

11

Surfaces

Beauty is only skin deep.

Proverb

The surface of a phase has a different environment than its bulk. Surface tension is a measure of the work that must be done to increase the surface area of a phase. For curved surfaces, pressure is higher on the concave side of the surface than on the convex side. As a result, liquids rise in capillaries that they wet and the vapor pressure of droplets is greater than that of flat surfaces. The contact angle between condensed phases depends on the attractive interactions at their interface. When these interactions are large, there will be spreading (of a liquid over a solid) or mixing (of two liquids). Surface excess concentration measures how a solute concentrates at the surface of a solution. Positive excess concentration lowers the surface tension of the solvent. Substances that strongly concentrate at an interface are called surfactants. Gases can chemisorb or physisorb on solids. The Langmuir isotherm describes adsorption of a monolayer on a surface, whereas the Brunauer, Emmet, and Tetter (BET) isotherm describes multi-layer adsorption. The latter can be used to estimate the surface area of a solid. Statistical mechanics can be used to calculate thermodynamic properties of adsorption and treat gas-surface

equilibria. Colloids are comprised of particles containing 10^5 – 10^9 atoms. Their properties are dominated by surface effects.

11.1 The Surface Region

So far, we have considered only homogeneous phases of matter, where concentrations and other properties are uniform throughout the phase. The surface of a phase or, more exactly, the *interfacial region*, extending a few molecular diameters from the surface, is clearly different from the bulk of the phase. Energies and concentrations (for multicomponent phases) may vary in this region. Molecules in the interfacial region experience reduced interactions with other molecules in the phase and may begin to interact with molecules in the adjacent phase.

Because systems usually interact with their surroundings only at their surface, the properties of the surface assume an importance disproportionate to the fraction of molecules in this region. The interfacial region is so small that it makes a negligible contribution to the bulk properties of the phase, unless the phase is composed of very small particles. Conversely, for those properties which depend on the surface (e.g., adhesion, wetting, foam formation, etc.), very small additions of materials can result in very large effects, if the added substance concentrates at the surface. Changing surface concentrations can, therefore, often be a very cost-effective way of modifying the properties of materials.

11.2 The Surface of the Single-Component Condensed Phase

In thermodynamics, we focus on the most important variables needed to describe a system. Although we are interested in the size of a system (or of a phase), we usually do not concern ourselves with the shape of the system. One way in which the shape of a system does influence its thermodynamic properties is through its surface area. The surface of a phase is a different environment than its bulk region. Molecules on the surface of a material do not experience attractive interactions to other molecules in all directions and, therefore, have higher energy than molecules in the bulk of the material. Energy is increased when the surface area of a condensed system (usually a liquid) is increased at constant volume and temperature. Because the Helmholtz free energy has T and V as its natural variables, we can immediately write

$$dA = \left(\frac{\partial A}{\partial T} \right)_{V, \sigma} dT + \left(\frac{\partial A}{\partial V} \right)_{T, \sigma} dV + \left(\frac{\partial A}{\partial \sigma} \right)_{T, V} d\sigma = -S dT - P dV + \gamma d\sigma \quad (1)$$

where the intensive variable γ is called the *surface tension* of the condensed phase. We are more likely to deal with condensed phases in air or in the presence of their vapors, rather than in vacuum. In such cases, to be exact, we should employ properties such as γ_{LG} or γ_{LV} , the liquid–air or liquid–vapor interfacial tensions in Eq. (1). However, at usual laboratory pressures, gas density is so low that these quantities are independent of the nature of the gas and the use of just γ , the surface tension of the condensed phase, is appropriate. We define partial derivatives of thermodynamic properties with respect to surface area, with volume and temperature constant, as the surface thermodynamic property (written lowercase, with superscript σ), so that

$$\gamma \equiv \left(\frac{\partial A}{\partial \sigma} \right)_{T,V} \equiv a^\sigma \quad (2)$$

that is, the surface tension is the surface Helmholtz free energy. We can also write

$$dU = d(A + TS) = T dS - P dV + \gamma d\sigma \quad (3)$$

showing that $\gamma = (\partial U / \partial \sigma)_{S,V}$.

Because $\gamma d\sigma$ is an additional work term, using Eqs. (39) and (40) of [Chapter 4](#), we define the enthalpy and Gibbs free energy as

$$H = U + PV - \gamma \sigma \quad (4)$$

and

$$G = U - TS + PV - \gamma \sigma. \quad (5)$$

The differential forms of these equations are

$$dH = T dS + V dP - \sigma d\gamma \quad (6)$$

and

$$dG = V dP - S dT - \sigma d\gamma \quad (7)$$

With these definitions, the natural variables for the Gibbs free energy (P , T , and γ) are all intensive functions.

A useful Maxwell relation can be derived from Eq. (1)¹

$$\left(\frac{\partial S}{\partial \sigma} \right)_{V,T} \equiv s^\sigma = - \left(\frac{\partial \gamma}{\partial T} \right)_{V,\sigma} \quad (8)$$

where s^σ is the surface entropy. Because $U = A + TS$,

$$\left(\frac{\partial U}{\partial \sigma} \right)_{V,T} \equiv u^\sigma = \left(\frac{\partial A}{\partial \sigma} \right)_{V,T} + T \left(\frac{\partial S}{\partial \sigma} \right)_{V,T} = \gamma - T \left(\frac{\partial \gamma}{\partial T} \right)_{V,\sigma} \quad (9)$$

where u^σ is the surface energy.

