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AND APPLIED CHEMISTRY
DIVISION OF PHYSICAL CHEMISTRY

MANUAL OF SYMBOLS AND
TERMINOLOGY FOR
PHYSICOCHEMICAL QUANTITIES
AND UNITS

APPENDIX II
Definitions, Terminology and Symbols in
Colloid and Surface Chemistry
PART I

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PREFACE TO THE INTERNET EDITION

In the past 30 years the *Manual on Definitions, Terminology and Symbols in Colloid and Surface Chemistry*, prepared by *Everett*, has lost very little of its significance for the community of people working in the field of colloid and surface chemistry. To make this Manual optimally available to the interested public the present IUPAC Commission on Colloid and Surface Chemistry including Catalysis has decided to reproduce the Manual for consultation through Internet. In order to bring further recommendations produced over the years by the various Commissions on Colloid and Surface Chemistry including Catalysis (CI.6) to the attention of the reader annotations are added as footnotes. In most cases these annotations just refer to other IUPAC documents. In the case of the sections 1.11 *Electrochemical terms in colloid and surface chemistry* and 1.12 *Electrokinetics* the annotations provide some new definitions and symbols. The new footnotes start with the marker (2001).

The Tentative Manuals on Optical properties, Rheology, Electrochemical nomenclature and the nomenclature in the field of Heterogeneous Catalysis, indicated in *Everett's* Preface have appeared in the meantime. A full list of recommendations published by CI.6. is presented below. The Manual on Electrochemical nomenclature is produced by the Commission on Electrochemistry (CI.3).

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December 2001

PREFACE

This Appendix to the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* (Butterworths: 1970 and *Pure and Applied Chemistry*, 1970, 21, No. 1) has been prepared by the Commission on Colloid and Surface Chemistry of the Division of Physical Chemistry of the International Union of Pure and Applied Chemistry. It is the outcome of extensive discussions within the Commission and its Sub-commissions, with other IUPAC Commissions, and with persons and organizations outside IUPAC, over the period 1961–1971¹. A tentative version of these proposals was issued by IUPAC as Information Bulletin No. 3 (January 1970): the text has been revised in the light of the criticisms, comments and suggestions which were received, and the present version was formally adopted by the IUPAC Council at its meeting in Washington, DC, in July 1971.

The present proposals are based on the general principles set out in detail in Section 1 of the Manual of Symbols and Terminology. Since colloid and surface chemistry are subdivisions of physical chemistry, and there is substantial overlap between these fields and others, in particular with electrochemistry and macromolecules, it is important that terms in colloid and surface chemistry should not be used in a sense different from that common to physical chemistry in general or to its other subdivisions. On the other hand, it is equally important to avoid inconsistencies between the meanings of terms employed in scientific aspects of colloid and surface chemistry, and the same terms used in industrial, engineering and technological contexts. It has also been necessary to balance the desirability of retaining terms because of historical connections or wide common usage against the need to develop a more consistent and logical structure as colloid and surface chemistry evolves into a more quantitative scientific discipline. It has not yet been possible to

¹The membership of the Commission during this period was as follows:

Chairman: 1961–67 Sir Eric Rideal (UK); 1967–69 J. Th. G. Overbeek (Netherlands); 1969– D. H. Everett (UK);

Secretary: 1961–67 W. A. Zisman (USA); 1967– H. van Olphen (USA);

Titular members: 1961–65 A. E. Alexander (Australia); 1967– S. Brunauer (USA); 1969– L. Burwell (USA); 1961–65 D. G. Dervichian (France); 1961–69 M. M. Dubinin (USSR); 1965–69 D. H. Everett (UK); 1961–65 K. Groth (Sweden); 1969– R. Haul (Germany); 1961–67 J. Horiuti (Japan); 1961–69 B. Kamienski (Poland); 1969 V. V. Kazansky (USSR); 1969– J. Mysels (USA); 1961–67 J. Th. G. Overbeek (Netherlands); 1965–71 M. Prettre (France); 1967– G. Schay (Hungary).

Associate Members: 1969– R. M. Barrer (UK); 1967– G. Borekov (USSR); 1967–69 R. L. Burwell (USA); 1969– S. Friberg (Sweden); 1967–69 R. Haul (Germany); 1967–71 J. Horiuti (Japan); 1969– C. Kemball (UK); 1969– A. V. Kiselev (USSR); 1969– H. Lange (Germany); 1967–69 K. J. Mysels (USA); 1967– Sir Eric Rideal (UK); 1967– A. Scheludko (Bulgaria); 1969– G. A. Schuit (Netherlands); 1965–1967 H. van Olphen (USA).

resolve all the consequent problems. For this reason, this Appendix will be issued in two parts.

Part II will include revised versions of the sections in the Tentative Manual on optical properties and rheology. Furthermore, the section on electrochemical nomenclature in Part 1 appears only in skeleton form, pending the finalization by the Commission on Electrochemistry of their nomenclature proposals. Proposals for nomenclature in the field of heterogeneous catalysis are also in preparation and are planned for inclusion in Part II.

This Appendix consists of three Sections: the first is concerned with definitions and terminology, and with recommendations for appropriate symbols; the second is a list of recommended symbols; and the third an alphabetical index of terms defined, together with the corresponding symbols.

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Bristol, UK.
6 January 1972

IUPAC recommendations for Colloid and Surface Chemistry including Catalysis.

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1 DEFINITIONS AND TERMINOLOGY

1.1 ADSORPTION AND SPREAD MONOLAYERS

1.1.1 Surface, interface

A boundary between two phases is called a surface or interface. The two words are often used synonymously, although *interface* is preferred for the boundary between two condensed phases and in cases where the two phases are named explicitly, e.g. the solid/gas interface², but the surface of a solid. In some instances the word *surface* is limited to its geometrical meaning while *interface* is used to describe the thin three dimensional layer (*surface layer* or *interfacial layer*, see §1.1.3) between the phases in contact. The area of the surface or interface is denoted by A , A_s or S (but *not* A^s); the symbol A_s may be used to avoid confusion with the Helmholtz energy A or with the entropy S . For curved surfaces the area depends on the choice of the surface defining the boundary.

When the area of the interface between two phases is proportional to the mass of one of the phases (e.g. for a solid adsorbent, for an emulsion or for an aerosol), the *specific surface area* (a , s or preferably a_s) is defined as the surface area divided by the mass of the relevant phase.

1.1.2 Position of the surface or interface

The location of the surface between two phases may be defined in relation to the mean positions, statistically averaged over their disordered thermal motion, of the molecules³ of one (or the) condensed phase at the phase boundary; or in terms of the distance of closest approach of the molecules of one phase to those of the other (condensed) phase. The latter is analogous to the definition of the cross-section of atoms or molecules with respect to their collision or interaction.

The term surface is also used in a geometrical sense in the Gibbs dividing surface defined in §1.1.8.

²The use of a solidus to separate the names of the bulk phases is preferred to the use of a hyphen which can lead to ambiguities. The same applies to the abbreviated notation for phase boundaries, i.e. S/L: S/G: L/L: L/G: S/L/G

³The term molecule is used here in the general sense to denote any molecular species : atom, ion, neutral molecule or radical.

1.1.3 Surface layer or interfacial layer

The region of space comprising and adjoining the phase boundary within which the properties of matter are significantly different from the values in the adjoining bulk phases, is called the *surface layer* or *interfacial layer*, as shown schematically in Figure 1 (p. 17).

In addition it may be expedient to be more explicit and to define a *surface* or *interfacial layer of finite thickness* (τ) bounded by two appropriately chosen surfaces parallel to the phase boundary, one in each to the adjacent homogeneous bulk phases; a layer of this kind is sometimes called a Guggenheim layer. For very highly curved surfaces (radii of curvature of the same magnitude as τ) the notion of a surface layer may lose its usefulness.

Quantities referring to the surface layer are indicated by the superscript s (e.g. the volume of the interfacial layer is $V^s = \tau A_s$).

1.1.4 Adsorption and related phenomena: general concepts and terminology

Adsorption is the enrichment (*positive adsorption*, or briefly, adsorption) or depletion (*negative adsorption*) of one or more components in an interfacial layer. In certain cases a decision as to whether the actual distribution of a component between the interfacial layer and the bulk phases should be looked upon as enrichment or depletion may depend on the choice of the reference system (see §1.1.8).

The material in the adsorbed state is called the *adsorbate*, while that present in one or other (or both) of the bulk phases and capable of being adsorbed may be distinguished as the *adsorptive*. In some cases of chemisorption (see §1.1.6) adsorptive and adsorbate may be chemically different species (e.g. in dissociative adsorption).

When adsorption occurs (or may occur) at the interface between a fluid phase and a solid, the solid is usually called the *adsorbent*; for gas/liquid interfaces it may be in some, but not in all, cases useful to call the liquid phase the adsorbent. For liquid/liquid interfaces an arbitrary unsymmetrical nomenclature may not be appropriate.

Adsorption complex is a molecular term used to denote the entity constituted by the adsorbate and that part of the adsorbent to which it is bound. The adsorbate may or may not be in thermodynamic equilibrium with the adsorptive, though normally such an equilibrium may be reached eventually in static systems, except in some cases of activated chemisorption (see §1.1.6(f)). Quantitative definitions of adsorption are given in §1.1.8.

When two phases are put into contact, the composition of one or both

bulk phases may be changed by the partition of one or more components between these phases. The transfer of a component from one phase to the other is other called *absorption*. In absorption the structure of the *absorbent* and/or the chemical nature of the *adsorptive* may be modified.

It is sometimes difficult or impossible to discriminate experimentally between adsorption and absorption: in such cases it is convenient to use the non-committal term: *sorption* (together with its derived terms *sorbent*, *sorbate*, *sorptive*). This term is also used as a general term to cover both adsorption and absorption when both are known to occur simultaneously.

When the adsorbate is substantially absent from the bulk of the phases forming the interface, it is said to form a *spread layer* (often *spread monolayer* when the layer is known to be only one molecule in thickness).

The term *adsorption* may also be used to denote the process in which molecules accumulate in the interfacial layer. When used in this sense, its counterpart, *desorption*, denotes the converse process, i.e. the decrease in the amount of adsorbed substance. Adsorption is also used to denote the result of the process of adsorption, i.e. the formation of adsorbate on an adsorbent. Adsorption and desorption may also be used adjectivally to indicate the direction from which experimentally derived adsorption values have been approached, e.g. adsorption curve (or point), desorption curve (or point).

Adsorption hysteresis is said to occur when the adsorption and desorption curves deviate from one another.

Adsorption from liquid mixtures. Adsorption from liquid mixtures is said to have occurred only when there is a difference between the relative composition of the liquid in the interfacial layer and that in the adjoining bulk phase(s) and observable phenomena result from this difference. A similar shift in relative composition occurs also generally (though not necessarily) in the case of adsorption from gaseous mixtures, in addition to the increase of total concentration in the interfacial layer which is the general characteristic of gas adsorption. For liquids, accumulation (positive adsorption) of one or several components is generally accompanied by depletion of the other(s) in the interfacial layer; such depletion, i.e. when the equilibrium concentration of a component in the interfacial layer is smaller than the adjoining bulk liquid, is termed *negative adsorption* and should not be designated as desorption. Negative adsorption may occur also in the case of adsorption from highly compressed gas mixtures.

Expulsion of a previously adsorbed component from the interfacial layer may be effected by subsequent stronger adsorption of another component; such a process is called *desorption* by displacement.

Adsorption isotherm is the relation between the quantity adsorbed (suitably defined, see §1.1.8) and the composition of the bulk phase (or the partial

pressure in the gas phase) under equilibrium conditions at constant temperature.

Equilibrium between a bulk fluid and an interfacial layer may be established with respect to neutral species or to ionic species. If the adsorption of one or several ionic species is accompanied by the simultaneous desorption (displacement) of an equivalent amount of one or more other ionic species this process is called *ion exchange*.

1.1.5 Adsorbent/fluid interface

It is often useful to consider the adsorbent/fluid interface as comprising two regions. The region of the fluid phase (i.e. liquid or gas) forming part of the adsorbent/fluid interface may be called the *adsorption space* while the portion of the adsorbent included in the interface is called the *surface layer of the adsorbent* (see Figure 2 p. 25).

With respect to porous solids^{4,5}, the surface associated with pores communicating with the outside space may be called the *internal surface*. Because the accessibility of pores may depend on the size of the fluid molecules, the extent of the internal surface may depend on the size of the molecules comprising the fluid, and may be different for the various components of a fluid mixture (*molecular sieve effect*).

When a porous solid consists of discrete particles it is convenient to describe the outer boundary of the particles as *external surface*.

It is expedient to classify pores according to their sizes:

- (i) pores with widths exceeding about 0.05 μm or 50 nm (500 \AA) are called *macropores* ;
- (ii) pores with widths not exceeding about 2.0 nm (20 \AA) are called *micropores* ;
- (iii) pores of intermediate size (20 nm < width < 50 nm) are called *mesopores*.

⁴(2001) A system of terms applicable to ordered microporous and mesoporous inorganic materials, such as zeolites, can be found in “*Nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic hosts*”, McCusker, L.B., Liebau, F., Engelhardt, G., *Pure Appl. Chem.* **73** (2001), 381–394

⁵(2001) A special class of materials with microporosity and mesoporosity are the pillared layer solids. The terminology used for these materials and their characterization are discussed briefly in “*Pillared clays and pillared layered solids*”, Schoonheydt, R.A., Pinnavaia, T., Lagaly, G., Gangas, N., *Pure Appl. Chem.* **71** (1999) 2367–2371.

The terms *intermediate* or *transitional* pores, which have been used in the past are not recommended.

In the case of micropores, the whole of their accessible volume may be regarded as adsorption space.

The above limits are to some extent arbitrary. In some circumstances it may prove convenient to choose somewhat different values⁶.

The area of the surface of the non-porous solid as defined in §1.1.2 is usually greater than that calculated from the macroscopic dimensions of the surface by a factor called the *roughness factor*.

1.1.6 Chemisorption and physisorption

Chemisorption (or *chemical adsorption*) is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. The problem of distinguishing between chemisorption and physisorption (see below) is basically the same as that of distinguishing between chemical and physical interaction in general. No absolutely sharp distinction can be made and intermediate cases exist, for example, adsorption involving strong hydrogen bonds or weak charge transfer.

Some features which are useful in recognizing chemisorption include:

- (a) the phenomenon is characterized by chemical specificity;
- (b) changes in the electronic state may be detectable by suitable physical means (e.g. u.v., infrared or microwave spectroscopy, electrical conductivity, magnetic susceptibility);
- (c) the chemical nature of the adsorptive(s) may be altered by surface dissociation or reaction in such a way that on desorption the original species cannot be recovered; in this sense chemisorption may not be reversible;
- (d) the energy of chemisorption is of the same order of magnitude as the energy change in a chemical reaction between a solid and a fluid: thus chemisorption, like chemical reactions in general, may be exothermic or endothermic and the magnitudes of the energy changes may range from very small to very large;

⁶(2001) Recommendations for the assessment of the porosity can be found in: (1) Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemieniowska, T., "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity", *Pure Appl. Chem.* **57** (1985) 603–619 and (2) Rouquerol, J., Avnir, D., Fairbridge, C.W., Everett, D.H., Haynes, J.H., Pernicone, N., Ramsay, J.D.F., Sing, K.S.W., Unger, K.K., "Recommendations for the characterization of porous solids", *Pure Appl. Chem.* **66** (1994) 1739–1758.

- (e) the elementary step in chemisorption often involves an activation energy;
- (f) where the activation energy for adsorption is large (*activated adsorption*), true equilibrium may be achieved slowly or in practice not at all. For example in the adsorption of gases by solids the observed extent of adsorption, at a constant gas pressure after a fixed time, may in certain ranges of temperature increase with rise in temperature. In addition, where the activation energy for desorption is large, removal of the chemisorbed species from the surface may be possible only under extreme conditions of temperature or high vacuum, or by some suitable chemical treatment of the surface;
- (g) since the adsorbed molecules are linked to the surface by valence bonds, they will usually occupy certain *adsorption sites* on the surface and only one layer of chemisorbed molecules is formed (monolayer adsorption, see §1.1.7).

Physisorption (or *physical adsorption*) is adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved. The term *van der Waals adsorption* is synonymous with physical adsorption, but its use is not recommended.

Some features which are useful in recognizing physisorption include:

- (a') the phenomenon is a general one and occurs in any solid/fluid system, although certain specific molecular interactions may occur, arising from particular geometrical or electronic properties of the adsorbent and/or adsorptive;
- (b') evidence for the perturbation of the electronic states of adsorbent and adsorbate is minimal;
- (c') the adsorbed species are chemically identical with those in the fluid phase, so that the chemical nature of the fluid is not altered by adsorption and subsequent desorption;
- (d') the energy of interaction between the molecules of adsorbate and the adsorbent is of the same order of magnitude as, but is usually greater than, the energy of condensation of the adsorptive;
- (e') the elementary step in physical adsorption from a gas phase does not involve an activation energy. Slow, temperature dependent, equilibration may however result from rate-determining transport processes;

- (f') in physical adsorption, equilibrium is established between the adsorbate and the fluid phase. In solid/gas systems at not too high pressures the extent of physical adsorption increases with increase in gas pressure and usually decreases with increasing temperature. In the case of systems showing hysteresis the equilibrium may be metastable;
- (g') under appropriate conditions of pressure and temperature, molecules from the gas phase can be adsorbed in excess of those in direct contact with the surface (multilayer adsorption or filling of micropores, see §1.1.7).

1.1.7 Monolayer and multilayer adsorption, micropore filling and capillary condensation

In *monolayer adsorption* all the adsorbed molecules are in contact with the surface layer of the adsorbent.

In *multilayer adsorption* the adsorption space accommodates more than one layer of molecules and not all adsorbed molecules are in contact with the surface layer of the adsorbent.

The *monolayer capacity* is defined, for chemisorption, as the amount of adsorbate which is needed to occupy all adsorption sites as determined by the structure of the adsorbent and by the chemical nature of the adsorptive; and, for physisorption, as the amount needed to cover the surface with a complete monolayer of molecules in close-packed array, the kind of close-packing having to be stated explicitly when necessary. Quantities relating to monolayer capacity may be denoted by subscript m .

The *surface coverage* (θ) for both monolayer and multilayer adsorption is defined as the ratio of the amount of adsorbed substance (see §§1.1.8 to 11) to the monolayer capacity.

The *area occupied by a molecule in a complete monolayer* is denoted by a_m ; for example, for nitrogen molecules $a_m(\text{N}_2)$.

Micropore filling is the process in which molecules are adsorbed in the adsorption space within micropores⁷.

The *micropore volume* is conventionally measured by the volume of the adsorbed material, which completely fills the micropores, expressed in terms of bulk liquid at atmospheric pressure and at the temperature of measurement⁸.

⁷(2001) In *micropore filling* the whole of the assessable volume present in the micropores is regarded as adsorption space, as distinct from *surface coverage* which takes place on the walls of macropores or mesopores.

⁸(2001) Recommendations on the use of gas adsorption for the measurement of the mi-

In certain cases (e.g. porous crystals) the micropore volume can be determined from structural data.

