Surface Energy of Solids

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1 Introduction

In the past few years, there has been a renaissance in surface chemistry. Classical aspects of the field, described in textbooks such as that of Adam[1] have been joined by new techniques[1a] including low energy electron diffraction (LEED), Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), field ion microscopy (FIM), and microprobe analysis. What these new techniques offer (apart from a proliferation of initials calculated to awe a listener) is the means to extract structural and chemical information about the surface region of a solid in a way, and to a precision, that was unavailable before. Because of this, many chemists, who previously avoided the study of surface phenomena because it was so difficult to know what was happening on or around the surface, have become interested in the surface region.

In surface chemistry, just as in any other branch of the subject, phenomena are largely controlled by, and can be interpreted with the aid of, thermodynamics and kinetics. Unfortunately, many standard text books do not deal comprehensively with the thermodynamics of solid surfaces; there is no general agreement on symbols and nomenclature with the result that chemists moving into the field may find several different parameters described by the phrases 'surface tension' and 'surface energy'.

Several recent reviews on surface thermodynamics have been written, notably those of Inman and Tipler,[2] Geguzin and Ovcharenco,[3] and Bikerman,[4] and a short book by Mykura.[5] These reviews deal fully with experimental determinations. In addition there has been a recent review[6] on theoretical calculations. This review aims to cover the thermodynamic parameters required to deal with solid surfaces, together with some techniques for measuring and calculating them. Only planar surfaces are considered, since complications arising from curvature are outside the scope of the article.

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[1] N. K. Adam, 'Physics and Chemistry of Surfaces', Dover, New York, 1968.
[1a] 'Surface and Defect Properties of Solids', ed. M. W. Roberts and J. M. Thomas (Specialist Periodical Reports), The Chemical Society, London, 1972, Vol. 1.
[2] M. C. Inman and H. R. Tipler, *Metallurg. Rev.*, 1963, **8**, 105.
[3] Y. E. Geguzin and N. N. Ovcharenko, *Soviet Phys. Uspekhi*, 1962, **5**, 129.
[4] J. J. Bikerman, *Physica Status Solidi*, 1965, **10**, 3.
[5] H. Mykura, 'Solid Surfaces and Interfaces', Routledge and Kegan Paul, London, 1966.
[6] G. C. Benson and K. S. Yun, in 'The Solid-Gas Interface', ed. E. A. Flood, Edward Arnold, London, 1967, chap. 8.

2 Surface Thermodynamics

A. What is a Surface?—To a layman, the surface of, say, a table is that aspect of the top of the table which he sees. He would probably agree with the suggestion that it was the boundary between the wood of the table and the air above. Replace the layman with a scientist and the table by a crystal and the notion of a boundary layer would still suffice. But how thick is this boundary layer or surface? The answer depends on the type of scientist rather than anything else. An engineer knows that a surface of, *e.g.*, a piece of 'flat' copper, is covered with asperities, and has a profile roughly that of a scaled down model of the Lake District. He knows that in air it is covered with layers of oxide and adsorbed gas contamination corresponding perhaps in scale to a metre of snow on our kilometre-high peaks. It is true that the surface can be polished down to a peak-to-valley separation of maybe 35 nm but, with the exception of cleaved mica, it is unlikely to be atomically flat. His measurement of the 'thickness' of a surface is likely to be the average peak-to-valley height. A chemist or physicist, on the other hand, will know that most 'physical' properties are fairly uniform in the bulk of the crystal until one comes somewhere near the surface, whereupon they start changing. They continue changing up to the top atomic layer of the crystal, and beyond into the surrounding fluid phase, until eventually one passes into a region where bulk, average, fluid phase properties take over. This is shown diagrammatically in Figure 1, where the region in which properties are changing is denoted by the 'surface phase, π, and lies between $A_1A_2A_3A_4$ and $B_1B_2B_3B_4$ and in Figure 2 where the value of some physical property of the system is plotted in the solid phase, α, the surface phase, π, and the gas, or more generally fluid, phase, β.

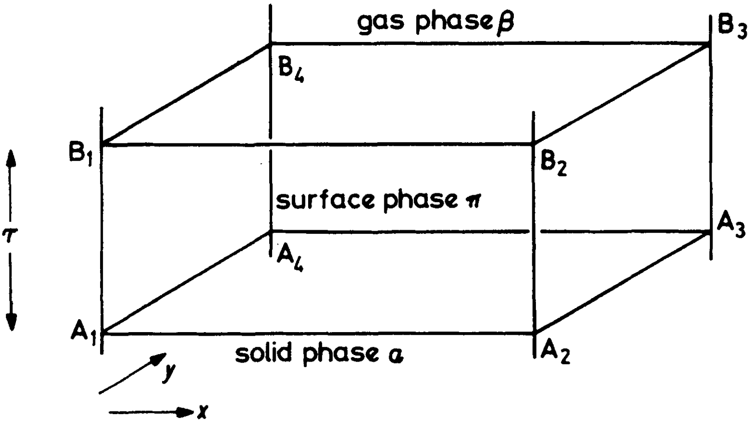

Figure 1

One can think, and indeed carry out calculations, in terms of either a two-dimensional or a three-dimensional surface region. The two-dimensional approach is usually ascribed to Gibbs[7] and the three-dimensional treatment to Guggenheim.[8] The three-dimensional approach has the advantage that it is easy to visualize, having boundaries at the vertical lines of Figure 2, *i.e.* at the places where the bulk fluid or solid properties start to change. A two-dimensional surface is fine as a mathematical fiction, a *dividing surface* positioned somewhere between the vertical lines. Its location can be chosen at will, to make some selected parameter zero for example, but this freedom of position means that the values of some types of parameter will vary according to the positioning of the dividing surface. It is also hard to give its position any physical interpretation as even if one wished to position it at the physical interface, one could not; the upper layer of solid atoms is neither static nor flat. From this it would appear that a three-dimensional system would be preferable, but it has one over-riding disadvantage. It involves a surface volume term which not only is of unknown magnitude but also which complicates considerably (and unnecessarily since being indeterminate it has perforce to be ignored) definition of, and equations involving, surface thermodynamic quantities.

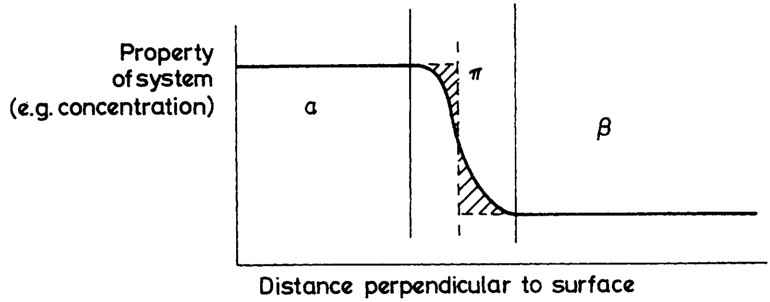

Figure 2

B. Can one consider the Surface 'Phase' on its own?—The answer to this question is that one cannot. A surface is of necessity a boundary region or phase separating two other phases. For equilibrium to occur, one must minimize the energy of the system, and the system must consist of the surface together with the two attendant phases that provide its reason for existence. For a solid, for example, one must consider the surface *plus* the bulk solid *plus* the surrounding fluid (*i.e.* liquid, gas, vapour, or vacuum).