Even though it is not the Gibbs or Helmholtz free energy, it is useful to consider the F function, $F \equiv U + PV - TS$, with differential

$$dF = V dP - S dT + \gamma d\sigma \quad (10)$$

This gives Maxwell relations

$$\left(\frac{\partial S}{\partial \sigma}\right)_{P,T} = -\left(\frac{\partial \gamma}{\partial T}\right)_{P,\sigma} \quad \text{and} \quad \left(\frac{\partial V}{\partial \sigma}\right)_{P,T} = \left(\frac{\partial \gamma}{\partial P}\right)_{\sigma,T} \quad (11)$$

To the degree that a single phase of one component has only two degrees of freedom, $(\partial V/\partial \sigma)_{P,T}$ is zero. Even with highly accurate measurements, we expect this quantity and, from Eq. (11), the pressure dependence of the surface tension to be very small.

Note also that

$$\gamma = \left(\frac{\partial F}{\partial \sigma}\right)_{P,T} \quad (12)$$

We can also write

$$\left(\frac{\partial U}{\partial \sigma}\right)_{P,T} = \left(\frac{\partial F}{\partial \sigma}\right)_{P,T} + T\left(\frac{\partial S}{\partial \sigma}\right)_{P,T} - P\left(\frac{\partial V}{\partial \sigma}\right)_{P,T} \quad (13)$$

Dropping the very small last term and using Eq. (11), we get

$$\left(\frac{\partial U}{\partial \sigma}\right)_{P,T} = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_{P,T} \quad (14)$$

which is analogous to Eq. (9).

11.3 Surface Tension of Single Components

Because intermolecular interactions of surface molecules are intermediate between those in the vapor and those in the bulk, we can expect surface tensions to be roughly proportional to energies of vaporization at the same temperature. Water is one of the exceptions to this rule. It has a particularly large value of γ , due to surface molecules being much less hydrogen-bonded than molecules in the bulk. The surface tensions of some common liquids is given in [Table 1](#). These values are measured in air, saturated with vapor at 1.0 atm total pressure.

One of the greatest difficulties in making surface tension measurements is ensuring the purity of the substance studied. Minute amounts of impurity, by concentrating at the surface, can make an appreciable difference in measured surface properties. Small amounts of reactive or condensable impurities in the gas phase can also greatly influence measured surface tensions.

TABLE 1 Surface Tension of Liquids at 298 K

Liquid	γ (10^{-3} J/m ²)	$d\gamma/dT$ (10^{-3} J/m ² K)
Ethyl alcohol	22.7	
Water	72.7	-0.15
<i>n</i> -Hexane	18.4	-0.10

Surface tensions of liquids decrease with increasing temperature and must equal zero at the critical temperature, where there is no longer a difference between the liquid and gaseous phase.² As a result, the temperature dependence of the surface tension is often expressed by the following empirical equation:

$$\gamma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^n \quad (15)$$

A value of $n = 1$ is often employed, although Guggenheim has found $n = 11/9$ gives a better fit for organic liquids.

Equations (8) and (15) indicate that the surface entropy of liquids is positive. This is because extending the surface creates an additional environment into which molecules can partition. When, in Eq. (15), $n = 1$ is employed, the surface energy is independent of temperature (problem 3). In practice, this is found not to hold when approaching the critical temperature, where the surface energy is also found to approach zero.

There is no reason to expect that as the dimensions of a phase are reduced to the point where it contains a small number of molecules, its surface tension remains constant. This question has obvious relevance to important problems, such as condensation of droplets from supersaturated vapors. Although a number of authors have considered this problem, in these days of supercomputers, it is probably best handled by considering individual intermolecular interactions rather than a bulk property, such as surface tension.

Solids also have “surface tension” because molecules on the surface of a solid particle are subject to fewer attractive forces than molecules in the bulk of the solid. Measurements of the surface tension of solids (usually called the surface energy) are difficult because solids are rarely pure and smooth on the molecular scale.

As shown in Example 1, surface effects only contribute appreciably to thermodynamic quantities for very small particles. This is because relatively few of the molecules of a macroscopic sample lie close enough to the surface to experience interactions noticeably different from those in the interior.

Example 1. For what diameter droplet size does the extra energy of surface molecules become 1% of the bulk cohesive energy of *n*-hexane at 298 K? For hexane, $\rho = 0.66 \text{ g/mL}$ and $\Delta_{\text{vap}}H = 31.9 \text{ kJ/mol}$.