Capillary condensation is said to occur when, in porous solids, multilayer adsorption from a vapour proceeds to the point at which pore spaces are filled with liquid separated from the gas phase by menisci⁹.

The concept of capillary condensation loses its sense when the dimensions of the pores are so small that the term meniscus ceases to have a physical significance. Capillary condensation is often accompanied by hysteresis.

1.1.8 Adsorption: quantitative definitions

A quantitative measure of adsorption may be, and usually is, based on the following general definition: Adsorption of one or more of the components, at one or more of the phase boundaries, of a multicomponent, multiphase system, is said to occur if the concentrations in the interfacial layers are different from those in the adjoining bulk phases, so that the overall stoichiometry of the system deviates from that corresponding to a *reference system* of homogeneous bulk phases whose volumes and/or amounts are defined by suitably chosen dividing surfaces, or by a suitable algebraic method.

Gibbs dividing surface (or *Gibbs surface*¹⁰) is a geometrical surface chosen parallel to the interface defined in §1.1.2 and used to define the volumes of the bulk phases in applying the foregoing definition to the calculation of the extent of adsorption, and of other surface excess properties.

For flat or only slightly curved surfaces one is free to define the position of the Gibbs surface in the manner most convenient for the discussion of a particular problem. In what follows it is assumed that this freedom exists; it must be remembered, however, that for surfaces whose radii of curvature approach molecular dimensions, the definitions become ambiguous.

Excess thermodynamic quantities referred to the Gibbs surface are denoted by superscript σ to distinguish them from quantities relating to the interfacial layer, for which superscript s is employed.

The *surface excess amount* or *Gibbs adsorption* of component i , n_i^σ which may be positive or negative, is defined as the excess of the amount of this component actually present in the system over that present in a *reference system* of the same volume as the real system and in which the bulk concen-

cropore volume, the mesopore volume and capillary condensation can be found in: Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemienińska, T., *Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity*, *Pure Appl. Chem.* **57** (1985) 603–619.

⁹(2001) See also previous footnote.

¹⁰The abbreviated form is generally preferred.

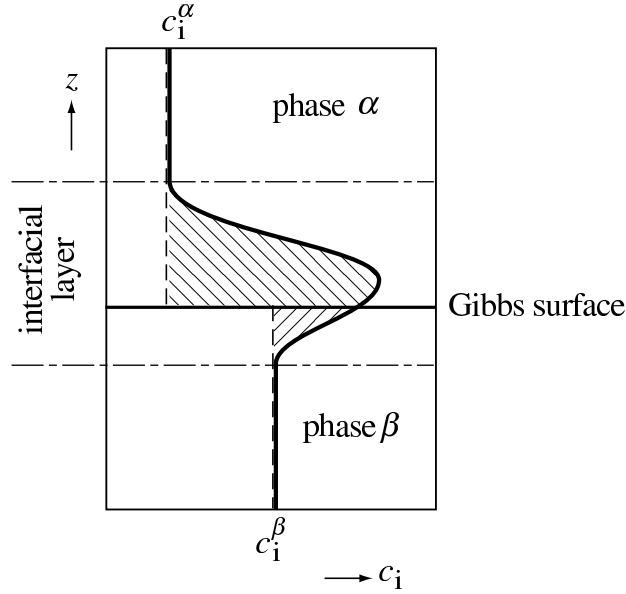


Figure 1: Schematic representation of the concentration profile (c_i) as a function of distance (z) normal to the phase boundary: full line (bold)—in the real system; broken line—in the reference system; chain-dotted line—boundaries of the interfacial layer. The surface excess amount per unit area (surface excess concentration n_i^σ/A_s) is given by the sum of the areas of the two shaded portions of the diagram.

trations in the two phases remain uniform up to the Gibbs dividing surface (see Figure 1).

That is

$$n_i^\sigma = n_i - V^\alpha c_i^\alpha - V^\beta c_i^\beta,$$

where n_i is the total amount of the component i in the system, c_i^α and c_i^β are the concentrations in the two bulk phases α and β , and V^α and V^β are the volumes of the two phases defined by the Gibbs surface. If c_i is the concentration of component i in a volume element dV , then

$$n_i^\sigma = \int_{\text{phase } \alpha \text{ up to Gibbs surface}} (c_i - c_i^\alpha) dV + \int_{\text{phase } \beta \text{ up to Gibbs surface}} (c_i - c_i^\beta) dV$$

Since in the bulk phases α and β , $c_i = c_i^\alpha$; $c_i = c_i^\beta$, the integrals may be taken, respectively, only over the volume of the interfacial layer adjacent to phase α up to the Gibbs surface, and over the volume of the interfacial layer adjacent to phase β , up to the Gibbs surface. The *total surface excess amount* of

adsorbed substance, n^α , is given by

$$n^\alpha = \sum_i n_i^\alpha.$$

If the area (A_s) of the interface is known, the *Gibbs surface concentration* or the *surface excess concentration* (formerly called the superficial density), Γ_i^σ , is given by

$$\Gamma_i^\sigma = n_i^\alpha / A_s.$$

The *total Gibbs surface concentration* or the *total surface excess concentration*, Γ^σ , is given by

$$\Gamma^\sigma = \sum_i n_i^\alpha / A_s.$$

Corresponding definitions can be given for the *surface excess number of molecules*, N_i^σ , and the *surface excess mass* of component i , m_i^σ and for the related surface excess molecular concentration and surface excess mass concentration.

The detailed application of the Gibbs definition of adsorption to interfaces of different kinds is discussed in the following sections (§§1.1.9; 1.1.10; 1.1.11).

1.1.9 Adsorption at the fluid/fluid interface

In general, the choice of the position of a Gibbs surface is arbitrary but it is possible to define quantities which are invariant with respect to this choice.

This is particularly useful for fluid/fluid interfaces where no experimental procedure exists for the unambiguous definition of a dividing surface.

The *relative adsorption* ($\Gamma_i^{(1)}$ or $\Gamma_{i,1}$). If Γ_i^σ and Γ_1^σ are the Gibbs surface concentrations of components i and 1, respectively, with reference to the same, but arbitrarily chosen, Gibbs surface, then the *relative adsorption* of component i with respect to component 1, defined as

$$\Gamma_i^{(1)} = \Gamma_i^\sigma - \Gamma_1^\sigma \left\{ \frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta} \right\},$$

is invariant to the location of the Gibbs surface.

Alternatively, $\Gamma_i^{(1)}$ may be regarded as the Gibbs surface concentration of i when the Gibbs surface is chosen so that Γ_1^σ is zero, i.e. the Gibbs surface is chosen so that the reference system contains the same amount of component 1 as the real system. Hence $\Gamma_1^{(1)} \equiv 0$.

In terms of experimental quantities

$$\Gamma_i^{(1)} = A_s^{-1} [n_i - V^\alpha c_i^\alpha - V^\beta c_i^\beta],$$

where

$$V^\alpha = \frac{n_1 - Vc_1^\beta}{c_1^\alpha - c_1^\beta},$$

and

$$V^\beta = \frac{Vc_1^\alpha - n_1}{c_1^\alpha - c_1^\beta},$$

and n_i , n_1 are the total amounts of i and 1 in the system, and V is the total volume of the system. V^α and V^β thus defined correspond to $\Gamma_1^\sigma = 0$.

For liquid/vapour interfaces the following approximate equation may be used in the domain of low vapour pressures:

$$\Gamma_i^{(1)} = A_s^{-1} \left(n_i - n_1 \frac{x_i^l}{x_1^l} \right),$$

where x_i^l and x_1^l are the mole fractions of i and 1 respectively in the bulk liquid phase.

The *reduced adsorption* ($\Gamma_i^{(n)}$) of component i is defined by the equation

$$\Gamma_i^{(n)} = \Gamma_i^\sigma - \Gamma^\sigma \left\{ \frac{c_i^\alpha - c_i^\beta}{c^\alpha - c^\beta} \right\},$$

where Γ^σ , c^α and c^β are, respectively, the total Gibbs surface concentration and the total concentrations in the bulk phases α and β :

$$\Gamma^\sigma = \sum_i \Gamma_i^\sigma,$$

$$c^\alpha = \sum_i c_i^\alpha,$$

$$c^\beta = \sum_i c_i^\beta.$$

The reduced adsorption is also invariant to the location of the Gibbs surface.

Alternatively, the reduced adsorption may be regarded as the Gibbs surface concentration of i when the Gibbs surface is chosen so that Γ^σ is zero, i.e. the Gibbs surface is chosen so that the reference system has not only the same volume, but also contains the same total amount of substance (n) as the real system.

Hence

$$\sum_i \Gamma_i^{(n)} \equiv 0.$$

In terms of experimental quantities

$$\Gamma_i^{(n)} = A_s^{-1} [n_i - V^\alpha c_i^\alpha - V^\beta c_i^\beta],$$

where now

$$V^\alpha = \frac{n - Vc^\beta}{c^\alpha - c^\beta}; i$$

$$V^\beta = \frac{Vc^\alpha - n}{c^\alpha - c^\beta}.$$

and

$$n = \sum_i n_i.$$

V^α and V^β thus defined correspond to $\Gamma^\sigma = 0$.

For liquid/vapour interfaces the following approximate equation may be used in the domain of low vapour pressures:

$$\Gamma_i^{(n)} = A_s^{-1}(n_i - nx_i^l).$$

Because both $\Gamma_i^{(1)}$ and $\Gamma_i^{(n)}$ are invariant to the position of the Gibbs surface, it is possible to dispense with the concept of the Gibbs surface and to formulate the above definitions without explicit reference to a dividing surface.

It may happen that component i is virtually insoluble in both of the adjoining phases, i.e. $c_i^\alpha = c_i^\beta = 0$, but is present as a monolayer between them. Such a layer can be produced by spreading and is called a *spread monolayer*¹¹. The relative and reduced adsorption become indistinguishable for such a component as does the difference between surface excess amount (n_i^σ) and amount of adsorbed substance n_i^s , (see §1.1.11). In this case the *surface concentration* (= surface excess concentration) is defined by

$$\Gamma_i^s = \Gamma_i^\sigma = n_i^s/A_s$$

The symbol for the (*average*) *area per molecule (in the surface)*¹² is a_i or $a_{i,s}$.

¹¹(2001) The principles for measuring and reporting experimental data on spread monolayers are discussed in: Ter-Minassian-Saraga, L., "Reporting experimental pressure-area data with film balances", *Pure Appl. Chem.* **57** (1985) 621–632.

¹²In the field of spread monolayers it has been customary to use A for the area per molecule and A_0 for its co-area (the two-dimensional analogue of the co-volume of a real gas). To avoid confusion with A_s for the total area and A for Helmholtz energy, the adoption of a_i (or $a_{i,s}$) and a_i^0 (or $a_{i,s}^0$) for *area* and *co-area* per molecule respectively is recommended.

1.1.10 Adsorption at the solid adsorbent/liquid interface¹³

For solid/liquid systems, two different definitions of the surface excess amount, $n_i^{\sigma(n)}$ and $n_i^{\sigma(v)}$, are frequently used. When the surface area of the solid is known, then these may be expressed as the *surface excess concentrations* $\Gamma_i^{(n)}$, (*reduced adsorption*), or $\Gamma_i^{(v)}$ (for which no specific name has been proposed), each relating to a particular procedure for calculating adsorption from solution. The corresponding specific quantities, $n_i^{\sigma(n)}/m (= A_s\Gamma_i^{(n)})$, or $n_i^{\sigma(v)}/m (= A_s\Gamma_i^{(v)})$ are used when the surface area of the solid is not known with certainty.

$\Gamma_i^{(n)}$ is the excess, per unit area of solid/liquid interface, of the amount of component i in the system, over the amount of i in a reference system containing the same total amount n^l , of liquid and in which a constant mole fraction x_i^l equal to that in the bulk liquid in the real system, is maintained throughout the liquid phase:

$$\Gamma_i^{(n)} = A_s^{-1}(n_i - n^l x_i^l) = A_s^{-1} n^l \Delta x_i^l.$$

The second form refers to the most usual experimental mode of determination: $\Delta x_i^l = (x_i^0 - x_i^l)$ is the change in mole fraction of i resulting from bringing a specified mass m of solid (of surface area $A_s = m a_s$) into contact with a specified amount of solution n^l , so that $n_i = n^l x_i^0$. $\Gamma_i^{(n)}$ is thus defined exactly in terms of experimental quantities without the introduction of any assumptions; it is therefore to be preferred generally over $\Gamma_i^{(v)}$ (see below).

It follows from the above definition that the *total reduced surface excess* of components in the liquid phase is zero:

$$\sum_{i=1}^k \Gamma_i^{(n)} = 0,$$

where the summation extends over all the k components of the liquid phase. This relation emphasizes the competitive character of adsorption from solution.

The above definition of $\Gamma_i^{(n)}$ is essentially algebraic (cf. end of first paragraph in §1.1.8), and is independent of the choice of a Gibbs dividing surface. It may be noted, however, that the Gibbs surface corresponding to this definition does not in general, coincide with the surface of the solid and, consequently $\Gamma_{\text{solid}} \neq 0$ according to this interpretation.

¹³(2001) A supplement to the present definitions and the operational determination of adsorption from solution, together with the interpretation of the data in thermodynamic terms is discussed in Everett, D.H., "Reporting data on adsorption from solution at the solid/solution interface", *Pure Appl. Chem.* **58** (1986) 967–984.

Similarly, as in the case of the fluid/fluid interface, it may sometimes be expedient to define and calculate from experimental data the *relative adsorption*, $\Gamma_i^{(1)}$, as the excess, per unit area of solid/liquid interface, of the amount of component i in the actual system, over the amount of i in a reference system containing the same amount of component 1 as the real system and in which a constant composition, equal to that of the bulk liquid in the real system, is maintained throughout the liquid phase:

$$\Gamma_i^{(1)} = A_s^{-1}(n_i - n_1 x_i^l / x_1^l),$$

so that $\Gamma_1^{(1)} = 0$, by definition. Note that for a binary system

$$\Gamma_2^{(1)} = \Gamma_2^{(n)} / x_1^l.$$

Analogous and completely equivalent definitions of reduced and relative adsorption may be formulated and used in terms of masses and mass fractions, respectively.

$\Gamma_i^{(v)}$ is the excess, per unit area of solid/liquid interface, of the amount of component i in the system over the amount of component i in the reference system containing the same volume V^l , of liquid and in which a constant concentration, equal to that in the bulk liquid in the real system, is maintained throughout the liquid phase.

V^l is defined as the difference between the total volume of the system and that of the solid, assuming that the latter is not changed by the adsorption process.

$$\Gamma_i^{(v)} = A_s^{-1}(n_i - c_i^l V^l).$$

$\Gamma_i^{(v)}$ corresponds to the choice of a Gibbs surface located at the geometrical surface of the solid so that component i does not penetrate into the surface layer of the solid.

If it is assumed that the volume of the liquid including adsorbed material is unchanged by contact with the solid, then $n_i = c_i^0 V^l$ where c_i^0 is the initial concentration of i in the liquid before contact with the solid, and

$$\Gamma_i^{(v)} = A_s^{-1} V^l \Delta c_i^l,$$

where $\Delta c_i^l = (c_i^0 - c_i^l)$ is the change in concentration resulting from bringing a specified mass of solid (of surface area A_s) into contact with a specified amount of solution (of volume V^l).

If it is assumed that V_i , the partial molar volume of i in the liquid, is independent of concentration and adsorption, the Gibbs surface concentrations of the various components defined in this way are related by the equation

$$\sum_i V_i \Gamma_i^{(v)} = 0$$

Because the calculation of $\Gamma_i^{(v)}$ from experimental measurements is based on the assumption of constant total volume, it is advisable to confine its use, and that of the corresponding specific quantity $V^l \Delta c_i^l / m$, where m is the mass of adsorbent, to practically ideal solutions, and in particular to ideal dilute solutions.

The *surface excess isotherm* is the function relating, at constant temperature and pressure, $\Gamma_i^{(n)}$, $\Gamma_i^{(1)}$ or $\Gamma_i^{(v)}$, or the respective specific quantities $n^l \Delta c_i^l / m$, $A_1 \Gamma_i^{(1)} / m$ or $V^l \Delta c_i^l / m$ to the mole fraction (or concentration) of component i in the equilibrium liquid phase. With solutions of more than two components such isotherms are unequivocal functions only when the ratios of the mole fractions (or concentrations) of all other components except i are kept constant.

The term *composite isotherm* has been used as a synonym for surface excess isotherm, but is not recommended.

The term *individual isotherm* or *partial isotherm* is the function relating, at constant temperature and pressure, the amount of a particular component in the interfacial layer per unit area (or per unit mass of adsorbent) with its mole fraction (or concentration) in the liquid phase. This function $n_i^s(x_i^l)$ (or $n_i^s(c_i^l)$) can be evaluated only when the location and the thickness of the interfacial layer has been defined. In this case, the surface excess can be expressed as $n_i^s - x_i^l \sum n_i^s$ (or $n_i^s - c_i^l V^s$), where $\sum n_i^s$ is the total amount of substance in the interfacial layer (and V^s is its volume). The amount n_i^s thus becomes identical with the experimentally accessible surface excess when the equilibrium concentration of i in the liquid is negligibly small.

In connection with strongly adsorbed solutes of limited solubility, the value of n_i^s reached in a saturated solution is called the *adsorption capacity* of the adsorbent for solute i ; its value depends also, in general, on the nature and, in the case of more than two components, on the relative composition of the bulk liquid.

1.1.11 Adsorption at the solid/gas interface

Surface excess amount of adsorbed substance (Gibbs adsorption), (n_i^σ) is the excess of the amount of component i actually present in the interfacial layer over that which would be present at the same equilibrium gas pressure in the reference system, in which the gas phase concentration is constant up to the Gibbs surface, and the reference concentration of component i is zero beyond the Gibbs surface in the surface layer of the solid (see Figure 2).

The general expression for n_i^σ (§1.1.8) becomes in this instance:

$$n_i^\sigma = \int_{\text{all adsorption space}} (c_i - c_i^g) dV + \int_{\text{surface layer of the solid}} c_i dV,$$

where the interfacial layer is divided into two regions, the adsorption space and surface layer of the solid (see §1.1.5), by the Gibbs surface. The second term is usually assumed to be zero or negligible.

For a multicomponent gas mixture the *total surface excess amount of adsorbed substance* is

$$n^\sigma = \sum_i n_i^\sigma$$

If the area A_s of the solid surface is known, then the *surface excess concentration* (or *Gibbs surface concentration*) of component i , denoted by Γ_i^σ , is

$$\Gamma_i^\sigma = n_i^\sigma / A_s$$

Similar definitions can be given for the *surface excess number of molecules* of component i , N_i^σ , and of the *surface excess mass* of i , m_i^σ , and of the *surface excess volume of gas of i* (V_i^σ) preferably expressed as the volume of gas calculated for 273.15 K and 101.325 kPa (0°C and 1 atm): the equation of state used in the calculation should be stated.

