliable, to compare the measured surface excess isotherms with those derived from a theoretical model. However, it is less easy to derive, in a general case, theoretical values for the enthalpy of immersion, since care has to be taken to establish the standard states for the enthalpies of the two components.

It is important to stress that monolayer models cannot be regarded as anything more than very crude approximations applicable only to near-ideal systems. If the influence of intermolecular potentials or molecular size differences are to be taken into account, then some form of multilayer theory must be developed since monolayer models are then thermodynamically inconsistent. So far those available are based on or equivalent to lattice models and clearly will need refinement before they can be applied to real systems. Attention must also be drawn to the fact that most existing models take no explicit account of entropy effects arising from changes in the molecular partition function caused by modification of the rotational degrees of freedom of adsorbed molecules. That these are important is becoming increasingly clear from experimental studies (Ref. 12).

The heterogeneity of the solid surface also plays a major role in determining the adsorption behaviour of real systems, and much work still has to be done to provide an adequate theoretical basis for the analysis of such systems.

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