A COMPREHENSIVE PRESENTATION OF THE THERMODYNAMICS OF ADSORPTION EXCESS QUANTITIES

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Abstract—A common general framework of thermodynamic relations between interfacial excess quantities in multicomponent systems is derived, based essentially on the fundamental Gibbsian treatment of adsorption phenomena. Both adjoining bulk phases are regarded as equivalent constituents of the system concerned—not only in the case of fluid interfaces, which are approached in this way in any current exact treatment, but also in the case of S/G and S/L interfaces, respectively. The algebraic mode of definition of the surface excesses of the components and of the coupled thermodynamic quantities is adopted, but without reference to imaginary Gibbs dividing surfaces positioned within the actual system, in order to avoid the necessity of admitting the concept of an adsorption excess of the solid, when considering the most common mode of evaluation of adsorption from liquid solutions by immersion experiments.

Applications of the general relations to L/G, S/G and S/L interfaces respectively are demonstrated. In connection with the latter two, no use is made of the controversial concept of surface tension of the solid. Instead an extra interfacial free energy term is introduced, as a mean specific quantity for adsorbents with a fixed colloidal texture, but whose surfaces are inhomogeneous, both geometrically as well as energetically.

The aim of the proposed representation is not the derivation of fundamentally new thermodynamic relations, but to obtain a unified picture of adsorption at different kinds of interfaces, and to rely as far as possible only on operational definitions.

1. THE GENERAL FUNDAMENTAL ENERGY EQUATION

According to the fundamental Gibbsian treatment we regard the following differential expression of the internal energy as valid for the whole of an open system consisting of two adjoining bulk phases separated by an interface and subject to a common hydrostatic pressure p:

$$dU = T\,dS - p\,dV + F\,dZ + \sum \mu_i\,dn_i \qquad (1)$$

where the term $F\,dZ$ represents an extra interfacial work term, with F as the intensive and Z the coupled extensive variable. Equation (1) is linked to the characteristic energy function

$$U = TS - pV + FZ + \sum \mu_i n_i \qquad (2)$$

and has as its corollary the generalized Gibbs–Duhem type equation

$$S\,dT - V\,dp + Z\,dF + \sum n_i\,d\mu_i = 0 \qquad (3)$$

which is valid for any displacement of the system along the multi-dimensional equilibrium surface.

In the case of plane fluid (L/G or L/L) interfaces F may be identified with the interfacial tension γ, and Z with the surface area A_s, both of which are measurable quantities. Then $F\,dZ$ is identified with $\gamma\,dA_s$, the well known expression of the differential surface work performed on the system when the interfacial area is extended.

The situation is not so simple, however, when one of the adjoining phases is a solid (S/G or S/L interface) for two reasons. Firstly, as a consequence of the particles of a

solid being bound to equilibrium positions, the effects of surface tension as a lateral force acting parallel to the surface, cannot be observed directly even in the case of a fairly smooth and energetically uniform surface. Furthermore, in reality a typical adsorbent has a surface which is microscopically heterogeneous, so the concept of such a force becomes even more meaningless. Secondly with compacted coherent solids, the surface area may be extended by plastic deformation or crushing, but both procedures involve the application of mechanical stress to some degree, and thus the structure and energetic state of the newly created surface will generally differ from the original one. No clear operational interpretation of the differential work $\gamma\,dA_s$ is possible in this instance.

Independent variation of the surface area becomes impossible, even in principle, with most solid adsorbents encountered in practice. This is because they either consist of particles of colloidal dimensions, dispersed or in more or less loose aggregation (e.g. carbon black pellets), or they are macromolecular structures consisting of coherent porous materials with a fixed characteristic texture (e.g. silica-gels, alumina powders for chromatographic purposes, not to speak of natural or synthetic zeolites). Evidently, the surface area of such adsorbents is proportional to the amount present† and the extensive factor Z in eqns (1–3) may be identified with m^a, the mass of the adsorbent. This identification is made with the proviso that dm^a be thought of as a "macrodifferential" representative of the textural properties of any macroscopic amount of the given adsorbent. It is common practice to refer to the mass m^a, and not to the amount of substance n^a, because adsorbents are not usually unambiguously characterized chemical systems. In accord with this convention, it is convenient to split the last sums in eqns (1–3) and separately write the terms $\mu^a\,dm^a$, $\mu^a m^a$ and $m^a\,d\mu^a$ respectively, where μ^a stands for the

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†For porous adsorbents this is strictly true only for a fixed grain size distribution, but generally the outer surface is negligibly small compared with the inner pore surface of the grains.

specific Gibbs energy of the bulk of the adsorbent. The sums in the above equations then need only be referred to the components of the fluid phase in contact with the adsorbent, with the tacit assumption that these components do not dissolve in the molecular structure of the adsorbent.

Let us denote the intensity factor corresponding to $Z = m^a$ by ϵ. If the specific surface area a_s of the adsorbent is supposed to be known and to have a clear meaning (which is questionable with highly microporous adsorbents), then ϵ/a_s is a quantity equivalent to a mean interfacial tension $\bar{\gamma}$. Because of the fixed texture, however, the complementary extensive factor A_s is, as explained above, not an independent variable as in the case of fluid interfaces and one would have to write $\bar{\gamma}a_s \, dm^a$ for $F \, dZ$.

By introduction of ϵ, the sum $\mu^a + \epsilon$ will appear as the factor before dm^a in eqn (1), and it may be noted that Hill[1] as well as Tykodi[2] and more recently Wagner[3] treat ϵ as being actually incorporated into μ^a. Such a procedure seems hardly acceptable, however, because ϵ is in fact tied up with the contact of the two phases and cannot be attributed to one or the other of them, and its occurrence in eqn (1) along with μ^a is only the consequence of the fact that the interfacial work term is proportional to m^a in the special case of solid adsorbents with fixed texture.

