Chapter 2C

Thermodynamics of Surfaces

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I. Mechanical Properties of an Interface

A. SURFACE TENSION

From a macroscopic point of view, the boundary between two fluid phases is regarded as a sharply defined mathematical surface. It is clear from either molecular or microscopic considerations that this assumption cannot rigourously apply. The interface between two phases is in reality a thin region of about 10^{-6} cm thickness whose physical properties vary sharply from the bulk properties of one phase to the bulk properties of the other phase.

A classical thermodynamic study for such systems is too complicated, and, in fact, it is a matter of common observation that a fluid behaves as though it consisted of two homogeneous fluids separated by a stretched isotropic surface or membrane of infinitesimal thickness. Any local deformation of this membrane without variation of the area requires no mechanical work. The surface thus has no rigidity and is called the surface of tension. Let us divide the surface of tension into two regions I and II by a curve l (Fig. 1). If, across an element δl, of l, the region I
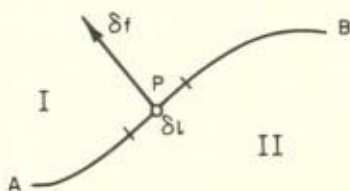

FIG. 1.   Definition of surface tension at a point P on a line AB in the surface.

exerts a force $\gamma \, \delta l = \delta f$ upon region II at a point P, then γ is called the surface (or interfacial) tension at this point.

The force δf is tangential to the surface of tension, perpendicular to δl, and independant of its orientation. The existence of a surface tension is, in fact, related to the thermodynamic instability of two phases in contact with one another, and thus to the free energy of contact. The contractile behavior of the transition layer minimizes this free energy and gives rise to the macroscopic experimental quantity. The unit often used in the measurement of γ is dyn cm^{-1}.

B. MECHANICAL EQUILIBRIUM

In a gravity field g (z axis), we have

$$dp^x/dz = -\varrho^x g; \qquad dp^\beta/dz = -\varrho^\beta g, \tag{1.1}$$

where p^x and p^β, ϱ^x and ϱ^β are, respectively, the hydrostatic pressures and the densities in the two phases α and β (Fig. 2).
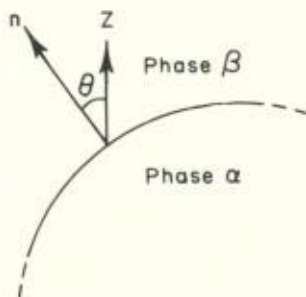
FIG. 2. Two phases α and β separated by a surface whose normal **n** is directed from α to β.

It is easy to show that the condition of local mechanical equilibrium of the surface of tension is given by

$$p^x - p^\beta = \gamma(K_1 + K_2) + g\Gamma \cos \theta \tag{1.2}$$

$$d\gamma/dz = g\Gamma, \tag{1.3}$$

where Γ is the surface density, K_1 and K_2 the two principal curvatures of the surface, and θ the angle between the z axis and the perpendicular to the surface directed from α to β.

Neglecting the gravity effect on γ ($\Gamma \simeq 10^{-7}$ g cm^{-2} and $d\gamma/dz = 10^{-4}$ dyn cm^{-2}), (1.2) reduces to the classical Laplace formula

$$p^\alpha - p^\beta = \gamma(K_1 + K_2), \tag{1.4}$$

with γ uniform on the surface.

Introducing the mean curvature defined by

$$\frac{1}{r_m} = \frac{1}{2}\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \tag{1.5}$$

where r_1 and r_2 are the principal radii of curvature, (1.4) becomes

$$p^\alpha - p^\beta = 2\gamma/r_m. \tag{1.6}$$

For a spherical surface of radius of curvature r, we then have

$$p^\alpha - p^\beta = 2\gamma/r. \tag{1.7}$$

The fundamental equation (1.4) shows that, because of its surface tension, a curved surface maintains mechanical equilibrium between two fluids at different pressure p^α and p^β.

Generally, because of the effect of gravity, $p^\alpha - p^\beta$, and thus $K_1 + K_2$, varies along the surface. In particular, $p^\alpha = p^\beta$ if $r = \infty$. Hence, a plane surface can exist only if the pressures of the fluids on the two sides are equal.

C. Application of the Laplace Formula

Consider a pure liquid forming a drop in thermodynamic equilibrium with its vapor. For mechanical equilibrium,

$$p^l - p^v = 2\gamma/r. \tag{1.8}$$

For physicochemical equilibrium

$$\mu^l = \mu^v, \tag{1.9}$$

where the superscripts l and v refer, respectively, to the liquid and vapor phases. For an equilibrium displacement, we obtain

$$\delta p^l - \delta p^v = \delta(2\gamma/r) \tag{1.10}$$

$$\delta\mu^l = \delta\mu^v. \tag{1.11}$$

The Gibbs–Duhem equation [Chapter 2A, Eq. (4.30)] may be applied to each coexisting phase, so that at constant temperature (1.11) gives

$$-v^l \, \delta p^l + v^v \, \delta p^v = 0 \qquad (T \quad \text{constant}). \tag{1.12}$$

Assuming the vapor to be a perfect gas and the liquid to be incompressible, (1.10) and (1.12) give, after integration, the well-known Kelvin equation

$$\ln(p^v/p^0) = (2\gamma/r) \, v^l/RT, \tag{1.13}$$

where p^0 is the saturation vapor pressure of the macroscopic liquid phase $(r \to \infty)$. This equation shows that the vapor pressure increases as the droplet decreases in size. An example for water at $18°$ $[(\gamma = 73 \text{ dyn cm}^{-1})]$ is given in Table I.

TABLE I

r (cm)	p^v/p^0	$p^l - p^v$ (bar)
∞	1	0
10^{-4}	1.001	1.46
10^{-5}	1.011	14.6
10^{-6}	1.115	146

The equilibrium of a drop initially satisfying (1.13) in an infinite volume of vapor of pressure p^v is unstable. If, by a small fluctuation, a little liquid evaporates, the droplet decreases in size and its vapor pressure exceeds that of the surrounding atmosphere: it will therefore continue to evaporate. Conversely, if a little vapor condenses, the vapor pressure of the droplet falls below that of the surroundings and further condensation will occur. This phenomenon leads to an explanation of the existence of supersaturated vapor (Dufour and Defay, 1963); this is a vapor which, in the absence of liquid, can exist at a given pressure p^v greater than the saturation pressure p^0 corresponding to the given temperature T.

D. EQUILIBRIUM OF A LINE OF CONTACT

The Laplace equation (partial derivatives of the second degree) determines the local form of the surface tension. Now let us consider the
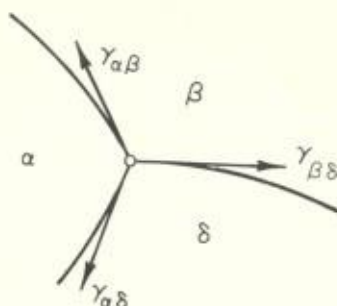
FIG. 3. Equilibrium at a line of contact: Neumann's triangle.

equilibrium of a line of contact formed by the interaction of three phases α, β, and δ (Fig. 3). As the total force acting on an element of line through P of length δl is zero, we find

$$\mathbf{1}_{\alpha\beta}\gamma_{\alpha\beta} + \mathbf{1}_{\alpha\delta}\gamma_{\alpha\delta} + \mathbf{1}_{\beta\delta}\gamma_{\beta\delta} + \mathbf{n}K\eta = 0, \qquad (1.14)$$

where $\gamma_{\alpha\beta}$, $\gamma_{\alpha\delta}$, and $\gamma_{\beta\delta}$ are the tensions related to the three surfaces, and the last term corresponds to a line tension η ($\mathbf{n}$ is the normal and K the curvature of the line of contact). In fact, the value of this line tension is quite negligible ($\simeq 10^{-6}$ dyn). Equation (1.14) then reduces to the Neumann equation

$$\mathbf{1}_{\alpha\beta}\gamma_{\alpha\beta} + \mathbf{1}_{\alpha\delta}\gamma_{\alpha\delta} + \mathbf{1}_{\beta\delta}\gamma_{\beta\delta} = 0. \qquad (1.15)$$

This equation may be applied to a line of contact formed by two liquid phases α and β and a solid surface s (Fig. 4). We obtain the Young equation

$$\cos \theta \gamma_{\alpha\beta} = \gamma_{\beta s} - \gamma_{\alpha s}, \qquad (1.16)$$

where θ is the contact angle of the surface $\alpha\beta$ with the solid and $\gamma_{\alpha s}$
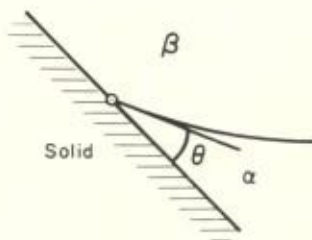

FIG. 4. Surface tension of a solid; the contact angle.

$\gamma_{\beta s}$ the solid–fluid tensions. If $|\gamma_{\beta s} - \gamma_{\alpha s}| > \gamma_{\alpha\beta}$, no equilibrium position of the line of contact can be found, and one of the two phases α or β covers the whole area of the solid: the liquid is said to wet the solid perfectly.

E. MECHANICAL WORK OF EXTERNAL FORCES

Let us consider a two-phase system α and β, with volumes V^α and V^β separated by a surface Ω of area A. In the absence of any external force fields, the work received by the system is (Fig. 5)

$$\delta\tau = -p^\alpha \, \delta V^\alpha - p^\beta \, \delta V^\beta + \gamma \, \delta A. \tag{1.17}$$
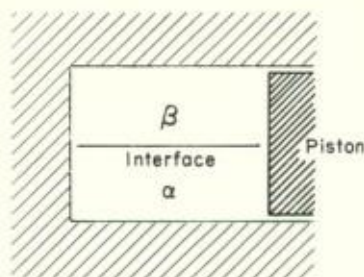
FIG. 5.   Mechanical work done by a capillary system: piston subjected to surface tension.

The piston is subjected to the pressure p^α and p^β of the two fluids α and β with $p^\alpha = p^\beta$ and to the surface tension γ of the surface Ω. In Fig. 6, the piston is not subjected directly to the surface tension. The system comprises a spherical drop of liquid of volume V^α separated from the vapor by the surface Ω. The whole system is contained in a cylinder of total volume $V = V^\alpha + V^\beta$. We have

$$\delta\tau = -p^\beta \, \delta V \tag{1.18}$$

$$\delta V = \delta V^\alpha + \delta V^\beta. \tag{1.19}$$

On the other hand, for a spherical surface $\alpha\beta$,

$$\delta V^\alpha = 2r \, \delta A, \tag{1.20}$$

and thus, from (1.18)–(1.20), we again find Eq. (1.17).
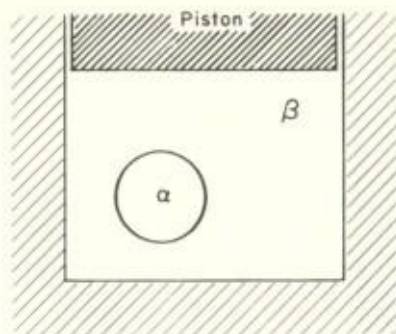
FIG. 6.   Mechanical work done by a capillary system: piston not subjected to surface tension.

Remark. For a multiphase system, (1.17) must be rewritten in the form

$$\delta\tau = -\sum_{\alpha} p^{\alpha}\,\delta V^{\alpha} + \sum_{\alpha\beta} \gamma^{\alpha\beta}\,\delta A^{\alpha\beta}. \tag{1.21}$$

F. Application of the Mechanical Work Relation

At constant temperature, we know that the free energy of a closed system is equal to the work received by the system (see Chapter 2A, Section III). For a two-phase system,

$$(\delta F)_{T_n} = -p^{\alpha}\,\delta V^{\alpha} - p^{\beta}\,\delta V^{\beta} + \gamma\,\delta A. \tag{1.22}$$

Let us now consider a supersaturated vapor of pressure p^{v} in an infinite volume. The free energy of formation of a droplet phase of size r is equal to

$$\Delta F = -(4\pi r^{3}/3)(p^{l} - p^{v}) + 4\pi r^{2}\gamma, \tag{1.23}$$

where p^{l} is the pressure in the droplet. From Eqs. (1.23) and (1.7), we thus obtain

$$\Delta F = 4\pi r^{2}\gamma/3 = \tfrac{1}{3}\gamma A, \tag{1.24}$$

where A is the area of the drop. The presence of a "germ" enables the condensation of this vapor. The germ is a droplet whose radius r can be calculated by Kelvin's equation. For water at 18°C, the free energy of formation of a germ ΔF_{g} (homogeneous nucleation) is given in Table II (Dufour and Defay, 1963).

