THERMODYNAMICS OF INTERFACIAL PHENOMENA

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Abstract — This paper reviews some of the problems associated with the formulation of the thermodynamics of interfacial phenomena. Special reference is made to the solid/liquid interface and stress is laid on the usefulness of making a thermodynamic analysis of experimental data before attempting an interpretation in terms of a molecular theory. An appropriate set of equations is developed, their application is discussed and a method of using adsorption data for the assessment of the relative wettability of surfaces is proposed. The thermodynamic characteristics, in terms of the surface tension, and the enthalpy and entropy of wetting, of some simple systems are presented and their relationship to current theories of adsorption from solution is discussed.

INTRODUCTION

There have been many expositions of the thermodynamics of interfacial phenomena emphasizing different aspects of the general problem. At one extreme are the most rigorous formulations which are not, however, always expressed in clearly operational terms, nor is it always easy to perceive their relationship to statistical mechanical models. On the other hand many treatments are linked either implicitly or explicitly to a molecular model of the interface, and it is then sometimes not easy to distinguish those features of the resulting equations which are independent of the chosen model from those which carry with them model-dependent characteristics. Since an increasing volume of experimental data on interfacial equilibria is becoming available, it is now an appropriate moment to establish the principles which should be followed in analysing and interpreting such information.

One objective of the present paper is to emphasize the importance of identifying the thermodynamic quantities which can be derived unambiguously from experimental measurements. Only when this has been done should one seek the connection between such quantities and molecular concepts which provide a statistical mechanical interpretation of the observed phenomena. To this end we first discuss some general problems, some of which, despite the large literature on the subject, seem to have been relatively neglected. We then use the case of solid/liquid interfaces as an example of the application of thermodynamics to interfacial phenomena, and illustrate the methods by some experimental data on simple systems. Finally, a brief discussion is given of the problems of the molecular interpretation of adsorption.

GENERAL THERMODYNAMIC PROBLEMS

A very general thermodynamic analysis of adsorption, applicable to gas/solid, solid/liquid, liquid/liquid and liquid/gas interfaces was given by Schay (Ref.1) at the 1st International Conference on Colloid and Surface Science. As he pointed out this quite abstract and formal treatment needs further specification to make it operational. An appropriate choice of operational variables has to be made, the most expedient choice being dependent on the particular kind of interface under consideration. Thus, for example, in the case of liquid/gas and liquid/liquid interfaces accurate direct measurement of adsorption is difficult (except in the case of insoluble films) while the surface tension is directly measurable (Note a).

Note a. It may be commented that for the liquid/gas interface it is in principle possible to determine the relative adsorption (defined later), although the experimental difficulties, in for example the McBain microtome method, are such that only a low accuracy is attainable.
measured (Note b), while the 'surface tension' has no practicable operational meaning. An important role of thermodynamics is that of providing a route between related quantities so that those which are either difficult or impossible to measure may be calculated from experimental measurements of other quantities. In a somewhat analogous fashion, while the surface area ($A_s$) of a liquid/gas or liquid/liquid interface is a well-defined quantity, that of a solid is in general not directly measurable. It is thus necessary, in a strictly operational approach, to express the contribution of the solid to the thermodynamic properties in terms of its mass and to use specific (per unit mass) rather than areal (per unit area) quantities. In this case, thermodynamics alone cannot provide a link and extra-thermodynamic procedures have to be used. Theoretical models of adsorption involve surface area as one parameter, so that if specific thermodynamic data calculated from experimental results can be brought into coincidence with theoretical equations by assigning a value to this parameter, then this may be taken as a measure of surface area. If agreement is found between areas derived from experiments on different types of interface involving the same solid, and interpreted through different (but mutually consistent) molecular models, then it is reasonable to assign to them a physical significance. Thus for some systems involving solids it is a reasonable assumption that the surface area can be known and it is then convenient to express the thermodynamic equations in terms of surface area. For other systems, however, (e.g. involving micro-porous solids where pore volume and pore size may be additional parameters) it may not be possible to arrive at a unique measure of surface area and the data must be related to the mass of solid.

In defining surface thermodynamic functions a fundamental choice has to be made between the Gibbs method in terms of surface excess quantities, the "surface phase" concept of Verschaffelt (Ref.2) and Guggenheim (Ref.3), and the 'algebraic' approach of Hansen (Ref.4), Goodrich (Ref.5) and Schay (Ref.6). The choice is largely a matter of taste and convenience since the final equations derived in the different ways are essentially identical. Although the 'surface phase' picture has certain attractions in terms of physical concepts, the Gibbs method when correctly interpreted is at least as powerful and will be adopted here. Other approaches which help to clarify the concept of surface excesses are also possible but will not be discussed in this paper.

Rather than elaborate the above considerations in the general case, it is convenient and possibly more useful to limit discussion to one particular example and for this purpose we choose the solid/liquid interface and consider the thermodynamics of adsorption by solids from binary liquid mixtures.

**THERMODYNAMICS OF ADSORPTION AT THE SOLID/LIQUID INTERFACE**

In this section we establish a phenomenological thermodynamic framework which enables a self-consistent description of adsorption from solution at a solid surface to be developed without recourse to any specific model. This involves the definition of the term adsorption and of other surface excess functions, and the derivation of equations relating them to one another and to experimentally observable quantities. Although much of what follows is to be found in other presentations, it is desirable that all important steps in the development should be made explicit so that the logical consistency of the arguments is clearly exposed.

We consider first the basic concept of adsorption and limit consideration to a binary liquid mixture. The presence of adsorption at a solid/solution interface may be inferred from two types of experiment. In the first, the fundamental observation is that when a solution is placed in contact with a solid surface and allowed to come to equilibrium, the composition of the bulk solution changes. If chemical reaction with the bulk solid, dissolution of the solid or penetration of the liquid into the bulk solid can be ruled out on the basis of independent experimental evidence, then the solid is said to have adsorbed one or more of the components of the solution. An inescapable conclusion, since the total amount of each substance in the liquid phase is unchanged in this process, is that the change in composition of the bulk liquid must have been accompanied by non-uniformity of composition in the neighbourhood of the surface, which may be represented schematically as in Fig. 1.

