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INTERPHASES IN SYSTEMS OF
CONDUCTING PHASES

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Interphases in systems of conducting phases

Abstract - The document is an Appendix to the Manual of Symbols and Terminology for Physicochemical Quantities and Units. Together with the other appendices notably that on Electrochemical Nomenclature, it expands the recommendations for nomenclature in the region of interphases containing charged particles. After suggesting terms for the description of the interphase itself, there are sections outlining nomenclature for electric potentials at free surfaces (a condensed phase in contact with vacuum or dilute gas) and in interphases (the boundary between two dense phases). These include a discussion of the electronic work function and the Volta (or contact) potential difference. Interphases between metals, semiconductors and electrolytes are discussed. Nomenclature for the thermodynamic properties of the interphase at equilibrium is recommended including capacitances and components of charge. Quantities related to the description of the structure of the interphase are discussed and terms consistent with the present knowledge of this structure are recommended for the situations of the adsorption of ions or molecules and the possibility of partial charge transfer. Some general remarks are made about adsorption isotherms. The report concludes with some recommendations for the nomenclature of the mechanical properties of solid surfaces.

PREFACE

The present document is intended to give an account of the nomenclature of adsorption phenomena at some electrified interphases by expanding previous recommendations to more specific systems. It must therefore be used in conjunction with the Manual of Symbols and Terminology (ref. 1) and its Appendices I, II (refs. 2,3) and III (ref. 4) since a number of quantities already defined in the other documents have been introduced here without any further comment. Some references can also be found to two documents of the Electrochemistry Commission dealing with transport phenomena in electrolytic systems (ref. 5), and with recommendations for publication of kinetic parameters (ref. 6).

The present recommendations are essentially based on concepts of general physics and adsorption thermodynamics while nonequilibrium dynamics as well as quantumchemical aspects have not been included. Much of the current discussion of the systems dealt with in this document depends on models. The purpose of the recommendations is to provide terms and symbols for the kinds of quantities, the components and the systems that may be described by measurement or by quantitative models. The attempt made here to codify the nomenclature should not be taken to imply endorsement of a particular model.

The document is necessarily incomplete and it is hoped that it will be supplemented in the future. As major examples, ionic solid/liquid and solid/solid electrolyte interphases are not dealt with, attention being primarily focussed on metal/electrolyte solution, and secondarily on electrolyte solution/air and metal/vacuum interphases.

At the end of the document, a list of symbols with the appropriate SI unit has been attached. Multiples or submultiples are equally acceptable and may frequently be preferred where justified by usage. Symbols already recommended in Appendix III (ref. 4) have not been included in the list.

1 GENERALITIES

1.1 Interface and surface

The plane ideally marking the boundary between two phases is called the *interface*. Although interfaces are always dealt with from a thermodynamic point of view, if attention is actually focussed on only one of the two phases, the plane ideally marking the boundary between the phase and the environment is called the *surface* of the phase.

This term is used particularly of a condensed phase in contact with a vacuum or an "inert" gas atmosphere. This condition is often emphasized by using the term *free surface*: e.g. the (free) surface of a metal in a vacuum or a dilute gas, the (free) surface of a liquid (much below the boiling point) in the air. "Free" surface should not be confused with "unoccupied" or "bare" surface which is normally used to indicate the part of a surface not covered by an adsorbate or to emphasize the condition of a surface without adsorbed species in contrast with the state of the surface with adsorbate.

The extent of the interface (surface) is measured by its area, A (or S). For solids, a *real* (true, actual) A_r , and a *geometric* A_g , surface (interface) area may be defined (ref. 4) if asperities are present whose height is orders of magnitude greater than the atomic or molecular size. The geometric surface is the projection of the real surface on a plane parallel to the macroscopic, visible phase boundary. The ratio $f_r = A_r/A_g$ is defined as the *roughness* (rugosity) *factor*. If asperities are of the order of the atomic size, the surface of the solid may be better described as *stepped*. High index faces of crystals are stepped surfaces but may be ideally smooth in the sense of the roughness factor.

1.2 Interphase and surface region

Particles of a condensed phase located near a newly created (free) surface are subjected to unbalanced forces. Modifications occurring to bring the system to equilibrium generally extend somewhat into the phase. The tridimensional region, extending from the free surface towards the interior, where the properties differ from the bulk is the *surface region*. The term "surface" may also be used in this sense.

The region between two phases where the properties vary between those in the bulk is the *interfacial region* (Fig. 1). It may also be regarded as a distinct - though not autonomous - phase and be called the interphase. The term "interface" used synonymously with "interphase" is not recommended. There is no clear boundary between the interfacial region and the bulk of the phases so that the thickness of the interphase depends on the model chosen to describe this region. Although only parameters relevant to the interphase as a whole can be thermodynamically defined it may be convenient and expedient for some purpose to split them into contributions of the two phases. Therefore, the interphase may be envisaged as consisting of the surface regions of the two phases in contact (Fig. 1). The properties of each of these generally differ from those of the free surfaces of the two phases because the local forces in play as a rule differ in the two cases.

1.3 Electrified interphase

Electrified interphases are those between phases containing free charged components which are usually accumulated or depleted in the surface regions thus giving rise to net charges on the phases. This definition includes the special case when the net charge on each of the phases reduces to zero.

When charged components are present in the two phases, electroneutrality must be fulfilled, on the time average, in any infinitesimal volume in the bulk of the phases. In the interphase electroneutrality is also fulfilled in any volume with constant cross-section parallel to the interface, extending into each bulk phase.

Charged components may or may not cross the interface between two phases. In this respect, interphases may be divided into the limiting types *unpolarizable* and *polarizable* respectively. Ideally *unpolarizable* interphases are those for which the exchange of common charged components between the phases proceeds unhindered. Ideally *polarizable* interphases are those for which there are no common components between the phases or the exchange of these is hindered. Real interphases may approach more or less well one of the above two idealized cases. Polarizability or non-polarizability is not an absolute property of an interphase but depends on a number of conditions, *e.g.* time scale of the experiment.

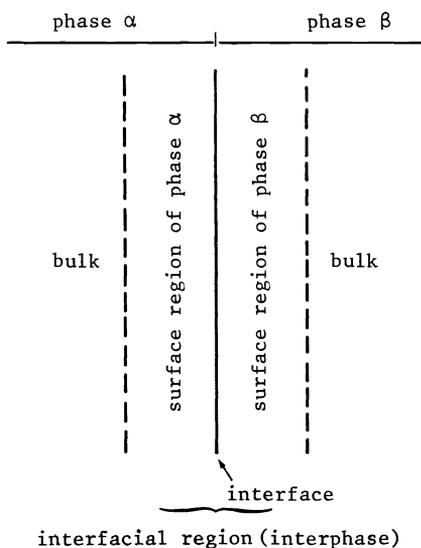


Fig. 1. Illustration of nomenclature.

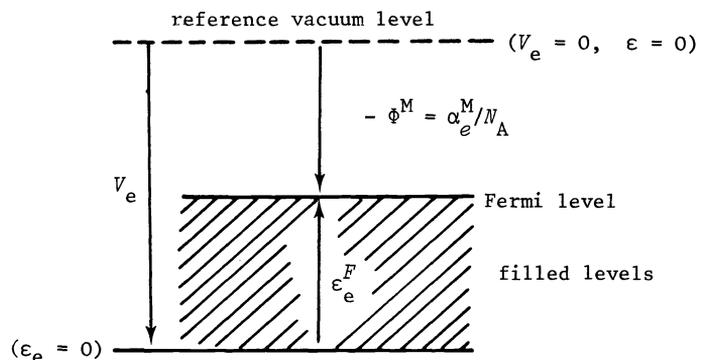


Fig. 2. Sketch of the energy diagram for electrons in uncharged metals.