TABLE II

p^v/p^s	r (cm)	ΔF_g (erg)	$\Delta F_g/kT$
1.011	10^{-3}	3×10^{-8}	0.75×10^6
1.115	10^{-6}	3×10^{-10}	0.75×10^4

As we know, the probability of obtaining a germ is given by the expression $\exp[-\Delta F_g/kT]$; we observe that the formation of a germ is not probable. A droplet lying on a solid surface may constitute a germ, but the free energy of formation is lower. For a spherical cap of radius r, we obtain (Fig. 7):

Volume of the liquid: $\frac{2}{3}\pi r^3(1 - \frac{3}{2}\cos\theta + \frac{1}{2}\cos^3\theta) = v$

Surface liquid–vapor: $2\pi r^2(1 - \cos\theta) = A$

Surface liquid–solid: $\pi r^2 \sin^2\theta = A'$ (1.25)

Laplace's equation: $p^l - p^v = 2\gamma/r$

Young's equation: $\gamma^{vs} - \gamma^{ls} = \gamma\cos\theta$

$$\Delta F = -(p^l - p^v)v + \gamma A + (\gamma^{ls} - \gamma^{vs})A'. \tag{1.26}$$

By combining these different equations, we obtain the relation

$$\Delta F = \frac{4}{3}\pi r^2\gamma(\frac{1}{2} - \frac{3}{8}\cos\theta - \frac{1}{8}\cos^3\theta). \tag{1.27}$$

A comparison between (1.27) and (1.24) for the same radius r leads to the conclusion that the condensation of vapor takes place preferentially on solid surfaces or on dust (heterogeneous nucleation).

Remark. If $\theta = \pi$, we find the value corresponding to homogeneous nucleation. If $\theta = 30°$, the free energy of formation is equal to one tenth of the corresponding energy of homogeneous nucleation.
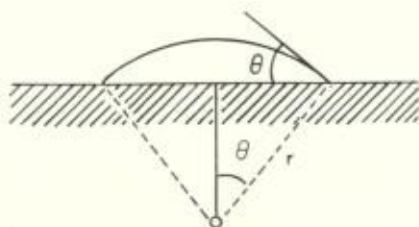

FIG. 7. Drop laid on a solid surface.

II. Pressure Tensor in Surface Layers

A. INTRODUCTION

From the molecular point of view, there exists, between two contiguous homogeneous phases in equilibrium, a zone of finite thickness with which the density, composition, and pressure tensor vary rapidly from the values characteristic of one phase to those characteristic of the other. A microscopic formulation of the surface tension may be introduced with the aid of the pressure tensor (Bakker, 1928; Kirkwood and Buff, 1949; Ono and Kondo, 1960, p. 134). In order to clarify these ideas, we shall first recall the force acting on a volume element of a fluid. We have (a) external local forces: the force $\mathbf{X}$ and the torque $\mathbf{C}$ per unit volume; and (b) the internal forces expressed by the pressure tensor in rectangular coordinates:

$$\mathbf{P} = \begin{pmatrix} P_{xx} & P_{xy} & P_{xz} \\ P_{yx} & P_{yy} & P_{yz} \\ P_{zx} & P_{zy} & P_{zz} \end{pmatrix}. \tag{2.1}$$

The motion equation of a fluid element is then given by

$$\int \delta V \varrho \, d\omega/dt = \int \delta V \mathbf{X} - \int \delta \mathbf{A} \cdot \mathbf{P}, \tag{2.2}$$

where ω is the velocity, $d\omega/dt$ the acceleration, and $-\delta \mathbf{A} \cdot \mathbf{P}$ is the force acting on the surface element δA by the adjacent fluid ($\delta \mathbf{A}$ is directed along the external normal).

Application of Green's formula gives the well-known Euler equation

$$\varrho \, d\omega/dt = \mathbf{X} - \boldsymbol{\nabla} \cdot \mathbf{P}, \tag{2.3}$$

where

$$\boldsymbol{\nabla} \cdot \mathbf{P} = \mathbf{1}_x \left(\frac{\partial}{\partial x} P_{xx} + \frac{\partial}{\partial y} P_{yx} + \frac{\partial}{\partial z} P_{zx} \right) + \mathbf{1}_y (\cdots) + \mathbf{1}_z (\cdots). \tag{2.4}$$

Now, we assume that the external local torque $\mathbf{C}$ is zero, and thus that the tensor $\mathbf{P}$ is symmetrical. The mechanical equilibrium condition of a fluid is given by [see Eq. (2.3)]

$$\boldsymbol{\nabla} \cdot \mathbf{P} = \mathbf{X}. \tag{2.5}$$

We shall restrict our development to systems for which $\mathbf{X} = 0$, and thus (2.5) reduces to

$$\boldsymbol{\nabla} \cdot \mathbf{P} = 0. \tag{2.6}$$

The influence of an electric field on the pressure tensor has been studied in great detail by Defay and Sanfeld (1967) (see also Sanfeld (1968)).

B. Pressure Tensor in a Plane Layer

Let us first consider rectangular axes x, y, and z, where the z axis is normal to the interface. The system is homogeneous in the directions x and y and the pressure tensor is

$$\mathbf{P} = \mathbf{P}(z) = \begin{pmatrix} p_T(z) & 0 & 0 \\ 0 & p_T(z) & 0 \\ 0 & 0 & p_N(z) \end{pmatrix}, \qquad (2.7)$$

where the normal pressure p_N acts on a face parallel to the interface and the tangential pressure p_T acts on a face perpendicular to the interface.
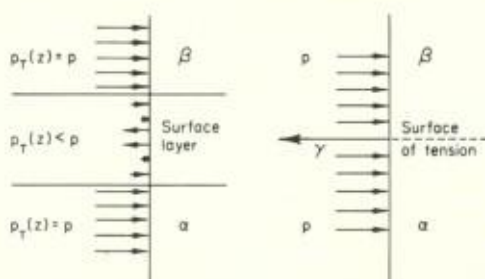
Fig. 8.   Real system and equivalent model with tension surface.

Outside the surface layer, in the isotropic regions α and β of the two fluids, $p_N = p_T$. The local mechanical equilibrium condition (2.6) here reduces to

$$dp_N/dz = 0. \qquad (2.8)$$

The normal pressure p_N is thus independent of z, so that, in the transition region, the normal pressure is equal to the scalar hydrostatic pressure p of the homogeneous phases. In contrast, there is no such condition for p_T. The tangential pressure may even take on negative values (Fig. 8).

The pressure deficit $\{p - p_T\}$ in the surface layer manifests itself macroscopically as a tension exerted by the fluid on the walls of the container.

The equivalence of the two models shown in Fig. 8 yields the expression

$$\int p_T(z)\, dz = \int p\, dz - \gamma \tag{2.9}$$

or

$$\gamma = \int \{p - p_T(z)\}\, dz, \tag{2.10}$$

where the region of integration is, in fact, the surface layer.

A second condition of equivalence can be expressed by the equality of the momentum forces. This determines the height z_0 of the surface of tension

$$\int z p_T(z)\, dz = \int z p\, dz - \gamma z_0; \tag{2.11}$$

thus,

$$z_0 = (1/\gamma) \int z\{p - p_T(z)\}\, dz = \int z\{p - p_T(z)\}\, dz / \int \{p - p_T(z)\}\, dz. \tag{2.12}$$

We note here that the value of γ is defined independently of the position of the surface of tension. Hence, for any transformation for which the interface remains plane, the height z at which γ is applied has no practical importance. However, this is not the case for curved surfaces.

C. Pressure Tensor in a Spherical Layer

In spherical coordinates, the pressure tensor is a function of the radius of the spherical surface involving the point under consideration:

$$\mathbf{P} = \mathbf{P}(r) = \begin{pmatrix} p_T(r) & 0 & 0 \\ 0 & p_T(r) & 0 \\ 0 & 0 & p_N(r) \end{pmatrix}. \tag{2.13}$$

In the bulk of the homogeneous phases, $\mathbf{P}$ is isotropic and independent of r; in phases α and β, we have

$$\mathbf{P} = p^\alpha \mathbf{l} \quad \text{and} \quad \mathbf{P} = p^\beta \mathbf{l},$$

where $\mathbf{l}$ is the unit tensor. In the transition region, p_T and p_N vary with r, and here the mechanical equilibrium condition (2.6) gives (Bakker, 1928)

$$-\partial p_N / \partial r = 2(p_N - p_T)/r. \tag{2.14}$$

Equation (2.14) may be rewritten

$$\partial(r^2 p_N)/\partial r = 2p_T r. \tag{2.15}$$
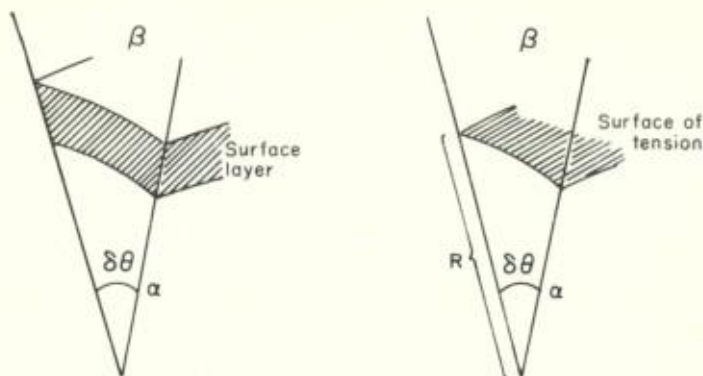
FIG. 9.   Section of a system; real and equivalent models with tension surface for spherical interface.

We shall now compare our system with the model surface of tension (Fig. 9). The mechanical forces and momentum equilibrium may be expressed by

$$\delta\theta \int p_T r \, dr = \delta\theta \int^R p^x r \, dr + \delta\theta \int_R p^\beta r \, dr - \delta\theta \gamma R \tag{2.16}$$

$$\delta\theta \int p_T r^2 \, dr = \delta\theta \int^R p^x r^2 \, dr + \delta\theta \int_R p^\beta r^2 \, dr - \delta\theta \gamma R^2, \tag{2.17}$$

where R determines the position of the surface of tension and where the integrals are limited to the thickness of the layer. Let us define the quantity $p^{x\beta}$ by the following relations:

$$\begin{aligned} p^{x\beta} &= p^x && \text{if } r < R \\ p^{x\beta} &= p^\beta && \text{if } r > R. \end{aligned} \tag{2.18}$$

Thus, we obtain the two fundamental equations

$$\gamma = (1/R) \int \{p^{x\beta} - p_T(r)\} r \, dr \tag{2.19}$$

$$R = \int \{(p^{x\beta} - p_T(r)\} r^2 \, dr / \int \{p^{x\beta} - p_T(r)\} r \, dr. \tag{2.20}$$

The knowledge of R is thus necessary to calculate γ. It is easy to verify that these equations are consistent with the Laplace relation

$$\gamma = (p^x - p^\beta) R / 2. \tag{2.21}$$

Remark. For $R \to \infty$, it is easy to show that (2.19) and (2.20) reduce to (2.10) and (2.12).

III. Gibbs's Surface Model

A. The Gibbs Dividing Surface

Let us now consider a point P in a transition layer separating two homogeneous phases α and β (Fig. 10). In the vicinity of P, we find other points P', P'', P''', ... equivalent to P (the intensive properties are identical at each of these points). Thus, we obtain a surface of uniform properties which includes P, P', P'', ... Through each point of a line perpendicular to the layer, there exists a surface of uniform properties. All these surfaces are parallel with one another and are characterized by the coordinate λ measured along a normal to the layer.

FIG. 10. Transition layer separating two homogeneous phases α and β.

In order to describe the macroscopic properties of the layer, Gibbs replaces the heterogeneous transition regions by a geometrical dividing surface which coincides with one of the surfaces of uniform properties. The dividing surface is thus in the interfacial region between the homogeneous phases α and β. In this model, the Gibbs surface is a two-dimensional phase without thickness but with well-defined physicochemical properties (Defay *et al.*, 1966). We restrict our study to a two-phase c-components equilibrium system without external field.