Note b. Even here the validity of adsorption measurements in solid/gas systems is limited by the need to know the volume of the solid so that 'dead-space' or buoyancy corrections can be made.
The observable quantities which characterise adsorption from a binary liquid mixture are the amount \( n^0 \) of initial solution of mole fraction \( x^0_2 \), the mass of solid \( m \), and the final equilibrium mole fraction in the liquid \( x^f_2 \) at a given temperature, \( T \), and pressure \( p \). The system thus contains an amount \( n^0 x^0_2 \) of component 2. If in the final state the liquid phase were of uniform composition \( x^f_2 \) throughout its extent it would contain an amount \( n^0 x^f_2 \). This latter hypothetical state in which the composition remains uniform up to the solid surface is taken as reference state. The real system thus contains an excess of component 2, over and above that in the reference system, given by

\[
n^0 (x^0_2 - x^f_2) = n^0 \Delta x^f_2,
\]

and defines one measure \( n^0_2(n) \) of adsorption called the reduced surface excess of component 2 (Ref. 7). This may be expressed in terms of the surface excess associated with unit mass of solid, the specific (reduced) surface excess,

\[
n^0_2(n)/m = n^0 \Delta x^f_2/m;
\]

or, if the specific surface area, \( a_s \), of the solid is known, in terms of unit surface area, the areal (reduced) surface excess, \( \Gamma^0_2(n) \),

\[
\Gamma^0_2(n) = n^0 \Delta x^f_2/ma_s.
\]

It follows that since \( x^f_1 + x^f_2 = 1 \), \( \Delta x^f_2 = -\Delta x^f_1 \) and \( \Gamma^0_2(n) = -\Gamma^0_1(n) \), which emphasizes the competitive nature of the adsorption process.

Adsorption can also be detected and measured in a flow system. If solution of constant composition is passed through a column of solid adsorbent, then initially the concentration in the solution leaving the bed is less than that in the feed. As equilibrium is approached the concentration in the effluent rises until it equals that of the feed. The integrated amount of component 2 leaving the column is less than the total amount fed in by an amount equal to the reduced surface excess of 2. If, when an amount, \( n \), of solution has passed into the column, the difference between the mole fractions at the inlet and outlet is \( \Delta x^f_2 \), then

\[
n^0_2(n) = n^0 \int_0^n \Delta x^f_2 \, dn,
\]

where \( n^0 \) is the amount of solution which has to be passed to reduce \( \Delta n^f_2 \) to zero, within some specified detection limit (Note c).

Note c. In practice, account must be taken of the amount of component 2 contained in the 'dead volume' of the apparatus.
These operational definitions of adsorption may be linked to the Gibbs definition which compares the real system with a reference system in which the compositions of two adjacent phases are supposed to remain constant up to an arbitrary dividing surface (a Gibbs dividing surface or GDS) drawn parallel to the real interface, and in which the volume of the reference system is the same as that of the real system. In the present case the value to be ascribed to the Gibbs surface excess $\Gamma_2$ is

$$\Gamma_2 = \frac{n_2^g}{m_{A_s}} = \frac{(n_2 - c_2^g V^g)}{A_s},$$

where $c_2^g$ is the bulk concentration and $V^g$ is the volume of liquid phase up to a chosen GDS, and it is assumed that the solid is impermeable to the components of the liquid ($c_2^g = 0$). If the GDS is moved parallel to the surface by a distance $dz$ (Fig. 1), $dV^g = A_s dz$, and

$$\frac{d\Gamma_2}{dz} = c_2^g = \frac{x_2^g}{v},$$

where $v$ is the molar volume of the liquid phase. The values of $\Gamma_1$ and $\Gamma_2$ thus vary with $z$ in the way shown schematically in Fig. 2. To obviate the problem of the arbitrary nature of $\Gamma$, Gibbs introduced the quantity $\Gamma_2^{(1)}$, called (Ref. 7) the relative adsorption of 2 with respect to 1, which is independent of the choice of GDS and for the type of system under consideration is defined by

$$\Gamma_2^{(1)} = \Gamma_2 - \Gamma_1 = \frac{c_2^g}{x_2^g} \left( \frac{x_1^g}{x_1^g} \right).$$

$\Gamma_1$ and $\Gamma_2$ are measured relative to the same but arbitrary GDS. An alternative interpretation of $\Gamma_2^{(1)}$ which follows from equation (7) is that it is the adsorption of 2 relative to the GDS chosen so that $\Gamma_1 = 0$ i.e. $z$ is chosen at $z^{(1)}$ in Fig. 2. Some authors call this GDS the Gibbs dividing surface. An alternative invariant quantity, the reduced adsorption of 2, $\Gamma_2^{(n)}$, is defined by

$$\Gamma_2^{(n)} = \Gamma_2 - \Gamma = \frac{c_2}{x_2^g},$$

where $c_2^g$ is the total concentration ($c_1^g + c_2^g$) and $\Gamma$ is the total adsorption, $(\Gamma_1 + \Gamma_2)$. The reduced adsorption may therefore be interpreted as the value of $\Gamma_2$ when the GDS is chosen so that $\Gamma = 0$. It follows that

$$\Gamma_2^{(n)} = -\Gamma_2^{(1)}.$$

and corresponds to the choice of the GDS at $z^{(n)}$ in Fig. 2; the condition of zero adsorption
means that the GDS coincides with the surface of the solid. As proved in the appendix, \(r_1\) defined by equation (8) is identical with the experimental quantity defined by equation (3). Insertion of (9) in (7) shows that

\[
\frac{r_{1}}{r_{1}} = \frac{r_{2}}{r_{2}}.
\]

(10)

Two important comments may be made at this point. First, as demonstrated by Hansen (Ref.4), Goodrich (Ref.6) and Schay (Ref.7), the Gibbs relative adsorption can be defined purely algebraically without reference to a dividing surface, although in effect certain volumes are ascribed to the phases in contact. Secondly, contrary to what has often been suggested in earlier literature, and in some textbooks, the Gibbs approach is nothing more than a book-keeping operation which ensures overall stoichiometric consistency. It should not be called the Gibbs model since it does not imply that the molecules comprising the surface excess are confined to the GDS which is a mathematical surface. The criticism that the Gibbs approach is physically unrealistic because molecules of finite size are required to be accommodated in a mathematical volumeless plane involves a complete misunderstanding of the nature of the Gibbs procedure. What the Gibbs method does is to recognise that the shape of the concentration profile which exists in the real system is not open to experimental determination, and provides a means of characterising the measurable global effect arising from non-uniformity near the surface.

