

# Chemical Reviews

Volume 78, Number 2

April 1978

## The Derivation of Thermodynamic Equations for Solid Surfaces

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Received December 7, 1977

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### I. Introduction

This review deals with aspects of the thermodynamics of capillary systems, that is, systems where surfaces are important. Examples of such systems include those where the surface to volume ratio is high and those containing colloidal and other disperse phases. Most systems involving solids are, in fact, capillary systems, because any interaction between the bulk solid and the remainder of the system takes place via the surface region, convection effects being precluded. The thermodynamics of the surface region plays a greater role for solids than for liquids. It is surprising therefore, but regrettably true, that solid surface thermodynamics is inadequately dealt with in most standard texts. Further, at the present time, knowledge of the physical and chemical behavior of solid surfaces has outstripped general understanding of the basic thermodynamics of this region. Commercial instruments have become available for a wide variety of techniques. Low-energy electron diffraction, Auger electron spectroscopy, x-ray and UV photoelectron spectroscopy, secondary ion mass spectrometry, and other surface analytical probes have enabled the solid surface to be studied in intimate detail. Considerable advances in areas of academic and industrial importance such as catalysis, solid–solid reactions, alloy behavior, powder sintering, and electronic device behavior have resulted from experimental studies using these techniques.

These advances in surface experimentation have not been

accompanied, however, by a corresponding increase in understanding of the thermodynamics of the solid surface region on the part of all surface scientists. Even those who are conversant with surface thermodynamics may not be fully aware of the quiet progress in this area that has accompanied the more spectacular advances in the experimental field. The subject has been clarified conceptually by two recent developments, the increasing use of the *Kramers energy function* and the introduction of the *generalized surface function*. These have enabled a number of apparently disparate equations to be unified and consequently the whole subject to be simplified. They have also made it less difficult to grapple with the question of which surface thermodynamic parameter is measured by a particular thermodynamic experiment.

The purpose of this review is to set out the thermodynamics of solid surfaces simply and concisely, taking advantage of recent theoretical advances. With honorable exceptions, the treatment of solid surface thermodynamics in textbooks is often brief, sometimes ambiguous, and occasionally misleading. It is not part of the aim of this paper to deal in depth with experimental thermodynamic techniques or calculation of solid surface thermodynamic properties as these topics have been reviewed elsewhere.<sup>1–8</sup> The effects of adsorption and of orientational dependence have also been covered recently<sup>5</sup> and will not be dealt with here.

An understanding of the thermodynamics of solid surfaces is of importance to all surface scientists. It is hoped that this is not without interest for the general reader, because thermodynamics is the study that relates quantities that can easily be measured to different quantities that are needed for the purposes of understanding or calculation. Consequently some emphasis has been given to elucidating which parameter is actually measured by a variety of experimental techniques.

The approach to the derivation of thermodynamic equations is only one of several that could have been used. In particular, no attempt has been made to incorporate a statistical mechanical treatment as exemplified, for example, by the work of Buff.<sup>9</sup> Although there are many advantages to such a treatment, it is conceptually and mathematically simpler to consider a macroscopic approach. Certainly when dealing with the use of thermodynamic equations for calculation and understanding, there is much to commend the comment of Hildebrand<sup>10</sup> that "it may be less 'correct' but more accurate to use macroscopic parameters to describe macroscopic properties, rather than integrating uncertain interatomic properties over an imprecise distribution function."

This article also does not deal with the irreversible thermo-

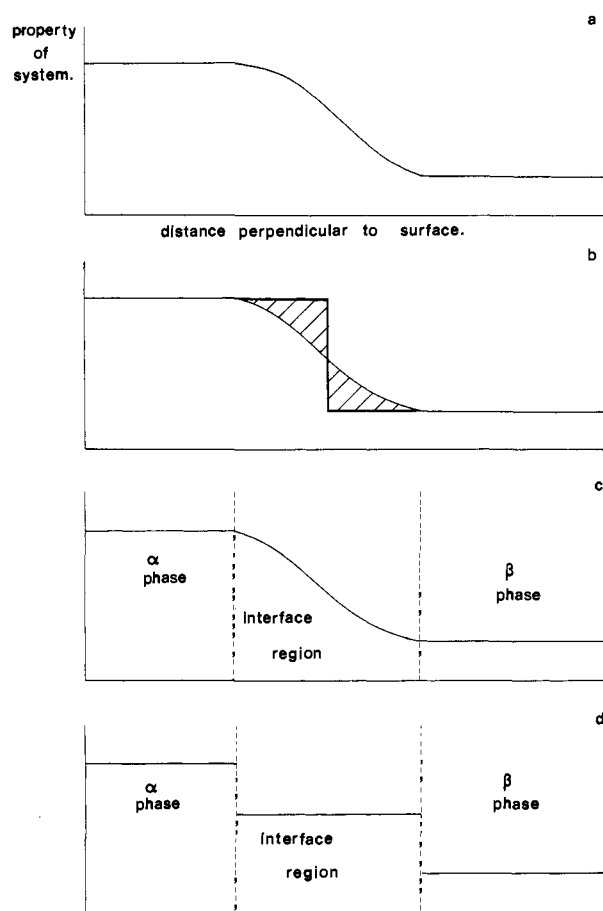


Figure 1.

dynamics of the surface region. Such an approach, which has been applied with considerable success by Defay and his co-workers<sup>11</sup> especially to adsorption problems, explicitly treats the entropy production terms which are the central quantities of any irreversible formulation. It differs from the presentation given here not only in using entropy rather than Kramers energy as the basic parameter but, more importantly, by utilizing the concept of local equilibrium of the surface region. This leads to a problem, described as "non-autonomy", which arises because the surface thermodynamic properties then depend not only on surface region compositions but also on those in the surrounding bulk phases. Defay overcomes this with the device of "cross chemical potentials", which are the partial derivatives of the surface energy with respect to component concentrations, not in the surface region but in the adjacent bulk phases. These are calculated from molecular models.

It should be noted that, in the approach used in this article, the use of the Kramers function modifies the definitions of enthalpy and Gibbs energy that are customary in bulk thermodynamics. This is discussed in detail below (section II.B.2).

## II. Surface Thermodynamic Parameters

The surface thermodynamics of liquid or solid systems requires a more detailed description of mechanical parameters than is normally demanded in the thermodynamics of bulk systems; use of the Kramers energy function is felt to be the simplest approach to fulfilling this requirement. For solid systems there is an additional complication, first noted by Gibbs,<sup>12</sup> that the work required to create unit area of surface by cleavage differs from the work required to form unit area by stretching. Consequently, more than one parameter is required but recent work<sup>13,14</sup> has ingeniously circumvented some of the difficulties arising from the presence of two parameters by proposing a

single path-dependent parameter, the generalized surface energy function.

In this section, the definition and properties of these parameters will be set out, but it is necessary first to clarify certain terms that will be used subsequently in describing the solid surface.

## A. The Solid Surface

### 1. Topography and Surface Area

With few exceptions, such as mica, solid surfaces are not flat. The superficial area, as represented by the product of the length and breadth of a rectangle enclosing part of a surface, is not the same as the actual surface area which takes into account the areas of the hills and valleys within the rectangle. If the surface is very rough, with very pronounced and irregular asperities, the superficial area is considerably smaller than the actual area. Such a surface is unlikely to be in a state of equilibrium and caution should be exercised when considering systems containing such surfaces. The properties of a portion of surface are dependent on orientation, and if there are many portions of different orientation, correct summation over the whole surface may be a difficult task.

Consideration will be restricted here to systems in which the difference between superficial and actual areas is not of overriding importance and, *unless otherwise stated, the area,  $\Omega$ , will refer to superficial, not actual, area*. This complication is not always dealt with in standard texts because they tend to concentrate on the surface thermodynamics of liquid systems which usually possess smooth surfaces.

### 2. Types of Surface

A surface does not exist in isolation. It is the interface region in a two-phase system and *valid thermodynamic conclusions can only be drawn by considering the system, namely, the interface and the two bordering regions, as a whole*.

There are many types of surface. *External surfaces* include those found in liquid-gas, liquid-vapor, solid-vapor, solid-(vapor + gas), and solid-vacuum systems. The last category might initially appear a surprising inclusion in a thermodynamic article concerned with systems in equilibrium, as one would expect a solid to be accompanied by its own vapor, even in the absence of other components. Certain substances such as tungsten, however, have such a low vapor pressure that, at room temperature, the whole of the earth's atmosphere is insufficiently large in volume to contain a single atom of vapor and consequently in these cases it is meaningful to consider a system where the solid is truly bounded by vacuum. *Internal surfaces* are those within the dense bulk phases of the system and include liquid-liquid, solid-liquid, and solid-solid interphase boundaries, and special cases of the last category such as grain boundaries. A complicated system may well include more than one type of surface.

Satisfactory treatments of liquid-gas and liquid-vapor systems are given in many standard texts, e.g., Adamson<sup>15</sup> and Lewis and Randall;<sup>16</sup> solid-liquid systems have been discussed by Chadwick<sup>17</sup> and grain boundary energies have also been reviewed.<sup>2,18,19</sup> This article therefore concentrates in its treatment on solid-vapor, solid-(vapor + gas), and solid-vacuum systems.

### 3. Gibbs Dividing Surfaces and the Guggenheim Surface Region

Many properties of a system, for example, concentration of a particular species, vary as a function of the distance perpendicular to the surface, as shown in Figure 1a. Gibbs<sup>12</sup> found it mathematically convenient to consider an idealized system, depicted in Figure 1b, with properties identical with those of the

whole real system. The "surface of discontinuity" or "dividing surface" in the idealized system is a two-dimensional region whose position is determined by the requirements that the property under consideration should maintain a uniform value in each bulk phase right up to the dividing surface. This corresponds to equating the two shaded areas in Figure 1b. A disadvantage of this approach is that the position of the dividing surface alters according to the property considered. This is of particular importance when considering adsorption.<sup>5,15</sup>

An alternative approach is that of Guggenheim;<sup>20</sup> here the surface is visualized as a region possessing thickness and hence volume, the boundaries of which lie at the positions where the actual bulk phase properties cease to be uniform, as shown in Figure 1c. In this approach two dividing surfaces, one at each boundary, are in fact employed as revealed in Figure 1d. A further disadvantage is that, in principle, terms dependent on surface volume are present in the equations, but it is difficult to assign values to these terms. This was of greater importance before the discovery of the modern surface analytical techniques mentioned in the introduction than it is now.

A more detailed discussion of the relative merits of the Gibbs and Guggenheim approaches together with an alternative formalism of Goodrich,<sup>21</sup> has been given elsewhere.<sup>5</sup> It is perhaps true to say that consideration of the relative niceties of the alternative dividing surface approaches has less bearing on the solid surface region than the giving of proper weight to decisions as to the correct surface parameter to use in a particular situation.

The approach used here roughly follows that of Guggenheim in considering a closed system shown in Figure 2 and consisting of a denser phase (denoted by superscript  $\alpha$ ) separated from a less dense phase (superscript  $\beta$ ) by a three-dimensional surface region (superscript  $\pi$ ); terms involving the surface volume  $V^\pi$  or the thickness of the surface phase,  $\delta$ , are usually neglected.