B. Surface Quantities

We consider a closed surface generated by a moving normal to the dividing surface s (Fig. 11). The closed surface is of such an extent that it includes portions of the homogeneous bulk phases α and β. The Helmholtz free energy of matter enclosed by the closed surface can be adequately described by relations of the type

$$F = F^\alpha + F^\beta + F^a, \tag{3.1}$$
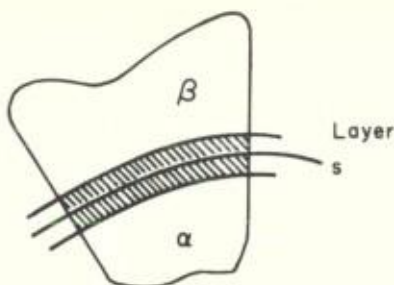
Fig. 11.   Dividing surface s in a surface layer.

where F^a is the surface free energy, F^α the energy of region α, and F^β the energy of region β. If V^α and V^β are the volumes of phases α and β, f_v^α and f_v^β the free energy densities, f_s^a the surface free-energy density, and A the area, we may write

$$F^\alpha = V^\alpha f_v^\alpha, \qquad F^\beta = V^\beta f_v^\beta, \qquad F^a = A f_s^a. \qquad (3.2)$$

In general, V^α, V^β, A, and f_s^a depend on the particular choice of the surface s of coordinate λ. Another dividing surface of coordinate $\lambda + d\lambda$ gives the variations

$$dV^\alpha = A \, d\lambda; \qquad dV^\beta = -A \, d\lambda; \qquad dA = (K_1 + K_2)A \, d\lambda, \qquad (3.3)$$

where $K_1 + K_2$ is the mean curvature of the surface s, assumed to have the same value at each point of the surface. Since the total free energy F is independent of the choice of the dividing surface, we obtain

$$f_v^\alpha - f_v^\beta + (K_1 + K_2)f_s^a + df_s^a/d\lambda = 0. \qquad (3.4)$$

A similar expression may be written for the entropies:

$$s_v^\alpha - s_v^\beta + (K_1 + K_2)s_s^a + ds_s^a/d\lambda = 0. \qquad (3.5)$$

However, if n_γ is the total number of molecules of species γ in the system and C_γ^α and C_γ^β the concentrations in the two phases α and β, we find

$$n_\gamma = n_\gamma^\alpha + n_\gamma^\beta + n_\gamma^a \qquad (3.6)$$

$$n_\gamma^\alpha = V^\alpha C_\gamma^\alpha, \qquad n_\gamma^\beta = V^\beta C_\gamma^\beta, \qquad n_\gamma^a = A\Gamma_\gamma, \qquad (3.7)$$

where n_γ^a is the number of molecules adsorbed on the dividing surface and Γ_γ is the specific adsorption. Similarly, we obtain

$$C_\gamma^\alpha - C_\gamma^\beta + (K_1 + K_2)\Gamma_\gamma + d\Gamma_\gamma/d\lambda = 0. \qquad (3.8)$$

C. Free Energy and Surface Work

For infinitesimal variations $\delta T, \ldots, \delta n_\gamma, \ldots$ and an external work $\delta\tau$, the variation of free energy is given by [see Chapter 2A, Eq. (4.14)]

$$\delta F = -S\,\delta T + \Sigma\,\mu_\gamma\,\delta n_\gamma + \delta\tau, \tag{3.9}$$

where $\delta\tau$ corresponds to displacements of the boundaries of the system and of the interface. In the case of the particular dividing surface s, we have

$$\delta\tau = -p^\alpha\,\delta V^\alpha - p^\beta\,\delta V^\beta + \bar\gamma\,\delta A + A(C_1{}^*\,\delta K_1 + C_2{}^*\,\delta K_2), \tag{3.10}$$

where $\bar\gamma$ is a tension which opposes the expansion of the layer, $C_1{}^*$ and $C_2{}^*$ are the rigidity coefficients which oppose a variation of the curvature. Substituting (3.10) in (3.9),

$$\delta F = -S\,\delta T + \sum_\gamma \mu_\gamma\,\delta n_\gamma - p^\alpha\,\delta V^\alpha - p^\beta\,\delta V^\beta + \bar\gamma\,\delta A$$

$$+ A(C_1{}^*\,\delta K_1 + C_2{}^*\,\delta K_2). \tag{3.11}$$

Let us now consider a virtual variation which corresponds to the choice of a new surface s' (s and s' are parallel); we may write

$$\delta V^\alpha = A\,\delta\lambda, \qquad \delta V^\beta = -A\,\delta\lambda, \qquad \delta A = (K_1 + K_2)A\,\delta\lambda, \tag{3.12}$$

$$\delta K_1 = -K_1{}^2\,\delta\lambda, \qquad \delta K_2 = -K_2{}^2\,\delta\lambda. \tag{3.13}$$

The real system being unmodified, $\delta\tau = 0$; thus, we obtain the relation

$$p^\alpha - p^\beta = \bar\gamma(K_1 + K_2) - C_1{}^*K_1{}^2 - C_2{}^*K_2{}^2, \tag{3.14}$$

which must be satisfied whatever the dividing surface.

If K_1 and K_2 are constant on the surface s and if the intensive variables $T, p^\alpha, p^\beta, \bar\gamma, \ldots, \mu_\gamma, \ldots$ are given, it is easy to show that (Euler's theorem)

$$F = \sum_\gamma \mu_\gamma n_\gamma - p^\alpha V^\alpha - p^\beta V^\beta + \bar\gamma A. \tag{3.15}$$

The invariance of F in comparison with the dividing surface then gives

$$p^\alpha - p^\beta = \gamma(K_1 + K_2) + d\bar\gamma/d\lambda. \tag{3.16}$$

A comparison with the expression for F obtained in the previous section

yields the following relations:

$$F^a = \sum_\gamma \mu_\gamma n_\gamma{}^a + \bar{\gamma}A \tag{3.17}$$

$$f_s{}^a = \sum_\gamma \mu_\gamma \Gamma_\gamma + \bar{\gamma}. \tag{3.18}$$

D. Primary Role of the Dividing Surface

If $K_1 = K_2$, then $C_1{}^* = C_2{}^*$; this is the special case of a plane interface. Since the thickness of the transition layer is always small with respect to the principle curvature radii, $C_1{}^*$ and $C_2{}^*$ are approximately equal to C^*, the coefficient corresponding to a plane interface. Equations (3.11) and (3.14) then become

$$dF = -S\,dT + \sum_\gamma \mu_\gamma\,dn_\gamma - p^x\,dV^x - p^\beta\,dV^\beta + \bar{\gamma}\,dA$$
$$+AC^*\,d(K_1 + K_2) \tag{3.19}$$

and

$$p^x - p^\beta = \bar{\gamma}(K_1 + K_2) - C^*(K_1{}^2 + K_2{}^2). \tag{3.20}$$

In comparison with the Laplace formula (1.4) for to the surface tension, it appears that the particular unrigid dividing surface ($C^* = 0$) coincides with the surface of tension. If λ_0 is the coordinate of this particular dividing surface, then $\gamma = \bar{\gamma}(\lambda_0)$, and the variations of free energy will be

$$dF = -S\,dT + \sum_\gamma \mu_\gamma\,dn_\gamma - p^x\,dV^x - p^\beta\,dV^\beta + \gamma\,dA. \tag{3.21}$$

From (3.16) and (3.20), we obtain

$$d\bar{\gamma}/d\lambda = -C^*(K_1{}^2 + K_2{}^2) = p^x - p^\beta - \bar{\gamma}(K_1 + K_2); \tag{3.22}$$

thus, on the surface of tension

$$d\bar{\gamma}/d\lambda = 0, \qquad d^2\bar{\gamma}/d\lambda^2 = \bar{\gamma}(K_1{}^2 + K_2{}^2) > 0. \tag{3.23}$$

It follows that, for the surface of tension, $\bar{\gamma}(\lambda)$ is minimum. This remarkable property was used by Gibbs (1928) in his fundamental work. On differentiation of (3.22), we see that

$$dC^*/d\lambda = -\bar{\gamma} + C^*[(K_1 - K_2)^2(K_1 + K_2)/(K_1{}^2 + K_2{}^2)]. \tag{3.24}$$

For a plane or spherical interface, Eq. (3.24) reduces to

$$dC^*/d\lambda = -\bar{\gamma}. \tag{3.25}$$

The ratio C^*/γ is more or less equal to 10^{-7} cm and we deduce therefore that a variation of λ of an amount of a few angströms is sufficient to modify the sign of C^*.

E. THERMODYNAMIC RELATIONS

We shall adopt here the surface of tension as the dividing surface. As we saw,

$$dF = -S\,dT + \sum_{\gamma} \mu_\gamma\,dn_\gamma - p^\alpha\,dV^\alpha - p^\beta\,dV^\beta + \gamma\,dA; \tag{3.26}$$

hence,

$$\gamma = (\partial F/\partial A)_{TV^\alpha V^\beta n}. \tag{3.27}$$

We can divide each of the extensive quantities F, S, and n_γ into three parts:

$$\begin{aligned}
F &= F^\alpha + F^\beta + F^a \\
S &= S^\alpha + S^\beta + S^a \\
n_\gamma &= n_\gamma^\alpha + n_\gamma^\beta + n_\gamma^a.
\end{aligned} \tag{3.28}$$

For the two volume phases

$$\begin{aligned}
dF^\alpha &= -S^\alpha\,dT - p^\alpha\,dV^\alpha - \sum_{\gamma} \mu_\gamma\,dn_\gamma^\alpha \\
dF^\beta &= -S^\beta\,dT - p^\beta\,dV^\beta - \sum_{\gamma} \mu_\gamma\,dn_\gamma^\beta,
\end{aligned} \tag{3.29}$$

and thus

$$dF^a = -S^a\,dT + \gamma\,dA + \sum_{\gamma} \mu_\gamma\,dn_\gamma^a. \tag{3.30}$$

The interface may thus be considered as a two-dimensional phase of area A and free energy F^a, with

$$S^a = -\left(\frac{\partial F^a}{\partial T}\right)_{An^a}, \qquad \mu_\gamma = \left(\frac{\partial F^a}{\partial n_\gamma^a}\right)_{TAn_\beta^a}, \qquad \gamma = \left(\frac{\partial F^a}{\partial A}\right)_{Tn^a}. \tag{3.31}$$

Furthermore, from (3.30), we have

$$\frac{\partial F^a}{\partial n_\gamma{}^a} = \frac{\partial F^a}{\partial n_\gamma{}^\beta} = \frac{\partial F^a}{\partial V^a} = \frac{\partial F^a}{\partial V^\beta} = 0. \tag{3.32}$$

This property is only true for extensive variables.

Indeed, the surface phase is nonautonomous; it depends directly on the intensive properties of the neighboring phases; for example, the dependence between F^a and $n_\gamma{}^a$ is given by

$$\mu_\gamma = \left(\frac{\partial F^a}{\partial n_\gamma{}^a} \right)_{Tn_\beta{}^a A}. \tag{3.33}$$

Let us now consider the specific surface free energy f^a defined by

$$f^a = F^a/A. \tag{3.34}$$

By differentiation, we obtain

$$df^a = \frac{dF^a}{A} - \frac{F^a}{A^2} \, dA. \tag{3.35}$$

From (3.35) and (3.30), we have

$$df^a = \frac{1}{A} \left[-S^a \, dT + \sum_\gamma \mu_\gamma \, dn_\gamma{}^a + \gamma \, dA \right] - \frac{F^a}{A^2} \, \delta A. \tag{3.36}$$

The variation of $n_\gamma{}^a$ may be expressed in terms of specific adsorption Γ_γ:

$$dn_\gamma{}^a = A \, d\Gamma_\gamma + \Gamma_\gamma \, dA. \tag{3.37}$$

If $dn_\gamma{}^a$ in Eq. (3.36) is replaced by the value given by (3.37), we obtain

$$df^a = s^a \, dT + \sum_\gamma \mu_\gamma \, d\Gamma_\gamma + (dA/A)(\gamma + \sum_\gamma \mu_\gamma \Gamma_\gamma - f^a), \tag{3.38}$$

where the specific entropy s^a is given by the ratio S^a/A. Because f^a is not function of A,

$$df^a = -s^a \, dT + \sum_\gamma \mu_\gamma \, d\Gamma_\gamma \tag{3.39}$$

$$f^a = \gamma + \sum_\gamma \mu_\gamma \Gamma_\gamma, \tag{3.40}$$

with

$$s^a = -(\partial f^a/\partial T)_\Gamma \tag{3.41}$$

$$\mu_\gamma = (\partial f^a/\partial \Gamma_\gamma)_{T\Gamma_\beta}. \tag{3.42}$$

Then, from the differential of (3.40) and (3.39), there follows the well-known Gibbs equation

$$d\gamma = -s^a \, dT - \sum_\gamma \Gamma_\gamma \, d\mu_\gamma. \tag{3.43}$$

Thus,

$$s^a = -(\partial\gamma/\partial T)_\mu \tag{3.44}$$

$$\Gamma_\gamma = -(\partial\gamma/\partial\mu_\gamma)_{T\mu_\beta} \tag{3.45}$$

where the subscript μ_β indicates that the derivative is taken keeping all the μ's except μ_γ constant. This can, however, be achieved only if the system has at least $c + 1$ degrees of freedom $T, \mu_1, \ldots, \mu_c$.