The operational definition of n_i^σ is

$$n_i^\sigma = n_i - c_i^g V^g,$$

where n_i is the total amount of component i present and V^g is the volume of the gas defined by the Gibbs dividing surface. The position of the Gibbs surface is often defined experimentally as that surface which encloses the volume of space from which the solid excludes helium gas (the so-called *helium dead-space*), and is associated with the assumptions that the volume of the solid is unaffected by the adsorption of i , and that helium is not adsorbed by the solid. This requires that the measurement of the helium dead-space be made at a sufficiently high temperature.

The *amount of adsorbed substance* is defined as

$$n_i^s = \int_{V^s} c_i dV,$$

where $V^s = \tau A_s$ is the *volume of the interfacial layer* which has to be defined on the basis of some appropriate model of gas adsorption and c_i is the local concentration of component i as exemplified in Figure 2. An equivalent, alternative, but somewhat more operational definition may be formulated as follows:

$$n_i^s = n_i^\sigma + c_i^g V^{s,g},$$

where $V^{s,g}$ is the volume of the adsorption space depicted schematically in Figure 2. When the adsorption of component i is not too weak and its

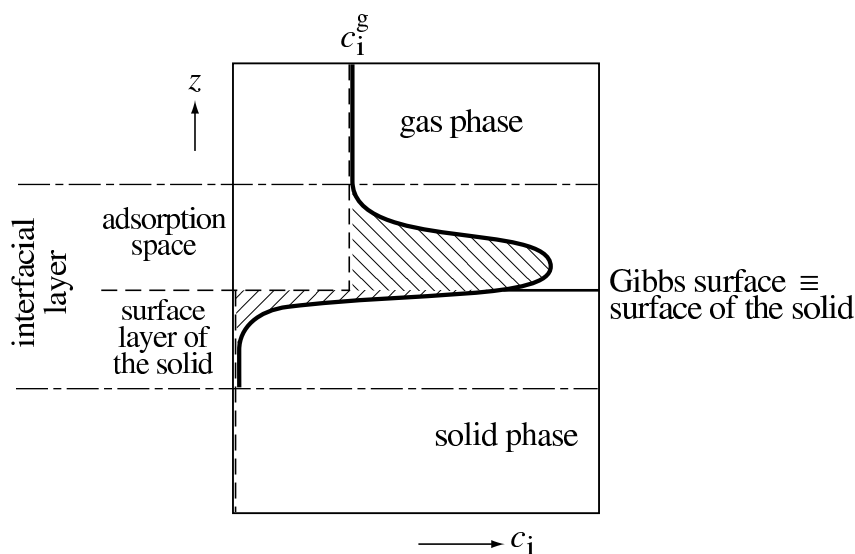


Figure 2: Schematic representation of the concentration profile (c_i) as a function of distance (z) normal to the surface: full line—in the real system; broken line—in the reference system; chain-dotted line—boundaries of the interfacial layer. The excess amount of adsorbed substance per unit area (n_i^σ/A_s) is given by the sum of the areas of the two shaded portions.

equilibrium partial pressure p_i^g sufficiently low, then the second term on the right hand side becomes negligibly small so that:

$$n_i^s \approx n_i^\sigma.$$

This last identification is usually justified in measurements of gas adsorption at lower pressures. Under these conditions the surface excess amount of adsorbed substance and the amount of adsorbed substance become indistinguishable and the latter term (often abbreviated to *amount adsorbed*) is usually used for both concepts.

The following definitions refer to the adsorption of a single adsorptive.

Adsorption isotherm, in the case of a single adsorptive, is the function relating the amount, mass or volume, or corresponding excess of substance adsorbed by a given amount of solid to the equilibrium pressure (p) at constant temperature (T)¹⁴

¹⁴(2001) The evaluation of gas adsorption isotherms is discussed in: Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A. Rouquerol, J., Siemieniowska, T., "Reporting physisorption data for gas/solid systems with special reference to the determinations of surface area and porosity", *Pure Appl. Chem.* **57** (1985) 603–619.

Adsorption isobar is the function relating the amount, mass, or volume, or corresponding excess of substance adsorbed by a given amount of solid to the temperature at constant pressure.

Adsorption isostere is the function relating the equilibrium pressure to the temperature at a constant value of the amount, or excess amount, of substance adsorbed by a given amount of solid.

When the *specific surface area* (a_s) is measured by adsorption methods¹⁵ then it is given by the product of the *specific monolayer capacity*, n_m^s/m , the Avogadro constant, and the area occupied by a molecule adsorbed in a complete monolayer (a_m):

$$a_s = \frac{n_m^s}{m} N_A a_m.$$

In the case of microporous solids the interpretation of adsorption measurements in terms of surface area may lose its significance when the size of the adsorbed molecules is comparable with the dimensions of the pores. Nevertheless it may be convenient to define a *monolayer equivalent area*, in which n_m^s is replaced in the above equation by the amount needed to fill the micropores (§1.1.7).

1.2 MECHANICAL AND THERMODYNAMIC PROPERTIES OF SURFACES AND INTERFACES

1.2.1 Surface tension, or interfacial tension (γ , σ)

The mechanical properties of an interfacial layer between two fluid phases can be expressed in terms of those of a geometrical surface of uniform tension called the *surface of tension* whose location is dependent on the distribution of the stress tensor within the interfacial layer.

The tension acting in the surface of tension is called the *surface tension* or *interfacial tension* and is expressed in terms of force per unit length. The surface tension between two bulk phases α and β is written $\gamma^{\alpha\beta}$ or $\sigma^{\alpha\beta}$, and, that between phase α and its equilibrium vapour or a dilute gas phase, γ^α or σ^α . The superscripts may be omitted if there is no danger of ambiguity.

The mechanical properties of the interfacial layer between two fluids, including the equilibrium shape of the surface, may be calculated by applying the standard mathematical techniques of mechanics to the forces associated

¹⁵(2001) Recommendations on the determination of specific surface areas by application of the BET-method to gas adsorption data are presented in: Sing et al. *Pure Appl. Chem.* **57** (1985) 603–619.

with the surface of tension. The resulting equations—which comprise the subject of *capillarity*—form the basis of experimental methods of measuring surface tension.

In particular, surface tension is the intensive factor in the differential expression for the work required to increase the area of the surface of tension. Measured under reversible conditions at constant temperature (and normally constant pressure) and referred to unit area, this work, the so-called (differential) *surface work*, is equal to the static (see below) surface tension. The surface tension may, therefore, also be expressed in terms of energy per unit area: it is not, however, in general equal either to the surface energy or to the surface Helmholtz energy per unit area (see §1.2.6).

In certain circumstances, for example with a rapidly expanding surface, one may measure surface tensions that are different from the equilibrium value. Such a surface tension is called the *dynamic surface* (or *interfacial*) *tension* (γ^{dyn} or σ^{dyn}). The equilibrium value is then called the *static surface* (or *interfacial*) *tension* (γ^{st} or σ^{st}). The modifying signs may be omitted if there is no danger of ambiguity.

In the case of solid surfaces it becomes difficult to define the surface tension in terms of mechanical properties.

1.2.2 Wetting

The general term *wetting* can be employed in the following ways: adhesional wetting, spreading wetting and immersional wetting.

Adhesional wetting is a process in which an adhesional joint is formed between two phases.

The *work of adhesion per unit area*, $w_A^{\alpha\beta\delta}$, is the work done on the system when two condensed phases α and β , forming an interface of unit area are separated reversibly to form unit areas of each of the $\alpha\delta$ - and $\beta\delta$ -interfaces.

$$w_A^{\alpha\beta\delta} = \gamma^{\alpha\delta} + \gamma^{\beta\delta} - \gamma^{\alpha\beta}.$$

The work of adhesion as defined above, and traditionally used, may be called the *work of separation*.

The *work of cohesion per unit area*, w_C^α , of a single pure liquid or solid phase α is the work done on the system when a column of α of unit area is split, reversibly, normal to the axis of the column to form two new surfaces each of unit area in contact with the equilibrium gas phase.

$$w_C^\alpha = 2\gamma^\alpha.$$

Spreading wetting—a process in which a drop of liquid spreads over a solid or liquid substrate.

A liquid, α , when placed on the surface of a solid or liquid, β , both previously in contact with a fluid phase δ , will tend to spread on the surface if the *spreading tension*, $\sigma^{\alpha\beta\delta}$, defined by

$$\sigma^{\alpha\beta\delta} = \gamma^{\beta\delta} - \gamma^{\alpha\delta} - \gamma^{\alpha\beta},$$

is positive. $\sigma^{\alpha\beta\delta}$ is also equal to the *work of spreading per unit area* (w_{spr}).

If adsorption equilibrium and mutual saturation of the phases is not achieved instantly, it is possible to distinguish the *initial spreading tension*, $\sigma_i^{\alpha\beta\delta}$, from the *final spreading tension*, $\sigma_f^{\alpha\beta\delta}$, when equilibrium has been reached.

In the case in which $\sigma_i^{\alpha\beta\delta}$ is positive, while $\sigma_f^{\alpha\beta\delta}$ is negative, the system is said to exhibit *autophobicity*.

When an area of liquid covered with a spread substance is separated from a clean area of surface by a mechanical barrier, the force acting on unit length of the barrier is called the *surface pressure*, π or π^s , and is equal to;

$$\pi^s = \gamma^0 - \gamma,$$

where γ^0 is the surface tension of the clean surface and γ that of the covered surface.

In the case of the spreading of a liquid or an adsorbed film on a solid where the surface pressure cannot be measured directly, the surface pressure may still be defined formally by the above equation.

When a liquid does not spread on a substrate (usually a solid), that is, when $\sigma_f^{\alpha\beta\delta}$ is negative, a *contact angle* (θ) is formed which is defined as the angle between two of the interfaces at the three-phase line of contact. It must always be stated which interfaces are used to define θ . When a liquid spreads spontaneously over an interface the contact angle, between the S/L and L/G surfaces, is zero.

It is of ten necessary to distinguish between the *advancing contact angle* (θ_a), the *receding contact angle* (θ_r) and the *equilibrium contact angle* (θ_e). When $\theta_r \neq \theta_a$ the system is said to exhibit *contact angle hysteresis*. When confusion might arise between θ used to denote contact angle, and to denote fraction of surface covered (§1.1.7) it is advisable to attach a subscript to θ for the contact angle.

Immersional wetting—a process in which a solid or liquid, β , is covered with a liquid, α , both of which were initially in contact with a gas or liquid, δ , without changing the area of the $\alpha\delta$ -interface.

The *work of immersional wetting per unit area*, or *wetting tension* ($w_W^{\alpha\beta\delta}$)¹⁶, is the work done on the system when the process of immersional wetting

¹⁶The use of the term *adhesion tension* is discouraged because it can be confused with the term *work of adhesion* (see above).

involving unit area of phase β is carried out reversibly:

$$w_W^{\alpha\beta\delta} = \gamma^{\beta\delta} - \gamma^{\alpha\beta}.$$

Note: in systems in which wetting is accompanied by adsorption the above definitions should, strictly speaking, be expressed in terms of the differential quotients of the work with respect to the relevant change in area.

1.2.3 Surface rheology¹⁷

The *surface (excess) shear viscosity* is denoted by η^σ . The inverse of η^σ is called *surface (excess) fluidity* and is denoted by φ^σ .

1.2.4 Thermodynamic properties

The thermodynamic properties associated with phase boundaries may be defined in terms either of excess quantities relative to a suitably chosen reference system, or of an interfacial layer of thickness τ and volume $V^s = \tau A_s$, in a manner analogous to that used for the definition of excess amounts and total amounts of substance adsorbed.

When expressed in forms which are invariant to the choice of dividing surface, on the one hand, or to the thickness of the interfacial layer on the other, the two methods lead to identical results. In the development of statistical mechanical theories of adsorption, however, many authors have preferred to express the problem in terms of an interfacial layer. For completeness, therefore, the appropriate definitions are given in relation to both formulations.

A Thermodynamic excess properties defined relative to a Gibbs surface.

Surface excess energy (U^σ) is defined by

$$U^\sigma = U - U^\alpha - U^\beta = U - V^\alpha \left(\frac{U_m^\alpha}{V_m^\alpha} \right) - V^\beta \left(\frac{U_m^\beta}{V_m^\beta} \right),$$

where V_m^α and V_m^β satisfy the condition

$$V_m^\alpha + V_m^\beta = V,$$

the total volume of the system.

¹⁷(2001) A set of terms of particular interest to colloid and surface chemists can be found in: Lyklema, J. and van Olphen, H., “*Terminology and symbols in colloid and surface chemistry - part 1.13: definitions, terminology and symbols for rheological properties*”, *Pure Appl. Chem.* **51** (1979) 1213–1218.

(U_m^α/V_m^α) and (U_m^β/V_m^β) are the energy densities in the two bulk phases where U_m^α and U_m^β are the mean molar energies and V_m^α and V_m^β are the mean molar volumes of the two phases.

Surface excess entropy (S^σ) is defined by

$$S^\sigma = S - S^\alpha - S^\beta = S - V^\alpha \left(\frac{S_m^\alpha}{V_m^\alpha} \right) - V^\beta \left(\frac{S_m^\beta}{V_m^\beta} \right).$$

(S_m^α/V_m^α) and (S_m^β/V_m^β) are the entropy densities in the two bulk phases, where S_m^α and S_m^β are the mean molar entropies of the two phases.

Surface excess Helmholtz energy (A^σ) is defined by

$$A^\sigma = U^\sigma - TS^\sigma.$$

Surface excess enthalpy (H^σ) is defined by

$$H^\sigma = U^\sigma - \gamma A_s.$$

Surface excess Gibbs energy (G^σ) is defined by

$$G^\sigma = H^\sigma - TS^\sigma = A^\sigma - \gamma A_s.$$

When the thermodynamics of surfaces is discussed in terms of excess quantities, $V^\sigma = 0$. There is thus only one way of defining the excess surface enthalpy and excess surface Gibbs energy (cf. case B, below).

The corresponding excess quantities per unit area may be denoted by lower case letters:

$$u^\sigma = U^\sigma / A_s,$$

$$s^\sigma = S^\sigma / A_s,$$

$$a^\sigma = A^\sigma / A_s,$$

$$h^\sigma = H^\sigma / A_s,$$

$$g^\sigma = G^\sigma / A_s.$$

Quantities invariant to the choice of dividing surface may be defined as follows:

Relative (excess) surface energy (with respect to component 1)

$$U^{\sigma(1)} = U^\sigma - n_1^\sigma \left[\left(\frac{U_m^\alpha}{V_m^\alpha} \right) - \left(\frac{U_m^\beta}{V_m^\beta} \right) \right] / (c_1^\alpha - c_1^\beta).$$

Analogous equations hold for $S^{\sigma(1)}$, $A^{\sigma(1)}$, $H^{\sigma(1)}$ and $G^{\sigma(1)}$.

Reduced (excess) surface energy

$$U^{\sigma(n)} = U^\sigma - n^\sigma \left[\left(\frac{U_m^\alpha}{V_m^\alpha} \right) - \left(\frac{U_m^\beta}{V_m^\beta} \right) \right] / (c^\alpha - c^\beta),$$

where n^σ is the total adsorption relative to an arbitrary choice of dividing surface and c^α and c^β are the total concentrations of the two phases.

Analogous equations hold for $S^{\sigma(n)}$, $A^{\sigma(n)}$, $H^{\sigma(n)}$ and $G^{\sigma(n)}$.

B Thermodynamic properties of an interfacial layer

The following definitions are useful only when V^s can be assessed unequivocally on the basis of a physical model of the interfacial layer, or when V^s can be taken as negligibly small.

Interfacial energy (U^s) is defined by

$$U^s = U - U^\alpha - U^\beta = U - V^\alpha \left(\frac{U_m^\alpha}{V_m^\alpha} \right) - V^\beta \left(\frac{U_m^\beta}{V_m^\beta} \right),$$

where U is the total energy of the system, and U^α and U^β are the energies attributed to the bulk phases α and β of volumes V^α and V^β subject to the condition

$$V = V^\alpha + V^\beta + V^s,$$

where V is the total volume.

Interfacial entropy (S^s) is defined by

$$S^s = S - S^\alpha - S^\beta = S - V^\alpha \left(\frac{S_m^\alpha}{V_m^\alpha} \right) - V^\beta \left(\frac{S_m^\beta}{V_m^\beta} \right),$$

where S is the total entropy of the system.

Interfacial Helmholtz energy (A^s) is defined by

$$A^s = U^s - TS^s.$$

The corresponding quantities per unit area may be denoted by lower case letters:

$$u^s = U^s/A_s,$$

$$s^s = S^s/A_s,$$

$$a^s = A^s/A_s.$$

Enthalpy and Gibbs energy. When the state of a system depends upon more than one pair of conjugate mechanical (or electrical) variables, i.e. more

than (p, V) , then it is possible to derive several sets of functions having the character of enthalpies and Gibbs energies. These functions are related in the following way

$$\begin{array}{ccc} \text{Energy} & \xrightarrow{-xY} & \text{Enthalpy} \\ \downarrow -TS & & \downarrow -TS \\ \text{Helmholtz energy} & \xrightarrow{-xY} & \text{Gibbs energy} \end{array}$$

where x is an intensive mechanical (or electrical) variable and Y the conjugate extensive variable.

The properties of interfacial layers depend on both (p, V^s) and (γ, A_s) . In defining an enthalpy in terms of the corresponding energy either $-pV^s$, γA_s or $-(pV^s - \gamma A_s)$ may be subtracted from the energy function. There are thus three possible definitions of *interfacial enthalpy*:

$$\begin{aligned} \mathcal{H}^s &= U^s + pV^s, \\ \hat{H}^s &= U^s - \gamma A_s, \\ H^s &= U^s + pV^s - \gamma A_s, \end{aligned}$$

and three definitions of the *interfacial Gibbs energy*

$$\begin{aligned} \mathcal{G}^s &= A^s + pV^s &= \mathcal{H}^s - TS^s, \\ \hat{G}^s &= A^s - \gamma A_s &= \hat{H}^s - TS^s, \\ G^s &= A^s + pV^s - \gamma A_s &= H^s - TS^s. \end{aligned}$$

No distinguishing names have been suggested for these different functions. A possible nomenclature, if one is needed, could be

$$\begin{aligned} \mathcal{H} &= pV\text{-enthalpy}, \\ \hat{H} &= \gamma A\text{-enthalpy}, \\ H &= pV\gamma A\text{-enthalpy}, \\ \mathcal{G} &= pV\text{-Gibbs energy}, \\ \hat{G} &= \gamma A\text{-Gibbs energy}, \\ G &= pV\gamma A\text{-Gibbs energy}. \end{aligned}$$

Of these \hat{H}^s and \hat{G}^s are not often used.

1.2.5 Surface chemical potentials

Surface chemical potentials are defined by

$$\begin{aligned} \mu_i^\sigma &= (\partial A^\sigma / \partial n_i^\sigma)_{T, A_s, n_j^\sigma} &= (\partial G^\sigma / \partial n_i^\sigma)_{T, p, \gamma, n_j^\sigma}; \\ \mu_i^s &= (\partial A^s / \partial n_i^s)_{T, V^s, A_s, n_j^s} &= (\partial G^s / \partial n_i^s)_{T, p, \gamma, n_j^s}. \end{aligned}$$

The quantities thus defined can be shown to be identical, and the conditions of equilibrium of component i in the system to be

$$\mu_i^\alpha = \mu_i^\sigma = \mu_i^s = \mu_i^\beta,$$

where μ_i^α and μ_i^β are the chemical potentials of i in the bulk phases α and β . (μ_i^α or μ_i^β has to be omitted from this equilibrium condition if component i is not present in the respective bulk phase.)