If electrically non-conducting phases are dealt with, injection of a few charges into them may lead to interphase thickness exceeding the size of the phases themselves. In what follows, electrically conducting charged phases are always to be understood.

2 ELECTRIC POTENTIAL AT FREE SURFACES

2.1 Surface of molecular liquids

Particles in the surface region of a phase are subjected to orienting forces as a result of the anisotropic force field. Polar molecules (*e.g.* permanent dipoles) may thus be preferentially oriented in the surface region, while polarizable molecules may be polarized (induced dipoles). The array of oriented polar and/or polarized molecules is called the *surface dipole layer* with which an electric potential drop is associated, called the *surface potential* of the phase, χ . Superscripts may be used to identify the phase. The sign of χ is positive when the dipole layer points its negative side towards the exterior of the phase.

If i is taken as the running index of different molecules present in the dipole layer then:

$$\chi = \sum_i n_i^s p_{\perp, i} / A\epsilon \quad (2.1.1)$$

where $p_{\perp, i}$ is the component of the permanent or induced dipole of molecule i normal to the interface. p is taken to contribute a positive surface potential if the positive end of the dipole points to the interior of the phase, ϵ is the effective (local) permittivity and n_i^s is the number of molecules of species i in the surface region.

Oppositely charged ionic components, if present in the phase, may penetrate the surface region differently and can be envisaged as being located on different planes there. This charge separation may also be expressed as a dipole contribution $p_{\perp, i}$. The surface potential drop of an electrolyte solution is thus the sum of an ionic and a dipolar contribution. The latter may differ from that of the pure solvent.

The adsorption of an uncharged molecule may also change χ both by changing the orientation or number of existing molecules and by contributing a dipole potential itself if it has a dipole [*cf.* eqn.(2.1.1)].

2.2 Surface of metals

Metals are usually envisaged as containing two constituents: ions (ion cores of metal atoms) and mobile (free) electrons (valence electrons of metal atoms). The term "electrons" is often used to mean "free electrons".

All free electrons in a metal experience the same *potential energy*, V_e , resulting from electron-ion and electron-electron interactions. V_e is measured with respect to electron at rest in a field-free vacuum where $V_e = 0$ (Fig. 2). It is a negative quantity and includes *bulk*, V_e^b , and *surface*, $-e\chi^M$, contribution, the latter being due to the surface potential of the metal:

$$V_e = V_e^b - e\chi^M \quad (2.2.1)$$

Free electrons are distributed in *energy levels* at increasing *kinetic energy*, ϵ_e (Note a). The highest level filled with electrons at 0 K is the *Fermi level* where the kinetic energy has the value ϵ_e^F . ϵ_e and ϵ_e^F are positive quantities (Fig. 2). At the Fermi level:

$$(V_e^b + \epsilon_e^F)N_A = \mu_e^M \quad (2.2.2)$$

where μ_e^M is the *chemical potential* (ref. 4) of electrons in the metal and N_A the Avogadro constant. The reference state for μ_e^M is constituted by electrons at rest in a field-free vacuum where $V_e = 0$, hence $\mu_e = 0$.

The total energy of electron in an uncharged metal at the Fermi level is the *Fermi energy*. The *molar Fermi energy*, measured with respect to the vacuum level, is the real potential α_e^M of electrons in the metal:

$$\alpha_e^M = (V_e^b + \epsilon_e^F)N_A - F\chi^M \quad (2.2.3)$$

or from eqn.(2.2.2):

$$\alpha_e^M = \mu_e^M - F\chi^M \quad (2.2.4)$$

in accord with the definition of the real potential. The surface potential χ^M originates from the local absence of charge balance in the surface region due here to the electron density profile not coinciding with the uniform positive background profile.

Note a: The symbol ϵ_e is preferred over E_k as suggested in (ref. 1) in view of the possibility of confusion with the symbol E used for the electrode potential.

2.3 Electron work function

The electron work function, Φ , of a metal M is the minimum work needed to extract electrons from the Fermi level of a metal across a surface carrying no net charge. It is equal to the sum of the potential energy and the kinetic Fermi energy taken with the reverse sign (Fig. 2):

$$\Phi^M = - (V_e + \epsilon_e^F) \quad (2.3.1)$$

As customarily defined, Φ , V and ϵ are *entitic* quantities, *i.e.* they are referred to a single entity (particle) of the system (one electron, in the present case). The electron work function, multiplied by the Avogadro constant, is therefore equal to the molar Fermi energy (or real potential of electrons) taken with the reverse sign:

$$\Phi_{N_A}^M = - \alpha_e^M = - \mu_e^M + F\chi^M \quad (2.3.2)$$

The work function depends on the structure of the surface at an atomic level. In this sense it is an anisotropic quantity. Stepped surfaces of metals exhibit lower work functions than smooth surfaces. Roughness at a macroscopic level is not a parameter relevant to the work function. The work function can be defined rigorously only for well defined crystal faces. Polycrystalline surfaces are made up of different crystal faces. If patchy surfaces are considered, each patch with true work function Φ_z^M occupying the area fraction θ_z of the real surface, the average work function of the polycrystalline surface may be defined by:

$$\langle \Phi^M \rangle = \sum_z \theta_z \Phi_z^M \quad (2.3.3)$$

However, the actual values of work functions measured with polycrystalline surfaces depend on the experimental technique used because a different average is obtained in each technique.

If a free charge density σ is present in the surface region of phase M, an extra work equal to $F\psi^M$ must be done to extract electrons, where ψ^M is the electrostatic potential (outer potential) (ref. 4) of the phase with respect to the vacuum level. Thus (Fig. 3):

$$N_A \Phi^M + F\psi^M = - \tilde{\mu}_e^M = - \mu_e^M + F\phi^M \quad (2.3.4)$$

where $\tilde{\mu}_e^M$ is the electrochemical potential (ref. 4) of electrons in the phase M and $\phi^M = \psi^M + \chi^M$ is the inner electric potential (ref. 4). $\tilde{\mu}_e^M$ is the energy binding electrons to the interior of a charged phase. Since the chemical potential is independent of charge on the phase and of the surface structure, eqn.(2.3.4) shows that the arbitrary separation of chemical and electric parameters implies constancy in χ^M with surface charge density, which is reasonable in view of the very low capacitance of the metal/vacuum interphase involving vanishingly small amounts of charge to change its electrical state.

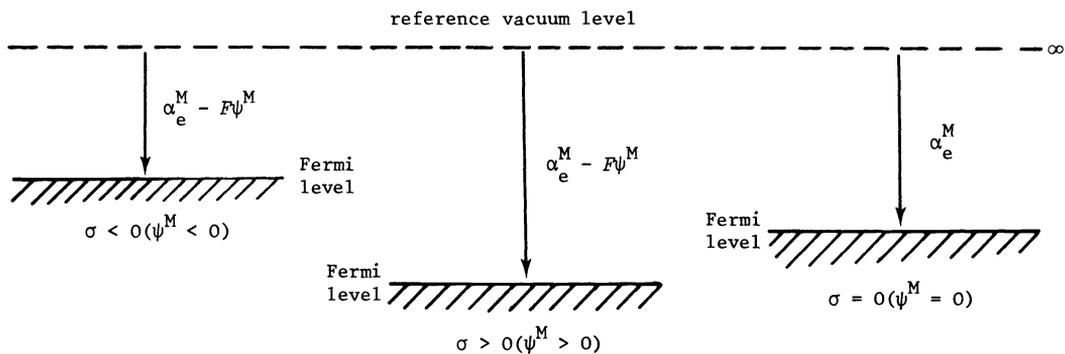


Fig. 3. Illustration of the effect of the presence of a free charge on the Fermi level position in a metal.