Solution: The extra energy of surface molecules per mole equals $u^\sigma \sigma_m$, where σ_m is the surface area per mole:

$$\begin{aligned}\mu^\sigma &= \gamma - T \frac{d\gamma}{dT} = 18.4 \times 10^{-3} + 298(0.1 \times 10^{-3}) \\ &= 48.2 \times 10^{-3} \text{ J/m}^2\end{aligned}$$

Taking the energy of vaporization of *n*-hexane,

$$\Delta_{\text{vap}}U = \Delta_{\text{vap}}H - RT = 31,900 - 8.314(298) = 29,400 \text{ J/mol},$$

as a measure of its cohesive energy, the molar area of σ_m required to give this energy is determined by

$$48.2 \times 10^{-3} \frac{\text{J}}{\text{m}^2} \sigma_m = 0.01 \left(\frac{29,400 \text{ J}}{\text{mol}} \right) \quad \text{or} \quad \sigma_m = 7000 \frac{\text{m}^2}{\text{mol}}$$

The surface-to-volume ratio is

$$\begin{aligned}4\pi r^2 / 4\pi r^3 / 3 &= 3/r \\ &= \frac{7000 \text{ m}^2}{\text{mol}} \frac{\text{mol}}{86 \text{ g}} \frac{0.66 \text{ g}}{\text{mL}} \frac{10^6 \text{ mL}}{\text{m}^3} \\ &= 5.4 \times 10^7 \text{ m}^{-1} \\ d = 2r &= 1.1 \times 10^{-7} \text{ m}\end{aligned}$$

11.4 Processes Involving One Interface

Even though surface effects may not be an appreciable contribution to total energy, there are phenomena for which they are dominant and which permit the surface tension to be measured.

11.4.1 Stretching of a Film

Consider a film of liquid on a wire balance as shown in [Fig. 1](#). A force is applied to a frictionless, movable wire, stretching the film, which adheres to the wire. The process occurs at constant temperature and volume of the liquid. The reversible work done as the movable wire moves a distance dx (at constant T and V) is equal to the increase in the Helmholtz free energy of the system:

$$\delta w_{\text{rev}} = f dx = dA = \gamma d\sigma = 2L\gamma dx \quad (16)$$

where the factor of 2 comes from the film having two sides. The surface tension can therefore be measured with such a balance as $\gamma = f/2L$. f is the force

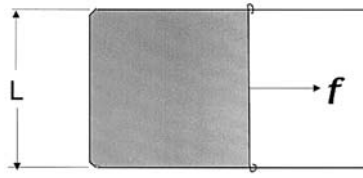


Figure 1 Wire balance for stretching a liquid film.

required to keep the movable wire at equilibrium. It is useful to also think of the surface tension as the force per unit length, directed parallel to the surface, which “pulls” to reduce the surface area (hence, “tension”). An oppositely directed force must be applied to keep the surface from contracting. In the absence of surface tension, zero force would be required to move the frictionless wire.

11.4.2 Falling Droplet

Water dripping from a tube will form a droplet supported by surface tension at the tube–water boundary, until the surface tension force can no longer support the droplet. Just before the droplet falls, as shown in Fig. 2, the gravitational force on the droplet is balanced by the surface tension force at the edge of the tube:

$$\gamma \pi d = mg \quad (17)$$

With suitable calibration, this phenomenon can be used to measure surface tension.



Figure 2 Falling droplet.

11.4.3 Cavities in Liquids

A cavity in a liquid filled with an insoluble gas will attain an equilibrium radius, where the pressure in the cavity is larger than that in the liquid. To see this, consider Fig. 3.

We imagine a slight increase, dr , in the radius of a cavity in a liquid. The system is the constant volume of a liquid between the cavity and an outer boundary whose radius increases as the cavity volume increases. The system is held at constant temperature, and because it has constant volume, Eq. (1) becomes

$$dA = \gamma d\sigma \quad (18)$$

If the system is at equilibrium, dA is the net work that must be done on the system for the change in r . This is (because $dV_l = 0$)

$$dA = \gamma d\sigma = -P_l dV_g + P_g dV_g \quad (19)$$

or

$$P_g - P_l = \gamma \left(\frac{d\sigma}{dV_g} \right) \quad (20)$$

For a spherical cavity, $\sigma = 4\pi r^2$, $d\sigma = 8\pi r dr$, $V = \frac{4}{3}\pi r^3$, and $dV = 4\pi r^2 dr$. Therefore, $d\sigma/dV_g = 2/r$, and

$$P_g - P_l = \frac{2\gamma}{r} \quad (21)$$

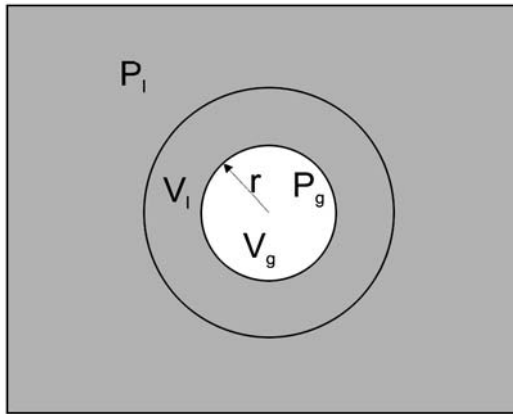


Figure 3 Cavity in a liquid.

This is for a spherical cavity. For a cavity with two principle radii of curvature, r_1 and r_2 , Eq. (21) becomes³

$$P_g - P_l = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (22)$$

This is known as the equation of Young and Laplace.