For a plane surface, the highest possible variance corresponds to systems where there are no chemical reactions among the components and where the surface has only one phase on it. For a plane surface, it is impossible to vary separately all the $c + 1$ variables $T, \mu_1, \ldots, \mu_c$. It follows that the Gibbs equation (3.43) does not enable the adsorption Γ_γ to be determined on a plane surface. A determination of the adsorption is theoretically possible on a curved surface, for, in this case, the variance is $c + 1$ (for the variance of a capillary system, see Section IV).

F. PLANE SURFACE AND RELATIVE ADSORPTIONS

For a plane surface, the variables $T, \mu_1, \ldots, \mu_c$ cannot be varied independently. We shall therefore examine the way in which μ_1 varies as a function of $T, \mu_2, \ldots, \mu_c$.

The Gibbs–Duhem equations for the two bulk phases may be written

$$dp^\alpha = s_v{}^\alpha \, dT + \sum C_\gamma{}^\alpha \, d\mu_\gamma$$
$$dp^\beta = s_v{}^\beta \, dT + \sum_\gamma C_\gamma{}^\beta \, d\mu_\gamma, \tag{3.46}$$

where $s_v{}^\alpha$ and $s_v{}^\beta$ are the entropy densities of phases α and β.

Moreover, for a plane surface, the mechanical equilibrium gives

$$p^\alpha = p^\beta, \tag{3.47}$$

so that we obtain for the variation of μ_1

$$d\mu_1 = -\frac{s_v{}^\alpha - s_v{}^\beta}{C_1{}^\alpha - C_1{}^\beta} \, dT - \sum_{\gamma \geq 2} \frac{C_\gamma{}^\alpha - C_\gamma{}^\beta}{C_1{}^\alpha - C_1{}^\beta} \, d\mu_\gamma. \tag{3.48}$$

We may now replace $d\mu_1$ in the Gibbs equation (3.43) to give

$$dy = -(s^a)_1\, dT - \sum_{\gamma \geq 2} \Gamma_{\gamma 1}\, d\mu_\gamma, \qquad (3.49)$$

where the quantities $(s^a)_1$ and $\Gamma_{\gamma 1}$ are, respectively, the relative surface entropy and the relative adsorption defined by

$$(s^a)_1 = s^a - \Gamma_1 \frac{s_v^\alpha - s_v^\beta}{C_1^\alpha - C_1^\beta}$$

$$\Gamma_{\gamma 1} = \Gamma_\gamma - \Gamma_1 \frac{C_\gamma^\alpha - C_\gamma^\beta}{C_1^\alpha - C_1^\beta}. \qquad (3.50)$$

Written in this form, the Gibbs equation is very much more useful, since the variables $T, \mu_2, \ldots, \mu_c$ can be completely independent. It is therefore possible to determine the relative surface entropy and relative adsorption by determining experimentally the differential coefficients

$$(s^a)_1 = -\left(\frac{\partial y}{\partial T}\right)_{\mu_1 \cdots \mu_c} \qquad (3.51)$$

$$\Gamma_{\gamma 1} = -\left(\frac{\partial y}{\partial \mu_\gamma}\right)_{T \mu_{\beta \neq 1}}. \qquad (3.52)$$

Example. The liquid phase consists of a saturated solution of nitrogen (subscript 2) in water (subscript 1) and the gaseous phase of nitrogen and water vapor. At moderately low pressures, the fugacity of nitrogen may be equated to the partial pressure p_2, so that, at constant temperature,

$$d\mu_2 = RT\, dp_2/p_2. \qquad (3.53)$$

The variation of the surface tension will be

$$dy = -\Gamma_{21}(RT/p_2)\, dp_2 \qquad (3.54)$$

and

$$\Gamma_{21} = -(p_2/RT)\, dy/dp_2. \qquad (3.55)$$

Suppose that we find that at 17°C the surface tension falls by 0.1 dyn cm^{-1} when the pressure is increased from 1 to 2 atm. Then, taking the mean pressure p_2 as 1.5 atm, we have (Defay et al., 1966, Chapter VII)

$$\Gamma_{21} \simeq 0.62 \times 10^{-11} \quad \text{mol cm}^{-2}.$$

Other examples can be found in the book by Defay and co-workers (1966, Chapter VII).

G. Influence of Curvature on the Surface Tension

We restrict our discussion to spherical surfaces and to one-component systems. At constant temperature,

$$dp^{\alpha} = C^{\alpha}\, d\mu, \qquad dp^{\beta} = C^{\beta}\, d\mu, \qquad d\gamma = -\Gamma\, d\mu. \tag{3.56}$$

For the surface of tension, the differential form may be written

$$dp^{\alpha} - dp^{\beta} = (2/r)\, d\gamma + 2\gamma\, d(1/r). \tag{3.57}$$

From (3.56) and (3.57), we get

$$\Gamma = -\frac{1}{2}\,(C^{\alpha} - C^{\beta})\,\frac{d\gamma}{d(\gamma/r)} = -\frac{1}{2}\,(C^{\alpha} - C^{\beta})\,\frac{d(\ln\gamma)/d(1/r)}{1 + (1/r)\,d(\ln\gamma)/d(1/r)}. \tag{3.58}$$

To determine Γ, we must measure the variation of γ with the curvature of the surface. From an experimental point of view, we are limited to radii $\geq 10^{-3}$ cm, and, in this range, it is impossible to observe a variation of γ.

By integration of (3.58) for small values of $1/r$, we obtain

$$\ln\left(\frac{\gamma}{\gamma_{\mathrm{p}}}\right) \simeq -\frac{2\Gamma}{C^{\alpha} - C^{\beta}}\left(\frac{1}{r}\right), \tag{3.59}$$

where γ_{p} is the surface tension of corresponding plane surface.

Example. Let us consider a drop of radius equal to 10^{-3} cm.

If $C^{\alpha} - C^{\beta} = 10^{22}$ molecules cm^{-3} and $\Gamma = 10^{15}$ molecules cm^{-2}, we find a relative variation for γ of about 0.01%.

H. Surface Activity

Every dissolved substance which modifies the surface tension of the solvent is called a surface-active agent. These substances tend to accumulate in the surface layer. They are made up primarily of a polar or an ionic soluble group and of an insoluble part (for example, an aliphatic chain). The Gibbs equation gives the relation between the relative adsorp-

tion of the surface-active agent (index s) and the slope of the γ–C_s curve,

$$\partial\gamma/\partial C_s = -\Gamma_{s1}kT/C_s. \tag{3.60}$$

The surface activity of a substance is defined as the initial value $-(\partial\gamma/\partial C_s)_{C_s\to 0}$ of the slope of the curve against C_s in the bulk phase (Fig. 12).

Traube showed that the surface activity is directly related to the length of the molecule. For different normal alcohols, he found that the surface activity was about three times higher than the previous value each time the chain was increased by one —CH_2— group. Detergents are surface-active agents at water–solid interfaces. They lower the surface tension of the interface and allow the wetting of the solid.
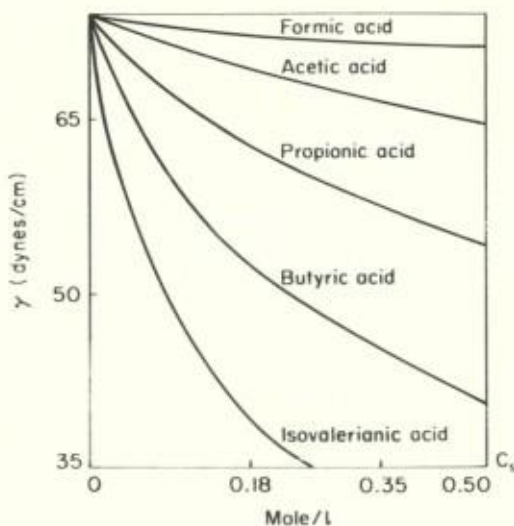
FIG. 12.   Surface tension as a function of the concentration of the dissolved substance.

Remark. It is well known that many surface-active agents are capable of profoundly affecting the state of dispersion of the particles of a disperse phase (solid, liquid, or gaseous) in a liquid medium. If the tendency for spontaneous mutual adhesion to occur among the disperse particles in a system is diminished by the addition of a surface-active agent, we can say that it has a "deflocculating" action; if, on the other hand, the tendency toward mutual adhesion is increased, then the surface-active agent can be conveniently referred to as a "flocculating agent." This problem is important in colloid chemistry (Frens, 1968).

IV. Phase Rule

Consider a system of c independent components and φ bulk phases separated by s surfaces, each comprising one or several surface phases (for a treatment of the phase rule in cases where there may be chemical reactions, see (Defay and Prigogine, 1951)). We denote by $\psi \geq s$ the total number of surface phases.

The physicochemical state of the system considered is defined by the intensive variables: T (uniform); $C_1, \ldots, C_e$ (in each volume phase); $\Gamma_1, \ldots, \Gamma_e$ (in each surface phase); and $r^1, \ldots, r^\psi$ (curvature of each surface phase). The system is defined by $1 + c(\varphi + \psi) + \psi$ intensive variables. If we wish the system to be in equilibrium, we can no longer arbitrarily fix all these variables, for, in equilibrium, they are limited by the following conditions:

(a) On a given surface, the different surface phases have the same surface tension.

(b) The Laplace equation must be satisfied for each surface phase.

(c) The chemical potential of each component has the same value for each bulk or surface phase.

The total number of conditions is thus $(\psi - s) + \psi + c(\varphi + \psi - 1)$, and the number of remaining independent variables at equilibrium, a number which we call the variance of the system (see Chapter 2A, Section V) is therefore

$$w = 1 + c - (\psi - s) \tag{4.1}$$

if we suppose, as above, that the only reactions within the system are transfer reactions.

Example. For a two-phase (liquid–gas), one-component system, the variance is $w = 2$, which means that the vapor pressure of a liquid drop depends on the temperature and on its radius. If the whole surfaces are plane, we have $\varphi - 1$ relations

$$p^1 = \cdots p^x = \cdots p^\varphi, \tag{4.2}$$

and the radii are infinite. It is easy to show (Defay *et al.*, 1966, Chapter VI) that, in this case,

$$w = 2 + c - \varphi - (\psi - s) \quad \text{(plane interfaces)}. \tag{4.3}$$

Finally, if each surface comprises only a single surface phase, $\psi = s$, and we again find the classical phase rule (see Chapter 2A, Section V)

$$w = 2 + c - \varphi. \tag{4.4}$$

V. Influence of Temperature on Surface Tension

We shall limit the study of the dependence on the temperature of the surface tension to single molecules (rare gases or quasispherical molecules). The surface tension decreases quite linearly with an increase in temperature from the triple point to the critical point. At the critical point, $\gamma = 0$, $s^a = 0$, and $\Gamma = 0$; thus, from the Gibbs equation, it follows that

$$d\gamma/dT = 0 \quad \text{(critical point)}; \tag{5.1}$$

the following experimental result is often used

$$\gamma \propto (T_c - T)^n, \tag{5.2}$$

where T_c is the critical temperature and n is a coefficient with $1.20 \leq n \leq 1.25$.

In the triple point–boiling point region, where $0.5 \leq T/T_c \leq 0.7$, Eq. (5.2) may be replaced by

$$\gamma \propto (aT_c - T), \tag{5.3}$$

with $a \simeq 0.93$. Experimental values of a are summarized (Fuks, 1967) in Table III.

TABLE III

	A	Kr	Xe	CH_4	N_2	O_2	CO
a	0.927	0.928	0.942	0.928	0.939	0.920	0.938

Other empirical equations are found in the literature:

1. *Eötvös Equation*

$$\gamma(v^l)^{2/3} = b(T_c - T), \tag{5.4}$$

where v^l is the molar volume of the liquid and where the coefficient b

is quite independent of the nature of the substance considered (for nonassociated substance) (see Table IV). Nevertheless, Eq. (5.4) is not valid in the neighborhood of the critical point [see Eq. (5.1)].