Let us define the reversible work required to create unit area of surface at constant temperature, T, volume, V, and chemical potential of the ith com-

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[7] J. W. Gibbs, 'The Scientific Papers of J. Willard Gibbs, Volume One. Thermodynamics', Dover, New York, 1906, reprinted 1961.
[8] E. Guggenheim, *Trans. Faraday Soc.*, 1940, **36**, 397.

ponent μ_i as the *specific* surface work*, γ_π. (The name is adopted here, following Mullins,[10] in preference to the usual terms 'surface energy' or 'surface tension' because of ambiguities in the use of these terms that will be outlined later.) Let us examine this quantity more closely to see how it relates to the energy of the whole system as described above, *i.e.* a bulk solid phase, α, separated from a fluid phase, β, by a surface phase, π. We can follow Herring[11] in calling the reversible work required to form a surface under the above conditions the *mechanical work*, ψ. He has shown that the condition for equilibrium of the system at constant T, V, and μ_i is that ψ is a minimum. The mechanical work ψ is an extensive quantity and Gibbs[7] showed that for a system of several phases like the one we have here, the contributions ψ_α and ψ_β of the phases α and β can be related to ψ by

$$\psi_\pi = \psi - \psi_\alpha - \psi_\beta \tag{1}$$

where ψ_π is the *surface work* of the system.

For a reversible change brought about by mechanical means at constant T, μ_i, and V, the work done on the system, $\Delta\psi$, is equal to the work done on the bulk phases plus the change, $\Delta\psi_\pi$, in the surface work. If new surface is created by cleaving the bulk solid in half very carefully so that the volumes of solid and fluid phase are unchanged and the stress distribution in the solid is affected as little as possible, then the work done on the bulk phases is negligible and $\Delta\psi$ becomes equal to $\Delta\psi_\pi$.

The specific surface work, γ_π, is the surface work per unit area under conditions of constant temperature and chemical potential of the system, *i.e.*

$$\gamma_\pi = \left(\frac{\partial\psi_\pi}{\partial\Omega}\right)_{\mu_i,T} \tag{2}$$

where Ω is area. The change in surface work, $\Delta\psi_\pi$, is therefore

$$\Delta\psi_\pi = \Delta \int\gamma_\pi \mathrm{d}\Omega \text{ (const. } T,\mu_i) \tag{2a}$$

Therefore if the volumes of liquid and solid phase (and the stress distribution in the solid) remain unchanged, then for the process of forming a surface the energy required, *i.e.* the change in mechanical work $\Delta\psi$, becomes equal to $\Delta \int\gamma_\pi \mathrm{d}\Omega$ (the integration being over the whole surface).

One of the complications of dealing with solids, compared to liquids, is that for liquids, unless the curvature at the surface changes,

$$\Delta \int\gamma_\pi \mathrm{d}\Omega = \gamma_\pi \Delta\Omega \tag{2b}$$

For a solid, equation (2b) is only true if the state of strain of the bulk solid

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*Despite the generally agreed convention[9] that the adjective 'specific' denotes 'per unit mass', it is more convenient here to use it to mean 'per unit area'.

[9] 'Symbols, Signs and Abbreviations recommended for British Scientific Publications', The Royal Society, London, 1969.

[10] W. W. Mullins, in 'Metal Surfaces: Structure, Energetics and Kinetics', American Society for Metals, Ohio, 1963, chap. 2.

[11] C. Herring, in 'Structure and Properties of Solid Surfaces', ed. R. Gomer and C. W. Smith, Univ. of Chicago Press, Chicago, 1952, chap. 1.

and the surface remain unchanged and also if the crystal orientation of the surface remains unaltered, since γ_π is a function of orientation.

If changes in the system are considered where T and μ_i are allowed to change but the surface work is kept constant, then the frequently used[12] *Gibbs adsorption equation*

$$d\gamma_\pi = -s_\pi dT - \Sigma\Gamma_i d\mu_i \tag{3}$$

can be derived.[8,10,11] Here s_π is the *specific surface entropy*, where

$$s_\pi = \frac{S_\pi}{\Omega} = \frac{S - S_\alpha - S_\beta}{\Omega} \tag{3a}$$

S is the entropy of the whole system and S_α, S_β, and S_π that of the solid, fluid, and surface phases, respectively; Γ_i is the *specific surface excess*, where

$$\Gamma_i = \frac{N_{i,\pi}}{\Omega} = \frac{N_i - N_{i,\alpha} - N_{i,\beta}}{\Omega} \tag{3b}$$

N_i, $N_{i,\alpha}$, $N_{i,\beta}$, and $N_{i,\pi}$ are the number of moles (or molecules) of the ith species in the whole system, the bulk solid, the fluid, and the surface region; the *chemical potential*, μ_i, is defined as

$$\mu_i = \left(\frac{\partial A_\alpha}{\partial N_i}\right)_{T,V,N_{j\neq i},\ \text{shearing strain}} = \left(\frac{\partial A_\beta}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial G_\alpha \text{ or } \partial G_\beta}{\partial N_i}\right)_{T,\ \text{stress},N_{j\neq i}} \tag{3c}$$

where A_α and A_β are the Helmholtz* energies and G_α and G_β are the Gibbs* energies of the solid and liquid phases, respectively. Equation (3) is further discussed in Section 6.

The mechanical work, ψ, was defined by Herring[11] as

$$\psi = A - \Sigma\mu_i N_i \tag{4}$$

where A is the Helmholtz energy and $\Sigma\mu_i N_i$ the Gibbs energy, G, for the whole system. An analogous equation can be written for the surface phase:

$$\psi_\pi = A_\pi - \Sigma\mu_i N_{i,\pi} \tag{4a}$$

and at constant temperature and chemical potentials this can be expressed per unit area as

$$\gamma_\pi = \mathrm{a}_\pi - \Sigma\mu_i\Gamma_i \tag{4b}$$

where A_π is the surface Helmholtz energy and a_π ($=A_\pi/\Omega$) is the *specific surface Helmholtz energy*.

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*Formerly[9] called 'Free' energies.

[12] E. D. Hondros, 'Interfaces, Conf. Melbourne', ed. R. G. Giffkins, Butterworths, London, 1969.

If the dividing surface is located so as to make Γ_1 zero, then for a one-component system (and *only* for such a system), γ_π becomes equal to the specific surface Helmholtz energy. (If the dividing surface is located elsewhere, it is a_π and Γ_i whose values change; for a planar surface the value of γ_π is completely independent of the position of the dividing surface.) In general, however, γ_π need not equal a_π, and the name 'surface free energy' for γ_π is misleading. Further, γ_π does not in general equal the internal energy (or perhaps here 'total' energy would be a more appropriate name) of the surface, or indeed of the whole system, and the name 'surface energy' for γ_π is also felt to be misleading as it could denote many other quantities equally well.