The surface chemical potentials are related to the Gibbs energy functions by the equations

$$\begin{aligned} G^\sigma &= \sum_i n_i^\sigma \mu_i^\sigma, \\ G^s &= \sum_i n_i^s \mu_i^s. \end{aligned}$$

1.2.6 Surface tension, surface Helmholtz and Gibbs energies, and entropies

The surface tension is related to the derivative of the Helmholtz energy by the equations

$$\begin{aligned} \gamma &= (\partial A^\sigma / \partial A_s)_{T, n_i^\sigma} = (\partial A^s / \partial A_s)_{T, V^s, n_i^s} \\ &= (\partial A / \partial A_s)_{T, V^\alpha, V^\beta, n_i^\alpha, n_i^\beta, n_i^\sigma} = (\partial A / \partial A_s)_{T, V, n_i}, \end{aligned}$$

where in the last equality A is the Helmholtz energy of the whole system, and V^α and V^β refer to the volumes of the bulk phases relative to the Gibbs surface; and to the derivative of the Gibbs energy by the equations

$$\begin{aligned} \gamma &= (\partial G^\sigma / \partial A_s)_{T, \gamma, n_i^\sigma} = (\partial G^s / \partial A_s)_{T, p^s, n_i^s} \\ &= (\partial G / \partial A_s)_{T, p^s, n_i^\alpha, n_i^\beta, n_i^\sigma}. \end{aligned}$$

Expressed in terms of integral quantities

$$\gamma A_s = A^\sigma - \sum_i n_i^\sigma \mu_i^\sigma = A^s - \sum_i n_i^s \mu_i^s,$$

or

$$\gamma = a^\sigma - \sum_i \Gamma_i^\sigma \mu_i^\sigma = a^s - \sum_i \Gamma_i^s \mu_i^s,$$

Under equilibrium conditions the superscripts s and σ attached to the μ_i terms may be omitted.

Note: Only when $\sum_i \Gamma_i \mu_i = 0$ is γ equal to the *surface (excess) Helmholtz energy per unit area*. In general, for a multicomponent system it is not possible to define either an interfacial layer, or a Gibbs surface, for which

this condition is satisfied. However, it is satisfied automatically when the system exhibits an adsorption azeotrope at which all the Γ_i are zero.

For a one-component system, treated in terms of a Gibbs surface it is always possible to choose this surface so that $\Gamma_1 = 0$, so that the surface tension is equal to the value of a^σ relative to this surface; on the other hand Γ_i^s must always be positive for an interfacial layer so that a^s and γ can never be equated.

The *surface excess entropy* is given by

$$-\left(\frac{\partial A^\sigma}{\partial T}\right)_{A_s, n_i^\sigma} = S^\sigma.$$

1.2.7 Solid adsorbent/gas interface: characteristic thermodynamic quantities of adsorption

The following definitions refer to the solid/gas interface. Changes in enthalpy and entropy associated with adsorption are usually attributed to changes in the thermodynamic state of the adsorbate only. It should be borne in mind, however, that the measured changes include contributions from the perturbation of the adsorbent.

Differential energy of adsorption

When the addition of a differential amount dn_i^σ or dn_i^s is effected at constant gas volume, the differential molar energy of adsorption of component i , $\Delta_a U_i^\sigma$ or $\Delta_a U_i^s$, is defined as:

$$\Delta_a U_i^\sigma = U_i^\sigma - U_i^g, \text{ or } \Delta_a U_i^s = U_i^s - U_i^g,$$

where the differential molar surface excess energy, U_i^σ , is given by¹⁸

$$U_i^\sigma = \left(\frac{\partial U^\sigma}{\partial n_i^\sigma}\right)_{T, m, n_j^\sigma} = \left(\frac{\partial U}{\partial n_i^\sigma}\right)_{T, m, V^g, p_i, n_j^\sigma},$$

and the differential molar interfacial energy, U_i^s , by

$$U_i^s = \left(\frac{\partial U^s}{\partial n_i^s}\right)_{T, m, V^s, n_j^s} = \left(\frac{\partial U}{\partial n_i^s}\right)_{T, m, V^g, V^s, p_i, n_j^s}.$$

U_i^g is the differential molar energy of component i in the gas phase, i.e. $(\partial U^g / \partial n_i^g)_{T, V, n_i^g}$.

¹⁸Mass is employed as extensive variable for the adsorbent in these equations because the area may change on adsorption.

Differential enthalpy of adsorption

When the addition of the differential amount dn_i^σ or dn_i^s is effected at constant pressure p , the *differential molar enthalpy of adsorption*, $\Delta_a H_i^\sigma$ or $\Delta_a H_i^s$, also called the *isosteric enthalpy of adsorption* (q^{st})¹⁹ is defined as²⁰

$$\begin{aligned}\Delta_a H_i^\sigma &= -q^{\text{st},\sigma} = U_i^\sigma - H_i^g; \\ \Delta_a H_i^s &= -q^{\text{st},s} = \mathcal{H}_i^s - H_i^g;\end{aligned}$$

where $\mathcal{H}_i^s = (\partial \mathcal{H}^s / \partial n_i^s)_{T,p,m,n_j^s}$, and H_i^g is the partial molar enthalpy of component i in the gas phase, i.e. $(\partial H^g / \partial n_i^g)_{T,p,n_j^g}$.

$\Delta_a U_i^\sigma$ and $\Delta_a H_i^\sigma$ are related by the equation:

$$\Delta_a U_i^\sigma - \Delta_a H_i^\sigma = pV_m^g \approx RT,$$

and the same applies to the difference between $\Delta_a U_i^s$ and $\Delta_a H_i^s$ when V^s/n_i^s is negligibly small compared with V_m^g .

When an excess n^σ of a single adsorptive is adsorbed on a surface initially free of adsorbate species, the *molar integral energy* and *molar integral enthalpy of adsorption* are given by

$$\Delta_a U_m^\sigma = \frac{1}{n^\sigma} \int_0^{n^\sigma} \Delta_a U^\sigma dn^\sigma \quad \text{and} \quad \Delta_a H_m^\sigma = \frac{1}{n^\sigma} \int_0^{n^\sigma} \Delta_a H^\sigma dn^\sigma.$$

Experimental calorimetric methods have to be analysed carefully to establish the appropriate procedure for deducing a particular energy or enthalpy of adsorption from measured data. The isosteric enthalpy of adsorption is usually calculated from adsorption isotherms measured at several temperatures by using the equation

$$\left(\frac{\partial \ln p}{\partial T} \right)_{n^\sigma} = \frac{q^{\text{st},\sigma}}{pV_m^g T} \approx \frac{q^{\text{st},\sigma}}{RT^2},$$

where p is the equilibrium partial pressure of the adsorptive when an amount n^σ is adsorbed at a temperature T .

Standard thermodynamic quantities. For different purposes it may be convenient to define standard changes of a thermodynamic quantity on adsorption in two alternative ways:

- (i) the change of the thermodynamic quantity on going from the standard gas state to the adsorbed state in equilibrium with gas at a partial pressure (fugacity) of p_i (f_i). Such quantities are sometimes called ‘half-standard’ quantities.

¹⁹Formerly called the isosteric *heat* of adsorption.

²⁰The naming of these quantities as enthalpies and their notation by $\Delta_a H$ is not strictly justified since $\Delta_a H^s$ is a difference between two differently defined enthalpies, and $\Delta_a H^\sigma$ is the difference between an energy and an enthalpy. A more complicated notation, which is hardly justified, would be needed to indicate these distinctions.

- (ii) the change of the thermodynamic quantity on going from the standard gas state to a defined standard condition of the adsorbed state.

It must always be stated clearly which of these conventions is being followed.

The *standard Gibbs energy of adsorption* is thus:

$$\Delta_a \mu_i^\ominus = RT \ln[f_i/f_i^\ominus],$$

where f_i^\ominus is the fugacity of i in the standard gas state and f_i the fugacity of gas in equilibrium with the (standard) adsorbed state. For most practical purposes the fugacity may be replaced by the (partial) pressure.

If unit pressure is chosen for the standard gas state, this may be written

$$\Delta_a \mu_i^\dagger = RT \ln[f_i/f_i^\dagger],$$

while if vapour in equilibrium with pure liquid i is chosen²¹, then

$$\Delta_a \mu_i^* = RT \ln[f_i/f_i^*].$$

Similarly, the *standard differential molar entropy of adsorption* is given by

$$\Delta_a S_i^\ominus = \frac{1}{T}(\Delta_a H_i^\ominus - \Delta_a \mu_i^\ominus),$$

where $\Delta_a H_i^\ominus$ is the *standard differential molar enthalpy of adsorption*.

The *standard integral molar entropy of adsorption* is

$$\Delta_a S_m^\ominus = \frac{1}{n_i^\sigma} \int_o^{n_i^\sigma} \Delta_a S_i^\ominus dn_i^\sigma.$$

The above definitions refer to equilibrium conditions, and their applicability in regions where adsorption hysteresis occurs is open to doubt.

1.2.8 Enthalpy of wetting or enthalpy of immersion

The enthalpy of wetting or enthalpy of immersion, $\Delta_w H$, $\Delta_{\text{imm}} H$, $-Q_w$ or $-q_w$ (when referred to unit of mass of the solid) is defined as the difference (at constant temperature) between the enthalpy of a solid completely immersed in a wetting liquid, and that of the solid and liquid taken separately. It must be specified whether the solid in the initial state is in contact with vacuum or with the vapour of the liquid at a given partial pressure. Measurements of the enthalpy of wetting of a solid equilibrated with varying relative pressures of the vapour of a pure wetting liquid may be used to derive the differential enthalpy of adsorption of the vapour.

²¹(2001) The superscript * is recommended for reference to a pure liquid.

1.3 DEFINITION AND CLASSIFICATION OF COLLOIDS

The term *colloidal* refers to a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 μm , or that in a system discontinuities are found at distances of that order. It is not necessary for all three dimensions to be in the colloidal range: fibers in which only two dimensions are in this range, and thin films, in which one dimension is in this range, may also be classified as colloidal. Nor is it necessary for the units of a *colloidal system* to be discrete: continuous network structures, the basic units of which are of colloidal dimensions also fall in this class (e.g. porous solids, gels and foams).

A *colloidal dispersion* is a system in which particles of colloidal size of any nature (e.g. solid, liquid or gas) are dispersed in a *continuous phase* of a different composition (or state).

The name *dispersed phase* for the particles should be used only if they have essentially the properties of a bulk phase of the same composition.

The term *colloid* may be used as a short synonym for colloidal system. The size limits given above are not rigid since they will depend to some extent on the properties under consideration. This nomenclature can be applied to coarser systems, especially when a gradual transition of properties is considered.

The description of colloidal systems often requires numbering of the components or constituents. It is felt that a fixed rule of numbering is unnecessarily restrictive. However, the author should make clear in all cases how he is numbering and in particular whether he is numbering by independent thermodynamic components (all neutral) or by species or constituents, of which some may be ionic, and which may be related by equilibrium conditions or by the condition of electroneutrality. In comparing English and French, it should be realized that the English word 'component' is usually equivalent to the French 'constituent' and the English 'constituent' to the French 'composant'.

A fluid colloidal system composed of two or more components may be called a *sol*, e.g. a protein sol, a gold sol, an emulsion, a surfactant solution above the critical micelle concentration (cf. §1.6), an aerosol.

In a *suspension* solid particles are dispersed in a liquid; a *colloidal suspension* is one in which the size of the particles lies in the colloidal range.

In an *emulsion* liquid droplets and/or liquid crystals are dispersed in a liquid. In emulsions the droplets often exceed the usual limits for colloids in size. An emulsion is denoted by the symbol O/W if the continuous phase: is

an aqueous solution and by W/O if the continuous phase is an organic liquid (an 'oil'). More complicated emulsions such as O/W/O (i.e. oil droplets contained within aqueous droplets dispersed in a continuous oil phase) are also possible. Photographic emulsions, although colloidal systems, are not emulsions in the sense of this nomenclature.

A *latex* (plural = latices or latexes) is an emulsion or sol in which each colloidal particle contains a number of macromolecules.

A *foam* is a dispersion in which a large proportion of gas by volume in the form of gas bubbles, is dispersed in a liquid, solid or gel. The diameter of the bubbles is usually larger than 1 μm , but the thickness of the lamellae between the bubbles is often in the usual colloidal size range.

The term *froth* has been used interchangeably with foam. In particular cases froth may be distinguished from foam by the fact that the former is stabilized by solid particles (as in *froth-flotation* q.v.) and the latter by soluble substances.

Aerosols are dispersions in gases. In aerosols the particles often exceed the usual size limits for colloids. If the dispersed particles are solid, one speaks of *aerosols of solid particles*, if they are liquid of *aerosols of liquid particles*. The use of the terms solid aerosol and liquid aerosol is discouraged. An aerosol is neither 'solid' nor 'liquid' but, if anything, gaseous.

A great variety of terms such as dust, haze, fog, mist, drizzle, smoke, smog are in use to describe aerosols according to their properties, origin, etc. Of these only the terms fog and smoke are included in this nomenclature.

A *fog* is an aerosol of liquid particles, in particular a low cloud.

A *smoke* is an aerosol originating from combustion, thermal decomposition or thermal evaporation. Its particles may be solid (magnesium oxide smoke) or liquid (tobacco smoke).

A *gel* is a colloidal system with a finite, usually rather small, yield stress. Materials such as silica gel which have passed a gel stage during preparation, are improperly called gels.

The term *xerogel* is used for such dried out open structures; and also for dried out compact macromolecular gels such as gelatin or rubber.

The term *aerogel* is used when the openness of the structure is largely maintained.

Colloidal dispersions may be *lyophobic* (*hydrophobic*, if the dispersion medium is an aqueous solution) or *lyophilic* (*hydrophilic*). *Lyophilic sols* are formed spontaneously when the dry coherent material (e.g. gelatin, rubber, soap) is brought in contact with the dispersion medium, hence they are thermodynamically more stable than in the initial state of dry colloid material plus dispersion medium. *Lyophobic sols* (e.g. gold sol) cannot be formed by spontaneous dispersion in the medium. They are thermodynamically unsta-

ble with respect to separation into macroscopic phases, but they may remain for long times in a metastable state.

Lyophilic sols comprise both *association colloids* in which aggregates of small molecules are formed reversibly and *macromolecules* in which the molecules themselves are of colloidal size.

Mixtures of lyophobic and lyophilic colloids, may form *protected lyophobic colloids* (cf. §1.5).

The terms *lyophilic* (*hydrophilic*, *lipophilic*, *oleophilic*, etc.) and *lyophobic*, (*lipophobic*, etc.) may also be used to describe the character of interaction of a particular atomic group with the medium. In this usage the terms have the relative qualitative meaning of ‘solvent preferring’ (water-preferring, fat-preferring etc.) and ‘solvent rejecting’ (water-rejecting, fat-rejecting, etc.) respectively.

The terms ‘*solvent preferring*’ or ‘*solvent rejecting*’ always refer to a differential process usually in the sense of preferring the solvent above itself or preferring itself above the solvent but sometimes preferring one solvent (e.g. water) above another (e.g. oil).

A *colloidal electrolyte* is an electrolyte which gives ions of which at least one is of colloidal size. This term therefore includes hydrophobic sols, ionic association colloids, and polyelectrolytes.

Ions of low relative molecular mass, with a charge opposite to that of the colloidal ion, are called *counterions*; if their charge has the same sign as that of the colloidal ion, they are called *co-ions*.

A *polyelectrolyte* is a macromolecular substance which, on dissolving in water or another ionizing solvent, dissociates to give *polyions* (*polycations* or *polyanions*)—multiply charged ions—together with an equivalent amount of ions of small charge and opposite sign. Polyelectrolytes dissociating into polycations and polyanions, with no ions of small charge, are also conceivable. A polyelectrolyte can be a *polyacid*, a *polybase*, a *polysalt* or a *polyampholyte*.

If all particles in a colloidal system are of (nearly) the same size the system is called *monodisperse*; in the opposite cases the systems are *heterodisperse*.

If only a few particle-sizes occur in a colloidal system the system is *pau-cidisperse* and if many particle-sizes occur *polydisperse*.

In heterodisperse systems the determination of particle mass or relative molecular mass gives averages, which depend on the method used. The most common averages are: $\bar{M}_{r,n}$, $\bar{M}_{r,m}$, and $\bar{M}_{r,z}$.

Number average relative molecular mass (= *number average molecular weight*)

$$\bar{M}_{r,n} = \frac{\sum n_i M_r(i)}{\sum n_i},$$

where n_i and $M_r(i)$ are the amount of substance and the relative molecular mass of the species i respectively.

Mass average relative molecular mass (= mass average molecular weight):

$$\bar{M}_{r,m} = \frac{\sum n_i \{M_r(i)\}^2}{\sum n_i M_r(i)}$$

Average relative molecular masses in which higher powers of $M_r(i)$ occur can be defined. Of these the Z-average (named after the Z-coordinate in the Lamm-scale method used in its determination) is applied fairly often. It is defined as follows:

Z-average relative molecular mass (= Z-average molecular weight):

$$\bar{M}_{r,Z} = \frac{\sum n_i \{M_r(i)\}^3}{\sum n_i \{M_r(i)\}^2}$$

The subscript r in the above definitions is generally omitted if there is no possibility of ambiguity.

1.4 PREPARATION AND PROCESSING OF COLLOIDAL SYSTEMS

Colloidal sols can be formed by *dispersion methods* (e.g. by mechanical subdivision of larger particles or by dissolution in the case of lyophilic sols) or by *condensation methods* (from supersaturated solutions or supercooled vapours, or as the product of chemical reactions) or by a combination of these two (e.g. in an electrical discharge).

When a condensation method is applied, molecules (or ions) are deposited on *nuclei*, which may be of the same chemical species as the colloid (*homogeneous nucleation*) or different (*heterogeneous nucleation*).

An aggregate of a small number of atoms, molecules or ions is called an *embryo*. A *critical embryo* has that size at which the Gibbs energy at constant pressure and temperature is a maximum. A larger embryo is called a *homogeneous nucleus*.

A *nucleating agent* is a material either added to or present in the system, which induces either homogeneous or heterogeneous nucleation.

The *rate of nucleation* is the number of nuclei formed in unit time per unit volume.

Dialysis is the process of separating a colloidal sol from a colloid-free solution by a membrane permeable to all components of the system except the colloidal ones, and allowing the exchange of the components of small molar mass to proceed for a certain time.

The colloid-free solution obtained at equilibrium in dialysis is called *equilibrium dialysate*. Its composition approaches that of the dispersion medium (more precisely, the limit to which the composition of the dispersion medium tends at large distances from the particles). In the dialysis equilibrium an osmotic pressure difference exists between sol and equilibrium dialysate.