Having established the method of defining a surface excess amount of substance relative to some chosen GDS, most authors (including Gibbs) have then extended the principle to define other surface excess quantities: there are, however, important features of these quantities not possessed by the surface excess amount. Thus the surface excess energy is defined as

\[
\sigma = U - V_{s}^{l} - V_{s}^{g},
\]

(11)

where \(U\) is the total energy of the system, \(V_{s}^{l}\) and \(V_{s}^{g}\) are the energy densities of the bulk liquid and solid and \(V_{s}^{l}\) and \(V_{s}^{g}\) are the volumes of the two phases measured up to the chosen GDS. In the first place, we see that the thermodynamic properties of the solid enter into this definition. This also means that, unlike the adsorption, the surface excess cannot be interpreted simply and unambiguously in terms of local energy densities. Thus the energy of an element of liquid near a surface arises both from its 'self-energy' (equal to that of the bulk far from the surface) and from the energy of interaction of the element with the whole of the solid; conversely the energy of an element of solid is in part determined by interactions with the whole of the liquid phase. One may, of course, adopt a convention by which, for example, van der Waals energies arising from interaction of an element of liquid with the solid are assigned to the liquid, while perturbations of energy arising from changes in the lattice parameters or lattice vibrations of the solid are attributed to the solid. But even here a unique subdivision is impossible since these various contributions to the total energy of the system are not strictly separable. This particular problem does not affect the overall thermodynamic formulation, but must not be overlooked in a detailed molecular interpretation. Another important potential source of confusion in molecular terms is that the excess surface energy is a property of all the molecules in the region of the surface and not just of the surface excess molecules: thus \(\sigma / n_{2}\) has no simple physical meaning.

Similar definitions can be written down for the surface excess entropy \(S_{s}\) and the excess Helmholtz energy \((F = U - TS)\) (Note d) \(F_{s}\), to which similar remarks apply. Since in the Gibbs formulation \(\gamma^{s} = 0\) (Note e) there is no distinction between \(F^{s}\) and the excess Gibbs \(G^{s}\). Similarly \(H^{s} = \sigma^{s}\). When related to the solid surface as GDS these reduced quantities are denoted by \(\sigma^{s}(n)\), \(G^{s}(n)\) and \(F^{s}(n)\) etc., while division by the surface area yields the areal excess quantities \(\sigma^{s}(a)\), \(G^{s}(a)\) and \(F^{s}(a)\) etc.

Note d. Reluctantly we depart from IUPAC recommendations, and use \(F\) rather than \(A\) for Helmholtz energy. Experience of using the IUPAC symbol shows that confusion can too often arise between \(A\), \(A^{s}\), \(a_{1}\), \(a^{s}\), etc. especially when they occur in the same equation.

Note e. This is at variance with the statement Schay (Ref.1) who says that, unlike in the cases of \(l/g\) and \(s/g\) interfaces, \(\gamma^{s}\) cannot be put equal to zero for \(s/l\) interfaces. This seems to arise from a difference in the definition of reduced quantities in his paper.
The total differential of the internal energy of a system involving a single interface can be deduced from the first and second laws of thermodynamics, together with the Gibbs postulate that the addition to a phase of an amount $dn_i$ of matter of type $i$, at constant $S$ and $V$, increases the energy by $\mu_i dn_i$, where $\mu_i$ is the chemical potential of $i$. Thus for a multicomponent system,

$$dU = TdS - p^dV^d - p^sV^s + \sigma dA + \sum_i \mu_i^d dn_i^d + \sum_i \mu_i^s dn_i^s + \sum_i \sigma_i^d d\sigma_i^d. \quad (12)$$

If $n_i = 0$ (i.e. the solid is not penetrated by $i$) then the term $\mu_i^s dn_i^s$ is zero. It is incidentally unnecessary to appeal to hypothetical 'surface pistons' in developing this equation, which can be extended to include more than one type of surface ($s/1, 1/l$ and $s/g$) by introducing the concept of 'effective area' (Ref.8). The quantity $\sigma$ is introduced as the potential factor conjugate with the surface area, and for lack of a better name is called the surface tension. The usual transformation converts equation (12) into the total differential of the Helmholtz energy

$$dF = SdT - p^dV^d - p^sV^s + \sigma dA + \sum_i \mu_i^d dn_i^d + \sum_i \mu_i^s dn_i^s + \sum_i \sigma_i^d d\sigma_i^d. \quad (13)$$

If adsorption equilibrium is established, it is readily shown that the chemical potential of each component is uniform throughout the system, so that for a closed system the last three terms on the right-hand side of equations (12) and (13) sum to zero. The surface tension may thus be defined as

$$\sigma = \left[ \frac{3U}{3S} \right]_{S,V, V^s,equal} = \left[ \frac{3F}{3S} \right]_{T,V^d,V^s,equal}. \quad (14)$$

Again, using the conventional procedure of integrating equation (13) at constant potential factors, re-differentiating and comparison back with (13), gives the generalised Gibbs-Duhem equation for the whole system:

$$\left( S^d + S^s + S^g \right) dT + V^d dp^d + V^s dp^s - A_s d\sigma - \sum_i \mu_i^d dn_i^d - \sum_i \mu_i^s dn_i^s - \sum_i \sigma_i^d d\sigma_i^d = 0. \quad (15)$$

Each bulk phase must, however, satisfy its own Gibbs-Duhem equation:

$$-S^d dT + V^d dp^d - \mu_i^d dn_i^d = 0, \quad (16)$$

$$-S^s dT + V^s dp^s - \mu_i^s dn_i^s = 0.$$

For a plane interface $dp^d = dp^s$, and equations (15) and (16) can be solved to give

$$-S^d(1) dT - d\sigma = \sum_i \mu_i^d(1) dn_i^d, \quad (17)$$

where

$$S^d(1) = S^d - \Gamma_i \left[ \frac{S^d - S^s}{c_i} \right], \quad (18)$$

and

$$S^d = \frac{1}{A} \left[ S - V^d \frac{\rho^d}{S} - V^s \frac{\rho^s}{S} \right]. \quad (19)$$

Here $\rho^d$ and $\rho^s$ are the densities of entropy in the two phases and $T^d$ and $T^s$ are defined relative to an arbitrary GDS. Equation (17) is the Gibbs adsorption equation.