For water, with a surface tension of 73 mJ/m², Eq. (21) gives $P_g - P_l = 0.0015$ bar for a 1-mm-radius cavity and 1.5 bar for a 1- μ m cavity (a very large pressure difference indeed!). Note that the surface acts like a membrane under tension, increasing the pressure on the concave side of the membrane. For a bubble, as shown in Fig. 4, there are two surfaces acting as membranes to increase the pressure of the gas inside the bubble over ambient pressure. The inside to outside pressure difference is thus twice that of Eq. (21):

$$P_{\text{in}} - P_{\text{out}} = \frac{4\gamma}{r} \quad (23)$$

11.5 Processes Involving More Than One Interface

11.5.1 Contact Angle and Spreading

When three phases are coexisting along an edge, we have three interfacial tensions. Assuming that one of the three phases is a gas (or a vapor), we will write these as γ_α , γ_β , and $\gamma_{\alpha\beta}$. The edge of the mobile α phase is at equilibrium under the tensions directed along the three interfaces. Equating the horizontal components of the forces in Fig. 5, we have

$$\gamma_\beta = \gamma_{\alpha\beta} + \gamma_\alpha \cos \theta \quad (24)$$

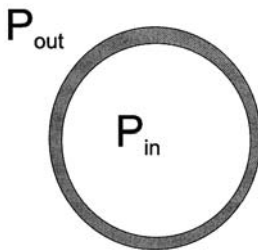


Figure 4 Pressure difference in a bubble.

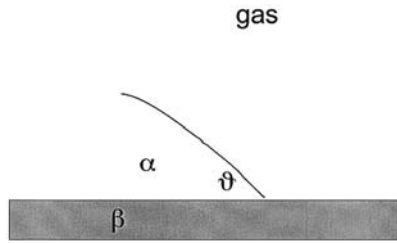


Figure 5 Interface among three phases.

or

$$\cos \theta = \frac{\gamma_{\beta} - \gamma_{\alpha\beta}}{\gamma_{\alpha}} \quad (25)$$

θ is called the (equilibrium) *contact angle*; $\cos \theta > 1$ represents a non-equilibrium situation and occurs if

$$\gamma_{\beta} - \gamma_{\alpha\beta} > \gamma_{\alpha} \quad (26)$$

or

$$\gamma_{\alpha} + \gamma_{\beta} - \gamma_{\alpha\beta} > 2\gamma_{\alpha} \quad (27)$$

$2\gamma_{\alpha}$ is called the *cohesive energy*, w_{coh}^{α} , of the α phase. It is the energy required to separate the α phase and produce two α -vapor interfaces. $\gamma_{\alpha} + \gamma_{\beta} - \gamma_{\alpha\beta}$ is called the *adhesive energy*, $w_{\text{adh}}^{\alpha\beta}$, of the α - β interface. It is the energy required to separate the α - β interface into separate α and β interfaces. We define the *spreading coefficient*, $S^{\alpha\beta}$, as

$$S^{\alpha\beta} \equiv \gamma_{\beta} - \gamma_{\alpha} - \gamma_{\alpha\beta} = w_{\text{adh}}^{\alpha\beta} - w_{\text{coh}}^{\alpha} \quad (28)$$

If $S^{\alpha\beta} > 0$, in the horizontal case, the liquid α will spread over the surface β . If β is a solid, α will completely wet it and enter its pores. This is called *complete wetting*, and is very useful (e.g., if we are using α to lubricate β). If the surface is not horizontal, the liquid will rise until the additional force of gravity balances the forces on the liquid edge. If β is also a liquid, α and β will mix and become a solution.

11.5.2 Wilhelmy Plate

When a plate is partially immersed in a liquid, the liquid adheres to the plate with contact angle θ , as shown in Fig. 6.

In order to suspend the plate in the liquid, the external force must balance the surface tension forces in addition to the gravitational and buoyancy forces on

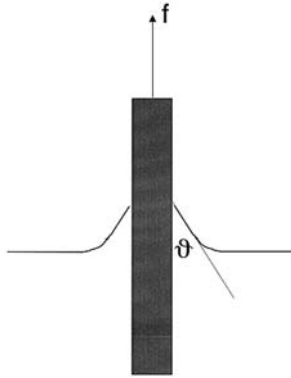


Figure 6 Plate suspended in a liquid.

the plate. Surface tension forces are exerted on the plate at the solid–liquid and solid–gas interfaces. The net downward surface tension force is

$$f_{st} = C(\gamma_{SG} - \gamma_{SL}) \quad (29)$$

where C is the circumference of the plate. Note that the direction of these forces on the plate are opposite to their directions on the mobile liquid interface. From Eq. (25),

$$f_{st} = C\gamma_{LG} \cos \theta \quad (30)$$

When the surface of the liquid is drawn up on the solid, we say that the liquid “wets” the solid. This results from a substantial attraction between the liquid and the surface of the solid, which is indicated by a small value γ_{SL} , the solid–liquid surface tension, and a large downward net surface tension force. A device that measures the force on a plate, such as shown in Fig. 6, is called a Wilhelmy balance.

11.5.3 Capillary Rise

Because the pressure is lower on the convex side of an interface, liquids will rise up in small tubes (capillaries), whose surface they “wet”, with *contact angle* θ less than 90° , as shown in Fig. 7.

