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The Thermodynamics of Solid-Solid Interfaces in Systems of Fixed Mass

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ABSTRACT

The textbook approach to interfacial excess quantities, due to Gibbs, is valid only at fixed volume. In the present work we develop an alternative approach to interfacial excess quantities, valid at fixed mass. For solid-solid interfaces this has several advantages over the Gibbs treatment such as (a) non-zero interfacial excess volumes appear naturally in the treatment, (b) analogues of the bulk phase Maxwell relations are readily obtained, and (c) formulae for the pressure dependence and temperature dependence of the interfacial tension are derived in a transparent way.

INTRODUCTION

The thermodynamics of interfaces has a long and distinguished history, stretching back to Gibbs [1]. Many books and review articles have been written on the topic, for example refs [2-12], and the symbols and terminology have been settled by international agreement [13]. Typically, an interface is said to exist when a thin inhomogeneous mass of material (γ) forms the transition zone between two homogeneous masses of material (α and β).

In the present work we focus on a special type of interface, namely the solid-solid interface between two one-component phases. Our goal is to derive explicit expressions for the temperature and pressure dependence of the interfacial tension of such an interface, in a form convenient for direct comparison with experimental data.

In the literature, several different approaches towards the thermodynamics of solid-solid interfaces have been suggested, having various degrees of user-friendliness. For example:

(i) *The Surface Phase Approach*, in which the interface is regarded as a third phase trapped between two bulk phases.
(ii) *The Surface Excess Approach (at Fixed Volume)* in which a system with an interface is regarded as the sum of a reference system without an interface, plus a correction. The actual system and the reference system have the same total volume.
(iii) *The Surface Excess Approach (at Fixed Mass)* in which a system with an interface is regarded as the sum of a reference system without an interface, plus a correction. The actual system and the reference system have the same masses of α and β, but possibly different volumes.

Approach (i) is widely associated with the name of Guggenheim [4], while approach (ii) is widely associated with the name of Gibbs [1]. Somewhat surprisingly, approach (iii) does not appear to have been considered in the literature (or at any rate is unknown to the present author) although Gibbs mentioned it as a possibility in a footnote in the *Transactions of the Connecticut Academy* in 1878 (reprinted at page 267 in ref [1]). We consider it in some detail below.

Guggenheim treated the interface as an inhomogeneous phase of arbitrary extent. Gibbs, on the other hand, regarded the interface as a departure from a hypothetical reference state of two homogeneous masses of α and β meeting at an abrupt *dividing*

surface. He called any difference between the actual system and the reference system an *interfacial excess quantity*.

Guggenheim's approach may aptly be described as the *Surface Phase Approach*. In his well-known book [4] he stated: "Since the surface layer is a material system with a well-defined volume and material content, its thermodynamic properties require no special definition." Although this is true, the statement actually hides a difficulty. This is that the surface layer is not *spatially homogeneous*, and so, to ensure that all the spatially-varying properties are included in the surface layer, the boundaries of the layer must be placed far inside the adjacent bulk phases.

An immediate corollary is that, on the Guggenheim model, the volume of the surface phase V^σ is completely arbitrary, and it therefore cannot be associated with the volume change of the total system that occurs upon formation of an interface within it. Assuredly, it is the volume of an arbitrarily large region that includes the surface, but the actual volume of the surface cannot be deduced from it without much more information. The only way around this problem is to define a dividing surface, but then we are back to the Gibbs approach.

Gibbs also considers two homogeneous phases with an inhomogeneous phase (the interface) in between. His approach is very different, however. He refers all measurements to a hypothetical reference state that has no inhomogeneities anywhere. This reference state consists of two homogeneous masses of α and β meeting at an abrupt *dividing surface*. To further simplify the analysis, he allows bulk matter to be continuously added to (or subtracted from) the system of interest so that its volume always matches the volume of the chosen reference system, which means that for him the surface excess volume V^σ is always (apparently) zero. As a result, terms such as $V^\sigma dP$ disappear from Gibbs' equations for surface excess quantities.

Gibbs understood and approved of this theoretical sleight-of-hand, but it leaves his approach open to misinterpretation. In particular, one must continuously remind oneself that Gibbs equations of surface thermodynamics do not apply to closed systems. This fact is insufficiently emphasized in the scientific literature, and the consequences are particularly troublesome in high pressure electrochemistry, where the disappearance of the term in $V^\sigma dP$ makes it difficult to derive explicit expressions for the pressure dependence of interfacial properties. A theory of surface thermodynamics based on *fixed quantities of matter* rather than *dividing surfaces* might therefore be easier to use.