2. QUANTITATIVE CHARACTERIZATION OF ADSORPTION BY EXCESS AMOUNTS AND A GENERAL FRAMEWORK OF THERMODYNAMIC RELATIONSHIPS BETWEEN INTERFACIAL EXCESS PROPERTIES

As we know nowadays, intermolecular forces are generally short range, and significant only between nearest neighbours (this is, for example, the supposition underlying the theory of regular solutions) and it is therefore a safe assumption that the thicknesses of interfacial adsorption layers are usually of the order of molecular dimensions. In this sense they may be regarded as two-dimensional phases, but thermodynamically they are not autonomous and the boundary between such a "phase" and the adjoining bulk phases cannot be defined in any exact, unquestionable way. In view of these circumstances, any attempts at a separate quantitative analysis of the contents of the adsorption layer such as the well-known microtome method of McBain for L/G systems, or radioactive tracer methods with S/L interfaces, can give only approximate results.† As recognized clearly by Gibbs, exact definitions can be given without detailed knowledge of the structure and thickness of the interfacial layer only for surface excess amounts (sometimes called Gibbs adsorptions). These are defined as differences between the actual real system and a reference system which is thought of as consisting only of suitably chosen portions of the equilibrium bulk phases actually present, without any contributions arising from interactions at their common interface. Such or equivalent[3] definitions are the only operational ones in the sense that they alone permit unambiguous computation of adsorption values from experimental data.

A general definition of surface excess amounts is therefore (with superscript σ to denote excess quantities):

$$n_i^\sigma = n_i - n^\alpha x_i^\alpha - n^\beta x_i^\beta \tag{4}$$

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†There are nevertheless exceptions, as, for example, the well-known monolayer films of insoluble "oils" on the surface of water, or well-defined chemisorbed films on solids.

where n_i is the total amount of component i present in the actual system, x_i^α and x_i^β its respective equilibrium mole fractions in the bulk phases adjoining the interface, and n^α and n^β the chosen reference amounts of the latter phases α and β respectively. Evidently the latter amounts have to be specified for n_i^σ to become definite and there are different ways of making this specification according to the nature of a particular problem. It may be noted incidentally that eqn (4) and all the following definitions and relationships can also be formulated in terms of masses and mass fractions respectively, provided chemical reactions are excluded (as was implied above for solid adsorbents).

Once the choice of n^α and n^β has been made, the corresponding surface excess X^σ of any extensive thermodynamic property (energy, entropy, volume etc.) is defined as:

$$X^\sigma = X - n^\alpha X_m^\alpha - n^\beta X_m^\beta \tag{5}$$

where X is the total value, while X_m^α and X_m^β represent the respective molar values of the property in question in the equilibrium bulk phases.

The object of the thermodynamics of interfaces is to establish functional relationships between the different surface excess quantities, in terms of their dependence on the relevant intensive thermodynamic variables. It is a remarkable fact in this context that a general thermodynamic framework can be set up formally without specifying the reference amounts n^α and n^β. On multiplying the fundamental eqns (1–3), referred to the molar properties of the respective bulk phases (i.e. without the interfacial term) by n^α and n^β, respectively, for example:

$$n^\beta U_m^\beta = n^\beta \left(TS_m^\beta - pV_m^\beta + \sum \mu_i x_i^\beta \right) \tag{6}$$

and

$$n^\beta \left(S_m^\beta \, dT - V_m^\beta \, dp + \sum x_i^\beta \, d\mu_i \right) = 0 \tag{7}$$

then from eqns (4) and (5), respectively, there results:

$$U^\sigma = TS^\sigma - pV^\sigma + FZ + \sum \mu_i n_i^\sigma \tag{8}$$

$$dU^\sigma = T \, dS^\sigma - p \, dV^\sigma + F \, dZ + \sum \mu_i \, dn_i^\sigma \tag{9}$$

$$S^\sigma \, dT - V^\sigma \, dp + Z \, dF + \sum n_i^\sigma \, d\mu_i = 0. \tag{10}$$

As explained in the foregoing section, one has to set

$$F = \gamma, \quad Z = A_s, \quad F \, dZ = \gamma \, dA_s \quad \text{(fluid interface)} \tag{11}$$

in these equations in the case of fluid interfaces. One may deal with A_s and a mean value $\bar{\gamma}$ in connection with fairly smooth solid surfaces, but for solid adsorbents with fixed texture it is more appropriate to select ϵ and m^a as the pertinent variables. It has to be considered, however, that the "free" surface of a solid in itself (i.e. in vacuo or in an "inert" gas atmosphere) has already an extra energy over the bulk value, and that this extra energy is decreased by the contact with an interacting fluid (exothermic heat of adsorption or of immersion). A value ϵ^a (or eventually $\bar{\gamma}^a$) characteristic of the "free" adsorbent must be thus taken into account when expressing the excess surface

energy. Under these conditions we substitute into eqns (8–10) and those which will follow below:

$$F = \epsilon' = \epsilon - \epsilon^a, \quad F\,dZ = \epsilon'\,dm^a,$$
$$\epsilon' < 0 \quad \text{(textured adsorbent).} \quad (12)$$