3 ELECTRIC POTENTIALS IN INTERPHASES

3.1 Dipolar contribution

Although at the interface between two phases distinct dipolar layers relevant to the two phases may not be experimentally distinguishable easily, it is often convenient for the purpose of modelling to distinguish separate contributions to the surface potential. The sharp separation rests on the assumption of absence of partial charge transfer between the two phases. The dipole potential of a phase at the interface with another phase is, anyhow,

more difficult to define. It differs in principle from that at the free surface and a different symbol must be used. Thus:

$$g_{(\beta)}^{\alpha}(\text{dip}) = \chi^{\alpha} + \delta\chi_{(\beta)}^{\alpha} \quad (3.1.1)$$

is the *dipole potential* of phase α at the boundary with phase β . Accordingly:

$$g_{(\alpha)}^{\beta}(\text{dip}) = \chi^{\beta} + \delta\chi_{(\alpha)}^{\beta} \quad (3.1.2)$$

is the dipole potential of phase β at the same interface. The total potential drop associated with dipolar layers in the interphase is:

$$g_{\beta}^{\alpha}(\text{dip}) = g_{(\beta)}^{\alpha}(\text{dip}) - g_{(\alpha)}^{\beta}(\text{dip}) \quad (3.1.3)$$

In principle:

$$g_{\beta}^{\alpha}(\text{dip}) \neq \chi^{\alpha} - \chi^{\beta} = \Delta_{\beta}^{\alpha}\chi \quad (3.1.4)$$

except the case of the quite fortuitous occurrence of $\delta\chi^{\alpha} = \delta\chi^{\beta}$. Owing to the high electrical capacitance of the region between two conducting phases, the charge density there is usually high and $g(\text{dip})$ must be regarded in principle as dependent on the electrical state of the interphase.

3.2 Metal/solution interphase

For ideally polarizable interphases in the absence of specific adsorption (see section 5.2) the electric potential drop may be written as the sum of a contribution arising from charge separation across the interface and one arising from dipole orientation:

$$\Delta_{\text{S}}^{\text{M}}\phi = g_{\text{S}}^{\text{M}}(\text{ion}) + g_{\text{S}}^{\text{M}}(\text{dip}) \quad (3.2.1)$$

$g_{\text{S}}^{\text{M}}(\text{ion})$ is the potential drop associated with free charges on the phases when the solvent molecules in the interphase are regarded as non-polar polarizable particles, while any fixed dipole contribution is included in $g_{\text{S}}^{\text{M}}(\text{dip})$. The potential drop in the diffuse layer (see section 5.2) is included in $g_{\text{S}}^{\text{M}}(\text{ion})$. At the *potential of zero charge* (ref. 4) $g_{\text{S}}^{\text{M}}(\text{ion}) = 0$ by definition, hence:

$$\Delta_{\text{S}}^{\text{M}}\phi_{\sigma=0} = g_{\text{S}}^{\text{M}}(\text{dip})_{\sigma=0} \quad (3.2.2)$$

By recalling eqn.(3.1.3), eqn.(3.2.1) may be written:

$$\Delta_{\text{S}}^{\text{M}}\phi = g_{\text{S}}^{\text{M}}(\text{ion}) + g_{(\text{S})}^{\text{M}}(\text{dip}) - g_{(\text{M})}^{\text{S}}(\text{dip}) \quad (3.2.3)$$

If ions are specifically adsorbed at a metal/electrolyte interphase, the contribution to $\Delta_{\text{S}}^{\text{M}}\phi$ from the ions on the electrolyte side of the interface does not vanish at $\sigma^{\text{M}} = -\sigma^{\text{S}} = 0$. Since the amount of ions specifically adsorbed is a function of the nature of the metal, the composition of the electrolyte etc., the potential of zero charge also depends on these factors. The presence of specifically adsorbed ions may also change the orientation of polar solvent molecules in the interface. Hence the analysis of $g_{\text{S}}^{\text{M}}(\text{dip})$, even at the potential of zero charge, is complex. $g_{\text{S}}^{\text{M}}(\text{dip})$ will also, in general, be a function of the free charge $\sigma^{\text{M}} = -\sigma^{\text{S}}$ on the interphase, *i.e.* of $g_{\text{S}}^{\text{M}}(\text{ion})$.

The adsorption of uncharged molecules may also change $g_{\text{S}}^{\text{M}}(\text{dip})$ in much the same way as χ^{S} is changed at a free liquid surface. However, because of the possibility of considerable variations of charge, the orientation of these molecules may vary and consequently their contribution to $g_{\text{S}}^{\text{M}}(\text{dip})$ is charge dependent.

3.3 Metal/metal interphase

When two uncharged metals, M_1 and M_2 are brought in contact, electrons flow from the metal with lower work function to that with higher Φ until their electrochemical potentials in the two phases become equal. This corresponds to the Fermi level becoming the same in the two phases (Fig. 4).

At equilibrium, free charges are present also at the free surfaces. These are responsible for the onset of a measureable *contact potential difference* (*Volta potential difference*), which is defined as the electric potential difference between one point in the vacuum close to the surface of M_1 and another point in the vacuum close to the surface M_2 . From eqn.(2.3.4) the contact potential difference is given by:

$$\Delta_{M_2}^{M_1}\psi = \Delta_{M_2}^{M_1}\phi/e \quad (3.3.1)$$

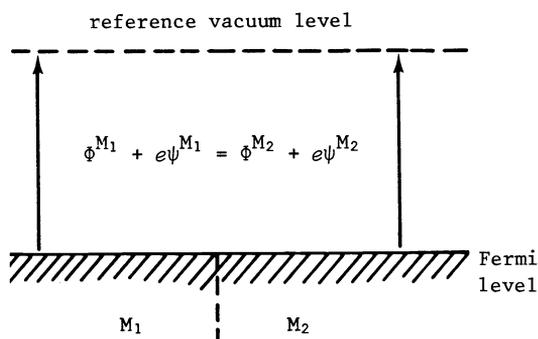


Fig. 4

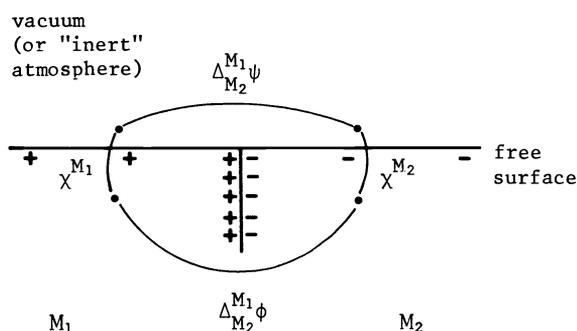


Fig. 5

Fig. 4. Schematic energy diagrams for two metals in contact.

Fig. 5. Illustration of the contact (Volta) potential difference. The point in the vacuum is at a distance from the phase such that charged particles there do not disturb the charge distribution in the surface region but are still subjected to the whole effect of the outer potential (ref. 4).

Since across the free surfaces of the phases the surface potential may be assumed to be independent of charge (*cf.* section 2.3) (Fig. 5):

$$\Delta_{M_2}^{M_1} \phi = \Delta_{M_2}^{M_1} \chi + \Delta_{M_2}^{M_1} \psi \quad (3.3.2)$$

where ϕ is the inner electric potential and $\Delta\phi$ is the Galvani potential difference (ref. 4).