It is interesting to ask why Gibbs rejected the *fixed-quantity-of-matter* approach in favour of the *dividing-surface* approach. The answer is found in a footnote on page 267 of his *Collected Works* [1]. (In what follows, the italics are mine.) He writes:

"It would ... be natural ... to regard the quantities of the homogeneous masses as determined by *... the total quantities of matter, and not by ... any other dividing surface*." However, the resulting "...nomenclature and method could not readily be extended so as to treat cases of more than two components with entire generality."

From these remarks it is clear that Gibbs had already explored a version of surface thermodynamics based on *total quantities of matter* rather than *dividing surfaces*, and had even decided that this approach was "natural" and "general" if no more than two components were involved. What a pity Gibbs didn't publish it! It is also clear that his reluctance to publish was connected with the difficulty of extending the theory to multi-component systems, which were his principal target. But in many practical systems this is not a pressing issue, and so need not delay us. Ironically, the comparatively contrived formulation that Gibbs did finally publish, which was based on dividing surfaces, and which he thought might be used only "in some cases", has become the accepted textbook standard!

In what follows, we reconstruct the lost theory of Gibbs, by developing a theory of interfacial thermodynamics based on *total quantities of matter* rather than *dividing surfaces*. Our ultimate goal is to obtain an expression for the pressure dependence of the solid-solid interfacial tension, valid for systems of fixed mass.

IN A NEW SET OF INTERFACIAL QUANTITIES, VALID FOR SYSTEMS OF FIXED MASS

In the laboratory we are often confronted with the problem of modelling systems in which interfaces are formed from fixed masses of starting materials. The classical approach to this problem is three-stage [13].

The first stage is to sum the free energies of the bulk phases in the system. The second stage is to sum the excess free energies of the interfaces. Then the third stage is to add all the free energies together.

However, conventional excess free energies, as derived by Gibbs [1], are difficult to apply to this problem. Gibbs excess free energies are defined *at fixed volume* rather than *at fixed mass*, and so cannot simply be added to the bulk free energies of the fixed masses to get the final result. To overcome this obstacle, a different approach is needed.

An idealized picture of an equilibrium solid-solid interface is shown in Fig 1. It is assumed that the phases α and β are single component phases which are ideally mutually insoluble. (Nevertheless, some interfacial mixing of α and β may occur despite their mutual insolubility, due to the finite surface entropy.) It is also assumed that there are sufficient amounts of the phases α and β to ensure that far from the interface they exhibit their bulk behaviours, although close to the interface some local expansion or contraction of both phases is allowed due to the changed intermolecular interactions.

Thermodynamic analysis of such an interface can be achieved by means of a thought experiment in which the bulk phases α and β are assumed to be initially separate and interface-free, but are then joined along a plane to create the α/β interface. Mass is conserved. Any changes in the thermodynamic parameters of the whole system are then ascribed to the new α/β interface. Such changes are accounted separately and

are here called *excess* values of the relevant parameters. However, these excess quantities are different to those of Gibbs, because we are working at fixed mass whereas he was working at fixed volume. To distinguish the two cases, we shall indicate our excess quantities by subscript γ, whereas Gibbs used subscript σ.
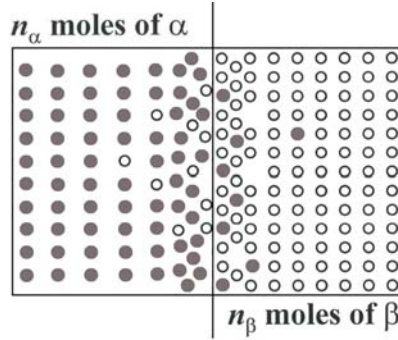

FIGURE 1. Formation of an interface from a fixed number of moles of α and β. Note that during interface formation the whole system changes its volume by an amount V_γ which we call the *interfacial excess volume*.