We may further define the excess Helmholtz free energy:

$$A^\sigma = U^\sigma - TS^\sigma = -pV^\sigma + FZ + \sum \mu_i n_i^\sigma \quad (13)$$

$$dA^\sigma = dU^\sigma - T\,dS^\sigma - S^\sigma\,dT$$
$$= -S^\sigma\,dT - p\,dV^\sigma + F\,dZ + \sum \mu_i\,dn_i^\sigma \quad (14)$$

the surface excess enthalpy:

$$H^\sigma = U^\sigma + pV^\sigma = TS^\sigma + FZ + \sum \mu_i n_i^\sigma \quad (15)$$

$$dH^\sigma = dU^\sigma + p\,dV^\sigma + V^\sigma\,dp$$
$$= T\,dS^\sigma + V^\sigma\,dp + F\,dZ + \sum \mu_i\,dn_i^\sigma \quad (16)$$

and the surface excess Gibbs free energy:

$$G^\sigma = H^\sigma - TS^\sigma = FZ + \sum \mu_i n_i^\sigma \quad (17)$$

$$dG^\sigma = dH^\sigma - T\,dS^\sigma - S^\sigma\,dT$$
$$= -S^\sigma\,dT + V^\sigma\,dp + F\,dZ + \sum \mu_i\,dn_i^\sigma. \quad (18)$$

It is usual to regard the characteristic functions $H^\sigma - FZ$ and $G^\sigma - FZ$ as the surface excess enthalpy and Gibbs free energy, respectively, when the reference amounts n^α and n^β are chosen so as to fulfil the condition $V^\sigma = o$ (see IUPAC Manual[4]).

From eqn (14) and (18) expressions of the surface excess entropy may be derived:

$$\left(\frac{\partial A^\sigma}{\partial T}\right)_{V^\sigma, Z, n_i^\sigma} = \left(\frac{\partial G^\sigma}{\partial T}\right)_{p, Z, n_i^\sigma} = -S^\sigma \quad (19)$$

and these lead to the Gibbs–Helmholtz type relations:

$$U^\sigma = A^\sigma - T\left(\frac{\partial A^\sigma}{\partial T}\right)_{V^\sigma, Z, n_i^\sigma}$$

and

$$H^\sigma = G^\delta - T\left(\frac{\partial G^\sigma}{\partial T}\right)_{p, Z, n_i^\sigma} \quad (20)$$

or in a more compact form:

$$\left(\frac{\partial J^\sigma}{\partial T}\right)_{V^\sigma, Z, n_i^\sigma} = \frac{U^\sigma}{T^2}$$

and

$$\left(\frac{\partial Y^\sigma}{\partial T}\right)_{p, Z, n_i^\sigma} = \frac{H^\sigma}{T^2} \quad (21)$$

where $J^\sigma = -A^\sigma/T$ and $Y^\sigma = -G^\sigma/T$ are the surface excess Massieu and Planck functions, respectively.

By differentiating both forms of Y^σ as they follow from eqn (17), namely:

$$Y^\sigma = -\frac{H^\sigma}{T} + S^\sigma = -\frac{F}{T}Z + \sum Y_i n_i^\sigma \quad (22)$$

where $Y_i = -\mu_i/T$ and making use also of eqn (16), we obtain:

$$\frac{H^\sigma}{T^2}\,dT - \frac{V^\sigma}{T}\,dp + Z\,d\left(\frac{F}{T}\right) - \sum n_i^\sigma\,dY_i = 0 \quad (23)$$

which is a Gibbs–Duhem type relationship similar to eqn (10), but possibly more advantageous in some respects because S^σ has been eliminated.

The relationships derived above show clearly that, apart from the necessity of including extra interfacial terms, the thermodynamic framework relating surface excess properties is formally similar to that referring to equilibria of homogeneous bulk phases. Probably because of this similarity, it is frequently erroneously believed that a set of such quantities defines a real "surface phase". It is with the object of dispelling this misconception that the above deductions have stressed the quite formal, abstract character of the thermodynamics of surface excess properties. Since no instructions have been given so far concerning the reference amounts n^α and n^β, respectively, there is no immediate link to any actual reality and the whole set of the derived relationships is no more than a logical structure at this stage. Further specifications are needed to establish useful relations with measurable quantities and thus to make the formalism operational. The most suitable choice of such specifications depends on the kind of real system under consideration, as will be shown in the following sections for L/G, S/G and S/L interfaces.

3. THE THERMODYNAMIC ADSORPTION ISOTHERM EQUATION OF GIBBS

Under isothermal and isobaric conditions, the first two terms in eqn (10) vanish. Imposition of the latter condition is reasonable in the case of S/L interfaces because moderate variations of the pressure (arising from variation of the vapour pressure with composition of liquid mixtures or of more or less dilute solutions) do not affect noticeably the thermodynamic properties of the adjoining condensed phases. If, however, one of the phases is a gas (L/G or S/G), then concentration changes in the latter at constant temperature correspond generally to pressure changes and vice versa, so that imposition of the condition $dp = 0$ would be incorrect. It is possible to envisage a series of varying relative compositions under constant pressure in the case of gas mixtures, but this is a very special case. Taking advantage of the freedom left by the general thermodynamic framework, it is the most useful convention to select the reference system in this context so that the surface excess volume vanishes, i.e.

$$V^\sigma = V - n^\alpha V_m^\alpha - n^\beta V_m^\beta = 0. \quad (24)$$

This equation, which can be traced back essentially to Guggenheim and Adam,[5] is the algebraic expression of the original procedure of Gibbs, who used for his deductions an imaginary surface called the Gibbs dividing surface, found in the actual system parallel to the interface.[4] For reference the homogeneous bulk phases should be thought of as extending with unchanged properties up to this surface, without any extra interfacial contributions at their contact. The concept of the Gibbs dividing surface may be intuitive in connection with smooth surfaces, but is difficult to visualize in the case of porous adsorbents, whereas eqn (24) has always a clear-cut meaning. It may be noted that adoption of the convention $V^\sigma = 0$ means that U^σ and A^σ become identical to H^σ and G^σ respectively.

After the above comments, there follows immediately

the generalized form of the differential Gibbs adsorption isotherm equation:

$$dF = -\sum \frac{n_i^\sigma}{Z} d\mu_i \quad (dT, V^\sigma dp = 0). \quad (25)$$

Further discussion of this equation is best undertaken separately for each kind of interface.