Up to this point no operational definition for $\sigma$ has been given, but we now have through equation (17) a route by which changes in $\sigma$ can be linked rigorously with experiment. The realisation of the importance of this equation in the analysis and interpretation of measurements of adsorption from solution has only developed in the last decade (Ref.9, 10) and a major objective of this paper is to stress the role that it, and equations derived from it, can play.

Since we already have a link between the experimental quantity $(n^d \Delta \chi^d/ma_s)$ and $\Gamma_2$ through equation (10), adsorption measurements as a function of solution concentration enable the differences between values of $\sigma$ in two chosen states to be calculated. For a binary system at constant temperature equation (17) becomes, on integration,
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\[ \sigma - \sigma^* = - \int_{x_2}^{x_2^0} \tau_2^{(1)} \, d\mu_2^L, \quad \text{(20)} \]

or since
\[ d\mu_2^L = RT \, d \ln x_2^L \gamma_2^L, \quad \text{(21)} \]

\[ \sigma - \sigma^* = -RT \int_{x_2}^{x_2^0} \frac{n \, \delta x_2^L}{x_2^L \gamma_2^L} \, d\left(x_2^L \gamma_2^L\right). \quad \text{(22)} \]

Here \( \sigma^* \) is the surface tension of the solid in contact with pure component 2, and \( \gamma_2^L \) is the activity coefficient of 2 in the bulk equilibrium solution. If the integration is taken from component 2 to pure component 1,
\[ \sigma_2^* - \sigma_1^* = RT \int_{x_2}^{x_2=0} \frac{n \, \delta x_2^L}{x_2^L \gamma_2^L} \, d\left(x_2^L \gamma_2^L\right), \quad \text{(23)} \]

thus enabling the difference between the surface tensions of the solid surface in contact with the two pure liquids to be calculated: the absolute values of \( \sigma_1^* \) and \( \sigma_2^* \) separately are not accessible.

It is now of interest to consider whether it is useful to try to interpret experimental data in terms of the surface excess free energy and the related enthalpy and entropy. The surface excess free energy (using now the Gibbs energy) is obtained by integrating equation (13) at constant potential factors and combining with the corresponding expressions for the two bulk phases:
\[ G^G = G - G' - G'' = \sigma A_s + \Sigma \mu_1 \gamma_1^L, \quad \text{(24)} \]
or
\[ \hat{g}^G = \sigma + \Sigma \mu_1 \gamma_1^L. \quad \text{(25)} \]

Two important comments must be made on equation (25). First, as written it involves values of \( \hat{g}^G \) and \( \gamma_1^L \) referred to an arbitrary GDS. However, \( \sigma \) has a value sensibly independent of the choice of GDS. It follows that if the choice of GDS is changed then variations in \( \hat{g}^G \) and \( \Sigma \mu_1 \gamma_1^L \) must cancel: we must have
\[ \frac{d\hat{g}^G}{dz} = \Sigma \mu_1 \left( \frac{d\gamma_1^L}{dz} \right) = \Sigma \mu_1 \gamma_1^L. \quad \text{(26)} \]

For a binary mixture, and using reduced adsorptions,
\[ \hat{g}^G(n) = \sigma + \Sigma \mu_1^G(n) \]
\[ = \sigma + \Gamma_2^G \left( \mu_2 - \mu_1 \right). \quad \text{(27)} \]

This directs attention to the second feature of (25), namely that since chemical potentials are defined with respect to a chosen standard state, the value of \( \hat{g}^G(n) \) also depends on this choice. Introducing the chemical potentials
\[ \mu_1 = \mu_1^0 + RT \ln a_1, \quad \text{(28)} \]
where $\mu_1^\Phi$ is a standard chemical potential and $a_1$ the corresponding activity,

$$
\hat{g}^\sigma(n) = \sigma + \frac{1}{2} \left[ (\mu_2^\Phi - \mu_1^\Phi) + RT \ln \left( \frac{a_2}{a_1} \right) \right].
$$

(29)

Bearing in mind that for the solid/liquid interface only differences in $\sigma$ are available we may write the following function of $\hat{g}^\sigma(n)$ which has a definite experimental meaning given by the right hand side.

$$
\hat{g}^\sigma(n) - \hat{g}_2^\sigma = \frac{1}{2} \left[ (\mu_2^\Phi - \mu_1^\Phi) = (\sigma - \sigma_2^\Phi) + \frac{1}{2} RT \ln \left( \frac{a_2}{a_1} \right). \right)
$$

(30) (Note f)

Whether the right-hand side is a convenient way of summarising the behaviour of a system remains to be seen.