C. Cleavage Parameters and Stretching Parameters.—Gibbs[7] pointed out that for liquids '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'. For solids, on the other hand, there is no such equivalence. The parameter that deals with formation of new surface is γ_π, the specific surface work. The reversible work required to form unit area of new surface by stretching is the *surface stress*, g_{ij}, which is related[10,11,13] to γ_π by

$$g_{ij} = \delta_{ij}\,\gamma_\pi + \left(\frac{\partial\gamma_\pi}{\partial\epsilon_{ij}}\right)_{\text{all other strains}} \tag{5}$$

where $\delta_{ij} = 0$ if $i \neq j$, $\delta_{ij} = 1$ if $i = j$, and ϵ_{ij} is the natural strain (*i.e.* increase in length per unit length).

As can be seen from the somewhat complicated subscripts, the surface stress is a tensor. (For those unfamiliar with the notation, the second subscript, j, gives the direction in which a force acts and the first subscript, i, specifies the plane in which the force acts.) A more formal definition of surface stress is that g_{ij} is numerically equal to the force acting in the jth direction, per unit length of exposed edge, the edge being normal to the ith direction, that must be applied to a terminating surface to keep it in equilibrium, the ith and jth directions lying in the plane of the surface. The surface stress g_{ij} has different values in different directions in a surface, but the specific surface work γ_π, which is a scalar quantity, does not. γ_π does vary, however, according to which surface is considered; the value for the 110 plane, γ_π^{110}, will not in general be the same as for the 100 plane, γ_π^{100}, for example.

Equation (5) is somewhat difficult to understand, and the meaning of the $\partial\gamma_\pi/\partial\epsilon_{ij}$ term will be dealt with in more detail below. The equation is simplified for an isotropic surface as here the shear stresses, g_{ij}, $i \neq j$, become zero and g_{ij} is replaced by the *mean surface stress*, g, where

$$g = (g_{ii} + g_{jj})/2 \tag{6}$$

and the strain ϵ_{ij} is replaced by the mean strain, $d\Omega/\Omega$, giving[14]

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[13] J. S. Vermaak, C. W. Mays, and D. Kuhlmann-Wilsdorf, *Surface Sci.*, 1968, **12**, 128.
[14] R. Shuttleworth, *Proc. Phys. Soc.*, 1950, **A63**, 444.

$$g = \gamma_\pi + \Omega\frac{\mathrm{d}\gamma_\pi}{\mathrm{d}\Omega} \tag{7}$$

The mean surface stress in fact has a relatively simple interpretation, since

$$\gamma_\pi + \Omega\frac{\mathrm{d}\gamma_\pi}{\mathrm{d}\Omega} = \frac{\mathrm{d}(\gamma_\pi\Omega)}{\mathrm{d}\Omega} \tag{8}$$

and so, from equations (7) and (8)

$$g = \frac{\mathrm{d}(\gamma_\pi\Omega)}{\mathrm{d}\Omega} \tag{8a}$$

For a liquid, surface stress and specific surface work are equal, and the name '*surface tension*' is suitable for the parameter. For solids, this name has been used by some authors[2,3,14–16] for surface stress and by others[11,13] for specific surface work, and its use is probably better discontinued for solids. A distinction is sometimes drawn between the units in which surface stress and specific surface work are measured, the former being described in terms of units of force per unit length, and the latter in units of energy per unit area. (These are, of course, dimensionally equivalent and indeed reduce to units of mass per unit time squared, one author[4] describing 'surface energies' in units of $\mathrm{g\,s^{-2}}$!) Problems of different units are sometimes avoided by ignoring the difference between g_{ij} and γ_π altogether, as can happen even in eminent thermodynamic textbooks.[17]

D. The Role of $\partial\gamma_\pi/\partial\epsilon_{ij}$; Elastic or Plastic Strains?—When a surface is stretched, initially the number of surface atoms remains constant, each atom occupying a larger area than normally, and the surface is *elastically strained.* If atoms migrate from the bulk to allow the elastically strained atoms to revert to their original interatomic separations, then the surface is *plastically strained.* Migration is possible in the case of liquids and of solids near their melting point; in such cases one cannot distinguish experimentally between surface stress and specific surface work. Because of this, Kuhlmann-Wilsdorf and her co-workers[13] suggested that only elastic strains entered into equation (5).

A migration of this type involves depletion of material from the underlying bulk solid which will result either in one (or some) of the underlying atomic layers being elastically strained or in a contraction in the volume of the bulk phase. In the case of an experiment where the tendency of the surface of a material near its melting point to expand or contract is opposed by an applied force (for example the zero-creep experiment discussed later), the *measured* surface stress equals the specific surface work, but the $\partial\gamma_\pi/\partial\epsilon_{ij}$ term is not zero. This apparent paradox occurs because[13,18] the applied load balances γ_π whereas the $\partial\gamma_\pi/\partial\epsilon_{ij}$ term is balanced by the elastic deformation in the bulk.

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[15] J. C. Eriksson, *Surface Sci.*, 1969, **14**, 221.

[16] E. Orowan, *Proc. Roy. Soc.*, 1970, **A316**, 473.

[17] G. N. Lewis and M. Randall, revised by K. S. Pitzer and L. Brewer, 'Thermodynamics', McGraw-Hill, New York, 1961, chap. 29.

[18] R. G. Linford, 'Solid State Surface Science II, ed. M. Green, Marcel Dekker, New York, 1973; D. Couchman, W. Jessel, and D. Kuhlmann-Wilsdorf, to be published.

Two points should be emphasized. A surface extended by a plastic strain is not identical with a surface formed by cleavage as the latter involves no elastic deformation of the underlying layers. Also, γ_π and g_{ij} are identical for liquids but not for solids, because of the higher mobility of the atoms in the case of liquids, but this does not mean that the difference is purely kinetic rather than thermodynamic. Herring[11] points out that a solid possesses long-range translational order and a liquid does not, and there may not be an energetically feasible way for atoms in a solid surface that has been elastically strained to revert to their original positions. In other words, one can certainly restore the *status quo* in liquids by migration, but this may not be true for solids.

A further complication arises when considering the role of mobility in determining which parameter one can *measure*.[13,18] At very high strain rates, mobility even in a liquid will be insufficient to prevent the surface strain being elastic. For elastic strain there is no compensating stress in the bulk to cancel out the effect of the $\partial\gamma_\pi/\partial\epsilon_{ij}$ term and so an experiment measures g_{ij} as given by equation (5). Conversely, for a solid at infinitesimal strain rates, all strains will be fully plastic, the bulk stress cancels with the $\partial\gamma_\pi/\partial\epsilon_{ij}$ portion of the surface stress, and the resultant, *measurable*, surface stress is equal to the specific surface work. To sum up this difficult point, in general for a solid

$$\begin{aligned} g_{ij\,\text{measurable}} &= g_{ij} + \text{bulk stresses} \\ &= \gamma_\pi + \frac{\partial\gamma_\pi}{\partial\epsilon_{ij}} + \text{bulk stress} \qquad (9) \end{aligned}$$

For elastic strains, the bulk stress is zero, whereas for plastic strains the bulk stress cancels[18] with $\partial\gamma_\pi/\partial\epsilon_{ij}$.

Theory and experiment show[13] that the sign of $\partial\gamma_\pi/\partial\epsilon_{ij}$ is in fact negative and therefore that g_{ij} is less than γ_π. Some calculations[14] on ionic crystals in fact predict that the mean surface stress itself is negative.