4. L/G INTERFACES

In accordance with the previous discussion in this case we define $V^\sigma = 0$, $F = \gamma$ and $Z = A_s$. Introducing further surface excess concentrations

$$\Gamma_i = n_i^\sigma / A_s. \quad (26)$$

Equation (25) assumes the well known form:

$$d\gamma_T = -\sum \Gamma_i \, d\mu_i. \quad (27)$$

Since in a two-phase equilibrium system of K components only $(K-1)$ chemical potentials are independent, one of the μ_i terms, say μ_1, may be eliminated from eqn (27). From the respective isothermal Gibbs–Duhem equations, each referred to unit amounts of the two equilibrium bulk phases, there follows (with superscripts l and g instead of α and β, respectively):

$$dp = \frac{1}{V_m^l} \sum x_i^l \, d\mu_i \equiv \sum c_i^l \, d\mu_i = \frac{1}{V_m^g} \sum x_i^g \, d\mu_i$$
$$\equiv \sum c_i^g \, d\mu_i \quad (28)$$

and thus:

$$d\mu_i = -\frac{\sum_{i=2}^{K} (c_i^l - c_i^g) \, d\mu_i}{c_1^l - c_1^g}. \quad (29)$$

Introducing this into eqn (27), this yields:

$$d\gamma_T = \sum_{i=2}^{K} \left(\Gamma_1 \frac{c_i^l - c_i^g}{c_1^l - c_1^g} - \Gamma_i \right) d\mu_i. \quad (30)$$

It has to be recalled now that no decision has been made hitherto the fix the reference amounts n^l and n^g, occurring in eqn (4), which define in a general way the excess amounts n_i^σ or, in the present context, the excess surface concentrations Γ_i. We are free to choose them so as to make Γ_1 vanish and then, if we define the Γ_i corresponding to this choice by $\Gamma_i^{(1)}$ the surface excess concentrations relative to component 1, eqn (30) simplifies to

$$d\gamma_T = -\sum_{i=2}^{K} \Gamma_i^{(1)} \, d\mu_i. \quad (31)$$

From this there follows the classical adsorption equation of Gibbs:

$$\Gamma_i^{(1)} = -\left(\frac{\partial \gamma}{\partial \mu_i} \right)_{T,\mu_{j\neq 1,i}} = -\left(\frac{\partial \gamma}{\partial \ln a_j} \right)_{T,a_{j\neq 1,i}}. \quad (32)$$

This equation enables the calculation of relative surface excess concentrations from measurements of the dependence of surface tension on composition provided the relevant activity coefficient data are available. If the gas phase may be assumed to behave ideally, the respective equilibrium partial vapour pressures may be used instead of the activities.

The convention $\Gamma_1 = 0$ or $n_1^\sigma = 0$ corresponds according to eqn (4) to:

$$n_1 - n^l x_1^l - n^g x_1^g = 0 \quad (33)$$

and this, together with the volume convention, eqn (24), determines unambiguously the reference amounts n^l and n^g, respectively. Simple algebra leads to:[4]

$$n_i^{\sigma(1)} = A_s \Gamma_i^{(1)} = n_i - \frac{n_1 - c_1^g V}{c_1^l - c_1^g} c_i^l - \frac{c_1^l V - n_1}{c_1^l - c_1^g} c_i^g. \quad (34)$$

This expression of the relative surface excess amounts is independent of surface tension measurements and is practically useful since all the quantities occurring on the right hand side are measurable, although it is questionable whether the necessary experimental accuracy can be ensured in practice.

Equation (34) provides for the possibility of an equivalent alternative definition of relative surface excess concentrations:[3]

$$\Gamma_i^{(1)} = \left(\frac{\partial n_i}{\partial A_s} \right)_{T,V,n_1,c_1,c_i}. \quad (35)$$

This definition is possibly more intuitive. It indicates the amount of i which has to be added (or removed in case of negative adsorption) in order to maintain the original values of c_1 and c_i when the interfacial area is increased, or in other words, in order to compensate for the changes caused by adsorption at the newly created portion of the interfacial area. This is assuming that the total volume of the system is kept constant.

The factors of c_i^l and c_i^g in eqn (34) are the respective volumes V^l and V^g of the reference amounts of the two equilibrium bulk phases so that:[4]

$$n_i^{\sigma(1)} = A_s \Gamma_i^{(1)} = n_i - V^l c_i^l - V^g c_i^g. \quad (34a)$$

Evidently, it is possible to remove arbitrary parts of the bulk phases from the actual system without disturbing the adsorption equilibrium, provided that the removals are made away from the interface. Especially, one may make the volumes in the two phases equal:

$$V^l = V^g = V/2 \quad (36)$$

and the expression of $n_i^{\sigma(1)}$ becomes then:

$$n_i^{\sigma(1)} = n_i - \frac{V(c_i^l + c_i^g)}{2} = n_i - \frac{c_i^l + c_i^g}{c_1^l + c_1^g} n_1 \quad (37)$$

with:

$$n_1 = \frac{V(c_1^l + c_1^g)}{2}. \quad (38)$$

In the domain of low vapour pressures, the gas phase concentrations may be neglected compared with those in the liquid (unless i is a very sparingly soluble gas component) and then the following approximate expression may be written:

$$n_i^{\sigma(1)} = A_s \Gamma_i^{(1)} = n_i - n_1 \frac{c_i^l}{c_1^l} = n_i - n_1 \frac{x_i^l}{x_1^l} \quad (39)$$

where n_i and n_1 are now the respective amounts present in the liquid phase. Equation (39) is the form quoted mostly in elementary textbooks, with the additional well-founded implication that adsorption at the "free" surface of solutions is effected practically by concentration shifts in the surface layer of the liquid only.