TABLE IV

	A	Kr	Xe	CCl_4	C_6H_6	C_6H_{12}	C_5H_{10}
b (ergs $^\circ K^{-1}$)	1.86	1.86	1.86	2.05	2.05	2.05	2.05

2. The Parachor

The concept of the parachor rests upon the equation of Kleeman (1910), Mac Leod (1923), and Sugden (1930), who found

$$\gamma^{1/4}[(v^l)^{-1} - (v^v)^{-1}] = P, \tag{5.5}$$

where v^v is the molar volume in the vapor phase and P is a constant characteristic of each substance. The experimental study of the critical region shows that

$$(v^l)^{-1} - (v^v)^{-1} \propto (T_c - T)^\beta, \tag{5.6}$$

with $0.3 \leq \beta \leq 0.35$. In the critical region, we then obtain the relation

$$\gamma \propto (T_c - T)^{4\beta} \propto (T_c - T)^{1.3 \pm 0.1}, \tag{5.7}$$

which is in a good agreement with (5.2).

The Eötvös formula breaks down in the immediate neighborhood of the critical point, and was modified by Nakayama, who replaced the factor $v^{2/3}$ by $y^{2/3}$,

$$\gamma y^{2/3} = b(T - T_c), \tag{5.8}$$

where $y^{-1} = (v^l)^{-1} - (v^v)^{-1}$. Away from T_c, $y \simeq v^l$, and (5.8) reduces to (5.4). From (5.8) and (5.7), we again find (5.2) with $n = 1 + \frac{2}{3}\beta \simeq 1.22 \pm 0.02$. Buff and Lovett (1968) recently obtained $n = 1.27 \pm 0.02$.

VI. Properties of Monolayers

A. INTRODUCTION

The study of the properties of monolayers spread out on a liquid has been the subject of numerous publications since the beginning of the present century (Davies and Rideal, 1961, Chapter 5; Gaines, 1966). Authors have, in particular, displayed great interest in the state equations deriving the various plausible formulations of surface pressure as well as of the chemical potential of the constituents in the layer. Monolayers are formed from molecules like higher fatty acids or polymers consisting of a hydrophobic and a hydrophilic part. These molecules, insoluble in water, spread out as a film with its end, the COOH group, wetted by water (hydrophilic), and its long hydrocarbon chain (hydrophobic) tending to leave the substrate. The same phenomenon arises at the oil–water interface. Interesting properties of monolayers can be investigated by pressure–area, surface-viscosity, and surface electrical-potential measurements (Guastalla, 1947; Davies and Rideal, 1961).

B. SURFACE PRESSURE

The surface pressure of a monolayer is the lowering of surface tension due to the monolayer. The molecules contained in the monolayer may be regarded as exerting a two-dimentional osmotic pressure; there is a repulsion in the plane of the surface which is measured on a floating barrier acting as a semipermeable membrane permeable to water only (Guastalla, 1947). It is this pressure opposing the contractile tension of the clean interface that is called the surface pressure Π

$$\Pi = \gamma_0 - \gamma, \tag{6.1}$$

where γ_0 is the surface tension of the clean surface. The variation of Π with the area available to the surface-active material is represented by a Π–Ω curve, where Ω is the area per molecule.

Some measurements of this type are shown in Fig. 13 for a homologous series of fatty acids. Qualitatively, the results are the same as for the isotherms of an imperfect gas condensing to a liquid. However, instead of changing temperature, which is difficult on a water surface, as the number of carbon atoms increases, the hydrophilic forces gain over the hydrophobic part of the molecule, and so the film has a great tendency
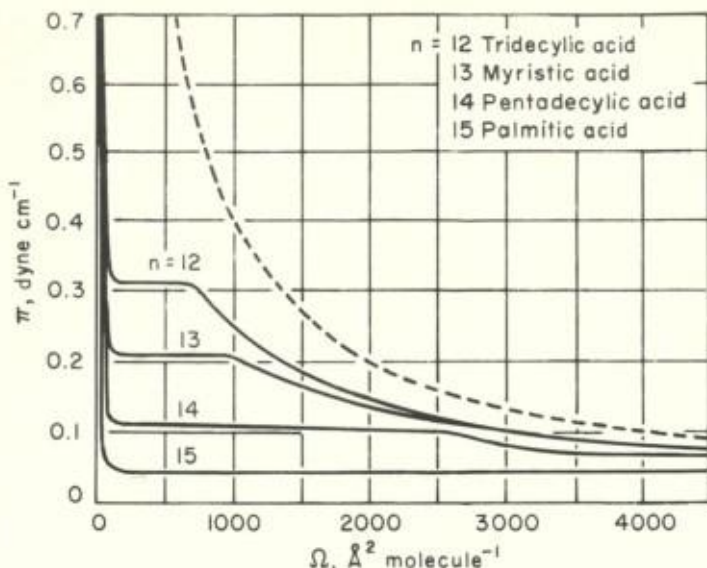
FIG. 13.   Pressure–area phase diagram for a fatty-acid film spread on a water surface.

to condense. The dashed curve in Fig. 13 is the ideal gas law in two dimensions,

$$\Pi = kT/a. \tag{6.2}$$

If the film is dilute enough, that is, if the area per molecule a is large enough, the ideal behavior is approached. At higher densities, two-dimensional condensation may take place. As the phase on the surface is further compressed, it is bound to break out of the two-dimensional film that is only one molecule thick. Ultimately, the surface film becomes thick enough so that it is properly treated as an ordinary three-dimensional phase. If molecules of the insoluble component are so tightly packed that further compression in the form of a film becomes impossible, then they pile up to form a crystal or a floating lens which grows steadily as the area of the surface is progressively decreased.

C. SURFACE VISCOSITY

A monolayer is resistant to shear stress in the plane of the surface just as, in bulk, a liquid is retarded in its flow by viscous forces. The viscosity of the monolayer may indeed be measured in two dimensions by flow through a canal in a surface or by its drag on a ring in the surface, cor-

responding to the Ostwald and Couette instruments for the study of bulk viscosities. The relation between surface viscosity η_s and bulk viscosity η is given by

$$\eta_s = \eta d, \qquad (6.3)$$

where d is the thickness of the surface phase (about 10^{-7} cm for many monolayers). From measurements of viscosities, it appears that hydrocarbon chains are strongly oriented.

Remark. A thermodynamic analysis of the surface potential was performed by Koenig twenty years ago (Koenig, 1951), on the base of the Volta effect. The air–water and oil–water surface potentials of monolayers in connection with the electrical double layer were developed in a great detail by Davies and Rideal (1961).

D. Gibbs's Surface Model

Let us first consider a solution of electrolyte in contact with a vapor phase. On the plane interface, a monolayer is spread out. We call $\gamma(1, \ldots, c)$ the constituents of the system, including the vapor and the liquid phases. We suppose that our system consists of laminae $\alpha = 1, \ldots, \infty$ each parallel to the interface, and containing constituents able to pass through it.

Only lamina β contains the monolayer, i.e., the insoluble nondissociated molecule (subscript 3) together with the insoluble ion of the dissociate molecule (subscript 2). For such an electrochemical system, Defay and colleagues (1966, Eq. (21.28)) have extended Gibbs's formulation outside thermodynamic equilibrium, in the molar form

$$A \, d\gamma = -\bar{S} \, dT + \sum_{\alpha} V^{\alpha} \, dp_e - \sum_{\alpha} \sum_{\gamma=3}^{c} n_{\gamma}{}^{\alpha} \, d\bar{\mu}_{\gamma}{}^{\alpha} - n_3 \, d\bar{\mu}_3{}^{\beta} - n_2 \, d\bar{\mu}_2{}^{\beta}, \qquad (6.4)$$

where $\bar{\mu}_{\gamma}{}^{\alpha}$ is the electrochemical potential of γ in phase α, equal to the sum $\mu_{\gamma}{}^{\alpha} + z_{\gamma}\varphi^{\alpha}$, where z_{γ} is the charge of γ and φ^{α} the electrical potential in phase α; A is the area of the plane interface; p_e is the external pressure (in the absence of gravity, p_e is equal to the pressure in the bulk phase); $\bar{S}$ is the total entropy of the system; and V^{α} is the volume of lamina α.

Let us now apply the Gibbs surface model to Eq. (6.4) for an insoluble monolayer $R-H$ spread on a surface β of a dilute aqueous solution of hydrochloric acid. We assume that thermodynamic equilibrium is achieved. We first place the dividing surface under the monolayer, and

call V' and V'' the two volumes (the liquid and the vapor phase) delimited by this surface of area A; we get

$$\Gamma_{\text{R-H}} = \frac{n^\beta_{\text{R-H}}}{A}, \quad \Gamma_{\text{R-}} = \frac{n^\beta_{\text{R-}}}{A}, \quad \Gamma_{j \neq 1,2} = \frac{n_j - V'C'_j - V''C''_j}{A}. \quad (6.5)$$

At constant temperature and pressure, we may write

$$(d\gamma)_{T,p_e} = -\Gamma_{\text{H}_2\text{O}} \, d\mu'_{\text{H}_2\text{O}} - \Gamma_{\text{H}^+} \, d\bar\mu'_{\text{H}^+} - \Gamma_{\text{OH}^-} \, d\bar\mu'_{\text{OH}^-} - \Gamma_{\text{Cl}^-} \, d\bar\mu'_{\text{Cl}^-}$$
$$- \Gamma_{\text{R-H}} \, d\mu^\beta_{\text{R-H}} - \Gamma_{\text{R-}} \, d\bar\mu^\beta_{\text{R-}}, \quad (6.6)$$

where the μ' are the chemical potentials in the bulk of the homogeneous liquid phase. The equilibrium condition may be written

$$\mu^\beta_{\text{R-H}} = \bar\mu^\beta_{\text{R-}} + \bar\mu'_{\text{H}^+}, \quad \mu'_{\text{H}_2\text{O}} = \bar\mu'_{\text{H}^+} + \bar\mu'_{\text{OH}^-}. \quad (6.7)$$

If the surface layer is neutral as a whole,

$$\Gamma_{\text{H}^+} = \Gamma_{\text{OH}^-} + \Gamma_{\text{Cl}^-} + \Gamma_{\text{R}^-}. \quad (6.8)$$

Combining (6.6), (6.7), and (6.8), we get

$$d\gamma = -\Gamma^t_{\text{H}_2\text{O}} \, d\mu'_{\text{H}_2\text{O}} - 2\Gamma_{\text{Cl}^-} \, d\mu'_{\text{H}^+\text{Cl}^-} - \Gamma^t_{\text{R-H}} \, d\mu^\beta_{\text{R-H}}, \quad (6.9)$$

where the total adsorptions are defined by

$$\Gamma^t_{\text{H}_2\text{O}} = \Gamma_{\text{H}_2\text{O}} + \Gamma_{\text{OH}^-}, \quad \Gamma^t_{\text{R-H}} = \Gamma_{\text{RH}} + \Gamma_{\text{R}^-} \quad (6.10)$$

and

$$d\bar\mu'_{\text{H}^+} + d\bar\mu'_{\text{Cl}^-} = 2 \, d\mu'_{\text{H}^+\text{Cl}^-}. \quad (6.11)$$

On the other hand, we know that, at T and p_e constant, the chemical potentials $\mu'_{\text{H}_2\text{O}}$ and $\mu'_{\text{H}^+\text{Cl}^-}$ appearing in Eq. (6.9) are not independent variables; actually, in the bulk phase, we may write

$$C'_{\text{H}_2\text{O}} \, d\mu'_{\text{H}_2\text{O}} + C'_{\text{H}^+} \, d\bar\mu'_{\text{H}^+} + C'_{\text{OH}^-} \, d\bar\mu'_{\text{OH}^-} + C'_{\text{Cl}^-} \, d\bar\mu'_{\text{Cl}^-} = 0 \quad (6.12)$$

and

$$C'_{\text{H}^+} = C'_{\text{OH}^-} + C'_{\text{Cl}^-}. \quad (6.13)$$

Now, combining Eqs. (6.7) and (6.11)–(6.13), we find that

$$C'^t_{\text{H}_2\text{O}} \, d\mu'_{\text{H}_2\text{O}} + 2C'_{\text{Cl}^-} \, d\mu'_{\text{H}^+\text{Cl}^-} = 0, \quad (6.14)$$

where

$$C_{H_2O}^{\prime t} = C_{H_2O}^{\prime} + C_{OH^-}^{\prime}. \tag{6.15}$$

Thus, from (6.14), in a dilute solution of HCl,

$$C_{H_2O}^{\prime t} \gg C_{Cl^-}^{\prime} \quad \text{and} \quad d\mu_{H_2O}^{\prime} \ll d\mu_{H^+Cl^-}^{\prime}.$$

If Γ_{Cl^-} is not too small compared with $\Gamma_{H_2O}^t$, (6.9) then becomes

$$d\gamma = -2\Gamma_{Cl^-} \, d\mu_{H^+Cl^-}^{\prime} - \Gamma_{R-H}^t \, d\mu_{R-H}^{\beta} \tag{6.16}$$

If the spread-out film is in a gaseous state, there are many water molecules in β; $\Gamma_{H_2O}^t$ is thus large for the reference surface, and $\Gamma_{Cl^-} \ll \Gamma_{H_2O}^t$ because the diffuse layer is not important. The term $d\mu_{H_2O}^{\prime}$ may no longer be neglected.