After (complete or incomplete) dialysis two solutions are obtained. The one free from colloidal material is called *dialysate*; the other one, containing the colloidal particles may be called *retentate*, *dialysis residue*, or simply *residue*, but should not be called dialysate.

The *ultrafiltrate*, prepared by *ultrafiltration* (filtration through a dialysis membrane), is in general not of the same composition as the equilibrium solution.

If dialysis is conducted in the presence of an electric field across the membrane(s) it is called *electrodialysis*. Electrodialysis may lead to local differences in concentration and density. Under the influence of gravity these density differences lead to large scale separation of sols of high and of low (often vanishingly low) concentrations. This process is called *electrodecantation* (*electrophoresis convection*).

Flotation is the removal of matter by entrainment at an interface. In particular, *froth flotation* is the removal of particulate matter by foaming (frothing).

Foam fractionation is a method of separation in which a component of the bulk liquid is preferentially adsorbed at the L/V interface and is removed by foaming.

1.5 STABILITY OF COLLOIDAL SYSTEMS, AGGREGATION, COAGULATION, FLOCCULATION

The terms stable and stability are used in rather special and often different senses in colloid science: the relationship between these usages and the formal thermodynamic usage is outlined below.

Thermodynamically stable or *metastable* means that the system is in a state of equilibrium corresponding to a local minimum of the appropriate thermodynamic potential for the specified constraints on the system (e.g. Gibbs energy at constant T and p). Stability cannot be defined in an absolute sense, but if several states are in principle accessible to the system under given conditions, that with the lowest potential is called the stable state, while the other states are described as metastable. Unstable states are not at a local minimum. Transitions between metastable and stable states occur at rates

which depend on the magnitude of the appropriate activation energy barriers which separate them. Most colloidal systems are metastable or unstable with respect to the separate bulk phases, with the (possible) exception of lyophilic sols, gels and xerogels of macromolecules.

Colloidally stable means that the particles do not aggregate at a significant rate: the precise connotation depends on the type of aggregation under consideration. For example, a concentrated paint is called stable by some people because oil and pigment do not separate out at a measurable rate, and unstable by others because the pigment particles aggregate into a continuous network.

An *aggregate* is, in general, a group of particles (which may be atoms or molecules) held together in any way: a colloidal particle itself (e.g. a micelle, see below) may be regarded as an aggregate. More specifically, aggregate is used to describe the structure formed by the cohesion of colloidal particles.

Aggregation is the process or the result of the formation of aggregates.

When a sol is colloidally unstable (i.e. the rate of aggregation is not negligible) the formation of aggregates is called *coagulation* or *flocculation*. These terms are often used interchangeably, but some authors prefer to introduce a distinction between *coagulation*, implying the formation of compact aggregates, leading to the macroscopic separation of a *coagulum*; and *flocculation*, implying the formation of a loose or open network which may or may not separate macroscopically. In many contexts the loose structure formed in this way is called a *floc*. While this distinction has certain advantages, in view of the more general (but not universal) acceptance of the equivalence of the words coagulation and flocculation, any author who wishes to make a distinction between them should state so clearly in his publication.

The reversal of coagulation or flocculation, i.e. the dispersion of aggregates to form a colloidally stable suspension or emulsion, is called *deflocculation* (sometimes *peptization*).

The rate of aggregation is in general determined by the frequency of collisions and the probability of cohesion during collision. If the collisions are caused by Brownian motion, the process is called *perikinetic aggregation*; if by hydrodynamic motions (e.g. convection or sedimentation) one may speak of *orthokinetic aggregation*.

In hydrophobic sols, coagulation can be brought about by changing the electrolyte concentration to the *critical coagulation concentration* (c.c.c.) (preferably expressed in $\text{mol m}^{-3} = \text{mmol dm}^{-3}$). As the value of the critical coagulation concentration depends to some extent on the experimental circumstances (method of mixing, time between mixing and determining the state of coagulation, criterion for measuring the degree of coagulation, etc.) these should be clearly stated.

The generalization that the critical coagulation concentration for a typical lyophobic sol is extremely sensitive to the valence of the counterions (high valence gives a low critical coagulation concentration) is called the *Schulze-Hardy rule*.

If the critical coagulation concentration of a mixture of two electrolytes A and B corresponds to concentrations of the two components of c_A and c_B whereas the c.c.c.'s of A and B taken separately are c_A^0 and c_B^0 then the effects of the electrolytes are said to be *additive* if $(c_A/c_A^0) + (c_B/c_B^0) = 1$; they are *synergistic* if $(c_A/c_A^0) + (c_B/c_B^0) < 1$; and *antagonistic* if $(c_A/c_A^0) + (c_B/c_B^0) > 1$. It is often found in the latter case that the individual values of (c_A/c_A^0) and/or (c_B/c_B^0) exceed unity.

Addition of small amounts of a hydrophilic colloid to a hydrophobic sol may make the latter more sensitive to flocculation by electrolyte. This phenomenon is called *sensitization*. Higher concentrations of the same hydrophilic colloid usually protect the hydrophobic sol from flocculation. This phenomenon is called *protective action*. Colloidally stable mixtures of a lyophobic and lyophilic colloid are called *protected lyophobic colloids*; although they may be thermodynamically unstable with respect to macroscopic phase separation, they have many properties in common with lyophilic colloids.

Sedimentation is the settling of suspended particles under the action of gravity or a centrifugal field. If the concentration of particles is high and interparticle forces are strong enough, the process of sedimentation may be better described as *compaction* of the particle structure with pressing out of the liquid. This particular kind of settling is also called *subsidence*.

Sediment is the highly concentrated suspension which may be formed by the sedimentation of a dilute suspension.

Coalescence is the disappearance of the boundary between two particles (usually droplets or bubbles) in contact, or between one of these and a bulk phase followed by changes of shape leading to a reduction of the total surface area. The flocculation of an emulsion, viz. the formation of aggregates, may be followed by coalescence. If coalescence is extensive it leads to the formation of a macrophase and the emulsion is said to *break*.

The *breaking of a foam* involves the coalescence of gas bubbles.

Coalescence of solid particles is called *sintering*.

Creaming is the macroscopic separation of a dilute emulsion into a highly concentrated emulsion, in which interglobular contact is important, and a continuous phase under the action of gravity or a centrifugal field. This separation usually occurs upward, but the term may still be applied if the relative densities of the dispersed and continuous phases are such that the concentrated emulsion settles downward. Some authors, however, also use

creaming as the opposite of sedimentation even when the particles are not emulsion droplets.

Cream is the highly concentrated emulsion formed by creaming of a dilute emulsion. The droplets in the cream may be colloiddally stable or flocculated, but they should not have coalesced.

As a rule all colloidal systems, initially of uniform concentration, establish, when subjected to the action of gravity or a centrifugal field, a concentration gradient as a result of sedimentation or creaming (see §1.10); but if the system is colloiddally stable the particles in the sediment or cream do not aggregate and can be redispersed by the application of forces of the same magnitude as those which caused sedimentation or creaming.

The loss of the stability of a lyophilic sol (equivalent to a decrease in the solubility of the lyophilic colloid) quite often results in a separation of the system into two liquid phases. The separation into two liquid phases in colloidal systems is called *coacervation*. It occurs also, though rarely, in hydrophobic sols. The phase more concentrated in colloid component is the *coacervate*, and the other phase is the *equilibrium solution*.

If coacervation is caused by the interaction of two oppositely charged colloids, it is called *complex coacervation*.

Coacervation usually begins with the separation of the second phase in the form of small droplets which may coalesce to a continuous phase. Sometimes with extremely anisotropy particles the droplets have the shape of spindles or cylinders (*tactoids*). If the colloidal system is highly concentrated, droplets of the dilute phase are formed in the concentrated one (*negative tactoids*). The phenomenon of tactoid formation is not restricted to lyophilic systems.

In some systems, sedimenting particles form layers separated by approximately equal distances of the order of the wavelength of light. This gives rise to strong colours when observed in reflected light and the system is said to form *iridescent layers* or *schiller layers*.

1.6 SURFACE ACTIVE AGENTS

A *surface active agent* (= *surfactant*) is a substance which lowers the surface tension of the medium in which it is dissolved, and/or the interfacial tension with other phases, and, accordingly, is positively adsorbed at the liquid/vapour and/or at other interfaces. The term surfactant is also applied correctly to sparingly soluble substances, which lower the surface tension of a liquid by spreading spontaneously over its surface.

A *soap* is a salt of a fatty acid, saturated or unsaturated, containing at least eight carbon atoms or a mixture of such salts.

A *detergent* is a surfactant (or a mixture containing one or more surfactants) having cleaning properties in dilute solution (soaps are surfactants and detergents).

A *syndet* is a synthetic detergent; a detergent other than soap.

An *emulsifier* is a surfactant which when present in small amounts facilitates the formation of an emulsion, or enhances its colloidal stability by decreasing either or both of the rates of aggregation and coalescence.

A *foaming agent* is a surfactant which when present in small amounts facilitates the formation of a foam, or enhances its colloidal stability by inhibiting the coalescence of bubbles.

The property of surface activity is usually due to the fact that the molecules of the substance are *amphipathic* or *amphiphilic*, meaning that each contains both a hydrophilic and a hydrophobic (lipophilic) group²².

Surfactants in solution are often association colloids, that is, they tend to form *micelles*, meaning aggregates of colloidal dimensions existing in equilibrium with the molecules or ions from which they are formed.

If the surfactant ionizes, it is important to indicate whether the micelle is supposed to include none, some, or all of the counterions. For example, *degree of association* refers to the number of surfactant ions in the micelle and does not say anything about the location of the counterions: *charge of the micelle* is usually understood to include the net charge of the surfactant ions and the counterions bound to the micelle: *micellar mass* and *micellar weight* usually refer to a neutral micelle and therefore include an equivalent amount of counterions with the surfactant ions.

The *relative molecular mass* (M_r) of a micelle is called the *relative micellar mass* or *micellar weight* and is defined as the mass of a mole of micelles divided by the mass of $\frac{1}{12}$ mole of ^{12}C .

There is a relatively small range of concentrations separating the limit below which virtually no micelles are detected and the limit above which virtually all-additional surfactant forms micelles. Many properties of surfactant solutions, if plotted against the concentration appear to change at a different rate above and below this range. By extrapolating the loci of such a property above and below this range until they intersect, a value may be obtained known as the *critical micellization concentration* (*critical micelle concentration*), symbol c_M , abbreviation c.m.c. As values obtained using different properties are not quite identical, the method by which the c.m.c. is determined should be clearly stated²³.

²²This assumes that one of the two phases is aqueous and the other non-aqueous. If both are non-aqueous (e.g. oil/air) molecules containing organophilic and organophobic groups may be amphipathic and surface active.

²³(2001) See also: K.J. Mysels, P. Mujerjee, "Reporting experimental data dealing with

Solubilization. In a system formed by a solvent, an association colloid and at least one other component (the *solubilizate*), the incorporation of this other component into or on the micelles is called *micellar solubilization*, or, briefly *solubilization*. If this other component is sparingly soluble in the solvent alone, solubilization can lead to a marked increase in its solubility due to the presence of the association colloid. More generally, the term *solubilization* has been applied to any case in which the activity of one solute is materially decreased by the presence of another solute.

Concentrated systems of surfactants often form *liquid crystalline phases*, or *mesomorphic phases*. Mesomorphic phases are states of matter in which anisometric molecules (or particles) are regularly arranged in one (*nematic state*) or two (*smectic state*) directions, but randomly arranged in the remaining direction(s).

Examples of mesomorphic phases are: *neat soap*, a lamellar structure containing much (e.g. 0.75%) soap and little (e.g. 0.25%) water; *middle soap*, containing a hexagonal array of cylinders, less concentrated (e.g. 0.50%), but also less fluid than neat soap.

A *soap curd* is not a mesomorphic phase, but a gel-like mixture of fibrous soap-crystals ('curd-fibers') and their saturated solution.

Myelin cylinders are birefringent cylinders which form spontaneously from lipid-containing material in contact with water.

Krafft point, symbol t_K (Celsius or other customary temperature), T_K , (thermodynamic temperature) is the temperature (more precisely, narrow temperature range) above which the solubility of a surfactant rises sharply. At this temperature the solubility of the surfactant becomes equal to the c.m.c. It is best determined by locating the abrupt change in slope of a graph of the logarithm of the solubility against t or $1/T$.

1.7 FLUID FILMS

When the thickness (t, h) of a fluid phase decreases sufficiently (below a few μm in most contexts) it becomes a *fluid film*.

The properties of fluid films depend on the nature of the film phase and on that of each of the two neighbouring bulk phases. By analogy with the accepted emulsion nomenclature (§1.3) these films should be described, where appropriate, by three capital letters such as A for air, W for 'water', O for 'oil', and S for solid, separated by solidi, the middle letter indicating the film phase. For *symmetrical films* the first and last symbols are the same,

critical micellization concentrations (c.m.c.'s) of aqueous surfactant systems", *Pure Appl. Chem.* **51** (1979): 1083-1089.

e.g. A/W/A: water film in air, or W/O/W/: oil film in water, whereas for *unsymmetrical films* these are different, e.g. W/O/A: oil film between water and air.

The term *soap film* has been established by usage for A/W/A films stabilized by surfactants although it is not a film of soap, nor is the stabilizing surfactant necessarily a soap (cf. §1.6). The term *lipid film* has been similarly established for W/O/W films.

A *film element* is a small homogeneous part of a film including the two interfaces and any fluid between them.

Except for free-floating bubbles, films have to be supported by frames, bulk surfaces or by other films. The transition zone separating these from the film proper, always containing some bulk liquid, is called a *Plateau border*.

A thin film is often, but not always, unstable with respect to *rupture*, that is, the formation of a hole which permits coalescence or direct contact of the two phases which it separates. There may also be a thickness, or thicknesses, at which the film is stable or metastable with respect to small thickness changes. Such a film is said to be an *equilibrium film*. Unless the area of the film is small, its composition may not be the same over its area and the (metastable) equilibrium thickness may be characteristic of the local condition only.

For films other than equilibrium films the thickness is often non-uniform and changes more (*mobile film*) or less (*rigid film*) rapidly with time. These differences are often associated with differences in surface shear rheology.

A film often thins gradually to a thickness at which it either ruptures or converts abruptly to an equilibrium film. This thickness is sometimes well enough defined statistically to be considered a *critical thickness*, t_c or h_c . Rupture under these conditions characterizes *unstable films*, whereas transition to an equilibrium film characterizes (*meta*)*stable films*. Liquids yielding the former give no foam or only a transient one, lasting generally less than twenty seconds, whereas liquids giving (meta) stable films form much longer-lasting foams under the same conditions.

When viewed in reflected white light against a black background, transparent films show the classical interference colours of thin plates which permit an estimate of their thickness to be made. When of the order of 100 nm (1000 Å) in thickness they appear white (*silver film*) and when thinner they appear gradually less intensely white, then grey and finally black. Hence, the term *black film* is a general one to designate films thinner than about $\frac{1}{4}$ wavelength of visible light. Black films are often equilibrium films, but equilibrium films may be considerably thicker under some conditions.

In soap films, two types of equilibrium film are often observed, sometimes successively in the same system: one characterized by thicknesses of the order

of 7 nm or more which varies significantly with minor changes in composition such as ionic strength, and the other having a lesser thickness relatively independent of such changes. It is recommended, that when a distinction is needed, the former be designated as *common black films*, and the latter as *Newton black films*. The current use of first or secondary for the common black film and of second, primary or Perrin's for the Newton black film is discouraged.

Conditions and quantities relating to the transition between common and Newton black films should be identified by the subscript N , thus c_N or t_N or ΔH_N .

Stratified films are films in which more than two thicknesses coexist in a fixed configuration over significant periods of time.

No pure liquid is known to give stable A/W/A films and many surfactant solutions give them only above a rather sharply defined concentration, c_{bl} . Above this concentration, under given experimental conditions, the film does not burst after it has thinned to t_c but gives equilibrium, often black, films.

The *film tension*, Σ_f , of an equilibrium film in contact with the bulk phase is measured by the contractile force per unit length exerted by this film.

For a symmetrical film $\Sigma_f/2$ may be called the *surface tension of the film*, σ_f or γ_f . σ_f is generally lower than the bulk surface tension, σ_0 . When $\sigma_f < \sigma_0$, the film and bulk phase form a macroscopic *film contact angle*, θ , analogous to the three-phase contact angle (see §1.2.2) and measured in the bulk phase between the limiting directions of the film and of the bulk liquid. θ is related to the surface tensions of the two surfaces in contact by

$$\sigma_f = \sigma_0 \cos \theta.$$

Gibbs film elasticity, E , pertains to a film element of a soap film changing in area at constant mass and is the differential change of its surface tension with relative change in area, $A(\partial\sigma/\partial A)_{T,p,n_i}$. Here σ is half the tension of the film element.

Some of the physical properties of a film such as its reflectivity for light or its parallel capacitance (for W/O/W or Hg/W/Hg films) are related to the film thickness. Determination of thickness from the measurement of such properties involves assumptions about the structure and properties of the film which at present are always somewhat uncertain and arbitrary. Unless the basic experimental data are reported, it is recommended that the method used in deriving from them any reported thickness or structure be given in sufficient detail to permit recalculation of these data in future work.

Because of this difficulty in obtaining accurately the thickness of a film, one sometimes expresses the experimental measurements in terms of an *equiv-*

alent film thickness which approximates to some extent the true film thickness and can be determined unambiguously. Such a thickness should be indicated by an appropriate subscript.

1.8 COLLIGATIVE AND RELATED PROPERTIES

Swelling is the increase in volume of a gel or solid associated with the uptake of a liquid or gas.

Imbibition is the uptake of a liquid by a gel or porous substance. It may or may not be accompanied by swelling.

Syneresis is the spontaneous shrinking of a gel with exudation of liquid.

Swelling pressure (Π_{sw} or Π) is that pressure difference which has to be established between a gel and its equilibrium liquid, to prevent further swelling of the gel.

Colloid osmotic pressure (Donnan pressure) (Π_D or Π) is the pressure difference which has to be established between a colloidal system and its equilibrium liquid to prevent material transfer between the two phases when they are separated by a membrane, permeable to all components of the system, except the colloidal ones.

Reduced osmotic pressure is the osmotic pressure divided by mass concentration.

1.9 ATTRACTION AND REPULSION

Two surfaces coming close together may repel each other for a variety of causes. The corresponding *Gibbs energy of repulsion* is indicated by G_r or G_{el} if the repulsion is due to electric effects (g_r or g_{el} is taken for unit area of each of two flat and parallel surfaces). G_r (or G_{el}) is defined as

$$G_r \text{ (or } G_{\text{el}}) = \left[\int_{\text{final distance}}^{\infty} \text{Force. d(distance)} \right]_{T,p}.$$

It is in general not equal to the difference in surface Gibbs energy between the final distance and infinite separation. The *Gibbs energy of attraction* (G_a or g_a for unit area) is similarly defined.

Van der Waals attraction constants are valid for small separations. Between molecules the *van der Waals-London constant* $\lambda = -\phi r^6$, where r is the distance between the centre of the molecules and ϕ the energy of attraction.