#### 4. Surface Excess Quantities

An extensive property,  $X$ , of the closed system shown in Figure 2 may be apportioned into three parts, one for each region of the system

$$X = X^\alpha + X^\beta + X^\pi \quad (1)$$

The quantity  $X^\pi$  is referred to as the *surface excess* of  $X$ . For example, the surface excess amount of substance of the  $i$ th component,  $n_i^\pi$ , is by definition

$$n_i^\pi = n_i - n_i^\alpha - n_i^\beta \quad (2)$$

where the lack of a superscript denotes the value of the property for the whole system.

#### 5. Superficial Quantities

A superficial quantity,  $x^\pi$ , is a surface excess quantity,  $X^\pi$ , per unit area  $\Omega$ , the area being the superficial area as defined in section II.A.1. Thus the superficial Helmholtz energy,  $a^\pi$ , is defined as

$$a^\pi = \frac{A^\pi}{\Omega} = \frac{(A - A^\alpha - A^\beta)}{\Omega} \quad (3)$$

The use of the symbol  $\Omega$  for area is to preserve the internationally agreed symbol,  $A$ , for Helmholtz energy. The whole question of nomenclature and symbolism in this field leaves much to be desired.<sup>22,23</sup> With the exception of amount of substance, upper case letters here denote surface excess parameters, and lower case letters are used for superficial quantities. In order to retain a symbol originally proposed by Gibbs, the superficial amount of substance of the  $i$ th component,  $n_i^\pi/\Omega$ , is denoted by  $\Gamma_i$ , and by convention  $\Gamma_1$  is the superficial concentration of the major

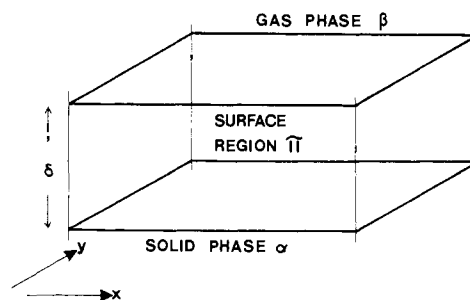


Figure 2.

component of the whole system. Because surface segregation of minor impurities from the bulk is of great importance in solid systems,  $\Gamma_1$  may well be much smaller than the values of  $\Gamma_i$  for some of the impurities, although in the bulk solid phase  $\alpha$ , component 1 completely predominates.

Superficial quantities have also been called<sup>4,5,8,23</sup> specific surface quantities. From their definition it can be seen that they are functions of the properties of the whole system rather than of the surface region alone.

#### 6. Elastic and Plastic Surface Strains

If one distorts the surface of a liquid, there is no barrier to prevent molecules from entering or leaving the surface. A new state of equilibrium can be reached, in which each surface molecule covers the same area as in the original undistorted state. The number of molecules in the surface region has changed, but the area per surface molecule has not. The surface strain,  $d\epsilon$ , i.e., the change in surface area per unit area, is said to be *plastic* in this case; plastic strains can also arise in solids near their melting points.

In the presence of long-range order, for example, in a solid far from its melting point, a distortion of the surface can be thought of as resulting in a change of area which cannot be accommodated by migration of atoms to and from the surface. While the distortion persists the number of molecules in the surface region therefore remains constant but the area occupied by each molecule differs from that in the undistorted case. Such a surface strain is said to be *elastic*.

If the stress causing a plastic strain is removed, the original state is regained by change in the number of molecules at the surface, whereas if an elastic strain is removed, the area occupied by each molecule returns to its original value, no migration taking place. It can be seen that the work required per unit area to produce new surface under plastic strain conditions is independent of the new area formed, because the new area is similar in nature to the existing area. Under elastic strain conditions, the work required is a function of area formed, because the greater the area formed, the greater the deviation from equilibrium intermolecular lattice spacing at the surface.

The above is a summary of what may be termed the historical approach to the subject, which is dealt with in detail elsewhere.<sup>4-8,24-27</sup> A more persuasive approach is to regard elastic and plastic strains as extreme cases of a generalized strain, in much the same way as ionic and covalent bonds may be considered as limiting descriptions of electron distribution between pairs of atoms. This idea has been developed by Couchman, first as a student in the school of Kuhlmann-Wilsdorf,<sup>28,29</sup> and subsequently in collaboration with Everett,<sup>13,14</sup> and is discussed in detail later (section III.B; section IV.A).

#### 7. Stretching and Cleavage

Gibbs<sup>12</sup> pointed out that when considering the interface between two perfectly fluid masses "the work spent in increasing the surface infinitesimally by stretching is identical with that which must be spent in forming an equal infinitesimal amount

of new surface. But when one of the masses is solid, and its states of strain are to be distinguished, there is no such equivalence between the stretching of the surface and the forming of new surface." He elaborated on the difference for solids between stretching and forming a surface or interface in the following words. "Let us consider a thin plane sheet of a crystal in a vacuum (which may be regarded as a limiting case of a very attenuated fluid), and let us suppose that the two surfaces of the sheet are alike. By applying the proper forces to the edges of the sheet, we can make all stress vanish in its interior. The tensions of the two surfaces are in equilibrium with these forces, and are measured by them. But the tensions of the surfaces, thus determined, may evidently have different values in different directions, and are entirely different from the quantity which we denote by  $\sigma$ , which represents the work required to form a unit of the surface by any reversible process, and is not connected with any idea of direction."

The work required to form unit area of new surface,  $\sigma$ , is a scalar quantity and is called the *superficial work*; it has previously been named the specific surface work,<sup>4,5,8,23</sup> the surface energy,<sup>30,31</sup> the surface tension,<sup>6,7,25,26</sup> and the surface free energy.<sup>1,2,21,24,27</sup> The analogous quantity that applies in a stretching situation is tensorial in nature and is here called the *surface stress*  $\Upsilon_{ij}$ ; other workers<sup>6-8,25,26,28,29</sup> have employed the same name but some<sup>1,2,24,27</sup> have preferred to use surface tension to refer to this parameter. It is clear that the name "surface tension" is unsafe to use when applied to solid surfaces; for liquid surfaces, on the other hand, where stretching, which can be an elastic process, is indistinguishable (at low rates of distortion) from cleavage, essentially a plastic process, the quantities  $\sigma$  and  $\Upsilon_{ij}$  are identical and the customary name "surface tension" is quite unambiguous.

## B. The Kramers Energy Function

### 1. Definition

Much early controversy revolved around the question of whether  $\sigma$  was identical with the superficial Helmholtz energy  $a^\pi$ , and if not whether  $\sigma$  or  $a^\pi$  was the appropriate parameter to use in a number of classical surface thermodynamic equations. A thorough discussion is given by Johnson.<sup>32</sup> Such a problem never arises if Herring's approach,<sup>7</sup> in which the superficial work is identified with the superficial Kramers energy, is employed.

It is unlikely that the general reader will have previously encountered the Kramers energy, also called the Legrand function or mechanical work function, and it is therefore worthwhile to discuss its origin. We begin with the definition of the internal energy,  $U$  of a reversible system in terms of heat,  $q$ , and work  $w$

$$dU = dq - dw \quad (4)$$

Both  $q$  and  $w$  are path dependent and are here defined for a reversible path. Equation 4 is a statement of the first law of thermodynamics; by combination with the second law

$$dS = dq/T \quad (5)$$

where  $S$  is entropy and  $T$  is temperature,

$$dU - TdS = dA = -dw \quad (6)$$

which always serves as a definition of the Helmholtz energy,  $A$ .

It is invariably helpful to divide the work,  $-dw$ , into two portions, which are normally the physico-chemical work  $\sum \mu_i dn_i$  (where  $\mu_i$  and  $n_i$  are the chemical potential and amount of substance of the  $i$ th species) and the work of expansion,  $-PdV$ , where  $P$  is pressure. Thus

$$dA = \sum \mu_i dn_i - PdV \quad (7)$$

and hence

$$dA + PdV = \sum \mu_i dn_i = dG \quad (8)$$

which normally serves as a definition of the Gibbs energy.

In the case of systems in which work other than work of expansion and physico-chemical work is involved, the definition of the Gibbs energy becomes ambiguous. Let us involve other terms, for example: (a) electrochemical work  $EdQ$ , where  $E$  is the potential and  $Q$  is the total charge; (b) magnetic work  $H^m dM$ , where  $H^m$  is the field strength and  $M$  the magnetization; (c) gravitational work  $\rho g dx$ , where  $\rho$  is the density,  $g$  the acceleration due to gravity, and  $x$  the vertical displacement; (d) surface work  $\gamma^s d\Omega$ , where  $\gamma^s$  is a symbol chosen so as not to preempt a decision as to whether  $\sigma$  or  $\Upsilon_{ij}$  would be appropriate, and  $\Omega$  is, as usual, area.

Now, we divide the work into two portions as before; to do this we must decide the essential attributes pertaining to each portion. In eq 7, the first portion, in that case solely the physico-chemical work term, was useful in the context of a chemical reaction whereas the second portion, the work of expansion, although capable of being harnessed by an appropriate machine, was an expender of energy *in the context of a chemical reaction*. A working criterion for deciding in which of the two categories a given work term belongs is that the first category contains work terms useful in the context of a chemical reaction and the second contains terms of a more mechanical nature. Thus

$$-dw = -dw_{\text{useful}} - dw_{\text{mechanical}} = dA \quad (9)$$

where

$$-dw_{\text{useful}} = (\sum \mu_i dn_i + EdQ) = dG \quad (10)$$

and

$$-dw_{\text{mechanical}} = (-PdV + \gamma^s d\Omega + H^m dM + \rho g dx) = d\Psi \quad (11)$$

Thus, combining eq 9, 10, and 11

$$dA = dG + d\Psi \quad (12)$$

which, with eq 11, serves to define the *Kramers energy or mechanical work function*  $\Psi$ .

The allotting of certain terms such as the magnetic work and the electrochemical work is, to an extent, dependent on circumstances; if, for example, in a particular situation the former can be harnessed within the context of a chemical reaction, then the term  $H^m dM$  belongs in eq 10 rather than eq 11.

Integration of eq 12 gives the relation

$$\Psi = A - G \quad (13)$$

### 2. Modification of Definition of Enthalpy and Gibbs Energy

The Gibbs energy function is defined in this formalism by eq 10 and 13, which differ but little from the normal definition, eq 8. A problem arises when considering enthalpy  $H$ , normally defined by the two following equations

$$H = U + PV \quad (14)$$

$$H = G + TS \quad (15)$$

For the simple situation where eq 6 and 8 are true, eq 14 and 15 are both valid. In the presence of other work terms such as (a) to (d) above, either eq 14 or eq 15 must be untrue. It has been found more helpful to retain eq 15 as a definition and to discard eq 14 in the general case. Thus, eq 15 serves as a definition of enthalpy, and in combination with eq 13 gives

$$H = A - \Psi + TS \quad (16)$$

which with the integral of eq 6 gives

$$H = U - \Psi \quad (17)$$

Combining eq 17 with the integral of eq 11

$$H = U + PV - \gamma^s \Omega - H_M^m - \rho gx \quad (18)$$

A useful formalism to distinguish between the "conventional" definitions of  $G$  and  $H$  applicable to simple systems, and the wider definitions set out here, has been proposed by Prigogine, Defay, et al.<sup>33</sup> They use

$$G = U - \Psi - TS = H - TS \quad (19)$$

but

$$G' = U + PV - TS = H' - TS \quad (20)$$

giving

$$G' = G + \Psi' \text{ and } H' = H + \Psi'$$

where

$$\Psi' = \Psi + PV \quad (21)$$

This point has also been discussed by Barnes.<sup>34</sup>

Occasionally,<sup>35</sup> an open system comprising bulk solid phase plus the surface region, which can exchange both energy and material with the surroundings, is employed in considering adsorption. Here a parameter, the open system energy function,  $J$ , is used where

$$J = U - \sum n_i \mu_i \quad (22)$$

so that, from eq 8 and 19

$$\Psi = J + TS \quad (23)$$

The above is also compatible with the definition of enthalpy,  $H$ , as being the sum of the internal energy  $U$  and the "external energy",  $Y$ , the latter arising from coupling with external mechanical forces.<sup>36</sup>

To summarize, eq 6, 9–13, and 15–19 are universally valid and will be used in this work, eq 7, 8 and 14 are not universally valid and will not be used here, and eq 20 and 21 are correct but will not find further application in this paper.