We refrain here from a detailed discussion of the other current type of surface excess quantities, based on the so-called reduced surface excess amounts[4] and denoted by $n_i^{\sigma(n)}$ or $\Gamma_i^{(n)}$. These correspond to a choice of a reference system which contains the same total amount of substance as the actual system, i.e.:

$$n^l + n^g = \sum n_i = n. \qquad (40)$$

The exact expression of $n_i^{\sigma(n)}$ is quite similar to the right hand side of eqn (34) (formally, one has only to drop the subscript 1 everywhere in the latter) and using the same approximation which led to eqn (39), we obtain:

$$n_i^{\sigma(n)} = A_s \Gamma_i^{(n)} = n_i - n x_i^l. \qquad (41)$$

From this as well as from the exact expression there follows:

$$\sum n_i^{\sigma(n)} = 0 \quad \left(\text{or} \quad \sum \Gamma_i^{(n)} = 0\right) \qquad (42)$$

demonstrating most impressively the strict displacement character of this kind of adsorption, that namely positive adsorption of one component must be compensated by negative adsorption of one or more of the others.

Although the Gibbs adsorption isotherm equation is by far the most important outcome of capillary thermodynamics, it is of interest to note further consequences of the general eqn (23) which reads, when applied to the present case:

$$(H^\sigma/T^2)\, dT + A_s\, d(\gamma/T) - \sum n_i^\sigma\, dY_i = 0. \qquad (43)$$

In view of

$$(\partial Y_i/\partial T)_{p,x^l} = H_i^l/T^2 \qquad (44)$$

where H_i^l is the partial molar enthalpy of i in the solution, the following expression of the temperature coefficient of γ/T at constant composition of the liquid solution can be derived:

$$\left(\frac{\partial(\gamma/T)}{\partial T}\right)_{p,x^l} = -\frac{H^\sigma - \sum n_i^\sigma H_i^l}{A_s T^2}. \qquad (45)$$

Neglecting the gas phase contributions, it follows from the general definitions given in eqns (4) and (5) and in view of eqns (39) and (41), respectively, that:

$$H^{\sigma(1)} - \sum n_i^{\sigma(1)} H_i^l = H^{\sigma(n)} - \sum n_i^{\sigma(n)} H_i^l = H - \sum n_i H_i^l$$
$$\equiv A_s h_\gamma \approx A_s u_\gamma \qquad (46)$$

where n_γ and u_γ are the extra surface enthalpy and energy, respectively, per unit surface area. Equation (45) thus assumes a simpler form:

$$\left(\frac{\partial(\gamma/T)}{\partial T}\right)_{p,x^l} = -h_\gamma/T^2$$

or:

$$h_\gamma = \gamma - T\frac{\partial\gamma}{\partial T} \qquad (47)$$

which is similar to the well-known relation connecting surface tension and extra surface energy per unit area in the case of a pure liquid. It may be noted that h_γ, though also a surface excess quantity, is not referred to some portion of the equilibrium bulk solution, but to a fictitious system in which the adsorbed amounts would have the same partial molar enthalpies as those characteristic of the bulk liquid.

Since the surface tension of solutions, like pure liquids, decreases with increasing temperature, it follows from eqn (47) that the extra surface energy is a positive quantity in the case of solutions also, and can be computed if the temperature coefficient of the surface tension at constant composition is measured. (As the extra surface energy in practice is attributed only to the condensed liquid phase, the condition of constant pressure indicated at the left hand side of eqn (47) is unimportant, at least in the domain of low vapour pressure.)

5. S/G INTERFACES[6]

As explained in Section 3, the generally adopted convention in connection with S/G interfaces is $V^\sigma = 0$ and according to the discussion in Section 2 we set $FZ = \epsilon' m^a$ (see eqn (12)) when adsorbents with fixed colloidal texture are involved. The general eqns (9–10) and (13–18), respectively, then assume the special forms:

$$U^\sigma = H^\sigma = TS^\sigma + \epsilon' m^a + \sum \mu_i n_i^\sigma \qquad (48)$$

$$dU^\sigma = dH^\sigma = T\, dS^\sigma + \epsilon'\, dm^a + \sum \mu_i\, dn_i^\sigma \qquad (49)$$

$$S^\sigma\, dT + m^a\, d\epsilon' + \sum n_i^\sigma\, d\mu_i = 0 \qquad (50)$$

$$A^\sigma = G^\sigma = \epsilon' m^a + \sum \mu_i n_i^\sigma \qquad (51)$$

$$dA^\sigma = dG^\sigma = -S^\sigma\, dT + \epsilon'\, dm^a + \sum \mu_i\, dn_i^\sigma \qquad (52)$$

where the indices i and thus the summations refer only to the gaseous components.

The operational definition of the adsorption excesses is now:

$$n_i^\sigma = n_i - x_i n^g = n_i - V^g c_i \qquad (53)$$

where the gas volume V^g is generally identified with the experimentally determined helium deadspace of the adsorption vessel; n^g and n_i are then the total amount of gas and the amount of i respectively present in the vessel under equilibrium adsorption conditions.

In contrast to L/G interfaces, the excess amounts n_i^σ are directly measurable quantities, whereas ϵ' can be computed only by referring to the thermodynamic adsorption equation of Gibbs, which reads, for the present case, as follows:

$$\left(\frac{\partial\epsilon'}{\partial\mu_i}\right)_{T,\mu_j} \approx \frac{1}{RT}\left(\frac{\partial\epsilon'}{\partial \ln p_i}\right)_{T,p_j} = -\frac{n_i^\sigma}{m^a} \quad (j \neq i). \qquad (54)$$

For a pure gas (or when the jth components are "inert" from the point of view of adsorption) this last equation may be written in the integrated form:

$$\epsilon' = \epsilon - \epsilon^a = -\frac{RT}{m^a}\int_0^p n^\sigma\, d\ln p \qquad (55)$$

and the prescribed integration can be carried out without any difficulty if the adsorption isotherm, i.e. the function

$n^\sigma(p)$ is known experimentally. It is evident that ϵ has to be smaller than ϵ^a, and decrease with increasing adsorption, in order to conform with the general Gibbsian principle that positive adsorption must be accompanied by a decrease of the interfacial free energy. It may be noted that in current literature the relationship corresponding to eqn (55) is usually written in terms of the highly problematic surface tension equivalent ϵ, and not with that of ϵ'. It is clear by our reasoning however that in fact only the value with respect to that of the solid/vacuum interface can be computed from experimental adsorption data.