Between semi-infinite flat plates the *van der Waals-Hamaker constant*

(Hamaker constant)²⁴ $A_H = -g_a \cdot 12\pi h^2$ where h is the distance between the surfaces of the semi-infinite plates and g_a is the Gibbs energy of attraction per unit cross-sectional area of the two plates. If the van der Waals forces between molecules are strictly additive, $A_H = \pi^2 n^2 \lambda$ where n is the number of molecules per unit volume.

Retarded van der Waals constants are valid for large separations. Between molecules, the retarded van der Waals constant is $\beta = -\phi r^7$.

Between semi-infinite flat plates, the Gibbs energy of the retarded van der Waals attraction per unit cross-sectional area is given by $g_a = -B/3h^3$. With strict additivity of retarded van der Waals forces, $B = \frac{1}{10}\pi n^2 \beta$.

The total Gibbs energy of interaction is indicated by G_t (g_t if taken per unit area of each of two flat and parallel plates). It is composed of the electrostatic, the van der Waals and possibly other components.

The curve representing the total Gibbs energy of interaction against the distance between the interacting surfaces frequently shows two minima. If this is the case, the minimum at the shorter distance is called the *primary minimum*, that at the larger separation the *secondary minimum*.

The total Gibbs energy of interaction is in general not equal to the difference in surface Gibbs energy between the final distance and infinite separation but it is equal to the change of Gibbs energy of the whole system as the separation changes.

Current usage often describes the Gibbs energies defined above as ‘potentials’ but this usage is to be discouraged.

The force per unit area which can be obtained as the derivative of $-g_t$ with respect to the distance is called the *disjoining pressure*, symbol Π_d .

1.10 SEDIMENTATION, CREAMING, CENTRIFUGATION AND DIFFUSION

Sedimentation volume (V_{sed}) or *cream volume* (V_{cr}) is the volume of sediment or cream formed in a suspension or emulsion. If the sediment is formed in a centrifugal field, the strength of this field should be explicitly indicated, otherwise normal gravity is understood.

Sedimentation equilibrium is the equilibrium between sedimentation and diffusion.

Rate of sedimentation is the *velocity of sedimentation* (v_{sed} or v).

Sedimentation coefficient (s) is the rate of sedimentation divided by acceleration, expressed in seconds (s) or in *Svedbergs* (Sv); Sv = 10^{-13} s.

²⁴(2001) In the original text the symbol A is used for the van der Waals-Hamaker constant. The present notation is recommended in the “Green Book”.

Limiting sedimentation coefficient, $[s]$, is the sedimentation coefficient extrapolated to zero concentration of the sedimenting component,

$$[s] = \lim_{c \rightarrow 0} s.$$

Reduced sedimentation coefficient, $s^0(20^\circ\text{C})$ ²⁵ is the sedimentation coefficient reduced to a standard temperature, usually 20°C and to a standard solvent, usually water.

$$s^0(20^\circ\text{C}) = s(t) \frac{\eta(t)}{\eta^0(20^\circ\text{C})} \cdot \frac{1 - v_s(20^\circ\text{C})\rho^0(20^\circ\text{C})}{1 - v_s(t)\rho(t)},$$

where $\eta(t)$ = coefficient of viscosity of the solution at temperature t ,
 $\eta^0(20^\circ\text{C})$ = coefficient of viscosity of standard solvent at 20°C ,
 $v_s(t)$ = partial specific volume of sedimenting substance at temperature t ,
 $\rho(t)$ = density of solution at temperature t ,
 $\rho^0(20^\circ\text{C})$ = density of the standard solvent at 20°C .

Reduced limiting sedimentation coefficient, $[s^0(20^\circ\text{C})]$, is the reduced sedimentation coefficient extrapolated to zero concentration of the sedimenting component:

$$[s^0(20^\circ\text{C})] = \lim_{c \rightarrow 0} s^0(20^\circ\text{C}),$$

Differential diffusion coefficient, D_i , of species i is defined by

$$D_i = -\mathbf{J}_i / \text{grad } c_i,$$

where \mathbf{J}_i is the amount of species i flowing through unit area in unit time and $\text{grad } c_i$ is the concentration gradient of species i . Different diffusion coefficients may be defined depending on the choice of the frame of reference used for \mathbf{J}_i and $\text{grad } c_i$. For systems with more than two components, the flow of any component and hence its diffusion coefficient depends on the concentration distribution of all components.

Limiting differential diffusion coefficient, $[D_i]$, is the value of D_i extrapolated to zero concentration of the diffusing species:

$$[D_i] = \lim_{c_i \rightarrow 0} D_i.$$

Self-diffusion coefficient, D_i^* , of species i is the diffusion coefficient in the absence of a chemical potential gradient. It is related to the diffusion coefficient D_i by

$$D_i^* = D_i \frac{\partial \ln c_i}{\partial \ln a_i},$$

²⁵It would be preferable to call this quantity the *standard sedimentation coefficient*.

where a_i is the activity of i in the solution. If an isotopically labelled species (i^*) is used to study diffusion, the *tracer diffusion coefficient*, D_{i^*} is practically identical to the self-diffusion coefficient provided that the isotope effect is sufficiently small.

Rotational diffusion coefficient, D_θ , is defined by the equation:

$$D_\theta = \frac{t_\theta}{\{\partial f(\theta, \varphi)/\partial \theta\} \sin \theta}$$

where $f(\theta, \varphi) \sin \theta d\theta d\varphi$ is the traction of particles whose axes make an angle between θ and $\theta + d\theta$ with the direction $\theta = 0$, and have an azimuth between φ and $\varphi + d\varphi$; $t_\theta d\varphi$ is the fraction of particles having an azimuth between φ and $\varphi + d\varphi$, whose axis passes from values $< \theta$ to values $> \theta$ in unit time. The axis whose rotational diffusion is considered has to be clearly indicated.

1.11 ELECTROCHEMICAL TERMS IN COLLOID AND SURFACE CHEMISTRY

Detailed basic definitions of electrochemical quantities are being developed by the Commission on Electrochemistry²⁶. Meanwhile the present appendix employs the names and symbols recommended in the Manual, and defines other quantities and concepts which have special relevance to colloid and surface chemistry.

Electrochemical double-layer. The electrical state of a surface depends on the spatial distribution of free (electronic or ionic) charges in its neighbourhood. This distribution is usually idealized as an electrochemical double-layer. Similar double-layers may also exist around micelles of association colloids or around polyelectrolyte molecules. Current views of electrical double-layers are based on a physical model in which one layer of the double-layer is envisaged as a *fixed charge* or *surface charge* attached to the particle or solid surface, while the other layer is distributed more or less diffusely in the liquid in contact with the particle. This layer contains an excess of *counterions*, opposite in sign to the fixed charge, and usually a deficit of *co-ions* of the same sign as the fixed charge. Counter and co-ions in immediate contact with the surface are said to be located in the *Stern layer*, and form with the fixed charge a molecular capacitor. Ions farther away from the surface form the *diffuse layer* or *Gouy layer*.

²⁶(2001) The definitions and terminology most relevant for colloid and surface chemists can be found in: Parsons, R., "Manual of Symbols and Terminology for Physicochemical Quantities and Units: Appendix III: Electrochemical nomenclature", *Pure Appl. Chem.* **34** (1974) 500–516.

The fixed *surface charge density* is denoted by σ^0 ; that in the Stern layer by σ^i and that in the Gouy layer by σ^{d27} . In a system which is electroneutral, $\sigma^o + \sigma^i + \sigma^d = 0$. The individual values attributed to the various charge densities depend on the precise definition adopted for surface charge.

A surface or a particle carrying no net fixed charge is said to be at the *point of zero charge* (abbreviation p.z.c.). The precise identification of this condition depends on the definition adopted for surface charge.

The *electrical potential* at the inner boundary of the Gouy layer is $\psi^{d28,29}$.

The *differential capacitance* of the electrical double-layer per unit area = $\partial\sigma/\partial\psi = C_{dl}^{30}$: the quantities held constant in this differentiation must be specified.

The *integral capacitance* of the electrical double layer per unit area =

²⁷(2001) In the original document, the symbols σ , σ_S and σ_G are used for respectively the charge densities at the surface plane, in the Stern layer and in the Gouy or diffuse layer. However, these notations are no longer recommended. The present notation is in accordance with the recommendations by (1) Parsons, R., “*Manual of Symbols and Terminology for Physicochemical Quantities and Units: Appendix III: Electrochemical nomenclature*”, *Pure Appl. Chem.* **34** (1974) 500–516 and (2) Lyklema, J., “*Electrified interfaces in aqueous dispersions of solid*, *Pure Appl. Chem.* **63** (1991) 895–906.

The inner boundary of the diffuse layer is called the *Stern plane* or *outer Helmholtz plane*. The charge σ^i in the Stern layer is generally assumed to be located at the *inner Helmholtz plane*, this is a plane situated between the surface plane and the Stern plane.

²⁸(2001) In the original document, the electrical potential is indicated as *inner* or *Galvani potential*, ϕ . For a solid phase immersed in a liquid phase this is the potential difference between a point in the bulk phase of the solid and a reference point R beyond the electric field of the solid in the liquid phase. The *outer* or *Volta potential*, ψ , for this situation is the potential difference just outside the solid phase and the reference point R in the liquid phase. The difference between ϕ and ψ is called the surface electric potential or “ χ ” potential.

If it is assumed that the surface potential is the potential at the outer boundary of the solid, no phase boundary is crossed between the surface and the reference point R . Under these conditions the *surface potential* can be considered as an *outer potential* ψ . Potentials inside the diffuse double layer are also defined with respect to point R in the liquid phase and these are outer potentials. Therefore, in colloid chemistry the surface potential and the potentials in the double layer are mostly all denoted as outer potentials, ψ .

In accordance with the distinctions of the double layer charges a distinction can be made between the *surface potential*, ψ^0 , the *potential at the inner Helmholtz plane*, ψ^i , and the *potential at the Stern layer* (the inner boundary of the diffuse layer), ψ^d . The course of the potential as a function of the distance to the interface is denoted as $\psi(z)$, or $\psi(r)$ where z or r is the distance to the surface. These potentials cannot be measured directly. In most cases a double layer model is used to convert the various charge densities into the corresponding potentials.

²⁹(2001) In the original text the symbol ϕ_G is used for the potential at the inner boundary of the diffuse layer, this symbol is not in accordance with more recent recommendations.

³⁰(2001) In the original text the symbols c_{dl} and k_{dl} are used, according to recent rules, capitals are preferred.

$$\sigma/\psi = K_{\text{dl}}^{31}.$$

A surface showing no electro-osmosis (see below) or a particle showing no electrophoresis is said to be at the *isoelectric point* (i.e.p.)³².

A macro-ion of a polyampholyte (in particular a protein) is said to be *isoelectric* if it exhibits no electrophoresis. It is *isoionic* if besides the polyampholyte and H⁺ or OH⁻ ions (in general ions of the solvent) no other ions are present in the system.

Potential determining ions are those species of ions which by virtue of their equilibrium distribution between the two phases (or by their equilibrium with electrons in one of the phases) determine the difference in Galvani potential between these phases. They are often, but not always, identical with the ions which stabilize a colloidal suspension formed from these phases, and which are sometimes called peptizing ions³³.

(Effective) *thickness of the* (diffuse electrical) *double-layer* = length characterizing the decrease with distance of the potential in the double layer = characteristic *Debye length* in the corresponding electrolyte solution = $1/\kappa$:

$$1/\kappa = [\epsilon_r \epsilon_0 RT / (F^2 \sum_i c_i z_i^2)]^{1/2} \text{ (rationalized four-quantity system);}$$

$$1/\kappa = [\epsilon_r RT / (4\pi F^2 \sum_i c_i z_i^2)]^{1/2} \text{ (three-quantity electrostatic system);}^{34}$$

where ϵ = static permittivity = $\epsilon_r \epsilon_0$; ϵ_r = relative static permittivity of solution; ϵ_0 = permittivity of vacuum; R = gas constant; T = thermodynamic temperature; F = Faraday constant; c_i = concentration of species i ; z_i = ionic charge on species i .

Donnan equilibrium is the equilibrium characterized by an unequal distribution of diffusible ions between two ionic solutions (one or both of the solutions may be gelled) separated by a membrane which is impermeable to at least one of the ionic species present, e.g. because they are too large to pass through the pores of the membrane. The membrane may be replaced by other kinds of restraint, such as gelation, the field of gravity, etc., which prevent some ionic components from moving from one phase to the other, but allows other components to do so.

³¹(2001) See previous footnote.

³²(2001) The difference between the p.z.c. and the i.e.p. is further explained by Lyklema, *Pure Appl. Chem.* **63** (1991) 895–906.

³³(2001) As pointed out by Lyklema, *Pure Appl. Chem.* **63** (1991) 895–906, for disperse systems the *surface charge density* is the primary parameter rather than the *surface potential*. The term *charge determining ions* is therefore in most cases more appropriate.

³⁴(2001) Presently, the rationalized four-quantity system (using S.I. units) is strongly recommended

Donnan emf (*Donnan potential*), E_D , is the potential difference at zero electric current between two identical salt bridges, usually saturated KCl bridges (conveniently measured by linking them to two identical electrodes) inserted into the two solutions in Donnan equilibrium.

Membrane emf: (*membrane potential*), E_m , is the potential difference between two saturated KCl bridges inserted into two solutions separated by a membrane. The solutions need not be in equilibrium with one another and need not contain any colloidal material.

Suspension effect (*Pallmann effect*, or *Wiegner effect*), E_s , is the Donnan emf between a suspension and its equilibrium liquid.

The relationships between these measured emf's and the behaviour of the membrane are complicated by a number of factors.

1.12 ELECTROKINETICS³⁵

Older equations for electrokinetic phenomena are often based upon the non-rationalized three-quantity electrostatic system. Transition to the internationally accepted rationalized four-quantity system (using S.I. units) is, however, recommended³⁶.

Electrophoresis is the motion of colloidal particles in an electric field. The term cataphoresis should be abandoned.

Electrophoretic velocity is the velocity of a particle during electrophoresis, symbol v .

Electrophoretic mobility is the electrophoretic velocity per unit field strength, symbol u_e or $u = v/\mathbf{E}$; u is positive if the particle moves towards lower potential and negative in the opposite case. According to the first paragraph of this section, the field strength should be expressed in Vm^{-1} (old: electrostatic c.g.s. units (statvolt) cm^{-1})³⁷.

Electrodeposition (which includes *electro-crystallization*) is the deposition of dissolved or suspended material by an electric field on an electrode.

Microscopic electrophoresis is the technique in which the electrophoresis of *individual* particles is observed with the aid of a microscope or ultramicroscope. This has been often referred to as microelectrophoresis, but it is recommended that the latter term be abandoned in view of likely confusion with the following definition.

³⁵To be distinguished from electrode kinetics.

³⁶(2001) A good example of consistent usage of modern notation can be found in J. Lyklema, *Fundamentals of Interface and Colloid Science*, Vol II, Academic Press (1995), Chapter 4.

³⁷(2001) Older units should be avoided. To avoid confusion, it is wise to indicate which units are used in each particular case.

Microelectrophoresis is the electrophoresis technique involving the movement of a mass of particles on a small scale (e.g. paper electrophoresis).

Electro-osmosis is the motion of a liquid through a membrane (or plug or capillary) as a consequence of the application of an electric field across the membrane. The spelling of electro-osmosis with two o's is preferred to electrosmosis with one o and to the older term electro-endosmosis.

Electro-osmotic velocity per unit field strength ($u_{e.o}$ or u) is the linear velocity of flow.

Electro-osmotic volume flow per unit field strength, J_v , is the volume flow per unit time through the whole plug; u and J_v are positive if the flow is in the direction of lower potential.

Electro-osmotic pressure, Δp , is the pressure difference across the membrane, plug, etc., needed just to stop electro-osmotic volume flow. Δp is positive if the higher pressure is on the high potential side.

Streaming potential difference (streaming potential), E_{st} or E , is the potential difference at zero current caused by the flow of liquid under a pressure gradient through a membrane, plug or capillary. Identical electrodes must be used on both sides of the membrane, plug, etc. E is positive if the higher potential is on the high pressure side.

Streaming current, I , is the electric current flowing in a streaming cell if the electrodes, which are supposed to be ideally depolarized, are short-circuited. I is positive if the current in the membrane, plug, etc., is from high to low pressure side (and in the outside lead from low to high pressure side).

Sedimentation potential difference (sedimentation potential) (also called *Dorn effect*), E_{sed} or E , is the potential difference at zero current caused by the sedimentation of particles in the field of gravity or in a centrifuge, between two identical electrodes at different levels (or at different distances from the centre of rotation). E is positive if the lower (peripheral) electrode is negative.

Sedimentation field strength, \mathbf{E}_{sed} , is the potential difference per unit length in a sedimentation or centrifugation cell. As the contributions of the interfacial potential differences at the electrodes are not included in \mathbf{E}_{sed} this quantity, although theoretically important, is not accessible to measurement.

Surface (excess) conductivity is the excess conductivity in the surface per unit length and width, symbol κ^σ ³⁸.

Electrokinetic potential (zeta potential), ζ , is the potential drop across

³⁸(2001) The *surface (excess) conductivity* can have contributions due to the diffuse layer charge outside the plane of shear (also called "*Bikerman*" *surface conductivity*) and due to the charge behind the plane of shear in the stagnant layer (*stagnant layer conductivity*).

the mobile part of the double layer, that is responsible for electrokinetic phenomena. ζ is positive if the potential increases from the bulk of the liquid phase towards the interface. In calculating the electrokinetic potential from electrokinetic phenomena it is often assumed that the liquid adhering to the solid wall and the mobile liquid are separated by a sharp *shear plane*³⁹. As long as there is no reliable information on the values of the permittivity, ϵ , and the viscosity, η , in the electrical double-layer close to the interface, the calculation of the electrokinetic potential from electrokinetic experiments remains open to criticism⁴⁰. It is therefore essential to indicate in all cases which equations have been used in the calculation of ζ . It can be shown, however, that for the same assumptions about ϵ and η , all electrokinetic phenomena must give the same value for the electrokinetic potential⁴¹.

A consistent use of signs requires that the electrophoretic mobility u_e and the streaming potential difference $E_{st}/\Delta p$ have the same sign as the electrokinetic potential, but the electro-osmotic velocity $u_{e.o.}$ and J_v/I have a sign opposite to that of ζ .

³⁹(2001) The *shear plane* is also called *slip(ping) plane*. The ζ potential is identified as the potential at the supposed slipping plane that separates the stationary and the mobile phases in tangential flow of the liquid with respect to the surface. Although there is still very little direct evidence to support the view of a slipping plane (instead of a slipping layer), the simple concept of a step function in the fluidity is generally accepted as convention for the analysis of electrokinetic phenomena.

In general, it is believed that the plane of shear is located in the diffuse part of the double layer, i.e. adjacent to the Stern plane at the boundary of the Stern layer. This means that the ζ potential is, in principle, lower than or at best equal to the potential at the onset of the diffuse double layer, ψ^d . At low ionic strength the decay of the electrostatic potential as a function of the distance perpendicular to the surface is weak, under such circumstances it seems reasonable to assume that $\zeta \approx \psi^d$.