Finally we consider the enthalpy of wetting or immersion of a solid in a liquid mixture. Equation (25) can be re-written

$$
\hat{g}^\sigma(n) = R^\sigma(n) = T \hat{g}^\sigma(n) = \sigma + \sum_{i=1}^n \mu_i^\Phi + \mu_i^\Phi.
$$

(31)

If this is divided by $T$, differentiated and use is made of the total differential of the areal excess enthalpy

$$
dH^\sigma(n) = T \frac{d\hat{g}^\sigma(n)}{\hat{g}^\sigma(n)} + \sum_{i=1}^n \mu_i^\Phi, d\Gamma_i.
$$

(32)

we obtain for a binary mixture

$$
\left[ \frac{\hat{g}(\sigma/T)}{\hat{g}(1/T)} \right]_{\hat{g}^\sigma(n)} = \frac{R^\sigma(n)}{\hat{g}^\sigma(n)} = \left( \frac{\hat{g}^\sigma(n)}{\hat{g}^\sigma(n)} \right) \left( \frac{h_2^\Phi - h_1^\Phi}{x_2} \right).
$$

(33)

This may be linked to the enthalpy of immersion in the following way. The initial enthalpy in an immersion experiment is

$$
H^i = n^o h^f(x_2^o) + m h^o
$$

(34)

where $h^o$ is the specific enthalpy of the solid and $h(x_2^o)$ the molar enthalpy of the initial liquid mixture. If we ascribe to the interface the whole of the excess enthalpy of the system after immersion and suppose that $h^o$ is unaffected (or if it is affected the perturbation is included in $H^\sigma(n)$) then the final enthalpy at the initial temperature is

$$
H^f = n^o h^f(x_2^o) + H^\sigma(n) + m h^o
$$

(35)

where $H^\sigma(n)$ is the reduced surface excess enthalpy. The enthalpy of immersion is thus

$$
\Delta_h^i = H^f - H^i = H^\sigma(n) + n^o \left[ h^f(x_2^o) - h^f(x_2^o) \right],
$$

(36)

where the last term refers to the change in enthalpy resulting from the change of solution composition. Now

$$
\frac{\partial h^f}{\partial x_2} = h_2^f - h_1^f,
$$

(37)

where $h_2^f$ and $h_1^f$ are the partial molar enthalpies at $x_2^f$. If the change in $x_2^f$ is sufficiently small (Note g)

$$
h^f(x_2^o) - h^f(x_2^o) = - (h_2^f - h_1^f) \Delta x_2^f,
$$

(38)

Note f. Since the values of activity coefficients depend on the choice of reference system, the numerical value of the r.h.s. will depend on the convention used for defining the activity coefficients.

Note g. The negative sign appears since we have defined $\Delta x_2^f$ as $(x_2^o - x_2^f)$. 
which on insertion in (36) leads to
\[ \Delta_w H = \int \Delta f(n) - \gamma_2(n) (h_2 - h_1), \]
where \( \Delta_w H \) is the enthalpy of immersion of unit area of solid in a volume of mixture large enough for equation (38) to hold. Comparison of (39) with (33) shows that
\[ \frac{\partial f(T)}{\partial (1/T)} = \Delta_w H. \]

Since only differences in \( \sigma \) are measurable in the present case
\[ \frac{\partial (\sigma_2 - \sigma_1)}{\partial (1/T)} = \Delta h_2 - \Delta h_1, \]
or
\[ \frac{\partial (\sigma_2 - \sigma_1)}{\partial (1/T)} = \Delta w_{2} - \Delta w_{1}, \]
which gives the difference between the enthalpies of immersion of the solid in pure liquids 2 and 1.

We thus derive a link between the adsorption isotherms at different temperatures and enthalpies of immersion via the surface tension. Similarly, combining expressions for free energy and enthalpy we obtain for the entropy
\[ T \Delta_s g(n) = \Delta w_{2} - \Delta w_{1}, \]
and
\[ \Delta w_{2} = \int [\sigma(n) - \gamma_2(n) (s_2 - s_1)]. \]

We stress that partial molar enthalpies and entropies (unlike partial molar volumes!) must also be referred to some chosen standard state and consequently \( h^*(n) \) and \( \sigma^*(n) \) have values which depend on this choice. The difficulty of ascribing a value to the area excess enthalpy was appreciated by Schay (Ref.11) and the generality of this problem is brought out by collecting together the appropriate equations:
\[ \sigma = \sigma(n) - \gamma_2(n) (\mu_2 - \mu_1), \]
\[ \Delta_{w_{2}} = \int \sigma(n) - \gamma_2(n) (h_2 - h_1), \]
\[ \Delta_{w_{2}} = \int \sigma(n) - \gamma_2(n) (s_2 - s_1). \]

Having now established a set of rigorous thermodynamic relations, we now examine their usefulness in handling experimental data.

THERMODYNAMICS OF ADSORPTION IN SOME TYPICAL SYSTEMS

Calculation of surface tension differences

Equations (22) and (23) are most conveniently applied using graphical integration of smoothed curves through the experimental points. This is illustrated by Fig. 3 which shows the curve of \( (n^0 \Delta x^2/m) (x \Delta x^2) \) against \( x \Delta x^2 \), and by Fig. 4 where the integrals of equation (22) to successive values of \( x \Delta x^2 \) and shown, for the system benzene + 1,2-dichloroethane at 25°C.

There is however, an unfortunate constraint on the use of these equations imposed by the lack, for many common organic mixtures, of reliable activity coefficient data for the bulk mixture over a range of temperature. Consequently the thermodynamic analysis of many systems for which adsorption data are now available is held up by the lack of adequate information on activity coefficients. Figure 3 also draws attention to the need to carry out adsorption measurements over the whole concentration range with special attention being paid to the two dilute solution regions at the extremes, otherwise extrapolation to \( x^2 \to 0 \).
Figure 3: $\frac{n^0 \Delta x_2/m}{x_1 x_2^{1/2}}$ versus $x_2^{1/2}$ for [benzene+1,2 dichloroethane]/Graphon at 298 K.

Figure 4: $[(\sigma - \sigma_2^e) a_s/RT]/10^{-4}$ mol g$^{-1}$ versus $x_2$
for [benzene+1,2 dichloroethane]/Graphon at 298 K.

Figure 5: (a) $[(\sigma - \sigma_1^e) + RT \Gamma_1^{(n)} \ln(a_1/a_2)]/mJm^{-2}$ versus $\Gamma_1^{(n)}/10^{-7}$ mol m$^{-2}$
for system [benzene(1) + cyclohexane(2)]/Graphon at 298 K.

(b) Slope of curves in (a) versus $\ln(a_1/a_2)$ kJmol$^{-1}$.
and 1 may present difficulties. This is especially true for systems showing large positive deviations from ideality for which measurements at very low values of \( x_2 \) are necessary to reach low enough values of \( \gamma_{22}^x \). For example for the ethanol + benzene system at 25°C, \( \gamma_{22}^x \approx 12 \) so that measurements to 0.005 mole fraction are needed to reach \( \gamma_{22}^x \) of 0.060.