3.4 Volta potential difference—metal/solution interface

A Volta potential difference is established at the equilibrium between a metal and a solution. Since the charges on the free surfaces are vanishingly small, χ^S may be assumed to remain constant. Thus (*cf.* Fig. 5):

$$\Delta_S^M \phi = \Delta_S^M \chi + \Delta_S^M \psi \quad (3.4.1)$$

In view of eqns.(3.1.2) and (3.2.1):

$$\Delta_S^M \psi = g_S^M(\text{ion}) + \delta\chi_{(S)}^M - \delta\chi_{(M)}^S \quad (3.4.2)$$

At the potential of zero charge, in view of eqn.(3.2.2):

$$\Delta_S^M \psi_{\sigma=0} = \delta\chi_{(S)}^M - \delta\chi_{(M)}^S \quad (3.4.3)$$

Equation (3.4.3) implies that at the potential of zero charge the Volta potential difference (cpd) between a metal and a solution in the absence of specific adsorption is in principle different from zero (*cf.* 3.1). Thus:

$$\begin{aligned} \Delta_S^M \psi &\neq g_S^M(\text{ion}) \\ \Delta_S^M \chi &\neq g_S^M(\text{dip}) \end{aligned} \quad (3.4.4)$$

Free charge and dipole contributions to potential drops are in principle different at different interphases of the same phase.

3.5 Metal/semiconductor interphase

The difference from the case in section 3.3 is that the electron density in semiconductors is as a rule so small that the free charge is a diffuse space charge and the surface region thus goes deeply into the phase (very many atomic diameters). Hence, most of $\Delta\phi$ is located in the surface region of the semiconductor, where the surface excess or deficiency of electrons constitutes a *space charge*.

The contribution of potential in the space charge region of the semiconductor results in a change in the electron energy levels with distance from the interface. This is usually described as "bending of the energy bands". Thus the bands are bent, *upwards* if $\sigma > 0$ and *downwards* if $\sigma < 0$. When $\sigma = 0$ the condition of *flat bands* is met, provided no surface states are present. *Surface states* are energy levels localized in the surface region of semiconductors which do not bear any direct relation to the bulk energy level distribution, but which can exchange electrons with the bulk. In such a case; a space charge may arise even

when $\sigma = 0$, in that $\sigma = \sigma_{sc} + \sigma_{ss}$, where σ_{sc} is the space charge density and σ_{ss} is the charge density associated with the surface states.

3.6 Semiconductor/solution interphase

For ideally polarizable interphases in the absence of specific adsorption (see section 5.2), the electric potential drop may be written:

$$\Delta_S^{SC} \phi = \Delta \phi^{sc} + g_S^{SC}(\text{ion}) + g_S^{SC}(\text{dip}) \quad (3.6.1)$$

where $\Delta \phi^{sc}$ is the potential drop associated with the space charge in the semiconductor and the last two terms have the same meaning as in eqn.(3.2.1). If effects of surface states are negligible, $\Delta \phi^{sc}$ vanishes as the charge on the semiconductor becomes zero. The potential of the semiconductor corresponding to this condition is the *flat band potential* which plays the same role as the potential of zero charge (ref. 4) for metals. At the flat band potential equation (3.6.1) may be written [cf. eqn.(3.2.2)]:

$$\Delta_S^{SC} \phi_{FB} = g_S^{SC}(\text{dip})_{FB} \quad (3.6.2)$$

Arguments given in section 3.1 and section 3.4 are applicable to this interface as well.

In the presence of surface states, $\sigma = 0$ does not necessarily imply the condition of flat band, for the charge trapped in the surface states may be balanced by a space charge of opposite sign in the semiconductor (cf. section 3.5).

3.7 Liquid/liquid interphase

When two immiscible, liquid, polar (or polarizable) phases S_1 and S_2 (e.g. water and nitrobenzene) are brought in contact, molecules at the newly created interface become preferentially oriented by the short-range, anisotropic forces located there. A dipolar layer thus arises to which a potential drop $g_{S_2}^{S_1}(\text{dip})$ is associated (cf. section 3.1). If electrolytes are dissolved in the liquid phases,² a further contribution due to the redistribution of free charges may be found. Therefore, the total electric potential drop may be written:

$$\Delta_{S_2}^{S_1} \phi = g_{S_2}^{S_1}(\text{ion}) + g_{S_2}^{S_1}(\text{dip}) \quad (3.7.1)$$

where, in the absence of ionic specific adsorption $g_{S_2}^{S_1}(\text{ion}) = 0$ when $\sigma^{S_1} = -\sigma^{S_2} = 0$. Hence:

$$\Delta_{S_2}^{S_1} \phi_{\sigma=0} = g_{S_2}^{S_1}(\text{dip})_{\sigma=0} \quad (3.7.2)$$

When $\sigma \neq 0$, a diffuse layer is present in each of the phases together with a compact layer consisting of the dipolar layers in the surface regions of the two phases.

Depending on the specific features, polarizable and unpolarizable liquid/liquid interphases can be defined. If i common ions are present in the two phases, the electric potential drop across the interphase is determined by the equality of the electrochemical potentials in the phases. Thus, for the cation B:

$$\Delta_{S_2}^{S_1} \phi = \Delta G_t^\circ(B)_{S_1 \rightarrow S_2} / z_B F + (RT/z_B F) \ln(\alpha^{S_2} / \alpha^{S_1}) \quad (3.7.3)$$

where $\Delta G_t^\circ(B)$ is the *standard Gibbs energy of transfer* of cation B from S_1 to S_2 (ref. 7). In the simple case of a common 1-1 electrolyte BA present in the two phases, the electric potential drop is defined by the equation:

$$\Delta_{S_2}^{S_1} \phi = \frac{RT}{2F} \ln \frac{K_B(S_1, S_2)}{K_A(S_1, S_2)} \frac{\gamma_B^{S_1} \gamma_A^{S_2}}{\gamma_B^{S_2} \gamma_A^{S_1}} \quad (3.7.4)$$

where the γ 's are ionic activity coefficients (here, on the molal concentration scale) and $K_i(S_1, S_2)$ is the *distribution coefficient* of ion i between solvents S_1 and S_2 . For electrolyte BA in this example the ionic distribution coefficients are related to the standard salt distribution coefficient by the equation:

$$(K_{BA}^\circ)^2 = K_B \cdot K_A \quad (3.7.5)$$

4 THERMODYNAMIC DESCRIPTION OF AN ELECTRIFIED INTERPHASE

4.1 General

The thermodynamic treatment of electrified interphases follows closely that of non-ionic systems in that surface composition is discussed in terms of surface excess quantities as already described in (ref. 2).

4.2 Ideally unpolarizable interphase

When at least one charged component is present in appreciable quantities in both phases adjoining the interphase and the interphase is permeable to at least one charged species the Gibbs adsorption equation for a plane interphase has the same form as that for a system of neutral molecules:

$$s dT - \tau dp + d\gamma + \sum_i \Gamma_i d\mu_i = 0 \quad (4.2.1)$$

where T is the temperature, p the external pressure, γ the interfacial tension and μ_i the chemical potential of the combination of species i whose net charge is zero (e.g. a salt or a metal etc.), s is the surface excess of entropy of unit area of interphase, τ is the thickness (or excess volume of unit area of the interphase and Γ_i is the surface excess of the group of species i . The summation is over all the chemical species i from which the interphase and its adjacent phases can be constituted, except one which is selected arbitrarily as a reference component.

Since eqn.(4.2.1) is in terms of the interfacial tension γ , it is implied that this treatment is for fluid interphases. The term required to replace $d\gamma$ for interphases including a solid is discussed in section 7. Much of the discussion of the other terms is common to both types of interphases.