E. Summary of Surface Energy Quantities.—As is apparent from the foregoing, surface thermodynamics is a somewhat confused subject, a situation that has not been helped by many authors failing to distinguish between the large choice of parameters available. To summarize, the most important parameters are

(i) *The specific surface work*, γ_π, being the reversible work required to form unit area of new surfaces by cleavage.

(ii) *The surface stress*, g_{ij}, which is the reversible work required to form unit area of new surface by stretching.

(iii) *The specific surface Helmholtz energy*, a_π, which is the Helmholtz energy per unit area of the surface phase, π, rather than of the whole closed system.

The surface stress is equal to the specific surface work for liquids but not usually for solids. The specific surface Helmholtz energy is equal to the specific surface work for a one-component solid surface but not for a multi-component surface. (Auger spectroscopy has shown that because of surface segregation the surface of even 99.995% pure nickel is covered by nearly a monolayer of sulphur,[19a] and that the surface concentration of Al in a 99.2%:0.8% Cu–Al alloy is over 35%.[19b] It is probable that the majority of solid metal surfaces are multi-component systems.)

Other surface excess parameters can be defined, *e.g.* the specific surface total energy, e_π, which is related to the specific surface Helmholtz energy

$$e_\pi = a_\pi + Ts_\pi \tag{10}$$

and which is identical with the specific surface enthalpy since

$$h_\pi = e_\pi + P\left(\frac{V_\pi}{\Omega}\right) \tag{10a}$$

and V_π is zero for a system with a two-dimensional surface. A further useful parameter, the heat of surface formation per unit area, q_s, is given by

$$q_s = Ts_\pi = -T\left(\frac{\partial\gamma_\pi}{\partial T}\right)_{\mu_i,V} \tag{10b}$$

The terms 'surface energy' and 'surface tension' have been used by different authors to denote probably each of the thermodynamic parameters mentioned so far; their use is better avoided (except in the collective term 'surface energy parameters'), but if the reader feels an irresistible desire to employ the term 'surface energy', γ_π would be the best quantity to which to apply it.

F. Interfacial and Surface Properties.—There is a difference between the behaviour of the boundary region of a system consisting of a solid in equilibrium with its vapour and one where other components, even air, are present in the fluid phase. Udin[20] distinguishes these systems by calling the boundary layer for the system where other components are present an interface, reserving the term surface for the system where only the solid and its vapour are present. He has shown that for silver at 930 °C, in air the specific interfacial work was $0.45\,\mathrm{J\,m^{-2}}$ whereas in vacuum γ_π was $1.14\,\mathrm{J\,m^{-2}}$ ($1\,\mathrm{J\,m^{-2}} = 10^3\,\mathrm{erg\,cm^{-2}}$). Hondros[21] has confirmed that true values of the specific *surface* work can be found for metals in ultra-high vacuum and also in helium, but that the presence of any other fluids, even argon, affects the results.

From now on, Udin's distinction will be adopted here when referring to surface properties, with the modification that if helium is the only 'foreign' component present, the boundary layer will be called a surface rather than an interface.

3 Experimental Methods for Measuring Surface Energy Parameters

A. Zero-creep Method.—This is a force measurement carried out on polycrystalline metal foils or wires at temperatures within 20% of the melting point. It depends on the phenomenon of high-temperature creep, which as pointed

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[19a] L. A. Harris, *J. Appl. Phys.*, 1968, **39**, 1428.

[19b] D. H. Buckley, *J. Adhesion*, 1969, **1**, 264.

[20] H. Udin, in 'Metal Interfaces', American Society for Metals, Ohio, 1952, 114.

[21] E. D. Hondros, *Acta Metallurgica*, 1968, **16**, 1377; *New Scientist*, 1969, **42**, no. 649, feature section, p. 8.

out by Hondros[21] was observed in 1857 by Faraday who heated gold foils and noted that they shrank. He also observed that gold foil held between sheets of glass became transparent when heated and deduced correctly that this was due to tearing, the foil shrinking under surface forces. It should perhaps be emphasized that the technique depends on the metal being in a form where the surface to volume ratio is high, otherwise any shrinkage is negligible. It should also be noted that the experiment is carried out at constant temperature and that the fact that a metal contracts when kept at a constant high temperature is quite compatible with the everyday observation that metals expand when heated.

Several wires or foils are examined at the same time, different loads being put on each, so that by interpolation the load, w, just sufficient to counterbalance the surface forces, *i.e.* for *zero* creep, can be found. (An excessive load will, of course, cause extension rather than contraction.) For a wire of radius r and length l, γ_π (or more properly the measurable surface stress which at high temperatures and low strain rates has been shown to be equal to γ_π) is related to w by[20]

$$w = \pi r\gamma_\pi - n\pi r^2\gamma^*/l \qquad (11)$$

n being the number of grain boundaries and γ^* being the grain boundary energy. Volume constancy is assumed and the weight of the wire is neglected; for equation (11) to be valid, the grain boundaries must also be aligned perpendicular to the surface in the so-called 'bamboo' structure. (This is achieved by keeping the wire lightly loaded at the desired temperature for a day or two.)

The presence of grain boundaries, whether in foils or wires, is necessary to the success of the experiment. It may be that the surface strains cannot be plastic unless the boundaries, which are conducive to high mobility, are present. This would be compatible with the mechanism usually ascribed to high-temperature creep, namely the Nabarro–Herring process[2] in which vacancies diffuse from the grain boundaries to the surface, thus causing contraction.

Limitations of the method are that the grain boundary energy (which is usually about one third of γ_π) must be known, and that the samples must have grain boundaries so that single crystals cannot be used. The method is capable of giving accurate results, but extrapolation to room temperature depends on uncertain surface entropy results.[22] The method has been criticized in detail by Bikerman[4] (as indeed have all the other methods mentioned here) and defended by Argon.[23]

(i) *The thermal grooving technique.* In a zero-creep experiment, the angles at the grain boundary-surface junctions vary around the perimeter of the wire. The junctions can be examined in an electron microscope subsequent to heating and stretching, and the variation of γ_π with crystallographic orientation determined.[24]

(ii) *The extruded filament technique.* This technique, like the zero-creep experi-

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[22] H. Jones and G. M. Leak, *Metal Sci. J.*, 1967, **1**. 211.

[23] A. S. Argon, *Physica Status Solidi*, 1965, **12**, K121.

[24] M. McLean and B. Gale, *Phil. Mag.*, 1969, **20**, 1033.

ment, involves a balance between surface forces and the load applied to a wire. A substance, *e.g.* paraffin wax, that exhibits considerable plasticity below the melting point, is formed into a filament by extrusion under gas pressure through a syringe of radius r. The length, l, of the filament changes with time, t, and from a plot of dl/dt against l the critical length L_0 at $dl/dt = 0$ is found. At L_0, which for a given substance is a function solely of r, the overall length of the filament is constant, although the upper portion is in fact extending and the lower portion contracting. For a material of density ρ and Poisson's ratio ν (*i.e.* the ratio of radial contraction to lateral extension), γ_π is given by

$$\gamma_\pi = rL_0\rho g/4(1 - \nu) \tag{12}$$

where g is the acceleration due to gravity. Results for paraffin wax[25] have shown unexpectedly that γ_π varies with r, which is attributed to two opposing effects. Visco-elastic relaxation within the syringe tends to keep the filament extruding after the gas pressure is cut off, which elongates the filament, whereas post-extrusion stress relaxation perpendicular to the filament tends to shorten it. Doubt has been cast[4,25] on whether surface properties in fact play any role in the behaviour of the filament.