In this case, it seems to be more convenient to use the relative adsorption in such a way that the Gibbs dividing surface yields $\Gamma_{H_2O}^t = 0$. The values of V' and V'' are then different from their values in the above cases, but the formulation remains valid and we may write, in terms of the relative adsorption Γ_{γ,H_2O}, the following equation:

$$d\gamma = -2\Gamma_{Cl^-,H_2O} \, d\mu_{H^+Cl^-}^{\prime} - \Gamma_{R-H,H_2O}^t \, d\mu_{R-H}^{\beta}. \tag{6.17}$$

Measuring γ for given values of Γ_{R-H,H_2O}^t at constant temperature, pressure, and $\mu_{H^+Cl^-}^{\prime}$, we then obtain the law

$$\gamma = \gamma(\Gamma_{R-H,H_2O}^t). \tag{6.18}$$

From the curve (6.18), we have

$$\frac{\partial \gamma}{\partial \Gamma_{R-H,H_2O}^t} = \frac{\partial \gamma}{\partial \mu_{R-H}^{\beta}} \frac{\partial \mu_{R-H}^{\beta}}{\partial \Gamma_{R-H,H_2O}^t} = -\Gamma_{R-H,H_2O}^t \frac{\partial \mu_{R-H}^{\beta}}{\partial \Gamma_{R-H,H_2O}^t}. \tag{6.19}$$

It is then possible to find the law $\mu_{R-H}^{\beta} = \mu_{R-H}^{\beta}(\Gamma_{R-H,H_2O}^t)$ for a given value of $\mu_{H^+Cl^-}^{\prime}$.

For example, if (6.18) is a linear law of the form

$$\gamma = \gamma^i - \theta_a \Gamma_{R-H,H_2O}^t, \tag{6.20}$$

where θ_a is a function of T, p_e, and $\mu_{H^+Cl^-}^{\prime}$ We obtain

$$\partial \gamma / \partial \Gamma_{R-H,H_2O}^t = -\theta_a, \tag{6.21}$$

and, from (6.19),

$$(\theta_a/\Gamma^t_{\text{R-H,H}_2\text{O}})\,d\Gamma^t_{\text{R-H,H}_2\text{O}} = d\mu^\beta_{\text{R-H}}. \tag{6.22}$$

Now integrating (6.22)

$$\mu^\beta_{\text{R-H}} = \mu^{\beta i}_{\text{R-H}} + \theta_a \ln \Gamma^t_{\text{R-H,H}_2\text{O}} \tag{6.23}$$

For different values of $\mu_{\text{H}^+\text{Cl}^-}$, it is now possible to know the variation of θ_a with $\mu_{\text{H}^+\text{Cl}^-}$.

Remark. It is possible that $\mu^{\beta i}_{\text{R-H}}$ is also a function of $\mu_{\text{H}^+\text{Cl}^-}$.

E. Various Explicit Formulations of the Chemical Potential in the Layer and in the Gibbs Dividing Surface

In absence of fields, for an ideal uncharged monolayer defined in the manner of Defay and Prigogine (see Defay *et al.* (1966), Chapter XII, § 5), we may write for each γ the expression:

$$\mu_\gamma^a = \zeta_\gamma^a(T, p) + RT \ln N_\gamma^c - \gamma\omega_\gamma, \tag{6.24}$$

where superscript c refers to the monolayer model and a to Gibbs' model. We also have

$$A = \sum_\gamma n_\gamma^c \omega_\gamma, \tag{6.25}$$

where ω_γ is the partial molar area of γ.

When the surface is saturated by only one component,

$$\omega_\gamma = A/n_\gamma^c = 1/\Gamma_\gamma^{c\infty}, \tag{6.26}$$

where $\Gamma_\gamma^{c\infty}$ is the saturation adsorption *in the layer* and not the Gibbs adsorption related to a division surface.

On the other hand, ω_γ may be a function of γ, i.e., the value of ω_γ may be slightly different in a saturated than in a nonsaturated layer. In the molecular models, it is always assumed that ω_γ is a constant quantity. For a nonideal monolayer in the absence of field, Eq. (6.24) must be replaced by (Defay *et al.* (1966), Chapter XII, § 5)

$$\mu_\gamma^c = \left(\frac{\partial F^c}{\partial n_\gamma^c}\right)_{T p \gamma n_\beta^c} + p v_\gamma^c - \gamma\omega_\gamma, \tag{6.27}$$

where v_γ^c is the molar volume of γ in the layer. The term $p v_\gamma^c$ is small

compared to $\gamma\omega_\gamma$. Equation (6.27) is valid for the solvent and also for the solutes. In the case of regular solutions, many authors give the explicit expressions of F^c and $\mu_\gamma{}^c$ (see, for example, Defay *et al.* (1966) Chapter XII, § 8). With the Gibbs model, we may write [see (Defay *et al.*, 1966) (12.13) and (12.14)]

$$\mu_\gamma{}^a = \left(\frac{\partial F^a}{\partial n_\gamma{}^a}\right)_{Tp\Lambda n_\beta{}^a} \tag{6.28}$$

$$\mu_\gamma{}^a = \left(\frac{\partial F^a}{\partial n_\gamma{}^a}\right)_{Tp\gamma n_\beta{}^a} - \gamma\omega_\gamma. \tag{6.29}$$

For nonideal uncharged systems in the absence of field, the use of the equation (Arcuri, 1966)

$$\mu_\gamma{}^a = \xi_\gamma{}^a(T, p) + RT \ln f_\gamma{}^a N_\gamma{}^a - \gamma\omega_\gamma \tag{6.30}$$

defines the activity coefficient $f_\gamma{}^a$.

Remark. Many authors have shown that the monolayer model is very coarse. Indeed, Defay *et al.* (1966, Chapter XII, § 10) proved that this model is inconsistent with the Gibbs formula. It seems better, following Defay *et al.* (1966) and Ono and Kondo (1960, p. 159), to use the multilayer model (infinite laminae) for which Eq. (6.24) may be written for each lamina with varying from lamina to lamina.

VII. Multilayer Model and Interfacial Orientation

A. INTRODUCTION

We know that, if a surface layer is many molecules thick, its composition may vary with position within the layer; this circumstance makes it physically reasonable to use the multilayer model developed by Defay and colleagues (1966), a model one could call intermediate between the continuous and the discontinuous models. The system is divided into uniform regions called phases; the nonuniform regions, such as the capillary layer, are subdivided into a number of laminae each sufficiently thin be considered as homogeneous.

Our purpose here is to develop capillary theory based on the multilayer model with a view to deriving an explicit formulation of interfacial orientation.

Excluding all microscopic fluctuation effects, this work deals only with systems for which orientation equilibrium occurs after the establishment of the diffusion equilibrium. All transport of matter from one region to another may be treated as a transfer of one or several components from one phase to another.

The only entropy production sources are, on the one hand, the chemical reactions and the transport from one phase to another, and, on the other hand, the orientation of every component which occurs in the laminae. Thus, in addition to the classical chemical and transport affinities, we shall have orientation affinities.

In Defay's work (1966), the orientation of the components is not treated as an independent variable. This means that the molecules, while moving from one phase to another, are supposed to be always in instantaneous orientation equilibrium with the dipole structure of the successive laminae.

If, on the contrary, the orientation equilibrium is reached after the diffusion equilibrium, orientation variables independent of diffusion variables should clearly appear in the thermodynamic formalism. This will enable us to show how the Gibbs formula may easily be extended to these systems and, for illustrative purposes, we shall discuss a very simple example of surface orientation.

Remark. The extension of our theory to electrocapillary systems has also been made (Sanfeld, 1968, Chapter 14).

B. Thermodynamics of a Closed Capillary System

We adopt the multilayer model in which each lamina, within the surface layer is considered as a homogeneous phase of infinitesimal thickness. Let us now consider a system at uniform temperature and in mechanical equilibrium, unable to exchange molecules with the surroundings. In particular, for a system containing only one plane interface, the work $d\tau$ done on the system by its surroundings is given by (1.17):

$$d\tau = -p_e \, dV + \gamma \, dA, \tag{7.1}$$

where p_e is the external (uniform) pressure acting on the system, and $V = \sum_\alpha V^\alpha$ is the total volume equal to the sum of the volumes of the individual phases (bulk phases I and II and laminae). The equations, derived from the first and second laws of thermodynamics, have the form

[see Chapter 1 and Chapter 2A, Eq. (1.11)]

$$dU = dQ - \sum_\alpha p_e \, dV^\alpha + \gamma \, dA \tag{7.2}$$

and

$$dS = d_e S + d_i S, \tag{7.3}$$

with $d_i S \geq 0$. Because of the way in which the system has been defined (no thermal flux, no hydrodynamic motion), the only possible sources of entropy production are the chemical reactions, the diffusion of molecules from one part of the system to another, and the orientation variations in each lamina within the surface layer. The variations in orientation are due to strong interactions between molecules or atoms belonging to the same lamina or to neighboring laminae.

We now define the degree of advancement introduced by De Donder (1922) [see Eq. (2.1) Chapter 2A] for all possible reactions (matter transport, i.e., passage of one or more components from one phase to another, chemical, and orientation reactions). We have

$$n_\gamma^\alpha - n_\gamma^{\alpha 0} = {}^{\alpha-1}\xi_\gamma{}^\alpha - {}^\alpha\xi_\gamma^{\alpha+1} + \sum_r v_{\gamma r}^\alpha \xi_r \tag{7.4}$$

$$\langle m_{x_{i\gamma}}^\alpha \rangle - \langle m_{x_{i\gamma}}^\alpha \rangle^0 = \xi_{x_{i\gamma}0}^\alpha \tag{7.5}$$

$$\langle m_{x_{i\gamma}}^{\alpha 2} \rangle - \langle m_{x_{i\gamma}}^{\alpha 2} \rangle^0 = \xi_{x_{i\gamma}Q}^\alpha, \tag{7.6}$$

where ${}^{\alpha-1}\xi_\gamma{}^\alpha$ and ${}^\alpha\xi_\gamma^{\alpha+1}$ are, respectively, the degrees of advancement of the transport reactions of constituent γ from phase $\alpha - 1$ to phase α and from α to $\alpha + 1$. The index r refers here to the chemical reactions, the superscript 0 to the time $t = 0$ (origin of ξ), and $\langle m_{x_{i\gamma}}^\alpha \rangle$ and $\langle m_{x_{i\gamma}}^{\alpha 2} \rangle$ are the orientation variables, i.e., the mean projection and the mean-square projection on the axes x_i ($i = 1, 2, 3$) of the dipole moment per mole of γ in the phase α. Let us remark that the distribution function of the orientation may be described by the six projections $\langle m_{x_i} \rangle$ and $\langle m_{x_i}^2 \rangle$ only if we assume the classical approximation of a Gaussian distribution. The degrees of orientation $\xi_{x_{i\gamma}0}^\alpha$ and $\xi_{x_{i\gamma}Q}^\alpha$ are defined by (7.5) and (7.6).

If the molecular orientation varies during the crossing from one lamina to another, then variables ${}^{\alpha-1}\xi_\gamma{}^\alpha$, $\xi_{x_{i\gamma}0}^\alpha$, and $\xi_{x_{i\gamma}Q}^\alpha$ vary together during the crossing.