### C. Definition of Surface Thermodynamic Parameters

It is only after the above preliminary considerations that it is possible to give definitions of the major surface thermodynamic parameters. Even at this stage the reasons for some of the constraints stated in the definitions will not be obvious. These will become clear in section III, and it was felt helpful to approach that section with some informed precognition of the terms employed!

#### 1. Superficial Work, $\sigma$

The superficial work,  $\sigma$ , is identical with the superficial Kraemer energy

$$\sigma \equiv \psi^\pi \quad (24)$$

where

$$\psi^\pi = \frac{\Psi}{\Omega} = \frac{A^\pi - G^\pi}{\Omega} = \frac{(A - A^\alpha - A^\beta)}{\Omega} - \frac{(G - G^\alpha - G^\beta)}{\Omega} \quad (25)$$

as described in sections II.A.4 and II.A.5.

As will be seen from section III.C.2, the superficial work may be defined as the reversible work at constant temperature, electric field, chemical potential, and elastic strain required to form unit area of new surface. It is a scalar quantity.

#### 2. Surface Stress, $\hat{\Gamma}_{ij}$

The surface stress is the reversible work required to form unit area of new surface by stretching with a linear stress, or a force

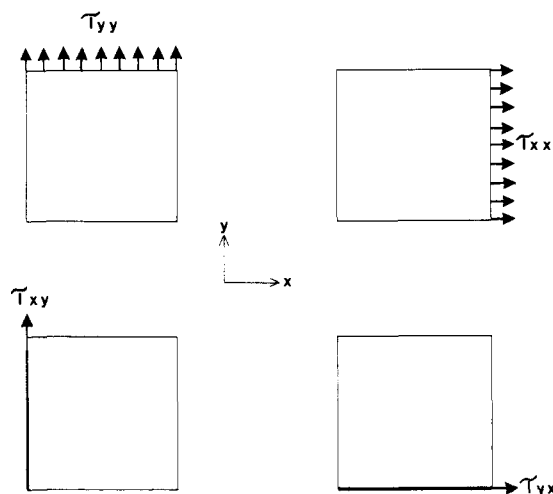


Figure 3.

per unit length, acting in the  $j$ th direction on an edge normal to the  $i$ th direction,  $i$  and  $j$  being in the plane of the surface, and conditions of constant temperature, electric field, and chemical potential applying. It is a tensorial quantity; for those unfamiliar with tensorial notation, reference to Figure 3 may be helpful.

For an isotropic solid, the directional dependence of the surface stress disappears, and in this case the surface stress becomes  $\hat{\Gamma}$ , the half-sum of the diagonal components of the surface stress tensor. The relationship between surface stress and superficial work will be discussed in sections III.B.1 and III.B.3.

#### 3. The Generalized Surface Intensive Parameter, $\gamma^s$

This is a superficial tensorial property<sup>14</sup> which is conjugate to the general (part plastic and part elastic) surface area change, and may be formally defined in terms of the superficial work,  $\sigma$ , and surface stress,  $\hat{\Gamma}$ , by the equation

$$\gamma^s = \frac{d\epsilon_p}{d\epsilon_{tot}} \sigma + \frac{d\epsilon_e}{d\epsilon_{tot}} \hat{\Gamma} \quad (26)$$

where  $d\epsilon_p$ ,  $d\epsilon_e$  are the plastic and elastic contributions to the total strain  $d\epsilon_{tot}$ .

It is of great conceptual use, as will be seen in connection with equations derived from the Gibbs–Duhem relation for a surface region. It is accurately but unmemorably named; a preferable alternative might well be the simple form "surface energy". This latter name is customarily used by metallurgists and materials scientists to denote some form of surface parameter. It is not unfair to say that they are often unclear as to precisely which parameter ( $\sigma$ ,  $a^\pi$ ,  $\hat{\Gamma}$ , etc.) they intend the term to refer, and  $\gamma^s$  would be as appropriate as any other alternative. Consequently the name "surface energy" will be used for  $\gamma^s$  in the remainder of this article. The relationship between surface energy and other parameters will be discussed in section III.

#### 4. Surface Free Energy, $a^\pi$

As is customary, this name will be given to the superficial Helmholtz energy,  $a^\pi$ , which has already been defined by eq 3. The surface free energy is related to the superficial work,  $\sigma$ , by the fundamental surface thermodynamic equation

$$\sigma = a^\pi - \sum \mu_j \Gamma_j - E q^\pi \quad (27)$$

the derivation of which is given in section III.C.1. The surface free energy is not an important parameter in solid systems.

#### 5. Surface Tension

As has been mentioned in section II.A.7 above, it is the present author's opinion that this name should not be used for

solid surface parameters as it has been variously used for both  $\sigma$  and  $\Upsilon_{ij}$ . As terminology in this field has not yet been authoritatively established, however, it is possible that in the future the use of the name "surface tension" for  $\gamma^s$  may be suggested, as an alternative to the present usage, "generalized surface intensive parameter" or "surface energy". The problem of differentiating between the name and the parameter that it denotes has been discussed elsewhere,<sup>23</sup> in terms of the distinction, analyzed in the White Knight's song in "Through the Looking Glass"<sup>37</sup> between the name of the song and the song itself.

For liquids, the term "surface tension" is not without its complications. In experiments such as the ripple method, it has been suggested<sup>25</sup> that more than one parameter is required on mechanical grounds. In less esoteric situations, it is also true that two parameters are necessary, but for compositional rather than mechanical reasons. Thus, one may carry out experiments on a static, reproducible liquid system in which complete equilibrium has been achieved throughout, so that the superficial excess concentration terms,  $\Gamma_1$ ,  $\Gamma_2$ , etc., assume their equilibrium values. The parameter in eq 27 is then the *equilibrium surface tension* and is clearly not equal to the surface free energy, unless (a) the term  $Eq^\pi$  is zero; (b) there is no elastic strain (section IV.A.1); and (c) the system contains but one component, and a dividing surface for which  $\Gamma_1 = 0$  is chosen; or (d) in a multicomponent system, a dividing surface for which  $\sum \mu_i \Gamma_i = 0$  is chosen.

One may also carry out experiments on an alternative system in which the surface is created and studied so rapidly that compositional equilibrium is not achieved. In such a dynamic system, the surface has the composition of bulk phase  $\alpha$ , and  $\sigma$  in eq 27 is equated to  $\sigma_{dyn}$ , the *dynamic surface tension*. If now (a) the term  $Eq^\pi$  is zero and (b)  $n_i^\alpha \gg n_i^\beta$  so that  $n_i \simeq n_i^\alpha$ , and/or (c)  $n_j^\beta \gg n_j^\alpha$  so that  $n_j \simeq n_j^\beta$ , and consequently  $\Gamma_i = \Gamma_j = 0$  for all  $i$  and  $j$  then, from eq 27

$$\sigma_{dyn} = a^\pi \quad (28)$$

which means that under certain conditions for liquid systems the surface free energy can be determined.

For solid systems, the distinction between equilibrium and dynamic properties cannot be made on compositional grounds alone, as the mechanical considerations concerned with cleavage and stretching assume a great importance.

## 6. Other Surface Thermodynamic Parameters

It is, of course, possible to define superficial and surface analogues of all the conventional extensive thermodynamic parameters; thus

$$u^\pi = \frac{U^\pi}{\Omega} = \frac{U - U^\alpha - U^\beta}{\Omega} \quad (29)$$

where  $u^\pi$  and  $U^\pi$  are the *superficial internal energy* and the *surface internal energy*, respectively. Care must be taken not to confuse  $U^\pi$  with the surface energy, or generalized surface intensive parameter,  $\gamma^s$ , defined above. Further

$$h^\pi = \frac{H^\pi}{\Omega} = \frac{H - H^\alpha - H^\beta}{\Omega} \quad (30)$$

where  $h^\pi$  and  $H^\pi$  are the *superficial enthalpy* and *surface enthalpy*, respectively.

From eq 17, it can be seen that

$$h^\pi = u^\pi - \sigma \quad (31)$$

The *superficial entropy* and *surface entropy* are defined as

$$s^\pi = \frac{S^\pi}{\Omega} = \frac{S - S^\alpha - S^\beta}{\Omega} \quad (32)$$

and, as expected

$$a^\pi = u^\pi - Ts^\pi \quad (33)$$

and

$$g^\pi = h^\pi - Ts^\pi \quad (34)$$

It is possible to relate  $S^\pi$  to independently measurable heat capacities. If  ${}^\pi C_p(T)$  denotes the heat capacity of a finely divided sample, then

$$(S^\alpha + S^\beta + S^\pi) - S_0 = \int_0^T {}^\pi C_p(T) \frac{dT}{T} \quad (35)$$

where  $S_0$  is the residual entropy at absolute zero.

If  ${}_0C_p(T)$  denotes the heat capacity for another solid sample identical in all respects to the first except that the surface area is minimized, then

$$(S^\alpha + S^\beta) - S^0 = \int_0^T {}_0C_p(T) \frac{dT}{T} \quad (36)$$

so that

$$S^\pi = \int_0^T \Delta_0^\pi C_p(T) \frac{dT}{T} \quad (37)$$

where

$$\Delta_0^\pi C_p(T) = {}^\pi C_p(T) - {}_0C_p(T) \quad (38)$$

In a similar manner

$$h^\pi - (h^\pi)^0 = \frac{1}{\Omega} \int_T^{298.15} \Delta_0^\pi C_p(T) dT \quad (39)$$

where  $(h^\pi)^0$  is the standard superficial enthalpy, namely  $h^\pi$  at  $T = 298.15$  K and  $P = 101325$  Pa.

Surface parameters of a rather different nature include the following.

### a. The Effective Fracture Surface Energy, $\gamma_{EFSE}$

This applies to an experimental situation in which a block of material is cleaved by initiating and subsequently propagating a crack. Initiation can be achieved by spark machining or cutting with a blade, propagation by pulling on either side of the crack with a tensile testing machine or similar device. The work needed to propagate the crack can be measured; this work is utilized in two ways: firstly to form the two new surfaces for which an energy of  $\sigma$  per unit area is required and, secondly, and indeed predominantly, for plastic deformation around the crack tip.  $\gamma_{EFSE}$  is defined<sup>38</sup> as the energy expended in such an experiment per unit area of surface formed at constant temperature. Numerically it is much larger than  $\sigma$ .