⁴⁰(2001) Common practice is to use the bulk values of ϵ and η for the region beyond the Stern plane. However, it is imperative to indicate any assumptions regarding ϵ and η within the Stern layer.

⁴¹(2001) When it is assumed that ϵ and η have bulk values beyond the plane of shear, one of the main remaining difficulties with the calculation of the ζ potential is the role of the *surface (excess) conductivity* due to the excess charge in the double layer. Classical models, such as the Helmholtz-Smoluchowski theory of electrokinetic phenomena, neglect surface conductivity entirely. Once the ζ potential is calculated, it is also possible to calculate the *electrokinetic charge density*, σ^{ek} , with a suitable double layer model. By comparing σ^{ek} with σ^0 an impression can be gained about the amount of charge in the stagnant layer. General experience shows that often $\sigma^{ek} \ll \sigma^0$. Under the assumption that $\zeta \approx \psi^d$, it follows that $\sigma^{ek} \approx \sigma^d$.

Notwithstanding the ambiguity in its determination, ζ potentials play an important role in colloid science. Often electrokinetic measurements are the only available techniques to obtain information on the electrical potential near the surface.

2 LIST OF SYMBOLS AND ABBREVIATIONS

2.1 ADSORPTION AND SPREAD MONOLAYERS

Area of surface ⁴²	A, A_s, S
Specific surface area (= surface area per unit mass) ⁴³	a, a_s, s
Thickness of surface layer	τ
Superscript, indicating quantities referring to the surface layer or interfacial layer	s
Volume of interfacial layer	V^s
Subscript, indicating quantities relating to monolayer capacity	m
Surface coverage (= amount of adsorbed substance divided by monolayer capacity)	θ
Area per molecule in complete monolayer of substance i	$a_m(i)$
Superscript, indicating excess quantities referring to the Gibbs surface	σ
Surface excess amount, Gibbs adsorption of component i ($= n_i - V^\alpha c_i^\alpha - V^\beta c_i^\beta$)	n_i^σ
Total surface excess amount (of adsorbed substance) ($= \sum_i n_i^\sigma$)	n^σ
Gibbs surface concentration, surface excess concentration ($= n_i^\sigma / A - s$)	Γ_i^σ
Total Gibbs surface concentration, total surface excess concentration ($= \sum_i \Gamma_i^\sigma$)	Γ^σ
Surface excess number of molecules (of component i)	N_i^σ
Surface excess mass (of component i)	m_i^σ
Relative adsorption of component i with respect to component 1	$\Gamma_i^{(1)}, \Gamma_{i,1}$

$$\left[= \Gamma_i^\sigma - \Gamma_1^\sigma \left(\frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta} \right) \right]$$

⁴²cf. footnote to section 1.1.9

⁴³The notions 'specific surface area' and 'average area per molecule in the surface' are rarely used both in the same context, but if this should happen, it is particularly important to indicate clearly, which choice of symbols has been made.

Reduced adsorption (of component i)	$\Gamma_i^{(n)}$
$\left[= \Gamma_i^\sigma - \Gamma^\sigma \left(\frac{c_i^\alpha - c_i^\beta}{c^\alpha - c^\beta} \right) \right]$	
Total concentration in phase α ($= \sum_i c_i^\alpha$)	c^α
Area per molecule in surface ^{37,38}	$a_i, a_{i,s}$
Co-area per molecule in surface ³⁷	$a_i^0, a_{i,s}^0$
Gibbs surface concentration (for solid/liquid systems) of component i , relative to a reference system with the same number of moles (reduced adsorption) ($= A_s^{-1} [n_i - n^l x_i^l]$)	$\Gamma_i^{(n)}$
Relative adsorption (for solid/liquid systems) ($= A_s^{-1} [n_i - n^l x_i^l / x_1^l] = \Gamma_i^{(n)} / x_1^l$ for binary system)	$\Gamma_i^{(1)}$
Gibbs surface concentration (for solid/liquid systems) of component i , relative to a reference system with the same volume of liquid ($= A_s^{-1} [n_i - c_i^l V^l]$)	$\Gamma_i^{(v)}$
Surface excess volume of gas calculated for 273.15 K and 101.325 kPa (0°C and 1 atm)	V_i^σ
Amount of adsorbed component i ($=$ amount of component i in the interfacial layer)	n_i^s
Total amount of adsorbed substance ($= \sum_i n_i^s$)	n^s
Monolayer capacity expressed as amount of substance	n_m^s
Monolayer capacity expressed in volume of gas calculated for 273.15 K and 101.325 kPa	V_m

2.2 MECHANICAL AND THERMODYNAMIC PROPERTIES OF SURFACES AND INTERFACES

Surface tension, interfacial tension	γ, σ
Surface tension of phase α in contact with equilibrium vapour or a dilute gas phase	$\gamma^\alpha, \sigma^\alpha$
Interfacial tension between phases α and β	$\gamma^{\alpha\beta}, \sigma^{\alpha\beta}$
Dynamic surface (or interfacial) tension	$\gamma^{\text{dyn}}, \sigma^{\text{dyn}}$
Static surface (or interfacial) tension	$\gamma^{\text{st}}, \sigma^{\text{st}}$
Surface tension of clean surface	γ^0, σ^0

Work of adhesion per unit area (between phases α and β , that were previously in contact with phase δ) ($= \gamma^{\alpha\delta} + \gamma^{\beta\delta} - \gamma^{\alpha\beta}$)	$w_A^{\alpha\beta\delta}, w_A^{\alpha\beta}, w_A$
Work of separation per unit area	$\equiv w_A^{\alpha\beta\delta}$
Work of cohesion of pure substance α per unit area ($= 2\gamma^\alpha$)	w_C^α
Spreading tension of phase α on phase β , both previously in contact with phase δ ($= \gamma^{\beta\delta} - \gamma^{\alpha\delta} - \gamma^{\alpha\beta}$)	$\sigma^{\alpha\beta\delta}, \sigma^{\alpha\beta}$
Work of spreading per unit area ($= \sigma^{\alpha\beta\delta}$)	w_{spr}
Initial spreading tension	$\sigma_i^{\alpha\beta\delta}, \sigma_i^{\alpha\beta}, \sigma_i$
Final spreading tension	$\sigma_f^{\alpha\beta\delta}, \sigma_f^{\alpha\beta}, \sigma_f$
Surface (or interfacial) pressure ($= \gamma^0 - \gamma$)	π^s, π
Contact angle	θ
Advancing contact angle	θ_a
Receding contact angle	θ_r
Equilibrium contact angle	θ_e
Work of immersional wetting per unit area (= wetting tension) ($= \gamma^{\beta\delta} - \gamma^{\alpha\beta}$)	$w_w^{\alpha\beta\delta}, w_w^{\alpha\beta}, w_w$
Surface (excess) shear viscosity	η^σ
Surface (excess) fluidity ($= 1/\eta^\sigma$)	φ^σ
Surface excess energy (referred to Gibbs surface)	U^σ
Surface excess energy per unit area ($= U^\sigma/A_s$)	u^σ
Surface excess entropy (and per unit area)	$S^\sigma (s^\sigma)$
Surface excess Helmholtz energy (and per unit area)	$A^\sigma (a^\sigma)$
Surface excess enthalpy ($= U^\sigma - \gamma A_s$) (and per unit area)	$H^\sigma (h^\sigma)$
Surface excess Gibbs energy ($= H^\sigma - TS^\sigma = \sum_i n_i^\sigma \mu_i^\sigma$) (and per unit area)	$G^\sigma (g^\sigma)$
Relative (excess) surface energy (with respect to component 1)	$U^{\sigma(1)}$
Reduced (excess) surface energy	$U^{\sigma(n)}$
Relative (excess) surface entropy, Helmholtz energy, enthalpy, Gibbs energy	$S^{\sigma(1)}, A^{\sigma(1)}, H^{\sigma(1)}, G^{\sigma(1)}$
Reduced (excess) surface entropy, Helmholtz energy, enthalpy, Gibbs energy	$S^{\sigma(n)}, A^{\sigma(n)}, H^{\sigma(n)}, G^{\sigma(n)}$
Interfacial energy (of interfacial layer)	U^s
Interfacial energy per unit area ($= U^s/A_s$)	u^s
Interfacial entropy (and per unit area)	$S^s (s^s)$
Interfacial Helmholtz energy (or interfacial free energy) (and per unit area)	$A^s (a^s)$

Interfacial enthalpy (pV -enthalpy) ($= U^s + pV^s$)	\mathcal{H}^s
Interfacial enthalpy (γA_s -enthalpy) ($= U^s - \gamma A_s$) (and per unit area)	\hat{H}^s (\hat{h}^s)
Interfacial enthalpy ($pV\gamma A_s$ -enthalpy) ($= U^s + pV^s - \gamma A_s$) (and per unit area)	H^s (h^s)
Interfacial Gibbs energy (pV -Gibbs energy) ($\mathcal{H}^s - TS^s$)	\mathcal{G}^s
Interfacial Gibbs energy (γA_s -Gibbs energy) ($= \hat{H}^s - TS^s$) (and per unit area)	\hat{G}^s (\hat{g}^s)
Interfacial Gibbs energy ($pV\gamma A_s$ -Gibbs energy) ($= H^s - TS^s = \sum_i n_i^s \mu_i^s$) (and per unit area)	G^s (g^s)
Surface chemical potential, relating to Gibbs surface	μ_i^σ
Surface chemical potential, relating to interfacial layer	μ_i^s
Differential molar energy of adsorption ($= (\partial U^\sigma / \partial n_i^\sigma)_{T,m,n_j^\sigma} - (\partial U^g / \partial n_i^g)_{T,V^g,n_j^g}$)	$\Delta_a U_i^\sigma$
Differential molar energy of adsorption ($= (\partial U^s / \partial n_i^s)_{T,m,V^s,n_j^s} - (\partial U^g / \partial n_i^g)_{T,V^g,n_j^g}$)	$\Delta_a U_i^s$
Differential molar enthalpy of adsorption (or isosteric enthalpy of adsorption) ($= (\partial U^\sigma / \partial n_i^\sigma)_{T,m,n_j^\sigma} - (\partial H^g / \partial n_i^g)_{T,p,n_j^g}$)	$\Delta_a H_i^\sigma, q^{\text{st},\sigma}$
Differential molar enthalpy of adsorption (or isosteric enthalpy of adsorption) ($= (\partial \mathcal{H}^s / \partial n_i^s)_{T,p,m,n_j^s} - (\partial H^g / \partial n_i^g)_{T,p,n_j^g}$)	$\Delta_a H_i^s, q^{\text{st},s}$
Molar integral energy of adsorption ($= \frac{1}{n^\sigma} \int_0^{n^\sigma} \Delta_a U^\sigma dn^\sigma$)	$\Delta_a U_m^\sigma$
Molar integral enthalpy of adsorption ($= \frac{1}{n^\sigma} \int_0^{n^\sigma} \Delta_a H^\sigma dn^\sigma$)	$\Delta_a H_m^\sigma$
Standard Gibbs energy of adsorption ($RT \ln f_i / f_i^\ominus$)	$\Delta_a \mu_i^\ominus$
Standard differential molar entropy of adsorption [$= \frac{1}{T} (\Delta_a H_i^\ominus - \Delta_a \mu_i^\ominus)$]	$\Delta_a S_i^\ominus$

Standard integral molar entropy of adsorption	$\Delta_a S_m^\ominus$
$(= \frac{1}{n^\sigma} \int_0^{n^\sigma} \Delta_a S^\ominus dn^\sigma)$	
Standard differential molar enthalpy of adsorption	$\Delta_a H_i^\ominus$
Enthalpy of wetting or enthalpy of immersion	$\Delta_w H, \Delta_{\text{imm}} H, -Q_w$
Enthalpy of wetting per unit mass of the solid	$-q_w$

2.3 DEFINITION AND CLASSIFICATION OF COLLOIDS

Number average relative molecular mass (= Number average molecular weight)	$\bar{M}_{r,n}$
$[\bar{M}_{r,n} = \frac{\sum n_i M_r(i)}{\sum n_i}]$	
Mass average relative molecular mass (= Mass average molecular weight)	$\bar{M}_{r,m}$
$[\bar{M}_{r,m} = \frac{\sum n_i (M_r(i))^2}{\sum n_i M_r(i)}]$	
Z-average relative molecular mass (= Z-average molecular weight)	$\bar{M}_{r,Z}$
$[\bar{M}_{r,Z} = \frac{\sum n_i (M_r(i))^3}{\sum n_i (M_r(i))^2}]$	

2.4 PREPARATION AND PROCESSING OF COLLOIDAL SYSTEMS

No symbols prescribed.

2.5 STABILITY OF COLLOIDAL SYSTEMS, AGGREGATION, COAGULATION, FLOCCULATION

Critical coagulation concentration	ccc
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2.6 SURFACE ACTIVE AGENTS

Relative micellar mass or micellar weight	M_r
Critical micellization (micelle) concentration	c_M ; cmc
Krafft point	t_K, T_K

2.7 FLUID FILMS

Film thickness	t, h
Critical (film) thickness	t_c, h_c
Film tension	Σ_f
Surface tension of film ($= \sigma_f/2$)	γ_f, σ_f
Film contact angle	θ
Gibbs film elasticity	E

2.8 COLLIGATIVE AND RELATED PROPERTIES

Swelling pressure	Π_{sw}, Π
Donnan pressure = colloid osmotic pressure	Π_D, Π

2.9 ATTRACTION AND REPULSION

Gibbs energy of repulsion (between two surfaces)	G_r
Gibbs energy of repulsion due to electric effects	G_{el}
Gibbs energy of repulsion per unit area of two parallel plates	g_r, g_{el}
Gibbs energy of attraction of two surfaces	G_a
Gibbs energy of attraction per unit area of two parallel plates	g_a
Van der Waals-London attraction constant between two molecules ($= \phi r^6$)	λ
(Van der Waals-)Hamaker constant between semi-infinite flat plates, distance h apart (n = number of molecules per unit volume) ($= -g_a \cdot 12\pi h^2 = \pi^2 n^2 \lambda$)	A_H
Retarded van der Waals constant between two molecules ($= -\phi r^7$)	β
Retarded van der Waals constant between semi-infinite flat plates, distance h apart ($= -3g_a h^3 = (1/10)\pi n^2 \beta$)	B
Total Gibbs energy of interaction (and per unit area of two parallel plates)	$G_t(g_t)$
Disjoining pressure ($= -dg_t/dh$)	Π_d

2.10 SEDIMENTATION, CREAMING, CENTRIFUGATION AND DIFFUSION

Sedimentation volume	V_{sed}
Cream volume	V_{cr}
Rate of sedimentation	v_{sed}, v
Sedimentation coefficient	s
Limiting sedimentation coefficient ($= \lim_{c \rightarrow 0} s$)	$[s]$
Svedberg unit	$S = 10^{-13} \text{ sec.}$
Reduced sedimentation coefficient (Standard sedimentation coefficient)	$s^0(20^\circ\text{C})$
Reduced limiting sedimentation coefficient ($= \lim_{c \rightarrow 0} s^0(20^\circ\text{C})$)	$[s^0(20^\circ\text{C})]$
Differential diffusion coefficient (of species i)	D_i
Limiting diffusion coefficient of species i ($= \lim_{c_i \rightarrow 0} D_i$)	$[D_i]$
Self-diffusion coefficient (of species i)	D_i^*
Tracer diffusion coefficient (of labelled species i^*)	D_{i^*}
Rotational diffusion coefficient	D_θ

2.11 ELECTROCHEMICAL TERMS IN COLLOID AND SURFACE CHEMISTRY

Surface charge density	σ^0, σ^s
Surface charge density in the Stern layer	σ^i
Surface charge density in the Gouy layer	σ^d
Point of zero charge	pzc
Surface potential	ψ^0, ψ^s
Electric potential at the inner boundary of the Gouy layer, Stern-plane potential	ψ^d
Differential capacitance (of the electrical double-layer per unit area) ($= d\sigma^0/d\psi^0$)	C_{dl}
Integral capacitance (of the electrical double-layer per unit area) ($= \sigma^0/\psi^0$)	K_{dl}
Isoelectric point	iep
Thickness of the diffuse electrochemical double layer ($=$ Debye length)	$1/\kappa$
[$= \sqrt{\epsilon_r \epsilon_0 RT / (F^2 \sum c_i z_i^2)}$ (rationalized four quantity system)]	
Donnan emf (Donnan potential)	E_D

Membrane emf (Membrane potential)	E_m
Suspension effect (Pallmann effect, Wiegner effect)	E_s

2.12 ELECTROKINETICS

Electrophoretic velocity	v
Electrophoretic mobility (+ for positive particle) (= v/E)	u_e, u
Electro-osmotic velocity (per unit field strength) (+ for flow to lower potential)	$u_{e.o.}, u$
Electro-osmotic volume flow	J_v
Electro-osmotic pressure (+ if high pressure on high potential side)	Δp
Streaming potential difference (+ if high potential is on high pressure side)	E_{st}, E
Streaming current (+ if electric current is in the same direction as the volume flow)	I
Sedimentation potential difference (+ if lower (peripheral) electrode is negative)	E_{sed}, E
Sedimentation field strength	\mathbf{E}_{sed}
Surface (excess) conductivity	κ^σ
Electrokinetic potential (zeta potential)	ζ

3 ALPHABETICAL INDEX

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	activated adsorption	1.1.6
	additive (<i>re</i> coagulation concentration)	1.5
	adhesional wetting	1.2.2
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n_i^s	amount of adsorbed substance (abbreviation: amount adsorbed)	1.1.11, 2.1
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	amphiphilic	1.6

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
	antagonistic (<i>re</i> coagulation concentration)	1.5
a_m	area per molecule in complete monolayer	1.1.7, 2.1
$a_i, a_{i,s}$	area per molecule (in the surface)	1.1.9, 1.1.10, 2.1
A, A_s, S	area of surface or interface	1.1.1, 2.1
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a, a_s	average area per molecule in surface	1.1.9, 2.1
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<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
θ_a	contact angle (advancing)	1.2.2, 2.2
θ_e	contact angle (equilibrium)	1.2.2, 2.2
	contact angle hysteresis	1.2.2
θ_r	contact angle (receding)	1.2.2, 2.2
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	counterion	1.3, 1.11
	cream, creaming	1.5, 1.10
V_{cr}	cream volume	1.10, 2.10
ccc	critical coagulation concentration	1.5, 2.5
t_c, h_c	critical film thickness	1.7, 2.7
$c_M; c_{mc}$	critical micellization concentration (critical micelle concentration)	1.6, 2.6
	critical embryo	1.4
	curd (soap)	1.6
$1/\kappa$	Debye length	1.11, 2.11
	deflocculation	1.5
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	dialysate	1.4
	dialysis	1.4
	dialysis residue	1.4
C_{dl}	differential capacitance (of electrical double-layer per unit area)	1.11, 2.11
$\Delta_a U_i^\sigma, \Delta_a U_i^s$	differential molar energy of adsorption	1.2.7, 2.2
$\Delta_a H_i^\sigma, -q^{st,\sigma}; \Delta_a H_i^s, -q^{st,s};$	differential molar enthalpy of adsorption	1.2.7, 2.2
	differential surface work	1.2.1
	diffuse layer	1.11
	diffusion	1.10
D_i	differential diffusion coefficient (of species i)	1.10, 2.10
Π_d	disjoining pressure	1.9, 2.9
	dispersed phase	1.3
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E_D	Donnan emf (Donnan potential)	1.11, 2.11
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Π_D, Π	Donnan pressure	1.8, 2.8