For an electrified interphase one of the chemical potentials μ_i may be replaced (ref. 8) by a quantity ξ which is the sum of the potential difference E between the terminals of an electrochemical cell (Note b) containing the interphase under consideration and a term consisting of chemical potentials of neutral species. Thus one of the terms, say $\Gamma_A d\mu_A$, in the sum of eqn.(4.2.1) is replaced by a term $Q_A d\xi_A$ where:

$$Q_A = z_A F T_A \quad (4.2.2)$$

is the charge on unit area of the interface - see eqn.(5.1.1) of (ref. 4) -. Since at constant temperature and pressure:

$$d\xi_A = dE_A \quad (4.2.3)$$

it follows from eqn.(4.2.1) that:

$$\left(\frac{\partial \gamma}{\partial E_A}\right)_{T,p,\mu_i \neq \mu} = - Q_A \quad (4.2.4)$$

which is the *Lippmann equation*. E_A is the potential of a cell in which the reference electrode has an interfacial equilibrium with one of the ionic components of A. Since more than one type of reference electrode may be chosen, more than one quantity Q may be obtained. Consequently Q cannot be considered as equivalent to the physical charge on a particular region of the interphase. It is in fact an alternative way of expression of a surface excess or combination of surface excesses of charged species.

The potential at which a given type of charge Q vanishes is often called *potential of zero total charge*, $E_{Q=0}$, to be distinguished from the *potential of zero free charge*, $E_{\sigma=0}$. The shorter term potential of zero charge is commonly used to indicate the latter quantity.

4.3 Ideally polarizable interphase

Differences from the behaviour of interphases containing only neutral species arise when the interphase may be described as *ideally polarizable*. This term is used when no charged component is common to both phases adjoining the interphase. This may arise as a result of the equilibrium conditions or from the kinetics of charge transfer and leads to an interphase impermeable to electric charge. In such an interphase it is convenient to divide the interfacial region into two parts: one containing the charged species from one phase (α), the other containing those from the other phase (β). The physical charge on unit area of either side of the interphase may then be defined in terms of the surface excesses of the charged species in the system:

$$\sigma^\alpha = \sum_i z_i F \Gamma_i^\alpha \quad (4.3.1)$$

$$\sigma^\beta = \sum_i z_i F \Gamma_i^\beta \quad (4.3.2)$$

Note b: When the interphase is between a metal (or a semiconductor) and an electrolyte, the cell would normally be made by combining this electrode (solid/electrolyte) with a reference electrode in equilibrium with the electrolyte. The potential E would then be measured between a contact attached to the metal under study and a contact attached to the reference electrode. When the interphase is between two electrolytes, two such reference electrodes would be used one in equilibrium with each electrolyte and E measured between contacts attached to these.

where the sum in eqn.(4.3.1) is over all charged components in phase α and that in eqn. (4.3.2) is over all charged components in β . The interphase as a whole is electrically neutral, *i.e.*

$$\sigma^\alpha + \sigma^\beta = 0 \quad (4.3.3)$$

The Gibbs adsorption equation for a ideally polarizable interphase must have a term in which the charge σ multiplies the change of a difference of electrochemical potentials between one charged species in each of the adjoining phase:

$$\sigma^\alpha d\xi \quad (4.3.4)$$

where

$$F\xi = (\tilde{\mu}_B^\alpha/z_B) - (\tilde{\mu}_C^\beta/z_C) \quad (4.3.5)$$

and B and C are particular charged species in phases α and β respectively.

The electrochemical potential difference in eqn.(4.3.5) may be expressed as the sum of chemical potentials of neutral groups of charged species (salts, metals etc.) and an electrical potential difference E between two electrodes *e.g.* between phase α if it is an electronic conductor and a reference electrode (ref. 8). When the reference electrode is in equilibrium with a cation (anion) in phase β , E is given the subscript + (-). At constant temperature and pressure:

$$d\xi = dE_{+(-)} \quad (4.3.6)$$

Thus the Gibbs adsorption equation takes the form:

$$sdT - \tau dp + d\gamma + \sigma^\alpha d\xi + \sum \Gamma_j d\mu_j = 0 \quad (4.3.7)$$

where j is an electrically neutral component of one or other of the phases and the sum is over all the components but one in each phase. It is not possible to eliminate the term $\sigma^\alpha d\xi$ to obtain an equation like eqn.(4.2.1).

Equation (4.3.7) is often called the *electrocapillary equation* because it includes the expression of the phenomenon of *electrocapillarity* - the dependence of the interfacial tension on the electrical state of the interphase. This is expressed by the Lippmann equation

$$(\partial\gamma/\partial E)_{T,p,\mu_j,\dots} = -\sigma^\alpha \quad (4.3.8)$$

which leads to a unique charge σ^α for a ideally polarizable interphase.

4.4 Cross-differential coefficients

Various cross-differential relationships can be obtained from the Gibbs adsorption equation by standard methods because it is a complete differential.

The left-hand side of one of these (when only one chemical potential is considered as variable):

$$(\partial E/\partial \mu)_{T,p,\sigma} = -(\partial \Gamma/\partial \sigma)_{T,p,\mu} \quad (4.4.1)$$

is called the *Esin and Markov coefficient*. Others provide useful routes for the analysis of experimental data.

4.5 Capacitances and ionic charges

The differential capacitance of unit area of interphase is defined by eqn.(5.5.1) of (ref. 4):

$$C = (\partial Q/\partial E)_{T,p,\mu_j} \quad (4.5.1)$$

It is most readily measured for a ideally polarizable interphase when it becomes:

$$C = (\partial \sigma^\alpha/\partial E)_{T,p,\mu_j} = -(\partial \sigma^\beta/\partial E)_{T,p,\mu_j} \quad (4.5.2)$$

Since the charge σ^α (or σ^β) is defined in terms of the surface excesses of the charged components by eqns.(4.3.1) and (4.3.2) it is often convenient to define the components of the charge attributable to a species i by

$$\sigma_i = z_i F \Gamma_i \quad (4.5.3)$$

where z_i is the charge number of that species in the bulk of the phase in which it is present. With this definition eqns.(4.3.1) and (4.3.2) may be written

$$\sigma^\alpha = \sum_i z_i \sigma_i^\alpha \quad (4.5.4)$$

$$\sigma^\beta = \sum_i z_i \sigma_i^\beta \quad (4.5.5)$$

and correspondingly the differential capacitance may be expressed in terms of partial capacitances C_i

$$C = \sum_i C_i^\alpha = - \sum_i C_i^\beta \quad (4.5.6)$$

where

$$C_i = (\partial \sigma_i / \partial E)_{T, p, \mu_i, \dots} \quad (4.5.7)$$

5 STRUCTURAL ASPECTS OF ADSORPTION AT ELECTRIFIED INTERPHASES

5.1 General

Due to adsorption, charged and uncharged components are distributed in the interphase in a non-random way. The array of charged particles at interfaces is called an *electrical double layer*. Adsorption on surfaces from solutions is to be regarded as a solvent replacement reaction:



where (sol) and (ad) stand for solution and adsorbed, respectively.

The theoretical interpretation of this process in terms of structure is at present based on rather simplified models. Here we outline current terminology for adsorption at an interphase between an electrolyte and another condensed phase (most often a metal). It should be remembered that further knowledge about the structure of interphases may render this terminology inexact or obsolete.

5.2 Adsorption of ions—non-specific adsorption

Ions approach the interface differently depending on the forces in play. Ions are *non-specifically* adsorbed (positively or negatively) when they are subjected in the interphase only to long-range coulombic interactions (attraction or repulsion). They are believed to retain their solvation shell, and in the position of closest approach to the interface they are separated from it by one or more solvent monomolecular layers. The locus of the electrical centers of non-specifically adsorbed ions in their position of closest approach is the *outer Helmholtz plane* (OHP).

The position of this plane for the anion and the cation of the electrolyte may differ. It may also differ for the different cations and the different anions of a mixed electrolyte solution. This is also the case with an electrolyte solution in mixed solvents in the composition range where more than one solvent species is present in the interfacial layer. The region in which non-specifically adsorbed ions are accumulated and distributed by the contrasting action of the electric field and thermal motion is called the *diffuse layer*. The region between the OHP and the interface is called the *inner (compact) layer*. If only non-specifically adsorbed ions are present in the interphase, it is often denoted by the term *ion free layer*.