### b. The Surface Layer or Cuticular Energy

This parameter is uniquely used by Bikerman.<sup>39</sup> It is difficult to do justice to his pungently expressed and idiosyncratic views which include repudiation of the majority of the concepts and definitions conventionally used in this subject. The interested reader is referred to his undeniably stimulating paper for further consideration of this parameter.

### c. The Heat of Adsorption

When a gas or vapor is adsorbed on a surface, the energy of the system changes as a function of coverage. This energy change can be expressed<sup>15</sup> as a differential or an integral quantity and is of great importance in adsorption studies, but detailed consideration is outside the scope of this article.

### d. The Surface Pressure, $\Pi$

The surface pressure<sup>15</sup> is the difference between the surface energy of a solution and the surface energy of the solvent. It is very useful in the surface thermodynamics of liquid systems, but plays a much smaller role in the solid systems discussed here. It is possible to construct surface pressure-area isotherms for

surface liquid film formation, and Barnes<sup>34</sup> has shown that the integral  $\int \Pi d\Omega$  is related to the quantity  $-\Delta G'$  defined in eq 20, whereas  $\int \Omega d\Pi$  is related to  $\Delta G$ .

Further surface parameters such as the disjoining pressure, which are of utility in such fields as colloidal systems, adhesion, and thin film studies, are also reviewed by Barnes.<sup>34</sup>

#### e. Surface Elasticity Modulus, $E^\pi$

As will be seen in a later section (III.B.1), the superficial work  $\sigma$  and the mean surface stress  $\Upsilon$  are related by the Shuttleworth equation

$$\Upsilon = \sigma + \Omega \frac{d\sigma}{(d\Omega)_e} = \sigma + \frac{d\sigma}{d \ln \Omega} = \sigma + E^\pi \quad (40)$$

The quantity,  $d\sigma/d \ln \Omega \equiv E^\pi$ , the surface elasticity modulus, is of considerable use in the study of surfactant solutions<sup>40</sup> and colloidal systems<sup>34</sup> and is a major stability parameter in irreversible surface mechanics of solid systems, but considerations of space preclude detailed consideration here.  $E^\pi$  is sometimes referred to<sup>11</sup> as the Gibbs elasticity. It should be noted that only elastic area changes are involved.

### III. Surface Thermodynamic Equations

Having defined the parameters necessary to describe the thermodynamic behavior of a system containing a solid surface, it is now possible to examine their interrelationships in detail. This section contains a consistent set of derivations of the major surface thermodynamic equations.

#### A. The Gibbs–Duhem Equation for a Surface

The Gibbs–Duhem relation is arguably the major equation of chemical thermodynamics. It is obtained by comparing the fundamental relationship involving the derivative of the internal energy, eq 41, with the integrated Euler relation for the internal energy, eq 42. In bulk-phase thermodynamics, a combination of the first and second laws gives, on ignoring magnetic and gravitational terms

$$dU = TdS + \sum \mu_i dn_i + EdQ - PdV \quad (41)$$

and integration of this relation yields

$$U = TS + \sum \mu_i n_i + EQ - PV \quad (42)$$

Differentiating eq 42 leads to

$$dU = TdS + SdT + \sum \mu_i dn_i + \sum n_i d\mu_i + EdQ + QdE - PdV - VdP \quad (43)$$

and consequently, from eq 41 and 43

$$0 = SdT + \sum n_i d\mu_i + QdE - VdP \quad (44)$$

so that, at constant electric field,  $E$ ,

$$\sum n_i d\mu_i = VdP - SdT \quad (45)$$

which is the normal form of the Gibbs–Duhem equation.

For systems containing surfaces, the predominant difficulty is to decide the nature of the surface terms that should appear in eq 41 and 42. This has been resolved by Everett and Couchman<sup>13,14</sup> who established that the appropriate term for incorporation in eq 41 is  $\gamma^s d\Omega$  whereas the surface term in eq 42 is  $\sigma \Omega$ . Substitution of these terms in eq 41 and 42, and conversion to surface excess quantities by use of eq 1 therefore gives

$$dU^\pi = TdS^\pi + \sum \mu_i dn_i^\pi + EdQ^\pi + \gamma^s d\Omega \quad (46)$$

and

$$U^\pi = TS^\pi + \sum \mu_i n_i^\pi + EQ^\pi + \sigma \Omega \quad (47)$$

so that the surface Gibbs–Duhem relation may be initially ob-

tained, from differentiation of eq 47 and subtraction of eq 46, in the form

$$0 = S^\pi dT + \sum n_i^\pi d\mu_i + Q^\pi dE + \sigma d\Omega + \Omega d\sigma - \gamma^s d\Omega \quad (48)$$

Conversion to superficial quantities may be achieved by dividing by  $\Omega$ , noting that

$$d\Omega/\Omega = d\epsilon_{\text{tot}}$$

where  $d\epsilon_{\text{tot}}$  is the total area strain;

$$0 = s^\pi dT + \sum \Gamma_i d\mu_i + q^\pi dE + \sigma d\epsilon_{\text{tot}} + d\sigma - \gamma^s d\epsilon_{\text{tot}} \quad (49)$$

where the superficial charge,  $q^\pi$ , is defined by

$$q^\pi = \frac{Q - Q^\alpha - Q^\beta}{\Omega} \quad (50)$$

The total strain may be divided into two contributions, the plastic strain  $d\epsilon_p$  and the elastic strain  $d\epsilon_e$ , so that

$$d\epsilon_{\text{tot}} = d\epsilon_p + d\epsilon_e \quad (51)$$

and substituting eq 26 and 51 into eq 49 gives

$$0 = s^\pi dT + \sum \Gamma_i d\mu_i + q^\pi dE + d\sigma + (\sigma - \Upsilon) d\epsilon_e \quad (52)$$

This is a most versatile form of the Gibbs–Duhem equation for a surface, from which three major thermodynamic equations, namely the Shuttleworth equation (section III.B.1), the Gibbs adsorption equation (section III.C.2) and the Lippman equation (section III.A.1) may be immediately obtained.

#### 1. The Lippman Equation

This equation is frequently used in electrocapillarity theory, and follows directly from eq 52 as pointed out by Couchman and Davidson<sup>42</sup>

$$(\partial\sigma/\partial E)_{T,\mu_i,\epsilon_e} = -q^\pi \quad (53)$$

The more conventional form of the Lippman equation involves the quantity  $(\partial\sigma/\partial E)_{T,\mu_i}$  which is related to  $q^\pi$  by

$$(\partial\sigma/\partial E)_{T,\mu_i} = -q^\pi - (\sigma - \Upsilon)(\partial\epsilon_e/\partial E)_{\mu_i,T} \quad (54)$$

The magnitude of the second term is highly uncertain, in view of the difficulty of obtaining unambiguous values of  $\Upsilon$  and also  $(\partial\epsilon_e/\partial E)_{\mu_i,T}$ .

### B. Elastic and Plastic Strain Interrelationships

#### 1. The Shuttleworth Equation

This equation was first derived in a classic paper by Shuttleworth<sup>27</sup> for solids of threefold or greater symmetry. He obtained from a cyclic approach

$$\Upsilon = \sigma + \Omega(d\sigma/d\Omega) \quad (40)$$

As Eriksson<sup>24</sup> originally showed, the final term in this equation should embody a partial derivative; Couchman and co-workers<sup>28,29</sup> also revealed that the strain term was solely elastic in nature. Thus, as can be seen clearly from eq 52

$$\Upsilon = \sigma + (\partial\sigma/\partial\epsilon_e)_{T,\mu_i,E} \quad (55)$$

#### 2. The Couchman–Everett Equation

From eq 49

$$\gamma^s = \sigma + (\partial\sigma/\partial\epsilon_{\text{tot}})_{T,\mu_i,E} \quad (56)$$

which was first derived by Couchman and Everett.<sup>14</sup> Considering eq 26 and 56, eq 55 can be seen to be a limiting case of eq 56, and likewise it is clear that

$$(\partial\sigma/\partial\epsilon_p)_{T,\mu_i,E} = 0 \quad (57)$$

### 3. The Herring–Mullins Equation

This is the tensor equivalent of the Shuttleworth equation and can be derived<sup>7,8</sup> by equating the work required initially to stretch and subsequently to cleave a unit solid cube with the work required to carry out the two processes in the reverse order. This gives, at constant  $T$ ,  $\mu_i$ , and  $E$

$$\Upsilon_{xx} = \sigma + d\sigma/d(\epsilon_e)_{xx} \quad (58)$$

and likewise for the  $yy$  and  $zz$  stretching process. Further, the work required initially to shear and subsequently to cleave a unit cube can be equated to that required to carry out the processes in the reverse order, giving

$$\Upsilon_{xy} = d\sigma/d(\epsilon_e)_{xy} \quad (59)$$

and likewise for  $yz$  and  $zx$  shear processes. Equations 58 and 59 may be combined by using the Kronecker delta function  $\delta_{ij}$  to suppress the  $\sigma$  term in the shear case. This function has the property

$$\begin{aligned} \delta_{ij} &= 1 \text{ if } i = j \\ \delta_{ij} &= 0 \text{ otherwise} \end{aligned} \quad (60)$$

Hence

$$\Upsilon_{ij} = \delta_{ij}\sigma + (\partial\sigma/\partial(\epsilon_e)_{ij})_{(\epsilon_e)_{kl} \neq ij, T, \mu_i, E} \quad (61)$$

which is the Herring–Mullins equation.

The surface energy  $\gamma^s$  is tensorial in nature, and consequently a tensorial equivalent of the Couchman–Everett equation can be derived.<sup>43</sup>

## C. Equations Embodying the Surface Excess Concentration

### 1. The Fundamental Surface Thermodynamic Equation

From eq 24 and 25

$$\sigma = a^\pi - g^\pi \quad (62)$$

Integrating eq 10 for the whole system gives

$$G = \sum \mu_i n_i + EQ \quad (63)$$

and similar equations hold for the solid,  $\alpha$ , and vapor,  $\beta$ , phases

$$G^\alpha = \sum \mu_i^\alpha n_i^\alpha + E^\alpha Q^\alpha \quad (64)$$

$$G^\beta = \sum \mu_i^\beta n_i^\beta + E^\beta Q^\beta \quad (65)$$

For physicochemical and electrochemical equilibrium, the conditions are

$$\mu_i = \mu_i^\alpha = \mu_i^\beta = \mu_i^\pi \quad (66)$$

$$E = E^\alpha = E^\beta = E^\pi \quad (67)$$

Hence

$$G^\pi = \frac{G - G^\alpha - G^\beta}{\Omega} = \sum \mu_i \frac{(n_i - n_i^\alpha - n_i^\beta)}{\Omega} + E \frac{(Q - Q^\alpha - Q^\beta)}{\Omega} \quad (68)$$

Therefore

$$g^\pi = \sum \mu_i \Gamma_i + Eq^\pi \quad (69)$$

and

$$\sigma = a^\pi - g^\pi = a^\pi - \sum \mu_i \Gamma_i - Eq^\pi \quad (70)$$

which is the fundamental surface thermodynamic equation. The conditions under which  $\sigma$  and  $a^\pi$  may be equated have been considered (section II.C.5). It should be noted that if the surface elastic strain is not zero, there is a depletion of material in the surface region. Hence, even for a one-component system,  $\Gamma_1$

is not zero in the presence of an elastic strain, and consequently, even in the absence of the electrochemical term  $Eq^\pi$

$$\sigma \neq a^\pi \text{ if } d\epsilon_e \neq 0 \quad (70)$$

It must be remembered that the choice of dividing surface affects<sup>15,33</sup> the values of  $a^\pi$  and  $\Gamma_i$ .