Usually, in capillary theory, orientations and diffusions are treated as independent variables, i.e., the orientation and diffusion occur simultaneously. Here, we consider the case of independent variables. An

extension of De Donder's equation (2.1) Chapter 2A for all the possible reactions leads to

$$T \, d_i S = \sum_\varrho A_\varrho \, d\xi_\varrho + \sum_{\alpha \gamma i} A^\alpha_{x_{i\gamma}0} \, d\xi^\alpha_{x_{i\gamma}0} + \sum_{\alpha \gamma i} A^\alpha_{x_{i\gamma}Q} \, d\xi^\alpha_{x_{i\gamma}Q}, \qquad (7.7)$$

where the summation symbol $\sum_{\alpha \gamma i}$ represents the triple summation $\sum_\alpha \sum_\gamma \sum_{i=1}^3$. The coefficient A_ϱ is the chemical affinity of the reaction ϱ (i.e., passage and chemical reactions). The orientation affinities $A_{x_{i\gamma}0}$ and $A_{x_{i\gamma}Q}$ are related to dipole moments $\langle m^z_{x_{i\gamma}} \rangle$ and $\langle m^{z2}_{x_{i\gamma}} \rangle$.

From Eqs. (7.2), (7.3), (7.7) and from Chapter 2A Eqs. (1.7) and (1.18), we obtain

$$dF = -S \, dT - \sum_\alpha p_\varepsilon \, dV^\alpha + \gamma \, dA - \sum_\varrho A_\varrho \, d\xi_\varrho - \sum_{\alpha \gamma i} A^z_{x_{i\gamma}0} \, d\xi^z_{x_{i\gamma}0}$$

$$- \sum_{\alpha \gamma i} A^z_{x_{i\gamma}Q} \, d\xi^z_{x \gamma_i Q}. \qquad (7.8)$$

The free energy F can thus be expressed in terms of variables T, V^α, A, ξ_ϱ, $\xi^z_{x_{i\gamma}0}$, and $\xi^z_{x_{i\gamma}Q}$, where $\alpha = 1, 2, \ldots$; $\gamma = 1, 2, \ldots, c$; and $i = 1, 2, 3$. The derivatives of F with respect to one variable, all others remaining constant, have the form

$$\frac{\partial F}{\partial T} = -S, \qquad \frac{\partial F}{\partial V^z} = -p_\varepsilon, \qquad \frac{\partial F}{\partial A} = \gamma, \qquad \frac{\partial F}{\partial \xi_\varrho} = -A_\varrho \quad (7.9)$$

and

$$\frac{\partial F}{\partial \xi^z_{x_{i\gamma}0}} = -A^z_{x_{i\gamma}0}, \qquad \frac{\partial F}{\partial \xi^z_{x_{i\gamma}Q}} = -A^z_{x_{i\gamma}Q}. \qquad (7.10)$$

C. Thermodynamics of an Open Capillary System

The previous discussion leads to the conclusion that F is a function of the variables which determine the physicochemical state of the phases, the mode of repartition of the components among the phases, and their orientation within each phase,

$$F = F(T, V^\alpha, A, n_\gamma{}^\alpha, \langle m^z_{x_{i\gamma}} \rangle, \langle m^{z2}_{x_{i\gamma}} \rangle), \qquad (7.11)$$

where the symbol $n_\gamma{}^\alpha$ represents $n^{1\ldots\alpha}_{1\ldots\gamma}$, the number of moles of each component in each phase of the system. The same will be true for an open system. Let us remark now that the orientation variables are intensive. If the system is subjected to a transformation in which all $n_\gamma{}^\alpha$, $\langle m^z_{x_{i\gamma}} \rangle$,

and $\langle m_{z_{(j}}^{z2}\rangle$ remain constant, the free energy will vary in exactly the same way as it would in a closed system where all ξ are constant. The three first equations (7.9) can thus be written

$$S = -\left(\frac{\partial F}{\partial T}\right)_x$$

where subscript $x = V^z n_y{}^z A \langle m_{z_{(j}}^z\rangle \langle m_{z_{(j}}^{z2}\rangle$

$$p_e = -\left(\frac{\partial F}{\partial V^z}\right)_y \qquad (7.12)$$

where subscript $y = T n_y{}^z A \langle m_{z_{(j}}^z\rangle \langle m_{z_{(j}}^{z2}\rangle$

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_z$$

where subscript $z = TV^z n_y{}^z \langle m_{z_{(j}}^z\rangle \langle m_{z_{(j}}^{z2}\rangle$. On the other hand, if the system is subjected to a transformation in which only $\langle m_{z_{(j}}^z\rangle$ varies, the free energy will vary in exactly the same way as it would in a closed system where all ξ are constant except $\xi_{z_{(j}0}^z$. From (7.5), (7.6), and (7.10), we obtain

$$\frac{\partial F}{\partial \langle m_{z_{(j}}^z\rangle} = \frac{\partial F}{\partial \xi_{z_{(j}0}^z} = -A_{z_{(j}0}^z$$

$$\frac{\partial F}{\partial \langle m_{z_{(j}}^{z2}\rangle} = \frac{\partial F}{\partial \xi_{z_{(j}Q}^z} = -A_{z_{(j}Q}^z. \qquad (7.13)$$

Furthermore, we define the quantity

$$\mu_\gamma{}^z = \left(\frac{\partial F}{\partial n_\gamma{}^z}\right)_{z'} \qquad (7.14)$$

where subscript $z' = TV^z A n_{j}{}^\delta \langle m_{z_{(j}}^z\rangle \langle m_{z_{(j}}^{z2}\rangle$, as the chemical potential of component γ in the phase α for a state where the mean orientations have given values. When these mean orientations take their equilibrium values, the chemical potential reduces to the classical equation (4.18). A derivative in which only $n_\gamma{}^z$ varies means that component γ added to phase α takes the preexistent orientation in this phase. From (7.4), (7.9), and (7.14), we have

$$A_\varrho = -\sum_{z\gamma} \frac{\partial F}{\partial n_\gamma{}^z} \frac{\partial n_\gamma{}^z}{\partial \xi_\varrho} = -\sum \nu_\gamma{}^z \mu_\gamma{}^z. \qquad (7.15)$$

Equation (7.8) can thus be written

$$dF = -S \, dT - \sum_{\alpha} p_e \, dV^{\alpha} + \gamma \, dA + \sum_{\alpha\gamma} \mu_{\gamma}{}^{\alpha} \, dn_{\gamma}{}^{\alpha}$$

$$- \sum_{\alpha\gamma i} A^{\alpha}_{z_{i\gamma}0} \, d\langle m^{\alpha}_{z_{i\gamma}0} \rangle - \sum_{\alpha\gamma i} A^{\alpha}_{z_{i\gamma}Q} \, d\langle m^{\alpha 2}_{z_{i\gamma}Q} \rangle. \tag{7.16}$$

The Function F is a homogeneous function of first degree in the variables V^{α}, A, $n_{\gamma}{}^{\alpha}$, and thus, from Euler's equation

$$F = - \sum_{\alpha} p_e V^{\alpha} + \gamma A + \sum_{\alpha\gamma} n_{\gamma}{}^{\alpha} \mu_{\gamma}{}^{\alpha} \tag{7.17}$$

where the chemical potentials $\mu_{\gamma}{}^{\alpha}$ depend on the orientations [see Eq. (7.14)] and where the summation over α includes all the bulk of both phases I and II and all the surface layers.

By differentiation of this relation, and subtracting (7.16), we obtain

$$A \, d\gamma = -S \, dT + V \, dp_e - \sum_{\alpha\gamma} n_{\gamma}{}^{\alpha} \, d\mu_{\gamma}{}^{\alpha}$$

$$- \sum_{\alpha\gamma i} A^{\alpha}_{z_{i\gamma}0} \, d\langle m^{\alpha}_{z_{i\gamma}} \rangle - \sum_{\alpha\gamma i} A^{\alpha}_{z_{i\gamma}Q} \, d\langle m^{\alpha 2}_{z_{i\gamma}} \rangle. \tag{7.18}$$

The above proof does not assume the existence of equilibrium with respect to the distribution of components among the surface layers, but does assume mechanical and thermal equilibrium.

But if orientation phenomena are much slower than diffusion, we can reach a partial equilibrium state, and, for each component γ,

$$\mu_{\gamma}{}^{I} = \mu_{\gamma}{}^{\alpha} = \mu_{\gamma}{}^{II}, \tag{7.19}$$

although the orientation affinities are different from zero. The superscript to μ_{γ} may then be dropped.

From (7.18) and (7.19), we find, in the Gibbs model,

$$d\gamma = -s^a \, dT - \sum_{\gamma} \Gamma_{\gamma} \, d\mu_{\gamma} - \sum_{\alpha\gamma i} A^{*\alpha}_{z_{i\gamma}0} \, d\langle m^{\alpha}_{z_{i\gamma}} \rangle - \sum_{\alpha\gamma i} A^{*\alpha}_{z_{i\gamma}Q} \, d\langle m^{\alpha 2}_{z_{i\gamma}} \rangle, \tag{7.20}$$

where $A^{*\alpha}_{z_{i\gamma}} = A^{\alpha}_{z_{i\gamma}}/A$. This is an extension of the Gibbs equation to chemical systems where orientation reaches equilibrium a long time after the diffuse equilibrium. At the true equilibrium (diffusion and orientation), $A^{*\alpha}_{z_{i\gamma}0} = 0$ and $A^{*\alpha}_{z_{i\gamma}Q} = 0$ and (7.20) reduces to the classical equation (3.43).

Let us now suppose that we maintain a constant temperature, pressure, and composition of the bulk phase, i.e., $d\mu_\gamma = 0$. The evolution of the surface from a state of partial equilibrium (i.e., from a state where the orientation is not in equilibrium) would be given, with the aid of (7.20),

$$d\gamma = -\sum_{\alpha\gamma i} A^{\ast\alpha}_{z_{i\gamma}O}\, d\langle m^{\alpha}_{z_{i\gamma}}\rangle - \sum_{\alpha\gamma i} A^{\ast\alpha}_{z_{i\gamma}Q}\, d\langle m^{\alpha2}_{z_{i\gamma}}\rangle. \tag{7.21}$$

This formula implies that each μ_γ is constant during the transformation, i.e., that diffusion occurs quickly enough to ensure continually that the equality (7.19) holds, by balancing the influence of the change in orientation of the local μ_γ.

D. EXAMPLES

We consider a system in a real equilibrium state. A short perturbation (friction or motion laying down the molecules) is applied so as to avoid diffusion (in the bulk phase, the temperature, the pressure, and the composition are constant and we suppose all the μ_γ are uniform in the medium). Nevertheless, this perturbation is able to reverse the molecular orientation in certain laminae. When the perturbation cancels out, the system returns to equilibrium in agreement with (7.21). This case may be related to the viscosity flow of monomolecular solutions.

From the experimental point of view (Defay and Pétré, 1970), it is well known that the rate of adsorption of sebacic acid, azelaic acid, and diols at the interface air/aqueous solution is not only diffusion-controlled; a barrier of potential energy between the substrate and the surface phase, related to the orientation of the adsorbed molecule, has to be taken into account in considering the rate of evolution to the equilibrium state.

Now we suppose that only one component of the upper lamina orients itself at the interface. Equation (7.21) may then be rewritten

$$d\gamma = -\left[\sum_i A^{\ast}_{z_iO}\, d\langle m_{z_i}\rangle + \sum_i A^{\ast}_{z_iQ}\, d\langle m^2_{z_i}\rangle\right]. \tag{7.22}$$

Let us suppose that initially (out of equilibrium) one half of the unde-formable or rigid dipoles are directed vertically upward and the other half vertically downward, while, at equilibrium, all dipoles turn vertically downward. If the x_1 axis is perpendicular to the surface of the layer, the rigid moments $\langle m_{z_1}\rangle$ and $\langle m^2_{z_1}\rangle$ may be written as $m\langle\cos\beta_1\rangle$ and $m^2\langle\cos \times \beta_1\rangle$, where m is the arithmetic value of the dipole moment and $\cos\beta_1$

the direction cosine of a unit vector on the axes of a dipole in comparison with the vertical axis x_1. Furthermore, let us assume that $A_Q{}^*$ varies only slowly with $\langle m \rangle$ in such a way that contribution of the second integral $\int_1^1 A_Q{}^* \, d\langle m^2 \rangle$ can be neglected. Integrating (7.22) from $\langle \cos \beta_1 \rangle = 0$ to $\langle \cos \beta_1 \rangle = -1$ and $\langle \cos^2 \beta_1 \rangle = 1$ to $\langle \cos^2 \beta_1 \rangle = 1$, one then has

$$\langle A_0{}^* \rangle = \Delta \gamma / m, \qquad (7.23)$$

where $\langle A_0{}^* \rangle$ is the mean value of the surface orientation affinity in the integration and $\Delta \gamma$ the variation of the surface or interfacial tension due to the change of orientation.