In the open capillary tube shown, the pressure in the gas phase at a and b are the same. Just below a in the liquid, we are on the convex side of the interface, so the pressure is lower by Eq. (21). At the bottom of the tube, the pressure must

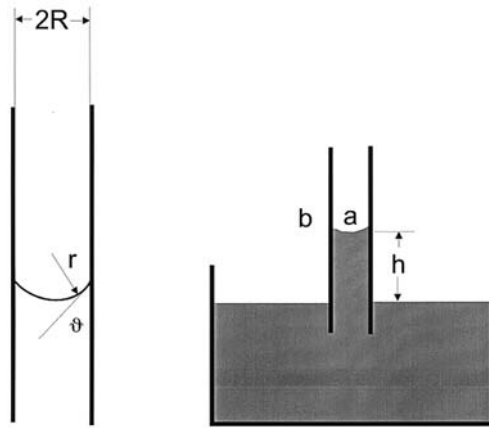


Figure 7 Capillary rise.

be the same inside and outside the tube, and so the liquid in the tube must rise a distance h , with

$$\frac{2\gamma}{r} = \rho gh \quad (31)$$

where ρ is the density of the liquid and r is the radius of curvature of the liquid interface. In the case of *perfect wetting*, when the adhesive energy between the liquid and the tube is greater than the cohesive energy of the liquid, the contact angle $\theta = 0^\circ$ and the radius of curvature of the liquid surface, r , becomes equal to the radius of the tube, R . In this case, the capillary rise is

$$h = \frac{2\gamma}{\rho g R} \quad (32)$$

Capillary rise is responsible for water being drawn into a sponge or a cloth. When the cloth is coated with a waterproofing material, such as silicone, the adhesive forces are reduced, the contact angle is greater than 90° , and there is no longer a tendency for water to be drawn into the cloth.

Example 2. What pressure above atmospheric must be applied in a 1.0-mm-diameter tube placed just below the surface of water at 25°C , in order to blow a bubble. (Assume perfect wetting of the tube.)

Solution: The excess pressure applied must be sufficient to counteract the tendency of water to rise in the tube plus that needed to form a cavity in the water.

$$\Delta P = \rho gh + \frac{2\gamma}{R} = \frac{4\gamma}{R} \quad [\text{using Eq. (31) for perfect wetting}]$$

$$\Delta P = \frac{4 \mid 72.7 \times 10^{-3} \text{ J/m}^2}{5 \times 10^{-4} \text{ m}} = 5.8 \times 10^2 \text{ Pa} = 4.3 \text{ torr}$$

11.6 Thermodynamics of Immersion

Heat is evolved when a finely divided solid is immersed in a liquid. At constant temperature, this heat can be taken as $\Delta_{\text{im}}U$ for the process. Writing $\Delta_{\text{im}}U$ for the formation of unit area of surface, we have

$$\Delta_{\text{im}}U = u_{\text{SL}}^\sigma - u_S^\sigma \quad (33)$$

Note that there are no internal surfaces in the liquid before immersion. Substituting Eq. (9) gives

$$\Delta_{\text{im}}U = \left[\gamma_{\text{SL}} - T \left(\frac{\partial \gamma_{\text{SL}}}{\partial T} \right)_{\nu, \sigma} \right] - \left[\gamma_S - T \left(\frac{\partial \gamma_S}{\partial T} \right)_{\nu, \sigma} \right] \quad (34)$$

Applying Eq. (25),

$$\Delta_{\text{im}}U = T \left(\frac{\partial(\gamma_L \cos \theta)}{\partial T} \right)_{\nu, \sigma} - \gamma_L \cos \theta \quad (35)$$

In order to obtain measurable heats of immersions, it is necessary to work with powdered solids with very small particle size.

11.7 Effect of Surface Curvature on Vapor Pressure

In this section, we will derive the vapor pressure of a spherical droplet of radius r . This vapor pressure is greater than that of a flat surface because the liquid is on the concave side of the surface and is thus at a higher pressure than the surroundings. As we saw in Eq. (61) of [Chapter 6](#), a higher pressure increases the escaping tendency of a condensed phase. The effect of surface curvature is only appreciable for very small droplets.

From Eq. (21), we have

$$dP_{\text{liq}} = -\frac{2\gamma}{r^2} dr \quad (36)$$

which gives a change of the chemical potential of the liquid of

$$d\mu_{\text{liq}} = V_m dP_{\text{liq}} = -\frac{2\gamma V_m}{r^2} dr \quad (37)$$

Equating this to the chemical potential of the vapor,

$$d\mu_g = RT \frac{dP}{P} = -2\gamma V_m \frac{dr}{r^2} \quad (38)$$

Integrating from an infinite radius, where the vapor pressure is P_∞ ,

$$\ln\left(\frac{P}{P_\infty}\right) = \frac{2\gamma V_m}{RT} = \frac{2\gamma M}{RT\rho r} \quad (39)$$

In the last step, we have written the molar volume in terms of the molecular weight and liquid density.

Example 3. At 25°C the surface tension of water is $73 \times 10^{-3} \text{ J/m}^2$ and its vapor pressure is 23.76 torr. What is the vapor pressure at 25°C of water droplets of radius 1.0 μm ? of radius 10 nm?