### 2. The Gibbs Adsorption Equation

From eq 52

$$d\sigma = -s^\pi dT - \sum \Gamma_i d\mu_i - q^\pi dE + (\Upsilon - \sigma)d\epsilon_e \quad (71)$$

which is the full form of the Gibbs adsorption equation. It can now be seen that, as stated in the definition (section II.C.1),  $\sigma$  is a function of  $T$ ,  $\mu_i$ ,  $E$ , and  $\epsilon_e$ .

It is common but incorrect to omit the last two terms of eq 71. A definition of the superficial entropy in terms of the variation of  $\sigma$  with  $T$  immediately follows from eq 71

$$s^\pi = -(\partial\sigma/\partial T)_{\mu_i, E, \epsilon_e} \quad (72)$$

emphasizing a point originally made by Herring<sup>7</sup> that the dependence of  $\sigma$  on temperature, and indeed on chemical potential, should only be measured under conditions of constant elastic strain if the results are to be meaningful.

### 3. The Gibbs Adsorption Isotherm

This takes the general form

$$\Gamma_i = -(\partial\sigma/\partial\mu_i)_{T, E, \epsilon_e, \mu_j \neq i} \quad (73)$$

The superficial excess of component  $i$ ,  $\Gamma_i$ , is related to the coverage of species  $i$ ,  $\theta_i$ , which is adsorbed from the gas or vapor phase. The chemical potential of species  $i$ ,  $\mu_i$ , is related to its partial pressure  $P_i$  and consequently eq 73 is an isotherm similar in nature to the Langmuir, BET, Freundlich, and other adsorption isotherms which also relate  $\theta_i$  to  $P_i$ .

Equation 73 is frequently applied to a particular idealized two-component system consisting of a solid phase  $\alpha$ , entirely composed of component 1 of negligible vapor pressure and a gas or vapor phase  $\beta$ , consisting entirely of component 2 which is insoluble in the solid phase  $\alpha$ , but which can be adsorbed in the surface region  $\pi$ .

Now

$$\mu_2 = \mu_2^0 + RT \ln f_2 \quad (74)$$

where  $f_2$  is the fugacity or escaping tendency of component 2. At low pressure, or for an ideal gas,  $f_2$  equals  $P_2$ , the partial pressure, so that

$$d\mu_2 = RT d \ln P_2 \quad (75)$$

and

$$RT\Gamma_2/P_2 = -(\partial\sigma/\partial P_2)_{T, E, \epsilon_e, \mu_1} \quad (76)$$

It can be seen from eq 76 that the more gas that is adsorbed, the greater the reduction in  $\sigma$ , thus illustrating that adsorption lowers the superficial work and that dirty surfaces have lower values of the superficial work than clean surfaces.

## D. Equations Applying to Curved Surfaces

In what has gone before, it has been implicitly assumed that the surface region is flat. Frequently, however, it is necessary to consider the vapor pressure or solubility of small solid particles, or their behavior on sintering, or the properties of gas or vapor bubbles entrapped in a solid matrix. In situations of this type, it is not permissible to ignore the surface curvature.

### 1. The Laplace Equation

This equation, first derived in 1806 for a liquid–vapor system, relates the hydrostatic pressures inside and outside a bubble to



the bubble radius and to a surface thermodynamic parameter. It probably will not surprise the reader that the correct choice of surface thermodynamic parameter has been a matter of some uncertainty. If one considers a system where the hydrostatic pressure in the solid phase  $\alpha$ ,  $P^\alpha$ , is not equal to the hydrostatic pressure in phase  $\beta$ , then under conditions of mechanical equilibrium, i.e., of constant Kramers energy for the whole system, ignoring changes in gravitational and magnetic work it can be seen from eq 11 that

$$d\Psi = 0 = PdV + \gamma^s d\Omega = -P^\alpha dV^\alpha - P^\beta dV^\beta + \gamma^s d\Omega \quad (77)$$

ignoring the surface volume term. Now, if the volume of the whole system remains constant

$$dV = 0 = dV^\alpha + dV^\beta \quad (78)$$

so that

$$\gamma^s d\Omega = dV^\beta (P^\beta - P^\alpha) \quad (79)$$

which is an analogous equation to that arrived at by Couchman and Jesser<sup>29</sup> from consideration of equilibrium conditions, without recourse to the concept of Kramers energy. The problem is now to ascertain the nature of  $\gamma^s$ . Couchman and Jesser take it as axiomatic that mechanical equilibrium of static systems concerns strain equilibrium solely of an elastic nature, so that

$$\epsilon_{\text{tot}} = \epsilon_e \text{ and } \epsilon_p = 0 \quad (80)$$

hence

$$\gamma_s = \frac{\epsilon_p}{\epsilon_{\text{tot}}} \sigma + \frac{\epsilon_e}{\epsilon_{\text{tot}}} \Upsilon = \Upsilon \quad (81)$$

Their assumption is persuasive, but it is fair to say that it is not adopted by all authors.<sup>44</sup>

Their conclusion is substantiated, however, if one starts from the integrated Euler relationship for the Kramers energy of the whole system, namely

$$\Psi = -PV + \sigma\Omega \quad (82)$$

Differentiating eq 82 gives, on noting that  $V^\pi = 0$

$$d\Psi = 0 = -P^\alpha dV^\alpha - P^\beta dV^\beta - V(dP^\alpha + dP^\beta + dP^\pi) + \sigma d\Omega + \Omega d\sigma \quad (83)$$

If the pressure is assumed to be constant in all regions, so that

$$dP^\alpha = dP^\beta = dP^\pi = 0 \quad (84)$$

then eq 83 reduces to

$$dV^\alpha(P^\alpha - P^\beta) = \sigma d\Omega + \Omega d\sigma \quad (85)$$

But, from the Shuttleworth equation (eq 40)

$$\begin{aligned} \sigma d\Omega + \Omega d\sigma &= \Upsilon d\Omega \\ dV^\alpha(P^\alpha - P^\beta) &= \Upsilon d\Omega \end{aligned} \quad (86)$$

confirming the conclusion reached on combining eq 79 and 81.

The Laplace equation is normally applied to a spherical drop of radius  $r$ , in which case

$$d\Omega/dV^\alpha = 2/r \quad (87)$$

so that

$$\Delta P = P^\alpha - P^\beta = 2\Upsilon/r \quad (88)$$

For a soap bubble, which is a duplex film containing an inner and an outer surface, the difference in pressure between the inside and the outside of the bubble is  $4\Upsilon/r$ .

## 2. The Kelvin Vapor Pressure Equation

The vapor pressure  $P_r$  of small radius solid or liquid particles is greater than the vapor pressure  $P_\infty$  of a flat surface of the same phase and the same composition. To show this, consider a one-component, two-phase system consisting of a spherical drop of radius  $r$  of bulk phase  $\alpha$  surrounded solely by its own vapor in phase  $\beta$ . At equilibrium

$$\mu^\alpha = \mu^\beta \quad (89)$$

and hence

$$d\mu^\alpha = d\mu^\beta \quad (90)$$

Applying eq 44 to the  $\alpha$  and  $\beta$  phases in turn, and ignoring the electrochemical work term  $QdE$

$$d\mu^\alpha = \frac{V^\alpha}{n^\alpha} dP^\alpha - \frac{S^\alpha}{n^\alpha} dT^\alpha = V_m^\alpha dP^\alpha - S_m^\alpha dT^\alpha \quad (91)$$

and

$$d\mu^\beta = \frac{V^\beta}{n^\beta} dP^\beta - \frac{S^\beta}{n^\beta} dT^\beta = V_m^\beta dP^\beta - S_m^\beta dT^\beta \quad (92)$$

where the subscript m denotes mean molar quantities. At thermal equilibrium

$$V_m^\alpha dP^\alpha = V_m^\beta dP^\beta \quad (93)$$

Hence

$$\frac{V_m^\beta}{V_m^\alpha} - 1 = \frac{dP^\alpha}{dP^\beta} - 1 \quad (94)$$

and

$$\frac{V_m^\beta - V_m^\alpha}{V_m^\alpha} = \frac{dP^\alpha - dP^\beta}{dP^\beta} \quad (95)$$

From the Laplace equation, eq 88

$$dP^\alpha - dP^\beta = d(2\Upsilon/r) \quad (96)$$

Hence

$$\frac{V_m^\beta - V_m^\alpha}{V_m^\alpha} = d \frac{(2\Upsilon/r)}{dP^\beta} \quad (97)$$

which is the rigorous form of the Kelvin equation. It may be transferred to a more usual form by making two assumptions identical with those used in deriving the Clapeyron–Clausius equation from the Clapeyron equation. They are:

$$V_m^\beta \gg V_m^\alpha \text{ so that } V_m^\beta - V_m^\alpha \simeq V_m^\beta \quad (98)$$

$$\text{the vapor is ideal, so that } V_m^\beta = RT/P^\beta \quad (99)$$

These in conjunction with eq 97 give

$$RTdP^\beta/V_m^\alpha P^\beta = d(2\tau/r) \quad (100)$$

and on integrating

$$RT/V_m^\alpha \int_{P_r}^{P_\infty} dP^\beta/P^\beta = \int_r^\infty d(2\tau/r) \quad (101)$$

$$P_r/P_\infty = \exp[2\tau V_m^\alpha/RT] \quad (102)$$

which is the Kelvin equation.