It is usual and expedient to refer the extensive thermodynamic excess properties to unit amounts of the adsorbates, i.e. to reckon with the partial molar values of these functions, defined generally as:

$$X_i^\sigma = \left(\frac{\partial X^\sigma}{\partial n_i^\sigma}\right)_{T, m^a, n_j^\sigma} \quad (j \neq i). \tag{56}$$

There follows from eqn (49):

$$U_i^\sigma = H_i^\sigma = TS_i^\sigma + \mu_i \tag{57}$$

and from eqn (52):

$$A_i^\sigma = G_i^\sigma = \mu_i. \tag{58}$$

This latter equality is evidently in conformity with the general requirements of thermodynamic equilibrium.

Any one of the μ_i terms can be expressed in terms of the equilibrium gas phase:

$$\mu_i = H_i^g - TS_i^g \tag{59}$$

and thus, eqn (57) can be transformed to give:

$$H_i^\sigma - H_i^g \equiv \Delta_a H_i^\sigma = T(S_i^\sigma - S_i^g) \equiv T\Delta_a S_i^\sigma. \tag{60}$$

This sequence of equations has to be interpreted as referring to the transfer of a unit amount of i from the gas phase into the adsorbed state without disturbing the equilibrium. Since such a transfer cannot involve more than an infinitesimal amount, the quantity $\Delta_a H_i^\sigma$ is a differential enthalpy and $\Delta_a S_i^\sigma$ the differential entropy of adsorption of component i, respectively.

It is easy to show that $\Delta_a H_i^\sigma$ is identical with the so-called isosteric heat of adsorption of i. From eqn (49) it follows that:

$$dH^\sigma = T\, dS^\sigma \quad (m^a, n_i^\sigma = \text{const}) \tag{61}$$

and further differentiation with respect to n_i^σ yields:

$$dH_i^\sigma = T\, dS_i^\sigma. \tag{62}$$

A comparison with the total differential of H_i^σ (eqn (57)) then gives the result:

$$S_i^\sigma\, dT + d\mu_i = 0 \tag{63}$$

along any isostere. For an ideal gas mixture, the expression of $d\mu_i$ is:

$$d\mu_i = -S_i^g\, dT + RT\, d\ln p_i \tag{64}$$

and by substituting this into eqn (63) we obtain:

$$(S_i^\sigma - S_i^g)\, dT + RT\, d\ln p_i = 0 \tag{65}$$

or, in view of eqn (60), the well-known expression of the isosteric heat of adsorption:

$$\Delta_a H_i^\sigma = R\left(\frac{\partial \ln p_i}{\partial (1/T)}\right)_{m^a, n_i^\sigma}. \tag{66}$$

For a single pure gas, $d\mu$ can be expressed, irrespective of whether the behaviour is ideal or not, as:

$$d\mu = -S_m^g\, dT + V_m^g\, dp \tag{67}$$

and there follows, by eqn (63), the Clausius–Clapeyron equation:

$$(\partial p/\partial T)_{m^a, n^\sigma} = -\Delta_a S_m^\sigma / V_m^g \tag{68}$$

or the equivlaent formulation:

$$(\partial \ln p/\partial T)_{m^a, n^\sigma} = -\Delta_a H_m^\sigma /(TpV_m^g) \approx -\Delta_a H_m^\sigma /(RT^2). \tag{69}$$

It may be noted that the equality of U_i^σ and H_i^σ does not involve equality of the differential energy and enthalpy of adsorption, respectively. The former is defined by:

$$\Delta_a U_i^\sigma = U_i^\sigma - U_i^g = \Delta_a H_i^\sigma + pV_i^g \approx \Delta_a H_i^\sigma + RT. \tag{70}$$

In the case of non-ideality of the gas phase, V_i^g is the partial molar volume of i according to Amagat's rule.

6. S/L INTERFACES[7,8]

In the case of adsorption from liquids onto solids, as with gas adsorption, the directly measureable quantities are the concentration and enthalpy changes brought about by adsorption. However, owing to the practically negligible compressibility of liquids under usual conditions, no perceptible concentration change occurs when a chemically inert pure liquid is brought into contact with a solid, so that we speak of adsorption only in connection with solutions (liquid mixtures). Furthermore, adsorption from the latter is not accompanied by a spectacular accumulation of matter as a whole in the interfacial layer as is seen with gases, where significant volume changes at constant pressure are observed. Rather, adsorption manifests itself only by shifts in composition of the solution.

Quantitative measurements of adsorption are carried out mostly by the immersion method: a weighed amount of adsorbent of mass m^a is immersed into a total amount n^0 of solution of known initial composition characterized by the mole fractions x_i^0 of its components, and the final equilibrium mole fractions x_i in the supernatant bulk liquid are determined by some suitable analytical method. Because $\Sigma x_i^0 = \Sigma x_i = 1$, some of the differences

$$\Delta x_i = x_i^0 - x_i \quad \left(\sum \Delta x_i = 0\right) \tag{71}$$

are positive and others negative, but the positive and negative adsorptions must occur simultaneously and be strictly complementary. It may be noted incidentally that such displacement effects are encountered also with adsorption of gas mixtures, but owing to the significant compressibility of the latter then are not bound to the condition of strict reciprocity.