**Thermodynamic consistency tests**

A very important, though perhaps unexciting, use of thermodynamics is in checking experimental data and the computations performed upon them for consistency. One such test can be applied in the present case if adsorption measurements are made on the same solid surface using three binary systems derived from three mutually miscible components 1, 2 and 3. The data should lead to surface tension differences which satisfy the following identity:

\[
(\sigma_1^* - \sigma_2^*) + (\sigma_2^* - \sigma_3^*) + (\sigma_3^* - \sigma_1^*) = 0 .
\] (46)

This test, incidentally, not only the adsorption data but also the activity coefficients used in the analysis. This test has been applied to the triads benzene, cyclohexane and n-heptane (Ref.12) and to benzene, n-heptane and ethanol (Ref.13) adsorbed by graphitised carbon black, and also to benzene, cyclohexane and heptane (Ref.14) and benzene, iso-octane and carbon tetrachloride (Ref.15) adsorbed by silica gel. Further applications of equation (46) are discussed later. Another test which as far as we know has not been used previously results from equation (25), from which it follows that

\[
d\Omega = d\phi + \sum \Gamma_i d\Gamma_i + \sum d\gamma_i = \sum \Gamma_i d\Gamma_i .
\] (47)

Applied to reduced quantities and to a binary mixture

\[
d\Omega(n) = (\nu_2 - \nu_1) d\Gamma_1(n) .
\] (48)

Differentiating equation (30) with respect to \( \Gamma(n) \), we have

\[
\frac{\partial}{\partial \Gamma(n)} \left[ (\sigma - \sigma_1^*) + \Gamma_2(n) RT \ln (a_2/a_1) \right] = \frac{\partial \Omega(n)}{\partial \Gamma_2(n)} - (\nu_2 - \nu_1) .
\] (49)

The r.h.s. of which from (48), is

\[
(\nu_2 - \nu_1) - (\nu_1 - \nu_2) = RT \ln (a_2/a_1) .
\] (50)

Thus if \( (\sigma - \sigma_2^*) + \Gamma_2(n) RT \ln (a_2/a_1) \) is plotted against \( \Gamma_2(n) \), the slope at each point should be RT ln \( (a_2/a_1) \). As an example, the data for (benzene + cyclohexane)/Graphon at 25°C are shown in Fig. 5: the data conform to equation (49) and (50) to within the precision of the numerical analysis.

**Thermodynamics of wetting**

Equation (46) has important applications in wetting thermodynamics. Thus if three liquids are chosen such that two binaries are completely miscible while the third (say 1 + 2) is immiscible, then measurements of adsorption from the miscible binaries enables \( (\sigma_2^* - \sigma_1^*) \) to be calculated. Now this difference is related to the contact angle \( \theta \), at the liquid 1/liquid 2/solid line of contact by Young's equation:

\[
\sigma_2^* - \sigma_1^* = \sigma_{12} \cos \theta ,
\] (51)

where \( \sigma_{12} \) is the interfacial tension between liquids 1 and 2. A thermodynamic route is thus available for the calculation of contact angles in circumstances where a direct measurement is impossible (e.g. in a powder). More importantly whereas all that one can deduce from contact angle measurements is that when \( \cos \theta = 1 \),

\[
\frac{\sigma_2^* - \sigma_1^*}{\sigma_{12}} > 1 ,
\] (52)

this proposed method gives quantitative information on \( (\sigma_2^* - \sigma_1^*) \) even when \( \cos \theta = 1 \). The present method thus enables the spreading tension

\[
\sigma_{spr} = \sigma_{12} - (\sigma_2^* - \sigma_1^*)
\] (53)

to be calculated, and opens the way, when \( \sigma_{spr} < 0 \), to possible investigations of the relationship between spreading tension (or net spreading pressure) and the speed of wetting.
Data are now becoming available which enable a table of values of $c_1^*$ for the graphite surface relative to a standard substance to be drawn up — this is in effect a table of relative wetting tensions, or relative wettabilities. Figure 6 gives a preliminary form of this table taking benzene as reference substance in which the variations of wetting tension with temperature are also shown. The relative wettability of graphite by water and an organic liquid with which it is immiscible can be assessed by reading off the difference ($c_{\text{water}}^* - c_{\text{org}}^*$) from the table and comparing this value with the interfacial tension at the water/organic interface: if the latter is less than ($c_{\text{water}}^* - c_{\text{org}}^*$) then the organic liquid will displace water spontaneously from graphite and a zero contact angle will be observed. Experiments to test this predictive method are in hand and appear to confirm the usefulness of this table.

Enthalpies and entropies of wetting

Equations (41) and (43) can be used to calculate the enthalpy and entropy of wetting as a function of composition of the wetting liquid. In Figures 7, 9 and 10 some typical results are shown. They highlight the way in which enthalpy and entropy tend to oppose one another in determining the surface tension and hence the adsorption. In these figures the components are numbered so that $(\Delta h_1^* - \Delta h_2^*)$ is negative so that if the adsorption were controlled by the enthalpy term, component 1 would be preferentially adsorbed. This is so for both (benzene + cyclohexane)/Graphon and (n-heptane + cyclohexane)/Graphon although in the latter case the entropy term is large and reduces the adsorption from the value it would have if enthalpy alone were the sole controlling factor. However for the (n-heptane + benzene)/Graphon system the enthalpy and entropy terms are of similar magnitude. At low heptane concentrations dominance of the enthalpy leads to preferential adsorption of heptane, while at higher concentrations the slope of the surface tension curve changes sign and benzene becomes the preferentially adsorbed component. If the temperature is lowered $T(\Delta h - \Delta s)$ decreases and the range of preferential adsorption of heptane increases, while conversely at higher temperatures benzene is adsorbed at all concentrations. An interesting and significant feature of these systems is that the entropy curves for the (n-heptane + benzene)/Graphon and (n-heptane + cyclohexane)/Graphon systems are almost exactly superimposable.