Solution:

For 1.0 $\mu\text{m} = 10^{-6} \text{ m}$:

$$\begin{aligned} \ln\left(\frac{P(10^{-6} \text{ m})}{P(r = \infty)}\right) &= \frac{2(72.0 \times 10^{-3} \text{ J/m}^2)(0.018 \text{ kg/mol})}{(10^3 \text{ kg/m}^3)(10^{-6} \text{ m})(8.314 \text{ J/mol K})(298 \text{ K})} \\ &= 0.00104 \\ P(10^{-6} \text{ m}) &= (23.76 \text{ torr}) \times \exp(0.00104) \\ &= (23.76 \text{ torr})(1.00104) = 23.78 \text{ torr} \end{aligned}$$

For 10 nm = 10^{-8} m :

$$\begin{aligned} \ln\left(\frac{P(10^{-8} \text{ m})}{P(r = \infty)}\right) &= 0.104(26.36 \text{ torr}) \\ P(10^{-8} \text{ m}) &= (23.76 \text{ torr})[\exp(0.104)] = 26.36 \text{ torr} \end{aligned}$$

The higher vapor pressure of very small droplets allows air to achieve a considerable *supersaturation* (partial pressure of water in air greater than the vapor pressure of water) before liquid droplets begin to form. In fact, most cloud droplets form on *nucleation centers*, which may be dust particles or minute droplets of sulfuric or nitric acid. Cloud seeding involves adding nucleation centers (usually iodide salts), in an attempt to encourage precipitation from supersaturated air.

Another consequence of the effect of surface area on vapor pressure is that large regions of liquids will grow at the expense of small droplets. Also, in

establishing the liquid–vapor equilibrium, the vapor will condense on flat surfaces or on large droplets of liquid, rather than form new microdroplets.

11.8 Thermodynamics of Solution Surfaces

We have defined solutions as homogeneous phases, with uniform concentrations throughout. Clearly, the surface of a solution provides a different environment than its bulk, and we should expect intensive properties (concentrations as well as intensive thermodynamic properties) to vary in this region. The mechanical and thermal variables, P and T , however, can be taken as uniform throughout the solution. It should be emphasized that the surface region of the solution is very thin, just a few molecular diameters thick. Bulk properties of the solution will, thus, only be affected by the surface if the solution is composed of very small droplets.

In treating interfacial (if) regions, we will follow the method of Gibbs and replace the nonuniform interfacial region by a two-dimensional *Gibbs surface phase* with uniform properties. Properties of this phase are called *surface excess properties* and their calculation is illustrated for the surface excess concentration of component i in Fig. 8. Here, the actual interfacial region, the region where properties vary, extends from z_1 to z_2 and is replaced by the surface phase located at position z_0 , with the uniform bulk α and β phases extended up to this position.

The number of moles of i must be the same in the actual and the Gibbs model system:

$$\sigma \int_{z_1}^{z_2} c_i^{if} dz = \sigma c_i^\alpha (z_0 - z_1) + \sigma c_i^\beta (z_2 - z_0) + n_i^\sigma \quad (40)$$

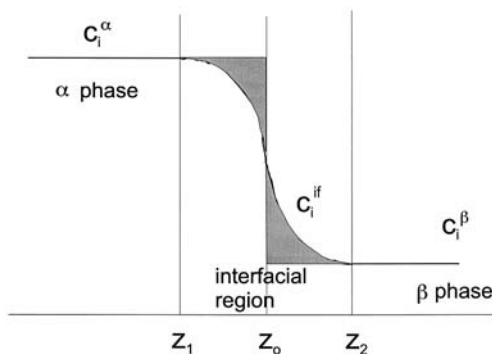


Figure 8 The Gibbs surface.

where σ is the area of the surface and n_i^σ is the *surface excess amount* of i . Rewriting gives

$$\frac{n_i^\sigma}{\sigma} \equiv \Gamma_i^\sigma = \left(\int_{z_0}^{z_2} c_i^{if} dz - c_i^B((z_2 - z_0)) \right) - \left(c_i^A(z_0 - z_1) - \int_{z_1}^{z_0} c_i^{if} dz \right) \quad (41)$$

where Γ_i^σ is the *surface excess concentration* of i . Note that Γ_i^σ is the difference between the shaded area to the right of z_0 and the shaded area to the left of z_0 . Surface excess concentrations have units of moles per unit area. z_0 , the position of the Gibbs interface, can be arbitrarily located anywhere in the interfacial region. Therefore, surface excess properties are arbitrary. It is customary, however, to select z_0 so that one surface excess concentration, usually that of the solvent, is zero (i.e., for the solvent, the shaded areas above and below the concentration curve just cancel). We will assume that this convention has been adopted in positioning the interface. In Fig. 8, the surface excess concentration is slightly positive, representing an accumulation of component i in the interfacial region. A negative value for Γ_i^σ denotes a deficiency of component i in the interfacial region.

We consider the change in the Gibbs free energy for arbitrary additions of the various components to the Gibbs surface phase. To do this, we generalize Eq. (7) to an open system:

$$dG = V dP - S dT - \sigma d\gamma + \sum_i \mu_i dn_i \quad (42)$$

Because the surface tension, γ , is an intensive property, it can depend on P , T and concentrations, but not on the area of the surface phase.