We proceed as follows. For a constant number of molecules, the first derivative of the Gibbs function in a single phase is

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T \qquad\qquad \text{Eq (1)}$$

Hence

$$\mathrm{d}G_1 = \left(V_\alpha + V_\beta\right)\mathrm{d}P - \left(S_\alpha + S_\beta\right)\mathrm{d}T \qquad\qquad \text{Eq (2)}$$

Similarly

$$\mathrm{d}G_2 = \left(V_\alpha + V_\beta + V_\gamma\right)\mathrm{d}P - \left(S_\alpha + S_\beta + S_\gamma\right)\mathrm{d}T + \gamma^*\mathrm{d}A \qquad\qquad \text{Eq (3)}$$

In the above equations, subscript 1 refers to the system *before* interface formation, and subscript 2 refers to the system *after* interface formation. In the terminology of surface thermodynamics, the system before interface formation is called the "reference state". In contrast to Gibbs' treatment of interfacial excess quantities, the numbers of atoms of α and β are the same in the reference state and the final state.

The asterisk denotes a "specific" quantity *i.e.* a quantity measured per unit area of interface. The subscript γ denotes a surface excess quantity measured relative to the reference state of bulk fixed masses of α and β.

The first derivative of the excess free energy between states 1 and 2 for the fixed masses n_α and n_β is thus

$$dG_\gamma = dG_2 - dG_1 \qquad\qquad\qquad \text{Eq (4)}$$

$$= V_\gamma dP - S_\gamma dT + \gamma^* dA \qquad\qquad \text{Eq (5)}$$

Because we are dealing with one-component phases, it follows that G_γ depends only on the *configurations* of the molecules at the surface and not on the *concentrations* of any dissolved species. Consequently, the specific interfacial excess free energy G_γ^* and the reorganization energy γ^* (*surface tension, interfacial tension*) are identical at constant temperature and pressure.

Eq (5) is more than just a mathematical equality; it contains genuine physical insight into the energetics of interface formation. For example, the term $\gamma^* dA$ is seen to be the mechanical work done against the *internal* force fields of the phases α and β by the movement of molecules from the bulk to create the surface. Likewise, the term $V_\gamma dP$ is seen to be the mechanical work done against the *external* force fields of the surroundings. The third term, $S_\gamma dT$, is the heat of formation of the interface. Because interfaces are always more disordered than bulk materials, S_γ is always positive, which explains why systems often tend to cool down as new interface is formed. As a result, heat must be supplied from the surroundings if the temperature is to be maintained constant.

γ^* is referred to in the literature as "the interfacial tension", though a better name might be *the specific reorganization energy of the interface*. It is always positive. It is always mechanical. Due to its mechanical character, γ^* can also be a function of interface curvature, though for present purposes we neglect this possibility.

Overall, G_γ is the excess free energy of formation of the interface at fixed masses of α and β. In other words, G_γ is not the total free energy required to form the interface from nothing, but is the additional free energy required to form the interface from fixed masses of the pre-existing bulk phases α and β. This is consistent with the common-sense notion that a surface cannot exist except when it is attached to a bulk phase! Analogously, the terms G_γ, V_γ, S_γ, and γ^* are all excess quantities.

In deriving the above equations, we used the *conservation of mass*

$$n_{\text{total}} = n_\alpha + n_\beta \qquad\qquad\qquad \text{Eq (6)}$$

and defined V_γ as

$$V_{\text{total}} = V_\alpha + V_\beta + V_\gamma \qquad\qquad \text{Eq (7)}$$

Here V_α and V_β are the volumes of the phases α and β before interface formation, and V_{total} is the combined volume after interface formation. V_γ is therefore the interfacial *excess* volume, which can have either a positive or negative value depending on whether the intermolecular interactions at the new interface involve a net expansion or contraction of the total volume of the system as a whole.

It is interesting to compare and contrast these equations with the *conservation-of-volume* approach of Gibbs. He assumes

$$V_{\text{total}} = V_\alpha + V_\beta \qquad\qquad \text{Eq (8)}$$

and

$$n_{\text{total}} = n_\alpha + n_\beta + n_\sigma \qquad\qquad \text{Eq (9)}$$

Here n_σ is the mass of material that must be added to (or subtracted from) the system to compensate for the volume loss (or gain) that accompanies the formation of the interface. The existence of n_σ, which is a supply of material from outside the system, means that the Gibbs model is always open.