B. Fracture Method.—A sample has a short crack introduced in it by a screw-driven wedge,[26] by spark machining,[27] or, in the case of a softer substance such as NaCl, with a razor blade.[28] The force required to extend the crack is measured on a tensile testing machine; for a wedge-induced crack it is related to γ_π by[26]

$$\gamma_\pi = 6P^2L^2/Yx^2t^3 \tag{13}$$

where P is the tensile force required to advance the crack, L is the initial crack length, x is the width of the crack, t is half the thickness of the specimen, and Y is Young's modulus.

This method on the face of it seems a very direct way of arriving at the work required for the reversible isothermal formation of unit area of new crystal surface by cleavage, *i.e.* γ_π. Unfortunately, much of the work required to propagate the crack is expended in plastic deformation, and only at low temperatures is the plastic deformation negligible. For example,[27] at 295 K, γ_π for the 100 face of tungsten was found to be $24 \pm 5\,\mathrm{J\,m^{-2}}$, whereas at 77 K (and also at 4 K) γ_π was $6.0 \pm 0.9\,\mathrm{J\,m^{-2}}$. A further complication is that heat has to be supplied to prevent the temperature of the surface layer from falling while the surface is being formed as q_s, the heat of surface formation, is positive. Since q_s is directly proportional to temperature, carrying out the experiments at low temperatures minimizes this effect as well as the plastic deformation term. The easiest way of lowering the temperature is to submerge the sample in liquid nitrogen, meaning of course that an interfacial rather than a surface property is measured. Any diminution of the surface area resulting from the cracking

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[25] A. C. Lowe and A. C. Riddiford, *J. Colloid Interface Science*, 1970, **32**, 292.

[26] J. J. Gilman, *J. Appl. Phys.*, 1960, **31**, 2208.

[27] J. E. Cordwell and D. Hull, *Phil. Mag.*, 1969, **19**, 951.

[28] S. M. Weiderhorn, R. L. Moses, and B. L. Bean, *J. Amer. Ceram. Soc.*, 1970, **53**, 18.

process is usually ignored.[4] The experimental conditions under which the crack is formed are of importance; spark machining is normally carried out in paraffin oil at room temperature, and for a crack initiated in this way and propagated in liquid nitrogen at 77K, γ_π for the 100 face of W was $6.0 \pm 0.9\,\mathrm{J\,m^{-2}}$ as mentioned above, but for a crack initiated in liquid nitrogen at 77K, it was $1.7 \pm 0.3\,\mathrm{J\,m^{-2}}$.[27]

For brittle materials such as glass, the crack initiation and propagation processes may be different, leading to different values of γ_π depending whether the work of fracture is averaged over the whole fracture process or not.[29]

C. Inert-gas Bubble Method.—The previous two methods do not usually provide values of γ_π near room temperature. This method, which consists of bombarding metal foils with argon or helium ions and annealing at raised temperatures to produce gas bubbles whose radius, r, is related to γ_π by

$$\gamma_\pi = 3mkT/8\pi r^2 n \tag{14}$$

(where n and m are the number of bubbles and gas atoms per unit volume, respectively)[30] has been used to give results near room temperature.[31a,b] The bubbles are observed in the electron microscope using replica techniques, and statistical methods can be used to find the mean bubble radius.[31b] From bubble shapes, γ_π for specific crystal faces can be measured. The surfaces formed are inside the crystal and are free from atmospheric contamination.

D. Other Methods for Determining Specific Surface Work.—(i) *Healing of Scratches.* Parallel scratches are made on a flat surface producing a sinusoidal surface profile. The rate of decay to flatness is related to γ_π.[32]
(ii) *Void annealing technique.* Voids (or empty bubbles) are introduced into wires by rapid quenching from high temperatures. They are annealed at carefully controlled, somewhat lower, temperatures under vacuum and the shrinkage in radii measured in an electron microscope.[33] The radius r after time t is related to γ_π by

$$r^3 = r_i^3 - 6D\omega\gamma_\pi t/kT \tag{15}$$

where r_i is initial radius at $t = 0$, D is diffusion coefficient and ω is atomic volume. In oxidizing atmospheres, voids tend to grow rather than shrink.[34]
(iii) *Neutral drop method.* This is a three-phase method where a droplet of metal that partly penetrates and imperfectly wets a solid substrate takes on a shape which minimizes γ_π for the system.[20] The liquid–solid (γ_{SL}) and liquid–vapour (γ_{LV}) specific interfacial works and the liquid–solid (ϕ) and liquid–vapour (θ) contact angles are related to γ_π of the metal by

$$\gamma_\pi = -\gamma_{\mathrm{SL}}\cos\phi - \gamma_{\mathrm{LV}}\cos\theta \tag{16}$$

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[29] R. W. Davidge and G. Tappin, *J. Material Sci.*, 1968, **3**, 165.
[30] R. S. Nelson, D. J. Mazey, and R. S. Barnes, *Phil. Mag.*, 1965, **11**, 91.
[31a] W. A. Miller, G. J. C. Carpenter, and G. A. Chadwick, *Phil. Mag.*, 1969, **19**, 305.
[31b] M. T. Lilburne, *J. Material Sci.*, 1970, **5**, 351.
[32] B. Mills and G. M. Leak, *Acta Metallurgica*, 1968, **16**, 303.
[33] K. H. Westmacott, R. E. Smallman, and P. S. Dobson, *Metal Sci. J.*, 1968, **2**, 177.
[34] T. A. Johnston, P. S. Dobson, and R. E. Smallman, *Crystal Lattice Defects*, 1969, **1**, 47.

where $\gamma_{SL}\sin\phi = \gamma_{LV}\sin\theta$. Imperfect wetting and low mutual solubility are essential for this method, which is normally carried out at high temperatures.
(iv) *Grain boundary grooving.* This involves a similar three-phase equilibrium between two grains and a fluid.
(v) *Pulsed Field Emission Microscopy (FEM).* Migration of material to try to reduce the curvature of an FEM tip is controlled by γ_π. A d.c. electric field can be applied to stop migration, and γ_π can be calculated. An experimental difficulty is that the electric field which has to be applied to produce an image on the phosphor screen interferes, but this can be pulsed to provide visual continuity with minimum interference with migration. There are some limitations on the materials that can be examined, but single-crystal faces can be studied and contamination is negligible in the ultra-high vacuum environment.[35]
(vi) *Evaporation of filaments.* A thin filament is evaporated in a sensitive (*e.g.* phase change) calorimeter to form a thin film and the energy of formation per unit area of this deposited film is measured.[36]
(vii) *Equilibrium crystal shape methods.* The shape adopted by a crystal during growth is influenced by γ_π and several methods, most of which yield poor results, depend on this.[37]

Values of the specific surface work for various materials are given in the Table.