If, by way of a perturbation, all the rigid dipoles are initially directed vertically upward and if, during equilibrium they turn downward, then, after integration, Eq. (7.22) becomes

$$\langle A_0{}^* \rangle = \Delta \gamma / 2m. \qquad (7.24)$$

A measurement of the surface tension for the two extreme positions of the orientations can give us a value of the mean affinity of orientation, as long as the dipoles are rigid and their moments are known.

Remarks. (1) If we assume that only one of variables $\xi_{z_0 0}^z$ varies, all others being kept constant in Eq. (7.8), and that, moreover, $\langle m_{z_1} \rangle$ varies from 0 to $-\langle m_{z_1} \rangle$ ($\langle \cos \beta \rangle$ varies from 0 to -1), we find

$$\Delta F = A \langle A_{z_{10}}^* \rangle \langle m_{z_1} \rangle. \qquad (7.25)$$

Putting (7.25) in (7.23), we get

$$\langle \Delta F \rangle = A \, \Delta \gamma. \qquad (7.26)$$

(2) It is easy to compare now the mean affinity $\langle A_0{}^* \rangle / \Gamma$ with $RT / \langle m \rangle$, where Γ is the number of moles per cm^2. At 15°C, $RT \simeq 2.3 \times 10^{10}$ ergs mol^{-1}. Let us choose, for example, a binary liquid whose surface is covered by 10^{-10} mol cm^{-2} of the surfactants. We suppose now that, if one half of the surface molecules of the surfactants are turning, the experimental value of $\Delta \gamma$ is 5 dyn cm^{-1}. Since the variation of the mean affinity per mole is only due to the surfactant in the upper lamina (we exclude the variation of the other component), it is easy to see from Eq. (7.23) that $\langle A_0{}^* \rangle / \Gamma$ is of order of magnitude $2.2 RT / \langle m \rangle$.

(3) The influence of orientation terms on the Lippmann electro-capillary equation has recently been studied (Sanfeld, 1968).

VIII. Capillary Condensation

A. THE BUBBLE

In order to interpretate the condensation of a vapor in the pores of a solid and thus the capillary condensation, we shall first treat the problem of the bubble.

Let us combine Eqs. (1.10) and (1.12) in such a way that

$$\delta\left(\frac{2\gamma}{r}\right) = \frac{v^l - v^v}{v^l}\,\delta p^v. \tag{8.1}$$

Then we neglect the molar volume of the liquid v^l compared with v^v and assume that the vapor behaves as a perfect gas. Equation (8.1) then becomes

$$\delta\left(\frac{2\gamma}{r}\right) = -\frac{RT}{v^l}\frac{\delta p^v}{p^v}. \tag{8.2}$$

On integrating (8.2) assuming v^l is constant, we obtain

$$\ln\frac{p^v}{p^0} = -\frac{2\gamma}{r}\frac{v^l}{RT}, \tag{8.3}$$

where p^0 is the normal vapor pressure (vapor pressure corresponding to a plane surface). Thus, the larger the curvature of the bubble, the smaller is the vapor pressure p^v. This equation explains the low vapor pressure exhibited by a liquid held in a porous solid whose walls are wetted by the liquid. When the pores are very small, then the liquid is separated from its vapor by a concave meniscus of small radius of curvature. Equation (8.3) also explains the superheating of liquids above the normal boiling point. Thus, for a bubble of vapor to form in water subjected to a pressure of 1 atm, it is necessary, because of the Laplace equation (1.7), for the pressure in the interior of the bubble to be greater than 1 atm. However, while the vapor pressure of a plane surface of water at 100°C is 1 atm, that of a concave surface will be less. Consequently, no bubbles can exist at 100°C and it is necessary to heat the water to above 100°C to achieve boiling. Powders or other impurities which favor the formation of large bubbles diminish the degree of superheating.

B. CAPILLARY CONDENSATION

The Kelvin equation (8.3) provides a ready interpretation of the condensation of a vapor in the pores of a solid. We consider the idealized

problem in which all the pores are supposed to be cylinders of the same radius r. We suppose that the pores are partially filled with a liquid in contact with its own vapor (Fig. 14) and assume furthermore that the walls of the pores are completely wetted by the liquid. So long as the menisci are away from the mouths of the pores, all the menisci will have hemispherical surfaces of radius r. The vapor pressure of the liquid in the pores is given by (8.3); this value, denoted by p_r^v, is less than the normal vapor pressure p^0. Consequently, liquid can exist in a porous medium in equilibrium with unsaturated vapor. If the vapor pressure is increased slightly, condensation will occur in all pores in which the
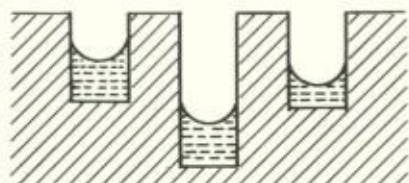

FIG. 14.   Condensation in capillary pores of uniform size.

meniscus has not yet reached the mouth of the pore. In pores where the meniscus has reached the mouth of the pore, further condensation would result in an increase in radius of curvature of the surface (Fig. 15); condensation in this pore therefore ceases when the radius of curvature reaches the equilibrium value corresponding to the pressure p^v ($>p_r^v$) which is being maintained in the vapor. Thus, condensation will proceed in the partially filled pores, and be halted in the filled pores, until a point is reached at which all the pores are similarly filled and the liquid in them has everywhere the radius of curvature corresponding to p^v. Further increase in p^v results in condensation in all the pores and the flattening of the menisci, which become plane when $p^v = p^0$. The vapor
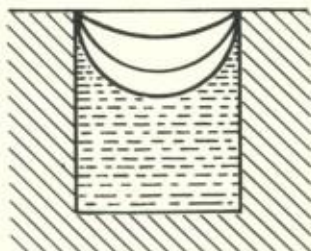

FIG. 15.   Variation of curvature of meniscus in a nearly filled pore approaching saturated vapor pressure.

is now saturated and any further increase in p^v is immediately offset by condensation of bulk liquid.

Thus, when an evacuated porous solid, in which all the pores are of equal size, is exposed to a vapor whose pressure is steadily increased, the following phenomena are to be expected (cf. Fig. 16). First, from O to A, vapor will be adsorbed by the whole solid surface. The shape of this curve may be explained in general terms by the theory of Brunauer et al. (1938) (see also Brunauer (1944)) in which it is supposed that the vapor forms, in succession, several adsorbed layers on the solid.
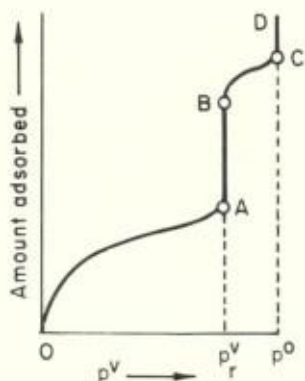

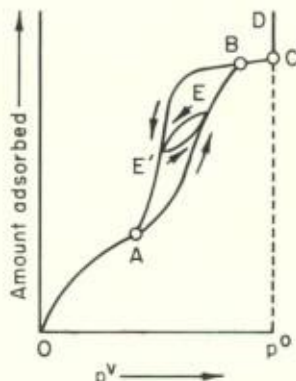FIG. 16. Isotherm for adsorption of vapor by an ideal porous body.

FIG. 17. Isotherm for adsorption of vapor by real porous body.

At A, capillary condensation commences, and the amount of liquid adsorbed increases at constant $p^v = p_r{}^v$ up to the point at which all the pores are just filled (B). Between B and C, further condensation causes the menisci to flatten until, at C, they are plane, the vapor is saturated, and condensation of bulk liquid can take place.

Real solids clearly do not have pores of the same size. Small pores will fill first and the largest will not begin to fill until the menisci in the smallest pores have already begun to flatten. It is for this reason that, for real solids (Fig. 17), the ideal vertical section AB becomes the oblique section AEB.

Furthermore, real solids are not always perfectly wetted, and their wettability may depend on various circumstances, such as the presence of an adsorbed layer of inert gas other than the vapor being studied. This problem has been developed in an exhaustive way by many authors (de Boer, 1953; Defay et al., 1966).

IX. Surface Tensions of Crystals

The surface tension, regarded as a mechanical force, poses some very complicated problems in the case of solids. In particular, its direct measurement is impossible except in special circumstances in which the molecules of the solid have a certain mobility, as, for example, in metals at temperatures very close to their melting points.

But, generally, if a rectangular crystalline sheet is stretched by a force applied to two of its sides, it is clear that the tensor in the sheet is anisotropic.
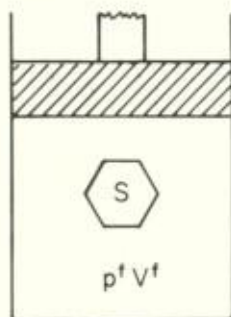

FIG. 18.   Equilibrium of a crystal immersed in a fluid (superscript f) (liquid or vapor).

Nevertheless, the growth of a crystal face is possible by deposition of fluid molecules on its faces. The external mechanical work received by the system is

$$d\tau = -p^f\, dV^f - p^s\, dV^s + \sum_\beta \gamma^\beta\, dA^\beta, \tag{9.1}$$

where the quantities $\gamma^1, \gamma^2, \ldots, \gamma^\beta$ are the surface tensions, respectively, of phases $1, 2, \ldots, \beta$, and the superscript f indicates fluid. As the work $d\tau$ is equal to the work done by the piston on the fluid (Fig. 18)

$$d\tau = -p^f\, dV = -p^f(dV^f + dV^s) = -p^f\, dV^f - p^s\, dV^s + (p^s - p^f)\, dV^s, \tag{9.2}$$

where we suppose the existence of a pressure p^s within the crystal far from the surface regions. For some internal point O, we draw a line h^β normal to each face β (Fig. 19). The change in volume is, to the first order in small quantities, equal to
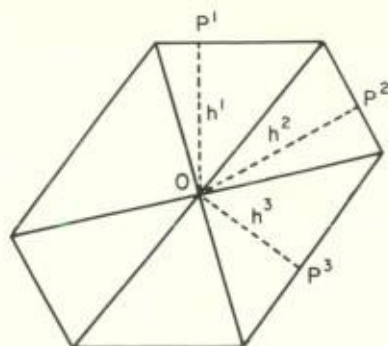
$$dV^s = \sum_\beta A^\beta\, dh^\beta. \tag{9.3}$$

FIG. 19. Geometrical variables defining the size and shape of a crystal.

Furthermore,

$$V^s = \sum_\beta \tfrac{1}{3} A^\beta h^\beta; \tag{9.4}$$

thus

$$dV^s = \tfrac{1}{3} \sum_\beta A^\beta \, dh^\beta + \tfrac{1}{3} \sum_\beta h^\beta \, dA^\beta. \tag{9.5}$$

From (9.2), (9.3), and (9.5), we obtain

$$d\tau = -p^t \, dV^t - p^s \, dV^s + \sum_\beta (p^s - p^t)\tfrac{1}{2}h^\beta \, dA^\beta. \tag{9.6}$$

By comparison of (9.6) and (9.1), we may assume that

$$\gamma^\beta = \tfrac{1}{2}(p^s - p^t)h^\beta. \tag{9.7}$$

Thus, one possible equilibrium form of a crystal is that for which

$$\frac{\gamma^1}{h^1} = \frac{\gamma^2}{h^2} = \cdots \frac{\gamma^\beta}{h^\beta}. \tag{9.8}$$

This form, in which the distance of each face from O is proportional to the surface tension of that face, is called the Wulff form, and the set of relationship (9.8) are called Gibbs–Wulff relations.

The concept of an isotropic pressure p^s in the interior of a crystal is self consistent provided that those faces for which the tensions are larger, are the most remote from the point O. In every crystal which is in the equilibrium form, there exists a point O such that the Wulff relations are satisfied.

Let us remark that (9.7) has a form like Laplace's equation. Moreover, if, in the demonstration of the Kelvin relations, (1.13), we use (9.7) in place of (1.8), we find the vapor pressure of a Wulff crystal

$$\ln \frac{p^t}{p^0} = \frac{v^1}{RT} \frac{2\gamma^\beta}{h^\beta}. \tag{9.9}$$

Small crystals have a larger vapor pressure than big ones. In the same vapor, big crystals grow while the small ones vanish. In the same way, in a liquid phase, small crystals are more soluble and disappear, to the benefit of big ones.

Remark. The surface tension of crystals and the thermodynamics of deformed elastic bodies have been studied in a more exhaustive way by many authors (see, for example, Gibbs (1928), Rice (1936), Herring (1953), Ghez (1968), Defay *et al.* (1966)).

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