Figure 8 shows another interesting example, where for the (1,2 dichloroethane + benzene)/Graphon system not only the surface tension but also the enthalpy curve changes sign. Moreover, while $(\Delta h_1^* - \Delta h_2^*)$ is small and positive, at intermediate concentrations of the mixture $(\Delta S_1^* - \Delta S_2^*)$ is negative and much larger.

These examples show that a purely thermodynamic analysis reveals rather clearly some striking characteristics of different systems, and points the way to possible molecular interpretations.

THEORIES OF ADSORPTION FROM SOLUTION

It is not the purpose of this paper to pursue in detail the various theories of adsorption which have been employed to interpret experimental data. Nevertheless some comments are relevant on the ways in which comparisons may be made between theory and experiment.

One method of making this comparison is to introduce the concept of surface activity coefficients to describe non-ideality of the surface layer in much the same way as for bulk phases. Although these activity coefficients can be calculated using thermodynamic procedures it is important to stress that to do this it is first necessary to make some assumptions about the thickness of the surface layer, and the areas associated with adsorbed molecules in that layer. Neither of these is experimentally determinable so that there is a degree of arbitrariness in the values obtained. This method is therefore only likely to be useful in simple cases where it is reasonable to suppose that monolayer adsorption of equal size molecules occurs.

Alternatively, one may follow the procedure often used for discussing the surface tension of liquid mixtures and compare the surface tension with that corresponding to a simple model. Frequently an excess surface tension is defined as the deviation of the observed surface tension from a linear relation, expressed in mole fractions, between surface tension and concentration. However, except when the surface tensions of the pure components are close together, this linear dependence does not correspond to any simple theoretical model. It seems preferable to make the comparison with the properties of a model the theoretical basis for which can be clearly defined, and for this purpose we choose monolayer adsorption from mixtures of equal size, which behave ideally in both bulk and surface regions, and where each molecule occupies an area $a$ on the surface:

$$\frac{(\sigma - \sigma_1^*)a}{RT} = \ln \left[ x_1^* + x_2^* \exp(- (\sigma_2^* - \sigma_1^*)a/RT) \right].$$  (54)
Figure 6: Surface tensions of liquid i/graphite interface relative to that of the benzene/graphite interface

Left hand: at 298 K
Right hand: as function of temperature

The data upon which this figure is based come from references 12,13; R. Bown, Ph.D. thesis Bristol 1973; R.W. Smith, Ph.D. thesis Bristol, 1978; C.E. Brown, unpublished; A.J.P. Fletcher, unpublished.
Figures 7-10: $\sigma - \sigma_2^*$, $\Delta h - \Delta h_2^*$, $\Delta s - \Delta s_2^*$ as functions of $x_2^*$ for the systems:

Figure 7 (benzene+cyclohexane)/Graphon; Figure 8 (1,2 dichloroethane+benzene)/Graphon
Figure 9 (n-heptane+cyclohexane)/Graphon; Figure 10 (n-heptane+benzene)/Graphon
Equation (54) is possibly more general than its derivation implies, for an essentially similar equation follows from the Polanyi potential theory if a discrete ideal adsorption layer (not necessarily a monolayer) is assumed (Ref.16). In practice, few bulk phases are ideal so that, to eliminate the influence of bulk phase non-ideality, it may be more meaningful to compare experimental data with a slightly more general form of equation (54) which includes the activity coefficients of the bulk phase: (Ref. 15)

\[
\frac{(\sigma - \sigma_1^*)a}{RT} = \ln \left[ \frac{x_1^a}{y_1} + \frac{x_2^*}{y_2} \exp \left\{ - \left( \frac{\sigma^* - \sigma_2^*}{a/RT} \right) \right\} \right].
\] (55)

Figure 11 makes these comparisons for the system (benzene + cyclohexane)/Graphon: the deviation of \(\sigma\) from ideal behaviour is almost completely accounted for by the non-ideality of the bulk solution which shows positive deviations from Raoult's law. The remaining discrepancy is to be attributed to a small positive deviation of the adsorbed layer from ideality, in agreement with the conclusion arrived at previously (Ref.12) on the basis of calculations of the surface activity coefficients. The extent to which bulk activity coefficients can influence the surface tension is brought out in Fig.12 which relates to the system (benzene + n-heptane)/Graphon. Here the non-ideality of the bulk phase alone gives rise to a change of sign of \(\sigma\) and to inversion of the preferential adsorption where \((\sigma^* - \sigma_2^*)\) goes through a minimum. This is partially offset by non-ideality of the surface region which is again positive but larger than in the previous example. In the present case the difference in the sizes of the two molecules makes it difficult to proceed through the surface activity coefficients. By contrast, in the case of (1,2 dichloroethane + benzene)/Graphon (Fig.13) the bulk phase is very nearly ideal at 298K, so that the deviation of the surface tension curve from ideality is caused entirely by non-ideality in the surface layer. These deviations are negative in agreement with the conclusion reached by Everett and Podoll (Ref.17) who found that the data for this system could be represented by treating the surface layer as a regular solution with a negative interaction parameter.

Further, more detailed study, involves a comparison of the enthalpy and entropy curves shown in Figs. 7 - 10 with those based on a simple model. For example, if in accordance with a simple monolayer model it is assumed that the enthalpy of the surface layer is a linear function of the surface mole fractions, then the equation given by Everett (Ref.18) can be re-arranged in the form

\[
\Delta h_1^s - \Delta h_2^s = A + B x_1^s.
\] (56)

where for an ideal system characterised by an adsorption equilibrium constant \(K\), \(A=(K-1)/K\) and \(B=1/K\). Figure 14 shows that this equation is followed by typical systems.

Moreover, the surface tensions may be represented by an analogous equation:

\[
\frac{\sigma - \sigma_2^*}{\sigma - \sigma_1^*} = A + \frac{B}{x_1^s}.
\] (57)

However, this equation does not follow exactly from the ideal monolayer model, but is a reasonable approximation to it for relatively weak preferential adsorption: at least provisionally it must be regarded as an empirical equation (Note h). Since both the entropy and surface tension curves follow equation (56) and (57), a similar relation must apply to the entropy curves.