Table *Measurements of specific surface work for various materials**

Material	*Temp.*/°C	γ_π/J m^{-2}	*Method*	*Ref.*
Ag	930	1.14 ± 0.09	Zero-creep	*a*
Al	180	1.14 ± 0.2	Void-annealing	*b*
Au	1040	1.37 ± 0.15	Zero-creep	*c*
Be	700	1·0	Inert-gas bubble	*d*
Cr	1550	2.2 ± 0.25	Grain boundary grooving	*e*
Cu	1000	1.71 ± 0.1	Zero-creep	*f*
Fe-δ	1410	2.32 ± 0.08	Zero-creep of foils	*g*
Mo	1427	2.2 ± 0.2	Field emission microscopy	*h*
Nb	2250	2.1 ± 0.1	Zero-creep	*i*
Ni	1220	1.86 ± 0.2	Healing of scratches	*j*
Pt	1310	2.3 ± 0.8	Healing of scratches	*k*
Sn	215	0.68	Extruded filament	*l*

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[35] J. P. Barbour, F. M. Charbonnier, W. T. Dolan, W. P. Dyke, E. E. Martin, and J. K. Trolan, *Phys, Rev.*, 1960, **117**, 1452.
[36] W. P. Gilbreath and D. E. Wilson, *Rev. Sci. Instr.*, 1970, **41**, 969.
[37] A. V. Belyustin, in 'The Growth of Crystals', ed. A. V. Shubnikov and N. N. Sheftal, Chapman and Hall, London, 1969, vol. 2.

Material	*Temp.*/°C	γ_π/J m^{-2}	*Method*	*Ref.*
Ta	1500	2.68 ± 0.5	Neutral drop	*m*
Ti	1600	1.7	Zero-creep	*n*
W	1750	2.9 ± 0.3	Field emission microscopy	*o*
Zn	380	0.83	Zero-creep	*p*
BaF_2(111)	25	0.28	Cleavage at 78K	*q*
CaF_2(111)	25	0.45	Cleavage at 78 K	*q*
KCl(100)	25	0.11	Cleavage at 298 K	*r*
LiF(100)	25	0.34	Cleavage at 78 K	*q*
MgO(100)	25	1.2	Cleavage at 78 K	*q*
MgO(100)	25	1.15	Cleavage at 298 K	*s*
	25	0.27	Solubility	*t,u*
NaCl(100)	25	0.37	Cleavage at 298 K	*v*
	−196	0.28	Cleavage in vacuum	*w*
Mica	25	0.31	Cleavage in dry conditions	*x*
Paraffin wax	20	0.07	Extruded filament	*l*, but see the comments of *y*
Ice	0	0.11	Grain boundary grooving	*z*
Soda glass	25	4.6 ± 0.3	Cleavage at 78 K	*aa*
Araldite	25	~10	Cleavage	*bb*

*Values for metals are given for polycrystalline specimens only, and for systems where the fluid phase is either high vacuum or high-purity helium, for reasons discussed in the text. Further values are given by Jones (*Metal Sci. J.*, 1971, **5**, 15), for metal values which do not meet these criteria.

[a] E. R. Funk, H. Udin, and J. Wulff, *Trans. Amer. Inst. Mining Metallurg. Eng.*, 1951, **191**, 1206; [b] K. H. Westmacott, R. E. Smallman, and P. S. Dobson, *Metal Sci. J.*, 1968, **2**, 177; [c] P. C. Mullick and G. B. Craig, *Canad. Metallurg. Quart.*, 1966, **5**, 129; [d] R. S. Barnes and G. B. Redding, *J. Nuclear Energy*, 1959, **10**, 32; [e] B. C. Allen, *Trans. Metallurg. Soc. A.I.M.E.*, 1969, **245**, 1621; [f] H. Udin, A. J. Shaler, and J. Wulff, *Trans. Amer. Inst. Mining Metallurg. Eng.*, 1949, **185**, 186; [g] E. D. Hondros, *Acta Metallurgica* 1968, **16**, 1377; [h] L. C. Crouser and R. W. Strayer, *J. Metals*, 1961, **13**, 74; [i] S. V. Radcliffe, *J. Less-Common Metals*, 1961, **3**, 360; [j] P. S. Maiya and J. M. Blakely, *J. Appl. Phys.*, 1967, **38**, 698; [k] J. M. Blakely and H. Mykura, *Acta Metallurgica*, 1962, **10**, 565, corrected by Jones, *loc. cit.*; [l] E. D. Greenhill and S. R. McDonald, *Nature*, 1953, **171**, 37; [m] E. N. Hodkin, M. G. Nicholas, and D. M. Poole, *J. Less-Common Metals*, 1970, **20**, 93; [n] V. I. Kostikov, A. V. Kharitonov, and V. Z. Savenko, *Phys. Metals Metallog.*, 1968, **26**, 181; [o] J. P. Barbour, F. M. Charbonnier, W. T. Dolan, W. P. Dyke, E. E. Martin, and J. K. Trolan, *Phys. Rev.*, 1960, **117**, 1452; [p] L. S. Bryukhanova, J. A. Andreeva, and V. I. Likhtman, *Soviet Material Sci.*, 1965, **1**, 82; [q] J. J. Gilman, *J. Appl. Phys.*, 1960, **31**, 2208; [r] A. R. C. Westwood and T. T. Hitch, *J. Appl. Phys.*, 1963, **34**, 3085; [s] A. R. C. Westwood and D. L. Goldheim, *J. Appl. Phys.*, 1963, **34**, 3335; [t] R. R. Weiler, J. Beeckmans, and R. McIntosh, *Canad. J. Chem.*, 1961, **39**, 1360; [u] F. Van Zeggeren and G. C. Benson, *Canad. J. Chem.*, 1957, **35**, 1150; [v] S. M. Weiderhorn, R. L. Moses, and B. L. Bean, *J. Amer. Ceram. Soc.*, 1970, **53**, 18; [w] P. L. Gross and G. E. Gross, *J. Appl. Phys.*, 1965, **36**, 2459; [x] A. I. Bailey and S. M. Kay, *Proc. Roy. Soc.*, 1967, **A301**, 47; [y] A. C. Lowe and A. C. Riddiford, *J. Colloid Interface Sci.*, 1970, **33**, 292; [z] W. M. Ketcham and P. V. Hobbs, *Phil. Mag.*, 1969, **19**, 1161; [aa] S. M. Weiderhorn, A. M. Shorb, and R. L. Moses, *J. Appl. Phys.*, 1968, **39**, 1569; [bb] R. Griffiths and D. G. Holloway, *J. Material Sci.*, 1970, **5**, 302.

E. Surface Enthalpy Measurements.—(i) *Heat of solution method.* This is a straightforward equilibrium thermochemical comparison of the heats of solution of equal masses of powdered and lump forms of a sample.[20] It has the disadvantages that the surfaces are easily contaminated, lattice strain can be introduced into the powdered form during preparation, an interfacial rather than a surface enthalpy is obtained, and the accuracy of the answer is strongly dependent on calculations of the surface area, which usually err on the low side. On the other hand, this is the only method that Bikerman[4] believes to be capable of measuring any sort of surface energy parameter at all. He asserts that it in fact measures the *surface-layer or cuticular* energy which he envisages as remaining unchanged even if the surface is stretched. (The 'surface layer' in his terms would seem to be like a stretch nylon sock, fitting any size of foot.) He states that the cuticular energy would disappear if impurities were absent, which would make it correspond to $\Sigma\mu_i\Gamma_i$ rather than h_π, but his is not the generally accepted view.