The nomenclature for distances and potentials in the double layer varies from one school to another. We recommend here a system based on the use of x as the coordinate perpendicular to the plane of the interface and ϕ for potentials since in this region the potentials are closest to inner potentials. However since they are not strictly inner potentials the location is denoted as a subscript and not a superscript, the latter being reserved for true inner potentials.

The origin of the coordinate system is taken at the interface and the OHP is at a distance from this x_2 , thus the inner layer thickness is x_2 (this is sometimes called d or δ). The diffuse layer stretches from x_2 to the bulk of the solution phase.

The potential of a metal phase is usually taken as uniform and equal to the inner potential ϕ^M while that of the electrolyte in the bulk is ϕ^S . The mean potential on the OHP is ϕ_2 . Thus the potential drop across the inner layer is $(\phi^M - \phi_2)$ and that across the diffuse layer is $(\phi_2 - \phi^S)$. It is often convenient to take ϕ^S as zero. The OHP potential is sometimes called ψ_0 , ψ_1 or ψ_d but these usages are not recommended because of confusion with outer potentials.

The areal free charge in the diffuse layer is denoted by σ^d and it may be regarded as made up of the charges contributed by an excess or deficiency of each ionic species

$$\sigma^d = \sum \sigma_i^d \quad (5.2.1)$$

the sum being over all ionic species in the solution. σ^d is the areal excess amount of charge contained in a tube of solution starting from the OHP and extending into the bulk of the solution. The thickness of the *diffuse* layer is often small compared to the thickness of the *diffusion layer* (ref. 5).

In a given system the existence of non-specific adsorption can only be verified by a number of tests most of which depend on the assumption that the behaviour of ions in the diffuse layer can be calculated from a model. The model most widely used is the Gouy-Chapman theory.

Model-independent tests include the absence of adsorption at $\sigma^M = 0$, and the identical behaviour of different cations or anions of the same charge, but such tests are not very widely useful.

Tests depending on the Gouy-Chapman theory depend on the calculated relations between ϕ_2 and σ^d , ϕ_2 and σ_i^d or σ_j^d and σ_j^d . Their sensitivity depends a great deal on the detailed conditions and must be carefully assessed.

Differential capacitances for the two parts of the interphase may be defined by noting that formally:

$$\frac{d(\phi^M - \phi^S)}{d\sigma^M} = \frac{d(\phi^M - \phi_2)}{d\sigma^M} + \frac{d(\phi_2 - \phi^S)}{d\sigma^M} \quad (5.2.2)$$

At constant composition the left-hand side is equal to the reciprocal of the differential capacitance of the whole interphase, so that eqn.(5.2.2) may be written:

$$C^{-1} = (C^i)^{-1} + (C^d)^{-1} \quad (5.2.3)$$

that is the interphase behaves in the absence of specific adsorption as a series combination of C^i the *inner layer capacitance* and C^d the *diffuse layer capacitance*. Note that this does not imply the existence of physical charge distribution equivalent to that in a system of two condensers.

In the case of the semiconductor/electrolyte interface, the space charge contributes one more capacitance C^{sc} in series with C^i and C^d .

5.3 Specific adsorption of ions

Ions become *specifically adsorbed* when short-range interactions between them and the interphase become important. They are believed then to penetrate into the inner layer and may (but not necessarily) come in contact with the metal surface. They are usually assumed to form a partial or complete monolayer. The locus of the electrical centers of this layer of specifically adsorbed ions is the *inner Helmholtz plane* (IHP) assumed to be at a distance x_1 from the metal surface. By *superequivalent adsorption* is meant that the specifically adsorbed amount of charge in the IHP (σ^i) is higher than the charge on the metal phase taken with the reverse sign. Thus the diffuse charge has the same sign as that on the metal.

Specific adsorption is detected by the deviation of the system from the behaviour described in the previous section, notably in that the surface excess of ions can no longer be explained in terms of an ion-free layer and a diffuse layer obeying Gouy-Chapman theory. The contribution to the solution charge from ions whose centers lie in the region $x_1 < x < x_2$ is denoted by σ^i so that the interphase electroneutrality condition is now written:

$$\sigma^M = -\sigma^S = -(\sigma^i + \sigma^d) \quad (5.3.1)$$

The separation of σ^S into σ^i and σ^d cannot be made without the introduction of a model. Use of the Gouy-Chapman theory and the assumption that one of the ionic components is not specifically adsorbed enables the other σ_j^d to be calculated and so the specifically adsorbed charge due to each other ion to be obtained:

$$\sigma_j^i = \sigma_j^S - \sigma_j^d \quad (5.3.2)$$

In view of the short-range of the forces causing specific adsorption the quantities σ_j^i are often equivalent to less than one monolayer of ions. Consequently the real distribution is often represented in models as a monolayer of ions with their centers on the IHP.

The capacitance of the interphase is still given by eqn.(5.2.2) but the second term on the

right-hand side is no longer equal to the diffuse layer capacity because the charge in the diffuse layer is now:

$$\sigma^d = -\sigma^M - \sum \sigma_j^i \quad (5.3.3)$$

and the differential capacitance of the diffuse layer is:

$$c^d = -d\sigma^d/d(\phi_2 - \phi^S) \quad (5.3.4)$$

Thus equation (5.2.2) must be replaced by

$$c^{-1} = (c^i)^{-1} + (c^d)^{-1}(1 + d\sum \sigma_j^i/d\sigma^M) \quad (5.3.5)$$

The inner layer capacity can be further analysed to express its dependence on specific adsorption. The potential drop across the inner layer may be assumed to depend on the charge σ^M and the specifically adsorbed charges σ_j^i . From this assumption it follows generally that

$$d(\phi^M - \phi_2) = \left[\frac{\partial(\phi^M - \phi_2)}{\partial \sigma^M} \right]_{\sigma_j^i} d\sigma^M + \sum \left[\frac{\partial(\phi^M - \phi_2)}{\partial \sigma_j^i} \right]_{\sigma^M, \sigma_k^i} d\sigma_j^i \quad (5.3.6)$$

or

$$\frac{d(\phi^M - \phi_2)}{d\sigma^M} \equiv \frac{1}{c^i} = \left[\frac{\partial(\phi^M - \phi_2)}{\partial \sigma^M} \right]_{\sigma_j^i} + \sum \left[\frac{\partial(\phi^M - \phi_2)}{\partial \sigma_j^i} \right]_{\sigma^M, \sigma_k^i} (d\sigma_j^i/d\sigma^M) \quad (5.3.7)$$

Thus the inner layer capacitance may be related to a series of partial capacitances which depend on σ^M :

$$c^i(\sigma^M) = \left[\partial \sigma^M / \partial (\phi^M - \phi_2) \right]_{\sigma_j^i} \quad (5.3.8)$$

and on each σ_j^i for the specifically adsorbed ions:

$$c^i(\sigma_j^i) = \left[\partial \sigma_j^i / \partial (\phi^M - \phi_2) \right]_{\sigma^M, \sigma_k^i} \quad (5.3.9)$$

Here the subscript σ_k^i means that all σ_j^i are kept constant except one.

Subject to the assumption of Gouy-Chapman theory (or other model of the diffuse layer) these quantities may be determined from experiment.

5.4 Partial charge transfer

The quantities defined above are in terms of the surface excesses of the ionic components Γ_i expressed as their equivalent charge using eqn.(4.5.3). In the real system, particularly when adsorption is specific the ionic charge may not retain the same value as in the bulk of the solution owing to electronic interaction during the formation of an adsorption bond. The fraction of charge shared by the adsorbed particle may be characterized by a *partial charge number*. This term, although conceptually correct when applied to the model, is not adequate to indicate the quantity accessible to experimental measurements on a thermodynamic basis.