Finally it is of interest to note that the entropy curves for the (benzene + n-heptane)/Graphon and (cyclohexane + n-heptane)/Graphon systems are virtually identical while for the (benzene + cyclohexane)/Graphon system the entropy term is zero within the experimental precision. This indicates strongly that the entropy effects in the two former systems are associated with restrictions on rotational degrees of freedom experienced by the n-heptane molecules when close to and adsorbed by a solid surface, whereas for benzene and cyclohexane these restrictions are roughly equal and much less than for n-heptane. Further study of alkane + benzene systems is in hand to elucidate the effect of chain-length on these entropy curves.

Note h. If \(A^*\) and \(B^*\) had the values \((K-1)/K\) and \(1/K\) respectively then \(K\) could be found. Since according to simple theory \((\sigma^*_1 - \sigma^*_2)a/RT = 1nK\), this would provide a means of obtaining \(a\). In fact values of \(a\) obtained in this way are very close those commonly accepted but in view of the empirical nature of equation (57) this is probably fortuitous.
Figure 11: [benzene(1)+cyclohexane(2)]/Graphon

Figure 12: [benzene(1)+n-heptane(2)]/Graphon

Figure 13: [benzene(1)+1,2 dichloroethane (2)]/Graphon

Figures 11, 12, 13

(\sigma - \sigma_1^*)a/RT versus x_1^*

(i) linear relation
(ii) ideal surface and bulk (equation 54)
(iii) ideal surface, non-ideal bulk (equation 55)

Figure 14: (i) (\sigma_2^* - \sigma_1^*)/(\sigma - \sigma_1^*) for [benzene+cyclohexane]/Graphon at 298 K.
(ii) (\sigma_2^* - \sigma_1^*)/(\sigma - \sigma_1^*) for [n-heptane+cyclohexane]/Graphon at 298 K.
(iii) (\Delta R_2^* - \Delta R_1^*)/(\Delta R - \Delta R_1^*) for [n-heptane+cyclohexane]/Graphon at 298 K.
SUMMARY AND CONCLUSIONS

This paper has advocated strongly that in the analysis and interpretation of experimental data on adsorption at interfaces greater attention should be paid in the first instance to a thermodynamic treatment and that only then should attempts be made to provide a molecular theory to account for the results. Suitable equations to enable this procedure to be followed are developed for the liquid/solid interface: similar equations may be derived for other types of interface. Selected examples from recent work illustrate the applications of the thermodynamic approach.

APPENDIX

We suppose the system to be contained in a rectangular box of area \( A_s \) in the \( x,y \) plane (the adsorption surface) and of height \( Z \). From figure 1 it follows that the total amount of component 2 in the system is

\[
\frac{Z}{x} \int_{z_0}^{Z} c_2 \, dz = \frac{Z}{x} \int_{z_0}^{Z} \frac{x_2}{v} \, dz,
\]

(A.1)

where \( c_2 \) and \( x_2 \) are, respectively, the local concentration and mole fraction at a distance \( z \) from the surface, and \( v \) is the corresponding molar volume. The total amount of substance in the liquid phase is

\[
n_2^o = A_s \int_{z_0}^{Z} c \, dz = A_s \int_{z_0}^{Z} \frac{1}{v} \, dz.
\]

(A.2)

Hence

\[
n_2^o = A_s \int_{z_0}^{Z} c \, dz = A_s \int_{z_0}^{Z} \frac{1}{v} \, dz = A_s \int_{z_0}^{Z} \frac{x_2 - x_2^o}{v} \, dz
\]

(A.3)

or

\[
\Gamma_2^{(n)} = \int_{z_0}^{Z} \frac{(x_2 - x_2^o)/v} \, dz.
\]

(A.4)

Since as \( z \) increases \( x_2 \rightarrow x_2^o \) the upper limit of integration may be taken as \( \infty \), so that \( \Gamma_2^{(n)} \) is independent of the choice of \( Z \).

The Gibbs adsorption at an arbitrary G.D.S. is

\[
\Gamma_2^{(v)} = \int_{z_0}^{Z} \left( c_2 - c_2^o \right) \, dz = \int_{z_0}^{Z} \left( \frac{x_2}{v} - \frac{x_2^o}{v} \right) \, dz = \int_{z_0}^{Z} \left( \frac{x_2^o - x_2}{v} \frac{v}{v} \right) \, dz.
\]

(A.5)

The relative adsorption of 2 with respect to 1 is (cf equation 7)

\[
\Gamma_2^{(1)} = \Gamma_2^{(v)} - \Gamma_1^{(v)} \left( \frac{x_2^o}{x_2^o} \right)
\]

\( \Gamma_2^{(1)} = \Gamma_2^{(v)} - \Gamma_1^{(v)} \left( \frac{x_2^o}{x_2^o} \right)
\]

The lower limit of integration could equally be taken as \( -\infty \) since within the solid \( c_1 = c_2 = 0 \).
\[ \begin{align*}
Z &= \left[ \frac{(x_2^v - x_1^v) - x_2^v (x_1^v - x_1^v)}{x_1^v} \right] dz \\
&= \frac{(x_2^v - x_1^v)}{x_1^v} - (x_1^v - x_1^v) \\
&= \frac{1}{x_1^v} \frac{dz}{dz}
\end{align*} \]  \quad (A.6)

which reduces to
\[ \Gamma_2^{(1)} = \frac{1}{x_1^v} \frac{dz}{dz} = \frac{1}{x_1^v} \Gamma_2^{(n)}. \]  \quad (A.7)

This shows that \( \Gamma_2^{(n)} \) defined by equation (3) is identical with that in (7) or (9).

REFERENCES

10. (a) G. Schay, L.G. Nagy and T. Szekrenyesy, Periodica Polytechnica, 6,91-111 (1962)
14. See ref 10 (c)
16. See e.g. ref. 9 (a), p.81

Corrections added in proof

p. 2183, penultimate line, for \( \Delta x_2^v \) read \( \Delta x_2^v \).

p. 2184, on the abscissa of figure 2 the right-hand \( \Gamma_2^{(n)} \) should read \( \Gamma_2^{(1)} \).