A similar equation, with activities or concentrations replacing pressures, governs the relative solubility of a small particle to the bulk material. The greater solubility of small particles is utilized in the coarsening of fine precipitates by digestion. The small particles dissolve, making the solution supersaturated with respect to large particles which then reprecipitate. A similar phenomenon is observed with gases, where nonequilibrium solubility can be observed, either if small gas bubbles are forced into a liquid or small liquid droplets are sprayed into a gas. Because of the surprisingly slow mixing of gases and vapors and

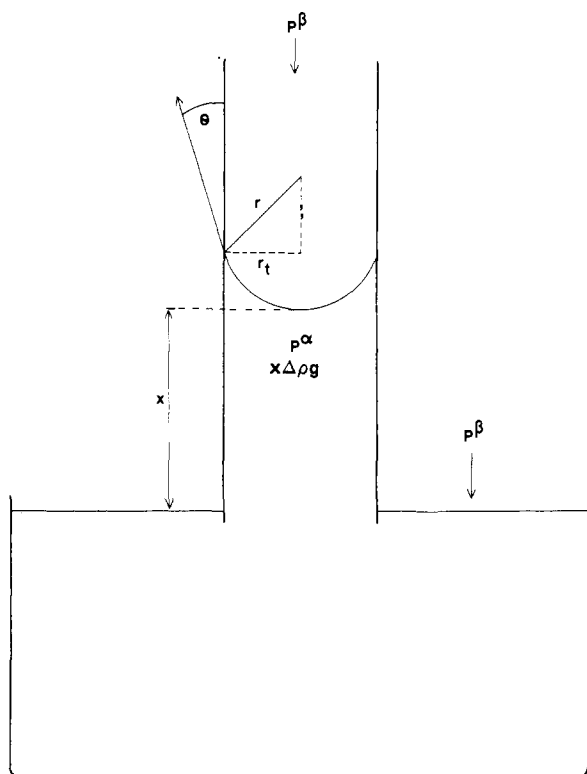


Figure 4.

also the limited diffusion of gases in liquids, anomalous solubilities can persist for several hours.<sup>45</sup>

### 3. The Lattice Contraction Equation

The compressibility of a solid or liquid spherical one-component particle  $k'$  is defined as

$$k' = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \approx -\frac{\Delta V}{V \Delta P} \quad (103)$$

Kuhlmann-Wilsdorf and co-workers<sup>25</sup> related the compressibility to the surface stress for a cubic solid of lattice constant  $a$  by assuming that

$$\Delta V/V \approx 3\Delta a/a \quad (104)$$

where  $\Delta a$  is the difference in lattice constant between that for a system subjected solely to ambient pressure and that for the bulk region of a small particle for which the pressure exceeds ambient by  $\Delta P$ . But  $\Delta P$  is given by the Laplace eq 88, and so

$$\Upsilon = -\frac{3}{2} \frac{\Delta a}{a} \frac{r}{k'} \quad (105)$$

which provides a means of determining  $\Upsilon$ . The contraction is very small; even for a relatively compressible material such as gold, the contraction  $\Delta a/a$  for particles of radius as small as 10 nm is of the order of 0.1%.

### 4. Capillary Rise

This phenomenon is observed in liquid but not solid systems. It is included here for completeness. At a reference surface just above the flat liquid surface shown in Figure 4 the applied pressure  $P^\beta$  is equal to the pressure of liquid in the capillary; this latter is the sum of  $P^\alpha$ , the pressure immediately below the curved surface, radius  $r$ , of the liquid in the capillary, and  $x\Delta\rho g$  where  $x$  is the vertical displacement,  $\Delta\rho$  the difference in densities between the  $\alpha$  and  $\beta$  phases, and  $g$  the acceleration due to gravity. Since  $r$  is related to the tube radius  $r_t$  by

$$r = r_t / \cos \theta \quad (106)$$

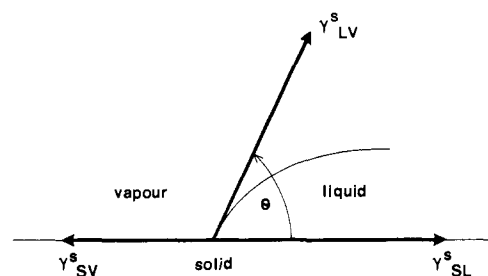


Figure 5.

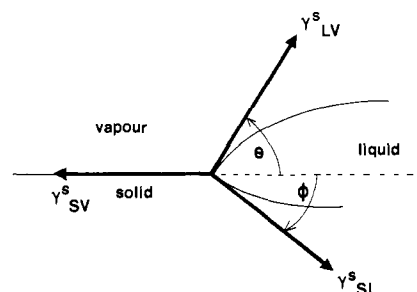


Figure 6.

and

$$P^\beta - P^\alpha = 2\Upsilon/r = x\Delta\rho g \quad (107)$$

Therefore

$$\Upsilon = \frac{x\Delta\rho g r_t}{2 \cos \theta} \quad (108)$$

Corrections for imperfections of meniscus shape can be applied.<sup>15,33</sup>

## E. Equations Concerning Spreading and Wetting

### 1. Young's Equation

This equation was derived by Thomas Young in 1805 and relates the "interfacial tensions" and the contact angle in a three-phase system, comprising a flat solid surface, above part of which is vapor and above another part of which is a liquid drop. The contact angle,  $\theta$ , is defined in Figure 5; it has been studied by statistical mechanics.<sup>46</sup> The interfacial tensions  $\gamma^{s_{SV}}$ ,  $\gamma^{s_{SL}}$ , and  $\gamma^{s_{LV}}$ , relating to the solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively, are classically related to the tensions required to keep the terminating surfaces in equilibrium. One might therefore suppose that they are identical with surface stresses, but all major workers<sup>7,15</sup> write such an equation in terms of superficial work. This is not the only conceptual difficulty surrounding this equation. The derivation is simple, the tensions being resolved horizontally to give

$$\gamma^{s_{SV}} = \gamma^{s_{SL}} + \gamma^{s_{LV}} \cos \theta \quad (109)$$

which is Young's equation. If one resolves horizontally, it can be seen that there is no force component to balance the term  $\gamma^{s_{LV}} \sin \theta$  and the situation appears to be one of partial mechanical equilibrium. If the liquid drop indents into the solid as shown in Figure 6, then eq 109 becomes

$$\gamma^{s_{SV}} = \gamma^{s_{SL}} \cos \phi + \gamma^{s_{LV}} \cos \theta \quad (110)$$

and in addition, by resolving vertically

$$\gamma^{s_{SL}} \sin \phi = \gamma^{s_{LV}} \sin \theta \quad (111)$$

For a further discussion on this point, the reader is referred elsewhere.<sup>5,15,33</sup>

A final conceptual difficulty with the Young's equation relates to the magnitude, if any, of the surface pressure  $\Pi$ . This relates

to the difference between  $\gamma^{s_{SV}}$  for a solid surmounted solely by its own vapor, and  $\gamma'_{sV}$ , the surface energy of a solid in the presence of its own vapor and of the vapor of the components of the liquid drop. Thus  $\gamma'_{sV}$  is the quantity that should appear in eq 109, and hence by substitution

$$\gamma^{s_{SV}} = \gamma^{s_{SL}} + \gamma^{s_{LV}} \cos \theta - \Pi \quad (112)$$

is often helpful to hope that  $\Pi$  is equal to zero.

## 2. Zisman's Equation and Rhee's Method

When a drop of liquid is placed on a solid surface, or indeed on another liquid with which it is immiscible, in some cases the liquid "wets" and spreads over the surface and in other cases it does not. A liquid that wets has a contact angle of zero, and one that forms drops has a contact angle greater than zero.

From a series of experiments, Zisman<sup>47</sup> found many cases of a linear relationship between the cosine of the contact angle and  $\gamma^{s_{LV}}$  for a homologous series of organic liquid drops on polymer solid surfaces. He noticed that, for a given solid surface, different homologous series of liquids gave lines of different slope but that they had the same value of  $\gamma^{s_{LV}}$  at  $\cos \theta = 1$ . He referred to this value, i.e., the surface tension of a hypothetical liquid that had a contact angle of exactly zero, as the *critical surface tension*  $\gamma^c$ . It is clearly a property of the solid surface. Zisman's relationship is

$$\cos \theta = 1 - b(\gamma^{s_{LV}} - \gamma^c) \quad (113)$$

where  $b$ , the slope of the Zisman plot, is characterized by the nature both of the solid surface and of the homologous series.

Rhee<sup>48</sup> related  $\gamma^c$  to  $\gamma^{s_{SV}}$ , the surface energy of the polymer, in the following way. Substituting the Zisman relationship eq 113 into Young's equation, eq 112, and assuming the surface pressure is zero, gives

$$\gamma^{s_{SL}} = \gamma^{s_{SV}} - \cos \theta \left[ \frac{(1 - \cos \theta)}{b} + \gamma^c \right] \quad (114)$$

This shows the parabolic dependence of  $\gamma^{s_{SL}}$  on  $\cos \theta$ . Now

$$\frac{d\gamma^{s_{SL}}}{d(\cos \theta)} = -\frac{1}{b} + \frac{2 \cos \theta}{b} - \gamma^c \quad (115)$$

and from eq 115,  $(\cos \theta)_m$ , the value of  $\cos \theta$  at the minimum, is given by

$$0 = -\frac{1}{b} + \frac{(2 \cos \theta)_m}{b} - \gamma^c \quad (116)$$

Rhee assumed that at the minimum  $\gamma^{s_{SL}}$  was, in fact, zero, an assumption supported by experimental evidence. Hence from eq 114

$$0 = \gamma^{s_{SV}} - (\cos \theta)_m \left[ \frac{(1 - (\cos \theta)_m)}{b} + \gamma^c \right] \quad (117)$$

giving  $\gamma^{s_{SV}}$  in terms of the experimental parameters  $b$  and  $\gamma^c$ . In a later paper Rhee<sup>49</sup> makes use of surface energy temperature dependence, i.e., surface entropy terms, to derive further relationships of this kind.

## 3. The Young-Dupre Equation and the Work of Adhesion

The work of adhesion  $W_{AB}$  between two phases A and B is defined as

$$W_{AB} = \gamma^{s_{AV}} + \gamma^{s_{BV}} - \gamma^{s_{AB}} \quad (118)$$

where AV, BV, and AB refer to the interfaces between the bulk phase A and the corresponding vapor phase, between the bulk phase B and its vapor phase, and between the A and B phases

in intimate contact. In a similar way the work of cohesion,  $W_{AA}$ , is defined as

$$W_{AA} = 2\gamma^{s_{AV}} \quad (119)$$

For a solid-liquid interface, where the subscript A is replaced by S and B by L,

$$W_{AB} = \gamma^{s_{SV}} + \gamma^{s_{LV}} - \gamma^{s_{SL}} \quad (120)$$

and substitution of Young's equation, eq 112, ignoring the surface pressure term, gives

$$W_{AB} = \gamma^{s_{LV}}(1 + \cos \theta) \quad (121)$$

which is the Young-Dupre equation.

## 4. The Spreading Coefficient

Spreading has already been considered in connection with the Zisman relationship. An alternative approach is to note that a liquid will spread on a solid or on the surface of a denser immiscible liquid if the work of adhesion exceeds the work of cohesion. The spreading coefficient  $S_{B/A}$  is then defined as

$$S_{B/A} = W_{AB} - W_{BB} = \gamma^{s_{AV}} - \gamma^{s_{BV}} - \gamma^{s_{AB}} \quad (122)$$

A positive value of  $S_{B/A}$  indicates that B will spread on A. Thus, benzene can be expected to spread on water at 20 °C, because

$$\begin{aligned} S_{\text{benzene/water}} &= \gamma^{\text{s}_{\text{water-water vapor}}} \\ &\quad - \gamma^{\text{s}_{\text{benzene-benzene vapor}}} - \gamma^{\text{s}_{\text{water-benzene}}} \\ &= 72.8 - 28.9 - 35.0 = +8.9 \text{ mJ m}^{-2} \text{ at } 20 \text{ }^\circ\text{C} \end{aligned} \quad (123)$$

Experimentally this is initially found to be the case. After a short time, however, the benzene retracts to form a lens or drop, floating on the liquid surface. This apparently puzzling behavior can be understood when it is realized that benzene and water are not totally immiscible and that mutual saturation occurs. The surface tension values for water saturated with benzene, and benzene saturated with water, then have to be used in eq 123, which gives

$$\begin{aligned} S_{\text{benzene/water}}^{\text{satd}} &= 62.2 - 28.8 - 35.0 \\ &= -1.6 \text{ mJ m}^{-2} \end{aligned} \quad (124)$$

The negative spreading coefficient indicates that spreading will not take place in the saturated system.