The accessible quantity is the *formal partial charge number* defined by

$$z_B = -(\partial \sigma^M / \partial \Gamma_B)_{E, \mu_i \neq \mu_B} / F = (\partial \mu_B / \partial E)_{\Gamma_B, \mu_i \neq \mu_B} / F \quad (5.4.1)$$

Physically, z_B measures the average number of unit charge supplied to the electrode from the external circuit when one molecule of species B is adsorbed at constant potential.

The term "electrosorption valency" and a different symbol have also been suggested for the quantity defined by eqn.(5.4.1). However, the former term is preferable on a conceptual basis. According to eqn.(5.4.1) $d\sigma^M$ is the charge which must be supplied to the system for E to remain constant as the adsorption changes by $d\Gamma_B$. z_B is the only parameter which can be obtained thermodynamically. The actual partial charge number can be obtained only on the basis of some model assumptions. The latter coincides with z_B only if adsorption does not affect the structure of the electrical double layer.

5.5 Adsorption of uncharged molecules

The absence of a charge on a molecule means that the long-range coulombic forces which form the diffuse double layer of ions play no role and adsorbed neutral molecules can be assumed to be present only in the inner layer although if they are larger than the solvent molecules previously present there, the thickness of the inner layer may be increased. Consequently

the adsorption of neutral molecules is normally treated as monolayer adsorption (although multilayers can be formed in some systems).

Since no charge is introduced into the inner layer by the adsorption, equation (5.2.2) remains valid. However the variation of the inner layer capacity can be expressed by an analogue of eqn.(5.3.7) by assuming that the potential drop in the inner layer depends on σ^M and the adsorbed amounts Γ_j of neutral molecules:

$$\frac{d(\phi^M - \phi_2)}{d\sigma^M} \equiv \frac{1}{c^i} = \left[\frac{\partial(\phi^M - \phi_2)}{\partial\sigma^M} \right]_{\Gamma_j} + \sum \left[\frac{\partial(\phi^M - \phi_2)}{\partial\Gamma_j} \right]_{\sigma^M} (\partial\Gamma_j/\partial\sigma^M) \quad (5.5.1)$$

Here:

$$\frac{1}{c^i(\sigma^M)} = \left[\frac{\partial(\phi^M - \phi_2)}{\partial\sigma^M} \right]_{\Gamma_j} \quad (5.5.2)$$

remains the inner layer capacity at constant composition as in eqn.(5.3.7).

The quantity in the second term on the right-hand side of eqn.(5.5.1) may be related to the effective perpendicular component of the dipole of the adsorbed molecule (less the corresponding quantity for the n solvent molecules it replaces - see section 5.1 -) by using the Helmholtz equation (2.1.1):

$$\partial(\phi^M - \phi_2)/\partial\Gamma_j = (p_{\perp,i}/\epsilon) - (np_{\perp,S}/\epsilon) \quad (5.5.3)$$

A formal partial charge number may be defined for neutral molecules in the same way as in equation (5.4.1); it includes effects due to change in thickness, effective permittivity or orientation of molecules rather than charge transfer.

6 ADSORPTION ISOTHERM

6.1 General

Adsorption in systems of neutral molecules is frequently expressed in terms of an adsorption isotherm which gives the amount adsorbed (or surface excess) as a function of bulk activity of the same species at constant temperature. The equation chosen to describe the isotherm may have some theoretical significance or may be empirical. In the former case an attempt may be made to learn about the interactions between species in the adsorbed state. This procedure is open to a number of difficulties. When the interface is ideally polarizable there is an additional difficulty in that the electrical state of the interphase must also be kept constant for the determination of the relation between surface and bulk concentration.

Two possibilities for this may be proposed: to determine the isotherm at constant σ^M or at constant $(\phi^M - \phi^S)$ (or at some constant cell potential which is equivalent to this) (Note c). From a formal thermodynamic point of view isotherms may be equally well calculated at constant charge or at any well-defined constant potential. However the physical significance of the relation thus obtained may depend on properties other than those of the interface, especially if constant cell potential is used. At present no completely satisfactory solution to this problem has been obtained so that no recommendation of the correct procedure can be made.

6.2 Surface pressure

By analogy with the two-dimensional pressure of spread films, it is possible to define a surface pressure as the change of interfacial tension caused by the addition of a given species to a base solution. At constant cell potential this is

$$\pi = \gamma_{\text{base}} - \gamma \quad (6.2.1)$$

while the analogue at constant charge is

$$\Phi = \xi_{\text{base}} - \xi \quad (6.2.2)$$

where

$$\xi = \gamma + \sigma E \quad (6.2.3)$$

Note c: Strictly speaking, isotherm should be determined at constant $(\phi^M - \phi_2)$ for according to section 5.5 the diffuse double layer plays no role.

In each case all other variables are kept constant. It must be noted that this approach allots the whole of the change in the interfacial tension to the added species. However it should be remembered that the interfacial concentration of other species may be changed by the introduction of the new species.

If the area occupied by the adsorbing species in question is put equal to $1/\Gamma$, the two-dimensional equation of state relating π or ϕ and $1/\Gamma$ is another expression of the adsorption isotherm and may be combined with it to obtain a relation between π or ϕ and the bulk activity of this species.

6.3 Specific types of adsorption isotherm

A number of different specific forms of isotherm has been proposed on the basis of more or less realistic physical models. Three approaches may be distinguished.

1. The assumption that the base solution may be regarded as a continuum and the adsorbed species behaves like the analogous adsorbate at the vapour/condensed phase interface.
2. The assumption that the adsorption process is a replacement reaction in which the adsorbing species replaces another species, normally the solvent.
3. The interphase is regarded as a two-dimensional solution and treated in a manner analogous to that used for bulk solutions.

No specific recommendations can be made at present, except that the tests used for assigning isotherm relations should be critical and that the procedures used should be clearly described.

Standard Gibbs energy of adsorption are frequently derived from the fitting of adsorption isotherms. It should be recognized that the use of a semiempirical equation to fit data that does not extend to very low coverage may lead to a quantity of limited significance.

It is recommended that the term standard Gibbs energy of adsorption should be reserved for the quantity which does not depend on surface coverage and it is essential that the standard states to which it refers should always be given, since like all other quantities of this type it is meaningless without this information.

7 INTERFACES BETWEEN PHASES OF WHICH ONE IS SOLID

7.1 General

The behaviour at a solid surface is more complicated than that at a liquid because it is not always possible to verify that the surface is in mechanical equilibrium. As a result the characterization of solid surfaces (except under high vacuum) is less well developed than that of liquids. This section is consequently more tentative than the previous ones. Further information may be obtained from the excellent review by Linford (ref. 9) on which these proposals are based.

7.2 Surface energies

The reversible work of formation of unit area of new surface by cleavage is called the *superficial work*. It has previously been called specific surface work, surface energy, surface tension or surface free energy. The symbol recommended here is γ_π , in preference to σ which is preferred by Linford, because of the confusion with surface charge density. The superficial work γ_π is a scalar quantity and consequently is isotropic.

The work required to form unit area of new surface by stretching under equilibrium conditions is the surface stress T_{ij} which is a tensor because it is generally anisotropic. T_{ij} is numerically equal to the force acting in the j th direction per unit length of exposed edge, the edge being normal to the i th direction, that must be applied to a terminating surface to keep it in equilibrium, the i th and j th directions lying in the plane of the surface.