By contrast, in the absence of deliberately added material from outside the system, the "fixed mass" model is always closed. Moreover, because the corresponding excess free energy G_γ is a state function, Eq (5) can be converted into three different partial differential equations by setting different pairs of dP, dT, and dA to zero. The results are surprisingly elegant:

$$\left(\frac{\partial \gamma^*}{\partial T}\right)_{P,A,n_\alpha,n_\beta} = -\left(\frac{\partial S_\gamma}{\partial A}\right)_{P,T,n_\alpha,n_\beta} = -S_\gamma^* \qquad\qquad \text{Eq (10)}$$

$$\left(\frac{\partial \gamma^*}{\partial P}\right)_{T,A,n_\alpha,n_\beta} = \left(\frac{\partial V_\gamma}{\partial A}\right)_{T,P,n_\alpha,n_\beta} = V_\gamma^* \qquad\qquad \text{Eq (11)}$$

$$\left(\frac{\partial V_\gamma}{\partial T}\right)_{A,P,n_\alpha,n_\beta} = -\left(\frac{\partial S_\gamma}{\partial P}\right)_{A,T,n_\alpha,n_\beta} \qquad\qquad \text{Eq (12)}$$

Here S_γ^* and V_γ^* are *the specific interfacial excess entropy* and *the specific interfacial excess volume*, respectively. These relations are, in fact, the interfacial analogues of the bulk-phase Maxwell relations, and represent our main results. It is particularly noteworthy that the analogues of the last two of these equations cannot be written down in the Gibbs "constant volume" approach, because of his requirement that $V_\sigma = 0$. The same requirement prevents the term $V_\sigma dP$ from appearing in the "constant volume" equivalent of Eq (5) — a curiosity of the Gibbs approach often left unexplained in undergraduate textbooks (see e.g. Atkins [14]).

Working at fixed mass, no such problems arise. In fact, only three important quantities remain to be derived – the specific interfacial excess free energy, the specific interfacial excess internal energy, and the specific interfacial excess enthalpy, all valid at fixed masses of α and β. The first is easy to derive; we simply integrate Eq (5) to yield

$$\left(G_\gamma\right)_{n_\alpha,n_\beta} = \gamma^* A \qquad\qquad\qquad \text{Eq (13)}$$

or equivalently

$$\left(G_\gamma^*\right)_{n_\alpha,n_\beta} = \gamma^* \qquad\qquad\qquad \text{Eq (14)}$$

This tells us that the *specific interfacial excess free energy* and the *interfacial tension* are identical at fixed masses of the one-component phases α and β. It follows that the temperature and pressure dependence of γ^* can be obtained by measuring the temperature and pressure dependence of G_γ^*. This is useful to solid-state electrochemists, because, as we intend to show elsewhere, the temperature and pressure dependence of G_γ^* can be derived from voltammograms of solid-solid phase transformations.

The *specific interfacial excess internal energy* is a little more difficult to derive. One must apply a Legendre transform to Eq (5) and then substitute the interfacial analogs of the Maxwell relations into the result. But after a little algebra one soon obtains:

$$\left(U_\gamma^*\right)_{n_\alpha,n_\beta} = \gamma^* + T S_\gamma^* - P V_\gamma^* \qquad\qquad \text{Eq (15)}$$

The *specific interfacial excess enthalpy* follows immediately:

$$\left(H_\gamma^*\right)_{n_\alpha,n_\beta} = \gamma^* + T S_\gamma^* \qquad\qquad\qquad \text{Eq (16)}$$

Finally, we identify H_γ^* as the "*surface energy*" ε. Thus

$$\varepsilon = \gamma^* - T\left(\frac{\partial \gamma^*}{\partial T}\right)_{P,A,n_\alpha,n_\beta} \qquad\qquad \text{Eq (17)}$$

It is very satisfying to note that the difference between the surface energy ε and the interfacial tension γ is simply the heat supplied by the surroundings when new interface is created isothermally.

CONCLUSIONS

The Gibbs approach towards interfacial excess quantities is valid only at fixed volume. In the present work we have described a parallel approach that is valid at fixed mass. For solid-solid interfaces this has several advantages over the Gibbs treatment such as (a) non-zero interfacial excess volumes appear naturally in the treatment, (b) analogues of the bulk phase Maxwell relations can be derived, and (c) formulae suitable for direct comparison with high pressure experiments are produced.

The temperature and pressure dependences of the specific interfacial excess free energy are of particular interest, because they can be investigated by electrochemical techniques [15]. Application of the present theory to data derived from high pressure electrochemical experiments will be reported in due course.

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