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
E_{sed}, E	Dorn effect	1.12, 2.12
$\gamma^{\text{dyn}}, \sigma^{\text{dyn}}$	dynamic surface (or interfacial) tension	1.2.1, 2.2
$1/\kappa$	effective thickness of the diffuse electrochemical double-layer	1.11, 2.11
ψ^0, ψ^s	electric potential at the surface	1.11, 2.11
ψ^d	electric potential (at the inner boundary of the Gouy layer)	1.11, 2.11
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	electrodialysis	1.4
ζ	electrokinetic potential (zeta potential)	1.12, 2.12
	electro-osmosis	1.12
Δp	electro-osmotic pressure	1.12, 2.12
$u_{\text{e.o.}}, u$	electro-osmotic velocity (per unit field strength)	1.12, 2.12
J_v	electro-osmotic volume flow	1.12, 2.12
	electrophoresis	1.4, 1.12
	electrophoresis convection	1.4
u_e, u	electrophoretic mobility	1.12, 2.12
v	electrophoretic velocity	1.12, 2.12
	embryo	1.4
	emulsifier	1.6
O/W or W/O	emulsion	1.3
$\Delta_a H_i, -q^{\text{st}}$	enthalpy of adsorption (isosteric) of substance i	1.2.7, 2.2
$\Delta_w H, \Delta_{\text{imm}} H, -Q_w, -q_w$	enthalpy of wetting or immersion (and per unit mass of solid)	1.2.8, 2.2
θ_e	equilibrium contact angle	1.2.2, 2.2
	equilibrium dialysate	1.4
	equilibrium film	1.7
	equilibrium solution (in coacervation)	1.5
	equivalent film thickness	1.7
	excess amount of adsorbed molecules, etc. (see surface excess amount etc.)	
	excess surface (or interfacial) energy, etc. (see surface excess energy, interfacial energy, etc.)	
	external surface	1.1.5

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
θ	film contact angle	1.7, 2.7
	film element	1.7
Σ_f	film tension	1.7, 2.7
t, h	film thickness	1.7, 2.7
$\sigma_f^{\alpha\beta\delta}, \sigma_f^{\alpha\beta}, \sigma_f$	final spreading tension	1.2.2, 2.2
	fixed charge	1.11
	floc	1.5
	flocculation	1.5
	flotation	1.4
	fluid film	1.7
	foam	1.3
	foam fractionation	1.4
	foaming agent	1.6
	fog	1.3
	froth	1.3
	froth-flotation	1.3, 1.4
	gel	1.3
n_i^σ	Gibbs adsorption (of component i)	1.1.8, 1.1.11, 2.1
	Gibbs dividing surface	1.1.8, 1.2.4
G_a	Gibbs energy of attraction	1.9, 2.9
g_a	Gibbs energy of attraction per unit area of two parallel plates	1.9, 2.9
G_r	Gibbs energy of repulsion	1.9, 2.9
G_{el}	Gibbs energy of repulsion due to electric effects	1.9, 2.9
g_r, g_{el}	Gibbs energy of repulsion per unit area of two parallel plates	1.9, 2.9
E	Gibbs film elasticity	1.7, 2.7
	Gibbs surface	1.1.8, 1.1.11, 1.2.4
Γ_i^σ	Gibbs surface concentration	1.1.8, 1.1.11, 2.1
$\Gamma_i^{(v)}$	Gibbs surface concentration (solid/liquid interface)	1.1.10, 2.1
$\Gamma_i^{(n)}$	Gibbs surface concentration (solid/liquid interface)	1.1.10, 2.1
	Gouy layer	1.11
A_H	Hamaker constant	1.9, 2.9
	helium dead-space	1.1.11
	heterodisperse	1.3

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
	heterogeneous nucleation	1.4
	homogeneous nucleation	1.4
	hydrophilic	1.3
	hydrophobic	1.3
	imbibition (of liquid by gel or porous substance)	1.8
	immersional wetting	1.2.2
	individual isotherm	1.1.10
$\sigma_i^{\alpha\beta\delta}$, $\hat{\sigma}_i^{\alpha\beta}$, σ_i	initial spreading tension	1.2.2, 2.2
K_{dl}	integral capacitance (of the electrical double-layer per unit area of interface)	1.11, 2.11
	interface	1.1.1
U^s (u^s)	interfacial energy (and per unit area)	1.2.4, 2.2
\mathcal{H}^s , \hat{H}^s , H^s	interfacial enthalpy	1.2.4, 2.2
(-, \hat{h}^s , h^s)	(and per unit area)	
S^s (s^s)	interfacial entropy (and per unit area)	1.2.4, 2.2
\mathcal{G}^s , \hat{G}^s , G^s	interfacial Gibbs energy	1.2.4, 2.2
(-, \hat{g}^s , g^s)	(and per unit area)	
A^s (a^s)	interfacial Helmholtz energy (and per unit area)	1.2.4, 2.2
indicated by superscript s	interfacial layer	1.1.1, 1.1.3, 1.2.4, 2.1, 2.2
γ , σ , $\gamma^{\alpha\beta}$, $\sigma^{\alpha\beta}$	interfacial tension (between phases α and β)	1.2.1, 2.2
	intermediate pore (use of this term is discouraged)	1.1.5
	internal surface	1.1.5
	ion exchange	1.1.4
	iridescent layer	1.5
	isoelectric	1.11
iep	isoelectric point	1.11, 2.11
	isoionic	1.11
$\Delta_a H_i^\sigma$, $-q^{\text{st},\sigma}$; $\Delta_a H_i^s$, $-q^{\text{st},s}$	isosteric enthalpy of adsorption of substance i (formerly isosteric heat of adsorption)	1.2.7, 2.2
t_K , T_K	Krafft point	1.6, 2.6
	latex	1.3
$[D_i]$	limiting differential diffusion coefficient (of species i)	1.10, 2.10
$[s]$	limiting sedimentation coefficient	1.10, 2.10

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>	
W/O/W	lipid film	1.7	
	lipophilic	1.3	
	lipophobic	1.3	
	lyophilic	1.3	
	lyophobic	1.3	
	macromolecules	1.3	
	macropores	1.1.5	
	$\bar{M}_{r,m}$	mass average relative molecular mass (molecular weight)	1.3, 2.3
	E_m	membrane emf (membrane potential)	1.11, 2.11
mesomorphic phase		1.6	
mesopore		1.1.5	
metastability		1.5	
micellar solubilization		1.6	
micellar mass		1.6	
micellar weight		1.6	
micelle		1.6	
microelectrophoresis		1.12	
micropore		1.1.5	
micropore filling		1.1.7	
micropore volume		1.1.7	
microscopic electrophoresis		1.12	
middle soap		1.6	
mobile film		1.7	
$\Delta_a U_m^\sigma$		molar integral energy of adsorption	1.2.7, 2.2
$\Delta_a H_m^\sigma$		molar integral enthalpy of adsorption	1.2.7, 2.2
		molecular sieve effect	1.1.5
M_r		molecular weight: see relative molecular mass	
	monodisperse	1.3	
	monolayer adsorption	1.1.7	
n_m^s, V_m	monolayer capacity	1.1.7, 1.1.11, 2.1	
	monolayer equivalent area	1.1.11	
	multilayer adsorption	1.1.7	
	myelin cylinder	1.6	
	neat soap	1.6	
	negative adsorption	1.1.4	
	negative tactoid	1.5	
	nematic state	1.6	
	Newton black film	1.7	

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
	nucleating agent	1.4
	nucleus	1.4
$\bar{M}_{r,n}$	number average relative molecular mass (molecular weight)	1.3, 2.3
	oleophilic	1.3
	orthokinetic aggregation	1.5
E_s	Pallmann effect	1.11, 2.11
	partial isotherm	1.1.10
	paucidisperse	1.3
	peptization	1.5
	perikinetic aggregation	1.5
	physisorption = physical adsorption	1.1.6
	Plateau border	1.7
pzc	point of zero charge	1.11, 2.11
	polyacid	1.3
	polyampholyte	1.3
	polyanion	1.3
	polybase	1.3
	polycation	1.3
	polydisperse	1.3
	polyelectrolyte	1.3
	polyion	1.3
	polysalt	1.3
	positive adsorption	1.1.4
	potential determining ion	1.11
	primary minimum	1.9
	protected lyophobic colloid	1.3, 1.5
	protective action (<i>re</i> coagulation and flocculation)	1.5
	rate of nucleation	1.4
u_{sed}, v	rate of sedimentation	1.10, 2.10
θ_r	receding contact angle	1.2.2, 2.2
$\Gamma_i^{(n)}$	reduced adsorption (of component <i>i</i>)	1.1.9, 1.1.10, 2.1
$U^{\sigma(n)}$	reduced (excess) surface energy	1.2.4, 2.2
$S^{\sigma(n)}$	reduced (excess) surface entropy	1.2.4, 2.2
$A^{\sigma(n)}$	reduced (excess) surface Helmholtz energy	1.2.4, 2.2
$H^{\sigma(n)}$	reduced (excess) surface enthalpy	1.2.4, 2.2
$G^{\sigma(n)}$	reduced (excess) surface Gibbs energy	1.2.4, 2.2

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
$[s^0(20^\circ\text{C})]$	reduced limiting sedimentation coefficient	1.10, 2.10
	reduced osmotic pressure	1.8
$s^0(20^\circ\text{C})$	reduced sedimentation coefficient	1.10, 2.10
	reference system	1.1.8
$\Gamma_i^{(1)}, \Gamma_{i,1}$	relative adsorption (of component i with respect to component 1)	1.1.9, 1.1.10, 2.1
$U^{\sigma(1)}$	relative (excess) surface energy (with respect to component 1)	1.2.4, 2.2
$S^{\sigma(1)}$	relative (excess) surface entropy	1.2.4, 2.2
$A^{\sigma(1)}$	relative (excess) surface Helmholtz energy	1.2.4, 2.2
$H^{\sigma(1)}$	relative (excess) surface enthalpy	1.2.4, 2.2
$G^{\sigma(1)}$	relative (excess) surface Gibbs energy	1.2.4, 2.2
M_r	relative micellar mass	1.6, 2.6
M_r	relative molecular mass of a micelle	1.6
	relative molecular mass :	
$\bar{M}_{r,n}$	number average	1.3, 2.3
$\bar{M}_{r,m}$	mass average	1.3, 2.3
$\bar{M}_{r,Z}$	Z-average	1.3, 2.3
	residue	1.4
β, B	retarded van der Waals constant	1.9, 2.9
	retentate	1.4
	rigid film	1.7
D_θ	rotational diffusion coefficient	1.10, 2.10
	roughness factor	1.1.5
	rupture (of a fluid film)	1.7
	schiller layer	1.5
	Schulze-Hardy rule	1.5
	secondary minimum	1.9
	sediment	1.5
	sedimentation	1.5, 1.10
s	sedimentation coefficient	1.10, 2.10
	sedimentation equilibrium	1.10
E_{sed}	sedimentation field strength	1.12, 2.12
E_{sed}, E	sedimentation potential difference (sedimentation potential)	1.12, 2.12
v_{sed}, v	sedimentation velocity	1.10, 2.10
V_{sed}	sedimentation volume	1.10, 2.10
D_i^*	self-diffusion coefficient (of species i)	1.10, 2.10

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
	sensitization (<i>re</i> coagulation and flocculation)	1.5
	shear plane (slipping plane)	1.12
	silver film	1.7
	sintering	1.5
	smectic state	1.6
	smoke	1.3
	soap	1.6
	soap curd	1.6
	soap film	1.7
	sol	1.3
	solubilization, solubilizate	1.6
	sorbate	1.1.4
	sorbent	1.1.4
	sorption	1.1.4
	sorptive	1.1.4
a, s, a_s	specific surface area	1.1.1, 1.1.11, 2.1
	spread layer	1.1.4
	spread monolayer	1.1.4, 1.1.9
$\sigma^{\alpha\beta\delta}, \sigma^{\alpha\beta}$	spreading tension	1.2.2, 2.2
	spreading wetting	1.2.2
	stability of colloidal systems	1.5
	stable film	1.7
$\Delta_a S_i^\ominus$	standard differential molar entropy of adsorption	1.2.7, 2.2
$\Delta_a H_i^\ominus$	standard differential molar enthalpy of adsorption	1.2.7, 2.2
$\Delta_a \mu_i^\ominus$	standard Gibbs energy of adsorption	1.2.7, 2.2
$\Delta_a S_m^\ominus$	standard integral molar entropy of adsorption	1.2.7, 2.2
$s^0(20^\circ\text{C})$	standard sedimentation coefficient	1.10, 2.10
$\gamma^{\text{st}}, \sigma^{\text{st}}$	surface (or interfacial) tension	1.2.1, 2.2
	Stern layer	1.11
	stratified film	1.7
I	streaming current	1.12, 2.12
E_{st}, E	streaming potential difference (streaming potential)	1.12, 2.12
	subsidence	1.5
	surface	1.1.1, 1.1.2
A, A_s, S	surface (area of)	1.1.1, 2.1

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
indicated by superscript σ	surface (excess quantities in the)	1.1.8, 2.1
	surface active agent = surfactant	1.6
	surface charge	1.11
σ^0, σ^s	surface charge density	1.11, 2.11
σ^d	surface charge density in the Gouy layer	1.11, 2.11
σ^i	surface charge density in the Stern layer	1.11, 2.11
μ_i^σ, μ_i^s	surface chemical potential	1.2.5, 2.2
Γ_i^s	surface concentration	1.1.9, 2.1
Γ_i^σ	surface concentration (Gibbs)	1.1.8, 1.1.11, 2.1
κ^σ	surface conductivity	1.12, 2.12
θ	surface coverage	1.1.7, 2.1
	surface energy etc., see interfacial energy	
	surface enthalpy etc., see interfacial enthalpy	
	etc.	
	surface entropy etc., see interfacial entropy	
	etc.	
n_i^σ	surface excess amount (of component i)	1.1.8, 1.1.11, 2.1
Γ_i^σ	surface excess concentration	1.1.8, 1.1.10, 1.1.11, 2.1
κ^σ	surface (excess) conductivity	1.12, 2.12
$U^\sigma, (u^\sigma)$	surface excess energy (and per unit area)	1.2.4, 2.2
$H^\sigma, (h^\sigma)$	surface excess enthalpy (and per unit area)	1.2.4, 2.2
$S^\sigma, (s^\sigma)$	surface excess entropy (and per unit area)	1.2.4, 1.2.6, 2.2
$G^\sigma, (g^\sigma)$	surface excess Gibbs energy (and per unit area)	1.2.4, 1.2.6, 2.2
$A^\sigma, (a^\sigma)$	surface excess Helmholtz energy (and per unit area)	1.2.4, 1.2.6, 2.2
	surface excess isotherm	1.1.10
m_i^σ	surface excess mass (of component i)	1.1.8, 1.1.11, 2.1
N_i^σ	surface excess number of molecules	1.1.8, 1.1.11, 2.1
V_i^σ	surface excess volume of gas	1.1.11, 2.1
φ^σ	surface (excess) fluidity	1.2.3, 2.2
η^s	surface (excess) shear viscosity	1.2.3, 2.2
indicated by superscript s	surface layer	1.1.1, 1.1.3, 2.1
	surface layer of the adsorbent	1.1.5, 1.1.11
π^s, π	surface pressure	1.2.2, 2.2
	surface rheology	1.2.3

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
$\gamma, \sigma, \gamma^{\alpha\beta}, \sigma^{\alpha\beta}$	surface tension (between phases (α and β))	1.2.1, 1.2.6, 2.2
$\gamma^\alpha, \sigma^\alpha$	surface tension (of α in contact with a dilute gas phase)	1.2.1, 2.2
γ_f, σ_f	surface tension of film	1.7, 2.7
	surface of tension	1.2.1
	surface work	1.2.1
	surfactant	1.6
	suspension	1.3
E_s	suspension effect	1.11, 2.11
S	Svedberg unit	1.10, 2.10
	swelling (of gel or solid)	1.8
Π_{sw}, Π	swelling pressure	1.8, 2.8
A/W/A, W/O/W	symmetrical film	1.7
	syndet	1.6
	syneresis	1.8
	synergistic (<i>re</i> coagulation concentration)	1.5
	tactoid	1.5
	thermodynamic stability	1.5
τ	thickness of surface (or interfacial) layer	1.1.3, 1.2.4, 2.1
$1/\kappa$	thickness of the double-layer	1.11, 2.11
n^s	total amount of adsorbed substance	2.1
G_t	total Gibbs energy of interaction	1.9, 2.9
g_t	total Gibbs energy of interaction per unit area of two parallel plates	1.9, 2.9
Γ^σ	total Gibbs surface concentration	1.1.8, 2.1
n^σ	total surface excess amount (of adsorbed substance)	1.1.8, 1.1.11, 2.1
Γ^σ	total surface excess concentration	1.1.8, 2.1
D_{i^*}	tracer diffusion coefficient (of labelled species i^*)	1.10, 2.10
	transitional pores (use of this term is discouraged)	1.1.5
	ultrafiltration, ultrafiltrate	1.4
	unstable films	1.7
W/O/A	unsymmetrical film	1.7
	van der Waals adsorption (use of this term is discouraged)	1.1.6
λ	van der Waals attraction constant	1.9

<i>Symbol or Abbreviation</i>	<i>Term</i>	<i>Section</i>
A_H	van der Waals-Hamaker constant	1.9, 2.9
λ	van der Waals-London constant	1.9, 2.9
v_{sed}, v	velocity of sedimentation	1.10, 2.10
V^s	volume of interfacial layer	1.1.3, 1.1.11, 1.2.4, 2.1, 2.2
	wetting	1.2.2
$w_w^{\alpha\beta\delta}, w_w^{\alpha\beta}, w_w$	wetting tension	1.2.2, 2.2
E_s	Wiegner effect	1.11, 2.11
$w_A^{\alpha\beta\delta}$	work of adhesion per unit area	1.2.2, 2.2
w_C^α	work of cohesion of pure substance α per unit area	1.2.2, 2.2
$w_W^{\alpha\beta\delta}, w_W^{\alpha\beta}, w_W$	work of immersional wetting per unit area	1.2.2, 2.2
$w_A^{\alpha\beta\delta}, w_A^{\alpha\beta}, w_A$	work of separation per unit area	1.2.2, 2.2
w_{spr}	work of spreading per unit area	1.2.2, 2.2
	xerogel	1.3
$\bar{M}_{r,Z}$	Z-average relative molecular mass (molecular weight)	1.3, 2.3
ζ	zeta potential	1.12, 2.12