(ii) *Kirchner and Chadwick's method.*[38] The ratios of γ_π in different crystallographic directions, say $\gamma_\pi^{110}/\gamma_\pi^{100}$, decrease with increasing temperature, linearly at first but more sharply at higher temperatures. For a one-component system where γ_π is equal to the specific surface Helmholtz energy, a_π, then equations (10) and (10a) may be rewritten to give

$$\gamma_\pi = h_\pi - Ts_\pi \tag{17}$$

and so

$$\frac{\gamma_\pi^{110}}{\gamma_\pi^{100}} = \frac{h_\pi^{110} - s_\pi^{110}\,T}{h_\pi^{100} - s_\pi^{100}\,T} = \frac{h_\pi^{110}}{h_\pi^{100}} + \left(\frac{h_\pi^{110}}{h_\pi^{100}} - \frac{s_\pi^{110}}{s_\pi^{100}}\right)\cdot\frac{T(s_\pi^{100}/h_\pi^{100})}{1 - T(s_\pi^{100}/h_\pi^{100})} \tag{17a}$$

If measurements are carried out at three or more temperatures, then the three unknowns, in this case h_π^{110}/h_π^{100}, s_π^{110}/s_π^{100}, and s_π^{100}/h_π^{100} can be obtained. Rewriting equation (17) as

$$\gamma_\pi^{100} = h_\pi^{100}\left(1 - \frac{s_\pi^{100}}{h_\pi^{100}}\,T\right) \tag{17b}$$

then a knowledge of γ_π^{100} at a temperature T, together with the value for s_π^{100}/h_π^{100} found from the analysis, yields h_π^{100}.

F. Surface Stress Measurements.—These are carried out using the *lattice-contraction* technique, which used to be described as a technique for measuring γ_π until the distinction between γ_π and g_{ij} was made clear. Small metal particles have their radii, r (usually ~1—50nm), measured in an electron microscope and their lattice constant, a, determined by electron diffraction in the same instrument. The mean surface stress, g, is given by

$$g = -\,3\Delta ar/2aK \tag{18}$$

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[38] H. O. K. Kirchner and G. A. Chadwick, *Phil. Mag.*, 1970, **22**, 449.

where Δa is the difference between a for the particles and a for the bulk material and K is the bulk compressibility.[39] For gold, Kuhlmann-Wilsdorf and her co-workers found $g = 1.140 \pm 0.07\,\mathrm{J\,m^{-2}}$ at 50 °C and $0.410 \pm 0.04\,\mathrm{J\,m^{-2}}$ at 985 °C; $d\gamma_\pi/d\epsilon_{ij}$ increased with temperature from $0.7\,\mathrm{J\,m^{-2}}$ at 50 °C to $1.0\,\mathrm{J\,m^{-2}}$ at 985 °C. The value of γ_π is higher than g, being $1.4\,\mathrm{J\,m^{-2}}$ at 1040 °C.

4 Calculations of Surface Energy Parameters

For crude estimates of the specific surface work, the relation[40]

$$\gamma_\pi \approx 4\gamma_{\mathrm{LV}}/3 \tag{19}$$

where γ_{LV} is the surface tension of the liquid, works quite well for metals at the melting point. For the grain boundary energy, γ^*, as has been already mentioned[2]

$$\gamma_\pi \approx 3\gamma^* \tag{20}$$

For a one-component system, the specific surface entropy can be estimated from data of the temperature variation of γ_π, a value of $0.0005\,\mathrm{J\,m^{-2}\,K^{-1}}$ being found for most metals,[22] but Kirchner and Chadwick[38] deduce values of s_π for hcp metals of *ca.* $0.0012\,\mathrm{J\,m^{-2}\,K^{-1}}$. As the grain boundary entropy is also about $0.0005\,\mathrm{J\,m^{-2}\,K^{-1}}$,[12] the higher value would be expected if equation (20) applied in addition to entropies.

Two types of calculation will now be considered; additional calculations for ionic solids have been extensively reviewed recently.[6]

A. The Nearest-neighbour Model.—A simple approach is to assume[41] that when a surface is formed by cleavage, half the nearest-neighbour bonds are broken for each surface atom. Each bond is considered to have an energy of l where

$$l = 2LW/XN \tag{21}$$

and L is the latent heat of vaporization in $\mathrm{J\,kg^{-1}}$, W is atomic weight, N is Avogadro's constant, and X is the number of nearest neighbours. If for a given crystal face there are n atoms $\mathrm{m^{-2}}$ and each atom has x bonds broken, then since *two* surfaces are formed, at the melting point

$$\gamma_\pi = xln/2 = LWnx/XN \tag{22}$$

Thus for the 111 face of an fcc crystal, $X = 12$, $n = 2/a^2\sqrt{3}$ (where a is the interatomic distance) and $x = 3$. The variation of γ_π with orientation can be estimated from this theory as the only parameters that change are n and x, the product (nx) being $6/a^2\sqrt{3}$ for the 111 surface of an fcc crystal, $4/a^2$ for a 100 surface,

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[39] J. S. Vermaak and D. Kuhlmann-Wilsdorf, *Surface Sci.*, 1968, **12**, 134; *J. Phys. Chem.*, 1968, **72**, 4150.

[40] J. W. Taylor, *J. Inst. Metals*, 1958, **86**, 456.

[41] H. Mykura, in ref. 5, p. 10.

$6/a^2\sqrt{2}$ for a 110 surface, and $14/a^2\sqrt{10}$ for a 210 surface, giving relative values for γ_π of 1.00:1.154:1.223:1.275.

A more refined approach is that of Skapski,[42] who calculates a parameter connected with increasing the area of existing solid surface at the melting point. Although this is properly a surface stress measurement, at the melting point mobility is high and surface stress equals the specific surface work. Skapski's equation is

$$\gamma_\pi = \frac{X_i - X_\pi}{X_i}\frac{L_F}{\Omega_s} + \left(\frac{\rho_s}{\rho_L}\right)^{2/3} \gamma_L + \frac{T_m}{2\Omega_s}(\Delta S_{L,\,\mathrm{config}} - \Delta S_{s,\,\mathrm{config}}) \qquad (23)$$

(where X_i and X_π are the number of nearest neighbours in the interior and on the surface, L_F is the latent heat of fusion, Ω_s is the molar area of a layer one atom thick of the solid, ρ_s and ρ_L are solid and liquid densities, T_m is the melting point and $\Delta S_{\mathrm{config}}$ is a configurational entropy change). The first term measures the energy difference between interior and surface atoms, the second the energy difference caused by difference in molar areas between liquid and solid, and the final term, *which is small and can be neglected,* the energy arising from the high mobility of surface atoms at the melting point.