The apparent amount adsorbed $n^0 \Delta x_i$ is identical with the reduced surface excess as defined formerly by eqn (41). Since $n_i (= n^0 x_i^0)$ is the total amount of i and $n (= n^0)$ is the total amount of all the solution components together in the actual system, we have:

$$n^0 \Delta x_i = n_i - n x_i = n_i^{\sigma(n)}, \quad \sum n_i^{\sigma(n)} = 0. \quad (72)$$

This latter definition is to be preferred because it is not applicable to the immersion experiment only, which is not the only possible way to determine $n_i^{\sigma(n)}$; this can be achieved, for example, also by frontal chromatography where the equilibrium mixture characterized by the x_i is fed onto the column so that the procedure does not rely on the determination of the Δx_i.[9]

By analogy with eqn (39), relative adsorption may also be defined as:

$$n_i^{\sigma(1)} = n_i - n_{\text{ref}} x_i = n_i - \frac{n_1}{x_1} x_i = n^0 \left(x_i^0 - \frac{x_1^0}{x_1} x_i \right). \quad (73)$$

The sum of the relative adsorptions of all the components,

$$\sum n_i^{\sigma(1)} = n^0 (1 - x_1^0 / x_1) = -n^0 \Delta x_1 / x_1. \quad (74)$$

For the case of a binary solution the different surface excess amounts are interrelated as follows:

$$n_2^{\sigma(n)} = -n_1^{\sigma(n)} = x_1 n_2^{\sigma(1)} = -x_2 n_1^{\sigma(2)}. \quad (75)$$

In view of the already mentioned fact that adsorption from solution is not accompanied by significant volume changes, it may appear somewhat surprising that according to the above definitions the surface excess volume V^σ cannot be set equal to zero. This would be possible only by admission of an adsorption excess of the solid adsorbent[4] which does not, however, undergo concentration changes. Such a formal procedure would be hardly realistic in our opinion (remembering that we do not speak of adsorption of a pure liquid, neither at the L/V nor at a S/L interface). Indeed, taking the amount and volume of the solid adsorbent in the reference system as equal to that in the actual system, and neglecting any variations of the partial molar volumes of the solution components caused by shifts in composition and/or by adsorption, there follows for the excess volume, based on the general definition (eqn (5)), the relationship:

$$V^\sigma = V_{\text{act}}^l - n_{\text{ref}}^l V_{m,\text{ref}}^l = \sum n_i V_i - n_{\text{ref}}^l \sum x_i V_i$$

$$= \sum (n_i - n_{\text{ref}}^l x_i) V_i = \sum n_i^\sigma V_i. \quad (76)$$

It may be seen that $V^{\sigma(n)}$ would vanish only in the case of all the V_i values being equal, but in view of eqn (74), even then this would not be true for $V^{\sigma(1)}$. As a consequence, the excess interfacial energy U^σ and the interfacial excess Helmholtz free energy A^σ cannot be equated with the enthalpy H^σ and the Gibbs free energy G^σ respectively, as was the case with L/G and S/G interfaces.

At constant pressure, which is the usual condition for the experimental determination of adsorption isotherms from solution, and assuming $F = \epsilon'$ and $Z = m^a$ as for adsorbents of a fixed texture, the general Gibbs adsorption isotherm eqn (25) becomes:

$$-d\epsilon' = \sum \frac{n_i^\sigma}{m^a} d\mu_i \quad (T, p = \text{const}). \quad (77)$$

Making use of the Gibbs–Duhem relation $\sum x_i \, d\mu_i = 0$, one of the $d\mu_i$ terms can be expressed as the function of the others and, especially for binary solutions, eqn (77) can be written in any one of the alternative forms:

$$-d\epsilon' = \frac{n_2^{\sigma(1)}}{m^a} d\mu_2 = \frac{n^0 \Delta x_2}{m^a x_1} d\mu_2 = \frac{n^0 \Delta x_1}{m^a x^2} d\mu_1$$

$$= RT \frac{n^0 \Delta x_2}{m^a x_1} d \ln a_2 = RT \frac{n^0 \Delta x_1}{m^a x_2} d \ln a_1. \quad (78)$$

Since all the quantities occurring at the right hand side are experimentally accessible, eqn (78) can be integrated, usually graphically, to give ϵ' as a function of the composition of the equilibrium solution. This function is evidently without maxima or minima if the adsorption of one of the components is preferred throughout, but will exhibit an extremum at any composition corresponding to an adsorption azeotrope. This is often met with in connection with pairs of completely miscible liquids. There follows also by eqn (78) that ϵ' decreases with increasing concentraation of the positively adsorbed component, in compliance with the general principle laid down by Gibbs. It may be noted that according to its definition in eqn (12), ϵ' is a negative quantity, although both of its terms, ϵ and ϵ^a, respectively, are positive. The latter, however, being a constant at constant temperature, means that a decrease in ϵ' corresponds to one in ϵ.