Combination of the Young-Dupre equation, eq 121 with eq 122, gives

$$S_{B/A} = \gamma^{s_{LV}} (\cos \theta - 1) \quad (125)$$

which is, of course, meaningful only for negative or zero spreading coefficients. In the case of the former, values of spreading coefficient can be obtained from contact angle measurements.

## IV. Parameters Obtained from Experimental Techniques

Detailed descriptions of the many techniques that have been used to measure the surface energy,  $\gamma^s$ , can be found elsewhere.<sup>2,3,5,30,50-54</sup> It is the intention here to concentrate on elucidating whether it is possible to identify  $\gamma^s$  with either the superficial work,  $\sigma$ , or the surface stress  $\bar{\Gamma}$  for certain prominent techniques. Values of the various parameters for different substances will then be summarized.

### A. Techniques and Parameters

#### 1. Zero Creep Method

This is the most common and most precise method for obtaining data on metal surfaces. Thin metal foils and wires shrink

when maintained at a constant high temperature because of the influence of surface forces. As pointed out by Hondros,<sup>55</sup> this was observed as long ago as 1857 by Faraday, who found that gold foil held between sheets of glass became transparent when hot, and correctly attributed this phenomenon to shrinkage and consequent tearing of the foil. The method depends on finding the tensile load needed exactly to counterbalance the effect of the surface forces, i.e., to produce a condition of zero creep, at which the strain rate is zero.

The first zero creep experiment was carried out in 1910 by Chapman and Porter<sup>56</sup> and subsequent progress has been reviewed by Udin<sup>57</sup> and Hondros.<sup>58</sup> The calculations are complicated by the need to account for grain boundary effects; also a number of practical constraints and necessary assumptions, which are discussed elsewhere,<sup>5</sup> make the experiments less straightforward than they might otherwise be. After making due allowance for grain boundary and other effects, the exactly counterbalancing load, divided by the length along which it acts, can be equated to the reversible work required to form unit area of new surface at constant temperature, chemical potential, and electric field. Following the recent papers of Everett and Couchman,<sup>13,14</sup> this work is the surface energy or the generalized surface energy or the generalized surface intensive parameter,  $\gamma^s$ .

The shrinkage effect manifests itself only when the sample (which, being a foil or wire, has a large surface to volume ratio) is heated to about nine-tenths of its melting point. Under such conditions, it is usually assumed that the strains are purely plastic, and consequently, from eq 26

$$\gamma^s = \frac{d\epsilon_p}{d\epsilon_{tot}} \sigma + \frac{d\epsilon_e}{d\epsilon_{tot}} \Upsilon \quad (26)$$

and since  $d\epsilon_p = d\epsilon_{tot}$ , therefore  $d\epsilon_e = 0$  and  $\gamma^s = \sigma$  under zero creep conditions. Consequently, the superficial work,  $\sigma$ , appears to be the measured parameter.

This point bears further examination. If the strain were not purely plastic in nature, then the measured parameter  $\gamma^s$  would be a composite of  $\sigma$  and  $\Upsilon$ . The surface strain will be purely plastic only if sufficient material is free to enter the surface region from the underlying bulk phase to preserve the surface density of material at its equilibrium value. For a normal sample, the surface-to-volume ratio is low and the bulk reservoir is effectively infinite. Transfer of material from bulk to surface does not therefore give rise to any significant work of expansion ( $-PdV^s$ ) term, nor is it necessary to suppose that the material leaving the bulk sets up any elastic strains. Under the conditions of a zero creep experiment, foils or wires of high surface-to-volume ratio are used. The transfer of material necessary to preserve plastically strained conditions at the surface can only be achieved at the expense of volume constancy of the bulk, or alternatively by setting up residual elastic strains in the bulk phase. It is normal<sup>5</sup> to assume conditions of volume constancy; if this is truly valid, then either the bulk or the surface is elastically strained and consequently  $\gamma^s$ , the measured parameter, is not identical with  $\sigma$ .

This interaction between surface and bulk strains was realized by Herring.<sup>7</sup> He postulated that the surface stress, which is, of course, a function of surface elastic strain, is, in fact, a surface excess property. This means that the measured parameter, which must always be a property of the whole system, embodies terms that depend on the strain state of both bulk and surface. Alternatively it may be said that the bulk Kramers energy is altered, and consequently the change in Kramers energy for the whole system is no longer described solely by the change in surface Kramers energy. In either case, it is clearly not sufficient to focus attention solely on the state of strain in the surface region when considering whether the whole system is in equilibrium. This argument has been developed previously<sup>5</sup> in order to show that, as later demonstrated by Everett and Couch-

man,<sup>13,14</sup> only elastic strains are significant in the Shuttleworth equation, eq 40.

The objection may be advanced that, in the above discussion, no account was taken of the fact that under zero creep conditions the strain rate is zero, regardless of whether elastic or plastic strains are involved. This is, of course, correct but it must be remembered from eq 26 that  $\gamma^s$  can only be equated to  $\sigma$  if the elastic strain, rather than the strain rate, is zero.

The true central point to any discussion of the parameter measured in the zero creep experiment, and indeed in any other experiment carried out at temperatures near the melting point of the solid, is the magnitude of the surface elastic modulus term  $E^\pi$  at this temperature. From eq 40 and 55

$$\Upsilon = \sigma + (\partial\sigma/\partial\epsilon_e)_{T,\mu_i,E} = \sigma + (\partial\sigma/\partial \ln \Omega) = \sigma + E^\pi \quad (126)$$

and if  $E^\pi$  is zero, then  $\Upsilon = \sigma = \gamma^s$ , irrespective of the nature of any strain involved. Arguments based on the inability of a liquid to support a shear stress can be advanced to show that, as the melting point of a solid is approached and providing the strain rate is low

$$E^\pi \rightarrow 0 \text{ as } T \rightarrow T_m \quad (127)$$

Consequently, despite conceptual difficulties related to the state of strain and/or the applicability of conditions of volume constancy, it can be stated that the zero creep experiment yields values of the superficial work,  $\sigma$ .

It should be noted that at lower temperature,  $E^\pi$  cannot be taken as zero. Certain zero creep experiments on foils have been carried out at temperatures substantially below the melting point, and for these  $\gamma^s$  cannot be identified with  $\sigma$ . Indeed, calculations of Drechsler and Nicholas<sup>60</sup> indicate that at such temperatures,  $E^\pi$  has a constant finite value irrespective of the size of the strain and there is no a priori reason to suppose that  $E^\pi$  becomes zero at either zero strain rate or, for that matter, zero strain. Further consideration is at present being given<sup>41</sup> to the magnitude of  $E^\pi$  as a function of strain, strain rate, and temperature.

## 2. Cleavage Methods

The chief problem with these techniques is that, although conceptually simple and directly in accord with the definition of  $\sigma$ , plastic deformation effects at the crack tip usually obscure the process of surface formation. The parameter obtained in practice is  $\gamma_{EFSE}$  (section II.C.6); the magnitude of the plastic deformation term is briefly considered later (section IV.B). It is possible,<sup>61</sup> with certain virtually ideal materials such as mica, to obtain values of  $\gamma^s$  which are then conventionally ascribed to the quantity  $\sigma$ . Nurse<sup>54</sup> has suggested that the plastic deformation term involves stresses and that it might be persuasive to argue that  $\gamma_{EFSE}$  under appropriately controlled conditions could be related to the surface stress  $\Upsilon$ . The more recent work described above, which restricts the strain terms involved in surface stress to those of an elastic nature, makes this suggestion unlikely.

## 3. The Lattice Contraction Technique

Following the discussion in sections III.D.1 and III.D.3, it is only necessary to state here that, providing that it is accepted that the appropriate parameter in the Laplace equation is  $\Upsilon$  and not  $\gamma^s$  or  $\sigma$ , then it is clear that this technique gives values for the surface stress.

## 4. Vapor Pressure of Small Particles

The Kelvin vapor pressure equation, eq 102, involves the surface stress  $\Upsilon$ . Listgarten and co-workers<sup>44</sup> modified this equation in such a way as to make it possible to obtain a surface thermodynamic parameter from measurement of particle radius

as a function of time. They made the usual assumptions of ideality of the vapor surrounding the particles and of negligible particle volume. They also assumed, however, that the particle density did not change with radius.<sup>5</sup> As the lattice contraction technique depends on measuring the change of density as a function of particle radius, this latter assumption appears questionable.

Listgarten et al. assumed that the surface thermodynamic parameter obtained by this technique was the superficial work,  $\sigma$ . Indeed, the results they obtained for solid silver particles were in excellent accord with values obtained from zero creep measurements. The primary reason for this is that the measurements were carried out near the melting point, where the value of the surface elasticity modulus is low and values of  $\sigma$  and  $\Upsilon$  can be expected to approach each other. Also the neglect of variation of particle density obscures the true nature of the parameter obtained from this technique.

In practice, experiments carried out at high temperatures by the method of Listgarten et al. and using their assumptions yield values near to these for  $\sigma$ . At lower temperatures and taking proper account of lattice contraction, values of  $\Upsilon$  would be obtained.

### 5. Other Methods

a. Inert Gas Bubble Method. This has been discussed in great detail elsewhere.<sup>5</sup> The essence of the arguments already presented for the zero creep technique apply here, but with the complication that these experiments are usually carried out at temperatures significantly below the melting point. The analysis of Lidiard and Nelson<sup>62</sup> concludes that  $\Upsilon$  is the parameter controlling the formation of bubble surface but that there is an elastic strain energy term in the surrounding bulk material that also needs to be considered. They suggest, in effect, that the surface elasticity modulus counteracts the bulk strain energy,  $E_b$ , so that the measured change in Kramers energy,  $d\Psi$ , is given by

$$d\Psi = \Upsilon + E_b = (\sigma + E^\pi) + E_b = \sigma \quad (128)$$

Consequently the parameter measured by this technique is  $\sigma$ . Similar reasoning can be applied to the time-dependent technique of void annealing and  $\sigma$  is again the quantity obtained.

b. Boundary Grooving and Multiphase Equilibrium Methods. These techniques are based on equations analogous to that of Young, eq 109. The point has already been made (section III.E.1) that  $\Upsilon$  rather than  $\sigma$  might well appear to be the more likely parameter to be involved. Values obtained from these techniques accord equally well with  $\sigma$  and  $\Upsilon$  values, but this may be due to the paucity of accredited measurements of  $\Upsilon$  with which to compare them. The present position is that most major authorities allow the assumption that these methods give values of  $\sigma$  to go unquestioned.

c. Healing of Scratches. This is based on the study of the rates of competing diffusion processes, and again it is generally, but perhaps uncritically, accepted that  $\sigma$  and not  $\Upsilon$  is the controlling parameter.

d. Equilibrium Shapes of Crystals. In this case, there is no serious likelihood that the parameter measured is other than  $\sigma$ .

## B. Values of Surface Parameters

The purpose of this article is to summarize recent advances in the conceptual understanding of the thermodynamics of solid surfaces. Consequently, it is not intended in this section to provide an up-to-date compendium of experimental data; reasonably complete tables are provided in earlier papers.<sup>5,63-65</sup> It is hoped that this section will provide an overview of typical values for certain of the parameters that have been mentioned.