B. Pairwise-potential Models.—(i) *Interatomic Potentials.* Nicholas[43] calculated the anisotropy of γ_π by summing the energies associated with all atomic pairs that were split up when the surface was created. He summed over all neighbours and used both Morse and Lennard-Jones pairwise potential functions; the constants in the potential functions for particular metals were selected to agree with experimental values of compressibility and sublimation energy for each metal. (ii) *Interplanar Potentials.* Linford and Mitchell[44] calculated values of γ_π at room temperature for a range of metals of different crystal structures, using a potential function between the two adjacent planes in the bulk that are separated to form two new surfaces. Bulk parameters are related to the values of derivatives of the potential at the equilibrium interplanar separation r_0, and a Buckingham (exp − 6) potential is preferred, giving

$$\gamma_\pi = Yr_0 f(b) \qquad (24)$$

where Y is Young's modulus and $f(b)$, which is 0.55 ± 0.06, is given by

$$f(b) = \frac{(b - 6)}{12b(b - 7)}$$

$$\text{where } b = (X^2 + 14 \times 56)^{\frac{1}{2}} - X;\ \text{where } X = \alpha Y r_0^3/k \qquad (25)$$

α being the linear coefficient of thermal expansion and k being Boltzmann's constant.

5 The Effect of Crystal Orientation

Several examples have been mentioned so far of the variation of γ_π with orienta-

[42] A. S. Skapski, *Acta Metallurgica*, 1956, **4**, 576.

[43] J. F. Nicholas, *Austral. J. Phys.*, 1968, **21**, 21.

[44] R. G. Linford and L. A. Mitchell, *Surface Sci.*, 1971, **27**, **142**.

tion and of the techniques that can be used to measure this. Apart from tabulation, two principal methods can be used to present this data, the Wulff plot and the γ-plot. A *Wulff plot*[45] is formed by drawing a set of vectors, normal to various crystal planes, and of lengths proportional to the values of γ_π for each plane. The set of planes normal to each vector and positioned at its end is constructed, giving a three-dimensional geometric figure which is the equilibrium shape of the crystal. A *γ-plot* is a stereographic projection[46] on which values of γ_π are superimposed as contours.

The value of γ_π for a low-index orientation is low but if an orientation at a small angle, θ, to the low index plane is considered, γ_π increases proportionally to θ, the quantity $d\gamma_\pi/d\theta$ being a *torque*. This can be calculated by the *step model*[47] for low θ, and by a *bond model*[47] for high θ. Avraamov[48] measured the torque of silicon–iron single crystals, finding that below $\theta = 20°$, $d\gamma_\pi/d\theta = +0.035\,\mathrm{J\,m^{-2}}$ (degree of rotation)$^{-1}$.

6 The Effect of Adsorbates

The Gibbs adsorption equation

$$d\gamma_\pi = -\, s_\pi dT - \Sigma\Gamma_i d\mu_i;\ \Delta \int \gamma_\pi dA = 0 \tag{3}$$

is valid for describing the change in γ_π due to changes in an adsorbed film on a solid unless the orientation or the state of strain of a crystal surface is changed.[11] It reduces to the adsorption isotherm

$$\left(\frac{d\gamma_\pi}{d\mu_i}\right)_{T,\mu_j} = -\Gamma_i \tag{26}$$

where

$$d\mu_i = kTd(\ln p_i) \tag{27}$$

At low coverage for physisorption of a gas on a solid, Γ varies with p, giving[49]

$$-\Delta\gamma_\pi = \Gamma kT \tag{28}$$

Hondros[21] has shown that γ_π for bcc iron falls by about 4% for every 10-fold increase in oxygen pressure between 10^{-20} and 10^{-15} atm O_2, implying the very high surface activity (fall of γ_π per unit solute content) of $10^4\,\mathrm{J\,m^{-2}}$(atm %O_2)$^{-1}$. This incidentally makes oxygen the most surface-active element, and the contaminant which causes the greatest interference with high-temperature surface studies.

The torque $d\gamma_\pi/d\theta$ can be greater in the presence of a solute adsorbed at the interface; at constant temperature[47]

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[45] A. W. Adamson, 'Physical Chemistry of Surfaces', 2nd edn., Interscience, New York, 1967.

[46] C. S. Barratt, 'Structure of Metals', 2nd edn., McGraw-Hill, New York, 1952.

[47] P. G. Shewman and W. M. Robertson, in 'Metal Surfaces: Structure, Energetics and Kinetics'. American Society for Metals, Ohio, 1963, p. 114.

[48] Y. S. Avraamov, A. G. Gvozdev, and B. G. Livshits, *Phys. Metals Metallog.*, 1966, **21**, 140.

[49] G. Ehrlich, in 'Metal Surfaces: Structure, Energetics and Kinetics', American Society for Metals, Ohio, 1963, p. 221.

$$-\frac{d\Gamma_i}{d\theta} = \frac{d\left(\frac{d\gamma_\pi}{d\theta}\right)}{d\mu_i} \qquad (29)$$

Consequently, adsorbates increase the anisotropy of the specific surface work.

7 The Use of Surface Energy Parameters

There is not space here to discuss the many applications of surface energy parameters in the physical sciences, but two unusual interdisciplinary applications connected with tribology will be mentioned.

(i) *Prediction of solid–solid adhesive strengths.* When two atomically clean surfaces are pressed together under light loads, they adhere. When they are pulled apart again, fracture normally occurs in the weaker material rather than at the interface. When the weaker material is very brittle, as in Buckley's[50] experiments on the adhesive force between single-crystal rhenium and quartz, the critical stress to fracture, or cohesive stress, σ_c, can be related to γ_π by

$$\sigma_c = (2Y\gamma_\pi/h)^{\frac{1}{2}} \qquad (30)$$

where Y is Young's modulus and h is the half-crack length.

If metals are arranged in order of decreasing γ_π, which also happens to be in order of decreasing Young's modulus, *i.e.* Pt > Ni > Cu > Au > Ag > Al > Pb, a given metal couple will break in the metal nearest the right hand end of the list, and transfer, *e.g.* of Au on to Cu, can be detected[19b] by LEED, Auger spectroscopy, or microprobe techniques. Adhesion strengths also vary as a function of crystal orientation, gold adhering more strongly to the 110 plane of Cu than to the 111 plane, despite the greater number of atoms to which to bond in the 111 plane. This is also contrary to what would be expected from the values of Young's modulus, but in accord with the values of γ_π.

(ii) *The 'Surface Energy Criterion' applied to friction and wear.* Rabinowicz[51] correlated the diameters, d, of wear particles formed when a solid, a, rubs on another solid, b, with a 'surface energy criterion'. This 'criterion' was defined as the ratio of the work of adhesion W_{ab} between a and b to the hardness of the weaker material; W_{ab} is related to the specific surface works $\gamma_{\pi,a}$ and $\gamma_{\pi,b}$ of a and b by

$$W_{ab} = \gamma_{\pi,a} + \gamma_{\pi,b} - \gamma_{ab}$$

where γ_{ab} is the interfacial work and usually is *ca.* $\frac{1}{2}(\gamma_{\pi a} + \gamma_{\pi b})$. Despite some assumptions Rabinowicz arrived at a relation between d and W_{ab}/H:

$$d = 60000\ W_{ab}/H \qquad (32)$$

The concept works passably well and has the attraction that W_{ab}/H has the dimensions of length, which is useful for a criterion dealing with lengths of sliding distances and with particle diameters.

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[50] D. H. Buckley, N.A.S.A. Technical Memorandum, NASA TMX-52589, 1969.

[51] E. Rabinowicz, 'Friction and Wear of Materials', Wiley, New York, 1966.

The author would like to thank A. A. Parry, L. A. Mitchell, A. Lowe, and M. Rowe for helpful discussions. This paper is published by permission of the Central Electricity Generating Board.