We now apply Eq. (42) to a process in which we start with a surface phase of very small area and add components to the phase in the proper ratio to keep its surface excess concentrations constant as we increase its area. Pressure and temperature are also held constant in this process. Because $\mu_i = \mu_i(P, T, c_i)$ and $\gamma = \gamma(P, T, c_i)$, μ_i and γ are constant in this process and Eq. (42) becomes

$$dG = \sum_i \mu_i dn_i \quad (43)$$

Integrating this equation from a very small area to the final area of the interface gives

$$G - G_0 = \sum_i \mu_i(n_i - n_{i,0}) \quad (44)$$

In the limit of the initial area of the surface approaching zero, this becomes

$$G = \sum_i \mu_i n_i \quad (45)$$

Following our development of the Gibbs–Duhem equation in [Chapter 8](#), we now apply Eq. (45) to a process at constant T and P , where components are added to the surface in an arbitrary ratio. In this process, the chemical potentials will vary:

$$dG = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \quad (46)$$

Equation (42), for the same process, becomes,

$$dG = -\sigma d\gamma + \sum_i \mu_i dn_i \quad (47)$$

Subtracting Eq. (47) from Eq. (46) and rearranging gives

$$d\gamma = -\sum_i \frac{n_i}{\sigma} d\mu_i = -\sum_i \Gamma_i d\mu_i \quad (48)$$

For a two-component solution, because z_0 has been positioned to make the surface excess concentration of solvent zero, Eq. (48) becomes

$$d\gamma = -\Gamma d\mu \quad (49)$$

where we have dropped the subscript for the single solute.

Because from Eq. (1) of [Chapter 9](#), $\mu = \mu^0 + RT \ln a$, Eq. (49) becomes

$$\frac{d\gamma}{d \ln a} = -RT\Gamma \quad (50)$$

In practice, the isothermal dependence of surface tension on concentration of solute in an aqueous solution is of three different types, shown in [Fig. 9](#).

With type 1 solutes, surface tension in aqueous solution mildly increases with concentration. Because activities generally increase with concentration, from Eq. (50), these solutes have a negative surface excess concentration (i.e., they are depleted in the surface layer). Inorganic electrolytes show this behavior. In the bulk solution, these ions are stabilized by interacting with the extended ionic environment of the solution. In the surface layer, this environment is limited in extent in one direction.

Type 2 solutes moderately decrease surface tension in aqueous solution and, thus, have positive surface excess concentrations. This class of solutes includes organic molecules with polar groups that give them some water solubility. Short-chain organic acids, amines, and alcohols are of this type.

Very small amounts of type 3 solutes produce a dramatic lowering of the surface tension of aqueous solutions. A substance with this property is called a *surfactant*. Usually, they consist of hydrocarbon chains, with $n = 10$ – 20 connected to polar groups (such as $-\text{OH}$, $-\text{CN}$, $-\text{COOH}$, $-\text{COOR}$, or $-\text{CONH}_2$) or ionic groups (such as $-\text{SO}_3^-$, $-\text{OSO}_3^-$, or $-\text{NR}_3^+$). They exclusively concentrate at the water–air interface. A monolayer of this type of

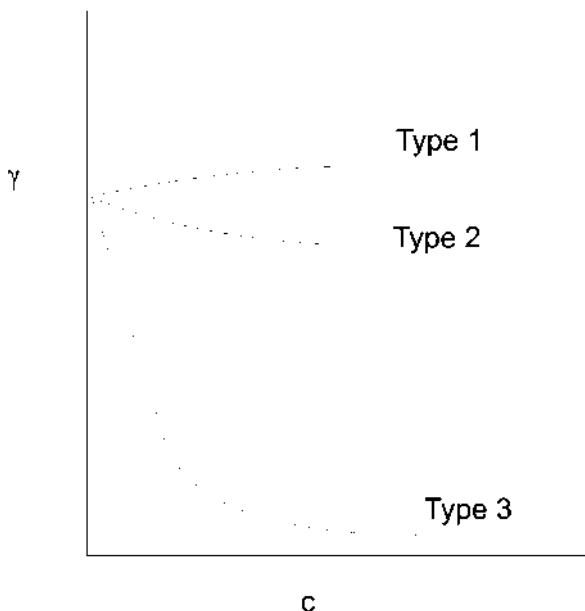


Figure 9 Concentration dependence of surface tension.

solute is called a *Langmuir layer*.⁴ After a complete monolayer of a surfactant is added, further addition produces a new phase and no further decrease in surface tension.

Soaps and detergents are examples of a surfactant. At the interface between water and a greasy phase, the hydrocarbon is attracted to the grease and the polar group to the water. The detergent molecules thus accumulate at the interface between these two phases and, by reducing surface tension at the interface, promote mixing (and the removal of grease from clothing).

11.9 Properties of Surface Films

The dependence of the surface tension of a Langmuir layer containing a given amount of surfactant, as a function of its area, reveals many of the properties of the surfactant. (At constant temperature, such measurements are analogous to determining the P - V isotherm of a gas.) One device for making such measurements is the Langmuir balance, the essential principles of which are shown in [Fig. 10](#).