The excess enthalpy and Gibbs free energy, either reduced or relative, can be specified now as follows:

$$H^\sigma = TS^\sigma + \epsilon' m^a + \sum \mu_i n_i^\sigma \quad (79)$$

$$G^\sigma = \epsilon' m^a + \sum \mu_i n_i^\sigma. \quad (80)$$

In the simplest possible case, of immersional wetting of an adsorbent by a pure liquid, since there is no adsorption (no change in the mole or mass fraction of the liquid), eqn (80) reduces to:

$$g^\sigma = G^\sigma / m^a = \epsilon' \quad (81)$$

so that ϵ' is equal in this case to the specific Gibbs free energy of immersional wetting and corresponds, if referred to unit surface area, to the quantity commonly called wetting tension. The quantity $h^\sigma = H^\sigma / m^a$ is, on the other hand, in this case the calorimetrically directly measurable specific enthalpy of immersional wetting by the pure liquid (the so-called heat of wetting, q_w).[4]

From the general eqn (23) there follows the counterpart of eqn (45):

$$\left(\frac{\partial (\epsilon'/T)}{\partial T} \right)_{p,x_i} = -\frac{H^\sigma - \sum n_i^\sigma H_i}{m^a T^2} = -\frac{H - \sum n_i H_i}{m^a T^2}. \quad (82)$$

It may be noted, however, that the analogy with eqn (45) does not extend to the sign: the wetting of a solid by a liquid is an exothermic process, and the numerator of the right hand side of eqn (85) is therefore a negative quantity. Equation (82) may also be written in the form of a Gibbs–Helmholtz type relation. Since in the case of wetting by a pure liquid, as mentioned above, the excess enthalpy is equivalent to the heat of immersional wetting, it follows that the latter, when referred to unit surface area, is also connected with the wetting tension through a

Gibbs–Helmholtz relationship, a fact generally passed over in the literature.

Excess enthalpy and the heat of immersional wetting cannot be equated, however, in the case of solutions where composition shifts caused by adsorption are also involved. The isothermal enthalpy of immersional wetting is defined as:

$$\Delta H_w = H - m^a h^a - n^0 H_m^{l,0} \quad (T, p = \text{const}) \quad (83)$$

where $H_m^{l,0}$ is the molar enthalpy of the solution before immersion of the solid and h^a the specific enthalpy of the solid *in vacuo*. ΔH_w is an experimentally accessible quantity, but practical difficulties may arise in its determination, especially with porous adsorbents where activated adsorption may occur. Any calorimetrically measured heat of immersion in a solution is therefore not necessarily equal to the true difference between the initial and final equilibrium values.

Since the immersion experiment is connected directly with the reduced excess amounts, we introduce the reduced excess enthalpy, defined as:

$$H^{\sigma(n)} = H - m^a n^a - n^0 H_m^l \quad (T, p = \text{const}). \quad (84)$$

It therefore follows that:

$$\Delta H_w = H^{\sigma(n)} + n^0 (H_m^l - H_m^{l,0}) = H^{\sigma(n)} + n^0 \Delta H_m^l \quad (85)$$

where ΔH_m^l is the change in the molar enthalpy of the bulk solution corresponding to the change of its composition caused by adsorption. Since this latter change depends not only on the kind of adsorbent and the composition of the solution in which it is immersed, but also on the ratio n^0/m^a used in the calorimetric experiment and/or the determination of a point of the adsorption isotherm, the measured specific heat of immersion, $\Delta H_w/m^a$, will also depend on this ratio and is thus not a quantity characteristic of the nature of the adsorbent and adsorbate alone. On the other hand, from experimental data, eqn (85) may serve for the computation of the directly not accessible excess enthalpy, provided the enthalpy of mixing as a function of solution composition is known.

Applying the general energy expression, eqn (2), to the present case we can write:

$$U + pV = H = TS + m^a(\mu^a + \epsilon) + \sum n_i \mu_i \quad (86)$$

further:

$$h^a = Ts^a + \mu^a + \epsilon^a \quad (87)$$

and

$$H_m^{l,0} = TS_m^{l,0} + \sum x_i^0 \mu_i^0. \quad (88)$$

There follows then, from eqn (83), an alternative expression for ΔH_w (noting that the respective amounts $n_i^0 x_i^0$ remain unchanged in the immersion experiment):

$$\Delta H_w = T\Delta S_w + m^a \epsilon' + n^0 \sum x_i^0 \Delta \mu_i \quad (T, p = \text{const}) \quad (89)$$

and for ΔG_w, the Gibbs free energy of immersional wetting:

$$\Delta G_w = \Delta H_w - T\Delta S_w = m^a \epsilon' \\ + n^0 \sum x_i^0 \Delta \mu_i \quad (T, p = \text{const}) \quad (90)$$

where $\Delta \mu_i (= \mu_i - \mu_i^0)$ represents the changes in the chemical potentials of the solution components brought about by adsorption. ΔS_w, which may be called the entropy of immersional wetting, is defined in a similar way as ΔH_w using eqn (85). ΔS_w can be computed from experimental data only for binary solutions because only in this case is ϵ' calculable by graphical integration of the Gibbs adsorption isotherm eqn (78). For a pure liquid, eqn (90) becomes identical with eqn (81), i.e. $\Delta G_w = G^{\sigma}$.

The excess adsorbed amounts $n_i^{\sigma(n)}$ do not appear in the last two equations because, as a consequence of the conservation of mass, all the Δn_i terms are zero, whereas energy, entropy etc. of the system are not conserved in the immersion experiment when carried out isothermally or nonadiabatically. It may be noted further that, as mentioned before, ΔV_w (the eventual volume change connected with the immersion experiment) can be considered negligibly small in general so that there is no practical need for a distinction between energy and enthalpy of immersional wetting on the one hand and between the corresponding Helmholtz and Gibbs free energies on the other hand.

CONCLUDING REMARKS

The aim of this lecture was to show that a generally valid exposition of the equilibrium thermodynamics of adsorption, based on the Gibbsian concept of interfacial excess amounts, appears possible only in a quite abstract, formal way. The characteristic quantities occurring in such a formal framework need further specification in order to make it operational, but the most expedient choice of these specifications has to be different for different types of interfaces, according to the special distinctive features of the latter. This has been shown in connection with three main kinds of interfaces. The quoted set of general relationships, as well as those referring to the special types of interfaces, are, of course far from complete, but can be amplified without difficulty by using standard methods of chemical thermodynamics to treat further problems of interest, such as the pressure dependence of adsorption at the interface between two immiscible liquids or at S/L interfaces.

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