In general, surface area changes will be neither wholly plastic (as in cleavage) or wholly elastic (as in equilibrium stretching). To deal with this situation, a generalized surface parameter γ^s may be defined which is conjugate to the general (part plastic, part elastic) surface area change. For an *isotropic* solid this will be sum of two contributions taken in proportion to the fractions of the two types of strain *i.e.*

$$\gamma^s = (d\epsilon_p/d\epsilon_{tot})\gamma_\pi + (d\epsilon_e/d\epsilon_{tot})T \quad (7.2.1)$$

where ϵ_p and ϵ_e are the plastic and elastic contributions to the total strain ϵ_{tot} .

In the more general case both γ^s and T are tensors. In addition surface thermodynamic parameters analogous to the usual bulk thermodynamic functions may be defined.

7.3 The Gibbs equation for solid surfaces

When one of the phases is an isotropic solid the interfacial tension term in eqn.(4.2.1) must be replaced by:

$$d\gamma_{\pi} + (\gamma_{\pi} - T)d\epsilon_e \quad (7.3.1)$$

This means that to recover the remaining equations in the form given in section 4 the elastic strain must be kept constant. Since this is not usually possible, the additional terms should be taken into account, e.g. the Lippmann equation becomes:

$$(\partial\gamma_{\pi}/\partial E)_{T,p,\mu_i\dots} = -\sigma - (\gamma_{\pi} - T)(\partial\epsilon_e/\partial E)_{T,p,\mu_i} \quad (7.3.2)$$

The magnitude of the contribution of the second term on the right-hand side of eqn.(7.3.2) is not known for certain at present.

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SYMBOLS (Note d)

		SI Unit	
1.	A, S	Surface (interface) area	m^2
	A_r	Real surface area	m^2
	A_g	Geometric surface area	m^2
	$f_r = A_r/A_g$	Roughness factor	
2.	n_B^s	Surface amount of species B	mol
	$p_{\perp, B}$	Normal component of dipole moment of species B	C m
	ϵ	Permittivity	$F m^{-1}$
	V_e	Potential energy for electrons in metals	$J mol^{-1}$
	ϵ_e^F	Kinetic energy of electrons at the Fermi level	$J mol^{-1}$
	μ_e^M	Chemical potential of electrons in metal	$J mol^{-1}$
	α_e^M	Real potential of electrons in metal (molar Fermi energy)	$J mol^{-1}$
	ϕ^M	Electron work function of a metal	J (eV)
	$\Delta_{\beta}^{\alpha}\psi$	Volta or contact potential difference between phases α and β	V
	$\Delta_{\beta}^{\alpha}\phi$	Galvani potential difference between phases α and β	V
3.	$g_{(\beta)}^{\alpha}$ (dip)	Dipolar contribution in phase α to the potential difference $\Delta_{\beta}^{\alpha}\phi$	V
	g_{β}^{α} (ion)	Ionic (free charge) contribution to the potential difference $\Delta_{\beta}^{\alpha}\phi$	V

Note d: Number refer to the section

$\delta\chi_{(\beta)}^{\alpha}$	Change in surface potential of phase α due to contact with phase β	V
$g_{\beta}^{\alpha}(\text{dip})_{\sigma}$	Dipolar contribution to the potential difference $\Delta_{\beta}^{\alpha}\phi$ when the free charge on the phases is σ	V
$\Delta\phi^{\text{sc}}$	Potential drop associated with the space charge in semiconductors	V
$\Delta G_{\text{L}}^{\circ}(\text{B})_{\alpha\rightarrow\beta}$	Standard Gibbs energy of transfer of ion B from liquid phase α to liquid phase β	J mol ⁻¹
$K_{\text{AB}}(\alpha, \beta)$	Distribution coefficient of the electrolyte BA between the liquid phases α and β	
4. γ	Interfacial (or surface) tension for fluid interphases (or surfaces)	N m ⁻¹
$\Gamma_{\text{B}}^{\sigma}, n_{\text{B}}^{\sigma}$	Surface excess concentration and surface excess amount of the substance B	mol m ⁻² , mol
$\Gamma_{\text{B}}^{\text{s}}, n_{\text{B}}^{\text{s}}$	Surface concentration and surface amount of the substance B	mol m ⁻² , mol
$\Gamma_{\text{B}}^{(1)}, n_{\text{B}}^{(1)}$	Relative surface excess concentration and relative surface excess amount of the substance B	mol m ⁻² , mol
τ	Thickness of the interphase	m
V^{s}	Volume of the interphase	m ³
p	Pressure	Pa(N m ⁻²)
s^{σ}, s^{s}	Areal surface excess entropy and areal surface entropy	J mol ⁻¹ K ⁻¹ m ⁻²
$s^{\sigma(1)}, s^{\text{s}(1)}$	Relative areal surface excess entropy and relative areal surface entropy	J mol ⁻¹ K ⁻¹ m ⁻²
ξ	Generalized potential	V
E_{+}	Electrode potential measured with respect to a cation reversible reference electrode	V
E_{-}	Electrode potential measured with respect to an anion reversible reference electrode	V
Q_{A}^{α}	Total surface charge density on phase α (areal amount of total charge on phase α) defined in terms of component A	C m ⁻²
$E_{Q=0}$	Potential of zero total charge	V
$E_{\sigma=0}$	Potential of zero (free) charge	V
E_{ecm}	Potential of the electrocapillary maximum	V
$\gamma_{Q=0}, \gamma_{\text{ecm}}$	Interfacial tension at the electrocapillary maximum with unpolarizable electrode	N m ⁻¹
σ^{α}	Free surface charge density on phase α (areal amount of free charge on the surface of phase α)	C m ⁻²
$\sigma_{\text{i}}^{\alpha}$	Component of free surface charge due to species i	C m ⁻²
$\gamma_{\sigma=0}, \gamma_{\text{ecm}}$	Interfacial tension at the electrocapillary maximum with polarizable electrodes	N m ⁻¹
C	Differential capacitance of an interphase	F m ⁻²
C_{i}	Component of differential capacitance of an interphase, due to species i	F m ⁻²
5. OHP	Outer Helmholtz plane	
IHP	Inner Helmholtz plane	
σ^{i}	Areal amount of charge adsorbed in the IHP	C m ⁻²
σ^{d}	Areal amount of charge in the diffuse layer	C m ⁻²

σ_B^d	Areal amount of charge due to species B in the diffuse layer	$C m^{-2}$
Γ_B^d	Surface excess concentration of B in the diffuse layer	$mol m^{-2}$
x_2 (d)	Thickness of the inner layer	m
x_1	Coordinate of the IHP	m
Γ_B^i	Surface excess concentration of species B adsorbed in the IHP	$mol m^{-2}$
$\Gamma_{B,m}$	Maximum surface excess concentration of B	$mol m^{-2}$
$\theta_B = \Gamma_B/\Gamma_{B,m}$	Surface fractional coverage with species B	
C^d	Differential capacitance of the diffuse layer	$F m^{-2}$
C^i	Differential capacitance of the inner layer	$F m^{-2}$
$C^i(\sigma)$	Differential capacitance of the inner layer at constant specifically adsorbed charge	$F m^{-2}$
$C^i(\sigma^i)$	Differential capacitance of the inner layer at constant charge density on the metal	$F m^{-2}$
C^{sc}	Differential capacitance of the space charge of a semiconductor	$F m^{-2}$
l_B	Formal charge transfer coefficient	
ϕ_2	Inner electric potential at the OHP	V
6. π	Surface pressure at constant potential	$N m^{-1}$
ϕ	Surface pressure at constant charge	$N m^{-1}$
ξ	Constant charge function ($= \gamma + \sigma E$)	$N m^{-1}$
7. γ_π	Superficial work	$J m^{-2}$
Γ	Surface stress	$J m^{-2}$
Γ^s	Generalized surface intensive parameter	$J m^{-2}$
ϵ_p	Plastic surface area change (strain)	
ϵ_e	Elastic surface area change (strain)	
ϵ_{tot}	Total surface area change (strain)	