The major surface thermodynamic parameter is undoubtedly the superficial work,  $\sigma$ . For a metal,  $\sigma$  is of the order of 1–2 J m<sup>-2</sup> near the melting point, and its temperature coefficient in that region is typically -0.5 to -1.2 mJ m<sup>-2</sup> K<sup>-1</sup>. For ionic solids at room temperature, values of  $\sigma$  are 0.3 ± 0.2 J m<sup>-2</sup>, although rather higher results have been reported for cleavage measurements on MgO, perhaps arising from plastic deformation effects at the crack tip. Polymeric materials possess low-energy surfaces, values in the region of 20–40 mJ m<sup>-2</sup> being usual for  $\sigma$ .

Values for  $\gamma_{EFSE}$  vary enormously according to the experimental conditions under which the crack is formed and also under which it is propagated. For tungsten, values<sup>66</sup> between 2 and 24 J m<sup>-2</sup> were found for a range of crack initiation and propagation conditions. It is clearly a difficult parameter to utilize, except in the context of a study of crack behavior.

Certain measurements have been made of the mean surface stress,  $\Upsilon$ , by the school of D. Kuhlmann-Wilsdorf who used the lattice contraction technique. They found<sup>67</sup> for gold that  $\Upsilon = 1.14$  J m<sup>-2</sup> at 50 °C and  $\Upsilon = 0.41$  J m<sup>-2</sup> at 985 °C, which may be compared with the value of Hondros and Gladman<sup>68</sup> of 1.4 J m<sup>-2</sup> for  $\sigma$  at 1040 °C. The temperature coefficient for  $\Upsilon$  is therefore ~ -0.8 mJ m<sup>-2</sup> K<sup>-1</sup>, i.e., of the same order as that for  $\sigma$ . Their results imply the surprisingly high value of 1 J m<sup>-2</sup> for the surface elasticity modulus,  $E^\pi$ , at ~1000 °C. Further measurements of surface stress have been carried out in South Africa by former members of this school. For silver, a value quoted<sup>69</sup> as 1.415 ± 0.3 J m<sup>-2</sup> was found for  $\Upsilon$ . This was compared with the literature value for  $\sigma$  of 1.14 ± 0.09 J m<sup>-2</sup> at 930 °C, which was adventurously extrapolated to a value of exactly 1.563 J m<sup>-2</sup> at 55 °C, yielding a value for  $E^\pi$  of -148 mJ m<sup>-2</sup> at this temperature. It is perhaps unfortunate that the authors omitted the error limits on this final value, which should have been reported as -150 ± 500 mJ m<sup>-2</sup>. Similar comments apply to their measurements on platinum, for which  $\Upsilon$  was found to be 2.574 ± 0.4 J m<sup>-2</sup>, and a similar audacious treatment, this time involving a value of  $\sigma$  for the liquid metal, yielded a value of  $E^\pi$  of -193 mJ m<sup>-2</sup>. It is not possible to be as confident as the authors that these measurements, in fact, indicate a negative value of  $E^\pi$  for these metals.

A general difficulty that arises when examining data for surface thermodynamic values of metals is that the most reliable values for  $\sigma$  are from high-temperature zero creep experiments, and in consequence it is not easy to be confident about the magnitude of  $\sigma$  at room temperature. This makes it difficult to draw firm conclusions as to the relative magnitudes of  $\sigma$ ,  $\Upsilon$ , and  $E^\pi$ .

## V. Conclusions

The thermodynamics of solid surfaces was studied by Gibbs,<sup>12</sup> who identified many of the conceptual difficulties such as those associated with the difference between cleavage and stretching parameters. During the ensuing 80 years the subject has gone through periods of darkness and periods of clarity. Important advances were made after the second world war; the work of Shuttleworth,<sup>27</sup> Herring,<sup>7</sup> and Buff<sup>9</sup> is particularly noteworthy. After a period of consolidation, further progress resulted from the general adoption of the Kramers energy formalism and the development of the concept of the generalized surface energy function; the work of Garcia-Moliner<sup>6</sup> and Couchman and Everett<sup>13,14</sup> is of especial relevance. It has been the purpose of the present review to consider the effect of these latest developments on the formalism of the subject. Coverage of this in some depth has precluded the possibility of even touching upon alternative approaches such as those based on statistical mechanics or irreversible thermodynamics.

It emerges from the subject matter covered here that the theoretical aspects of the subject have received some recent attention, but there is still an urgent need for more thermody-

dynamic measurements of surface parameters. Until these have been carried out, a complete clarification of the parameters measured by the various techniques will not be possible, and advances in understanding comparable to those resulting from the recent strides in analytical and structural surface studies will not occur.

## VI. List of Symbols

$A$	Helmholtz energy of whole system
$A^\alpha, A^\beta$	Helmholtz energy of solid and vapor phases
$A^\pi$	surface excess Helmholtz energy (II.A.4)
$a$	lattice constant (III.D.3)
$a^\pi$	superficial Helmholtz energy (II.A.5)
$b$	slope of Zisman plot (II.E.2)
${}^\pi C_p(T)$	heat capacity of finely divided sample (II.C.6)
${}_0 C_p(T)$	heat capacity of bulk sample (II.C.6)
$E$	electric field
$E^\pi$	surface elasticity modulus (II.C.6)
$E_b$	bulk elastic strain energy (IV.A.5)
$f_2$	fugacity of vapor component (III.C.3)
$G$	Gibbs energy of whole system
$G'$	Gibbs energy under restricted conditions (II.B.2)
$G^\alpha, G^\beta$	Gibbs energy of solid and vapor phases
$G^\pi$	surface excess Gibbs energy (II.A.4)
$g$	acceleration due to gravity
$g^\pi$	superficial Gibbs energy (II.A.5)
$H$	enthalpy of whole system
$H'$	enthalpy under restricted conditions (II.B.2)
$H^m$	magnetic field strength (II.B.1)
$H^\alpha, H^\beta$	enthalpy of solid and vapor phases
$H^\pi$	surface excess enthalpy (II.C.6)
$h^\pi$	superficial enthalpy (II.C.6)
$(h^\pi)^0$	standard superficial enthalpy (II.C.6)
$J$	open system energy function (II.B.2)
$k'$	bulk compressibility (III.D.3)
$M$	magnetization of whole system (II.B.1)
$n_i$	amount of $i$ th substance
$n_i^\alpha, n_i^\beta$	amount of $i$ th substance in solid and vapor phases (II.A.4)
$n_i^\pi$	surface excess amount of $i$ th species (II.A.4)
$P$	hydrostatic pressure
$P^\alpha, P^\beta$	hydrostatic pressure over curved and flat surfaces (III.D.2)
$P_r, P_\infty$	hydrostatic pressure over curved and flat surfaces (III.D.2)
$P_i$	partial pressure of $i$ th species (III.C.3)
$Q$	electric charge on whole system
$Q^\alpha, Q^\beta$	electric charge in the solid and vapor phases (III.A)
$Q^\pi$	surface excess electric charge (III.A)
$q$	path dependent heat (II.B.1)
$q^\pi$	superficial charge (III.A)
$R$	gas constant
$r$	radius of bubble, drop, or curved surface (III.D.1)
$r_t$	radius of capillary tube (III.D.4)
$S$	entropy of whole system
$S^\alpha, S^\beta$	entropy of solid and vapor phases
$S^\pi$	surface excess entropy (II.C.6)
$S_m$	mean molar entropy (III.D.2)
$S_0$	residual entropy at absolute zero (II.C.6)
$s^\pi$	superficial entropy (II.C.6)
$S_{B/A}$	spreading coefficient of liquid B on solid or liquid A (III.E.4)
$T$	temperature
$T_m$	melting point of solid (IV.A.1)
$U$	internal energy of whole system
$U^\alpha, U^\beta$	internal energy of solid and vapor phases
$U^\pi$	surface excess internal energy (II.C.6)

$u^\pi$	superficial internal energy (II.C.6)
$V$	volume of whole system
$V^\alpha, V^\beta$	volume of solid and vapor phases
$V^\pi$	volume of surface region (II.A.3)
$V_m$	mean molar volume (III.D.2)
$W_{AB}, W_{AA}$	work of adhesion and cohesion (III.E.3)
$w$	path-dependent work (II.B.1)
$X$	any extensive property of the whole system
$X^\alpha, X^\beta$	any extensive property of the solid and vapor phases (II.A.4)
$X^\pi$	any surface excess extensive property (II.A.4)
$x$	vertical displacement of system (II.B.1)
$x^\pi$	any superficial extensive quantity (II.A.5)
$Y$	external energy (II.B.2)
$\alpha$	superscript denoting solid bulk phase
$\beta$	superscript denoting vapor phase
$\Gamma_i$	superficial amount of $i$ th species (II.A.5)
$\Gamma_1$	superficial amount of major component of whole system (II.A.5)
$\gamma^c$	critical surface tension (III.E.2)
$\gamma^s$	generalized surface intensive parameter or surface energy (II.C.3)
$\gamma_{EFSE}$	effective fracture surface energy (II.C.6)
$\gamma_{AV}^s, \gamma_{BV}^s, \gamma_{AB}^s$	$\gamma^s$ for interface between solid A and vapor, liquid B and vapor, and solid A and liquid B (III.E.3)
$\gamma_{SV}^s, \gamma_{SL}^s, \gamma_{LV}^s$	$\gamma^s$ for solid-vapor, solid-liquid, and liquid-vapor interfaces (III.E.1)
$\gamma'_{sv}$	$\gamma^s$ for a solid in the presence of multicomponent vapor (III.E.1)
$\delta$	thickness of surface region (II.A.3)
$\delta_{ij}$	Kroenecker delta (III.B.3)
$d\epsilon$	surface strain (III.A.6)
$d\epsilon_{tot}, d\epsilon_e, d\epsilon_p$	total surface strain, elastic surface strain, plastic surface strain (II.C.3)
$\theta$	contact angle (III.E.1)
$\theta_i$	surface coverage of $i$ th species (III.C.3)
$\phi$	solid-liquid angle of contact (III.E.1)
$\mu_i$	chemical potential of $i$ th species
$\mu_2^0$	standard chemical potential of vapor (III.C.2)
$\Pi$	surface pressure (II.C.6)
$\pi$	superscript denoting surface region
$\rho$	density
$\sigma$	superficial work (II.A.7; II.C.1)
$\sigma_{dyn}$	dynamic surface tension (II.C.5)
$\bar{\Upsilon}$	mean surface stress (II.C.2)
$\bar{\Upsilon}_{ij}$	tensorial surface stress (II.A.7; II.C.1)
$\Psi$	Kramers energy of whole system (II.B.1)
$\Psi'$	Kramers energy under restricted conditions (II.B.2)
$\Psi^\alpha, \Psi^\beta$	Kramers energy of solid and vapor phases
$\Psi^\pi$	surface excess Kramers energy (II.C.1)
$\psi^\pi$	superficial Kramers energy (II.C.1)
$\Omega$	superficial area (II.A.1)

**Acknowledgments.** The author wishes to acknowledge extensive and helpful discussions on section II.B with D. A. Armistage.

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