Here, a monolayer film is prepared by dissolving a surfactant molecule in a volatile organic solvent. (The surfactant is assumed nonvolatile.) The solution is

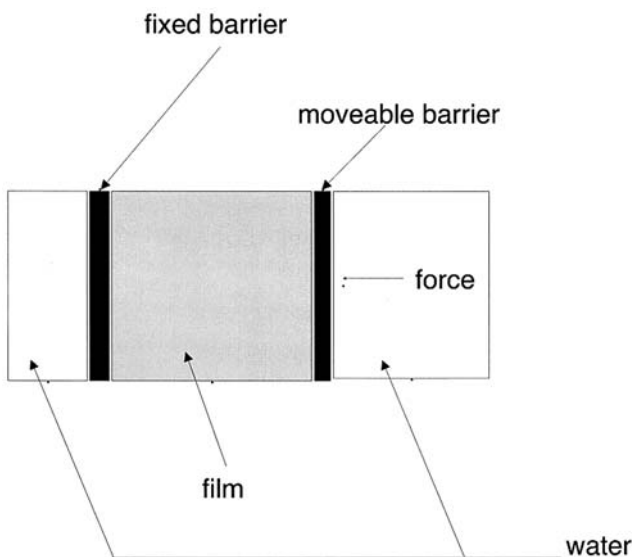


Figure 10 Langmuir balance.

added to the surface of clean water in a trough, in the region between a fixed and movable barricade. The surfaces are coated with a material, such as Teflon, that has negligible interaction with the surfactant. The force needed to hold the movable barricade at different positions, corresponding to different film areas, is recorded. As shown, the force per unit length of the barricade, the *surface pressure*, π , is given by

$$\pi = \gamma_0 - \gamma \quad (51)$$

where γ_0 is the surface tension of pure water and γ is that of the surfactant layer.

The shape of the typical π versus σ isotherm observed for a surfactant is shown in [Fig. 11](#).

At large areas, as the area is decreased the concentration of surfactant is increased and the surface tension is decreased. From Eq. (51), the surface pressure increases in this region (but only slowly). At a critical area, σ_0 , surface pressure rises quite abruptly if additional compression is attempted. This area, σ_0 , called the *Pockels point*,⁵ is considered to be the area at which the surfactant molecules are in contact in a monolayer. Any further compression requires a much larger force to “buckle” the monolayer. The surface tension is negative in this region. For a group of acids, $\text{CH}_3(\text{CH}_2)_n\text{COOH}$, with $n = 14\text{--}24$, Langmuir found no change in the Pockels point area, indicating that these molecules take up very similar space in the monolayer. This suggest that at the Pockels point, the

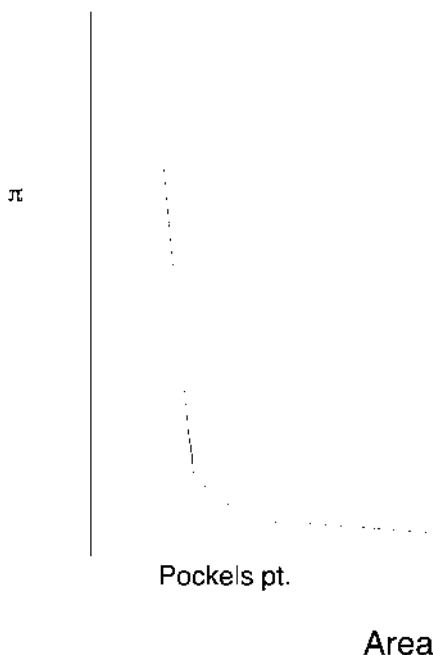


Figure 11 Isotherm for a surfactant.

organic chains of the different acids are sticking up out of the solution, so that it is the cross-sectional area of the chain that is important.

We can also analyze the part of π versus σ isotherm at large σ . When the film's area is very large, the surfactant molecules are sufficiently far apart that we can assume that their behavior is ideally dilute. In this case, the activity in Eq. (50) can be written in the usual ideally dilute solution approximation, $a = c = n/\sigma$, $d \ln c = dn/n$. We use moles/area for the interfacial concentration. Equation (50) then becomes

$$d\gamma = -RT\Gamma \frac{dn}{n} \quad (52)$$

For a surfactant, the concentration of solute in the aqueous layer is essentially zero. All of the surfactant is in the interfacial region and $\Gamma = n/\sigma$. Equation (52) then becomes

$$d\gamma = -\frac{RT}{\sigma} dn \quad (53)$$

Integrating from $n = 0$, $\gamma = \gamma_0$,

$$\gamma_0 - \gamma = \frac{nRT}{\sigma} = \pi \quad (54)$$

(i.e., the two-dimensional analog of the ideal gas law).

11.10 Adsorption on Solids

Adsorption on solids is an important step in the industrially important process of heterogeneous catalysis. Adsorption, which takes place on the surface (including that of the pores) of the solid, should be distinguished from absorption, which occurs throughout its bulk. The latter is illustrated by the taking up of water by anhydrous calcium chloride.

In adsorption, we call the gas or solution solute the *adsorbate* and the solid the *adsorbent*. *Monolayer adsorption* involves up to one layer of adsorbate on the adsorbent, whereas *multilayer adsorption* involves more than one layer of adsorbate. Adsorption may be either *physical adsorption* (*physisorption*), where the adsorbate is bound to the surface by relatively weak physical forces ($\Delta H_{\text{desorp}} < 40$ kJ/mol) or *chemical adsorption* (*chemisorption*), where the binding forces are stronger ($\Delta H_{\text{desorb}} > 40$ kJ/mol).⁶ Because chemical adsorption involves chemical-type bonds between adsorbate and adsorbent, it is limited to the first monolayer on the surface. Physical adsorption can involve multiple layers and physical adsorption can occur on top of chemisorbed layer.

In adsorption, the amount adsorbed on a surface is most fundamentally characterized by the fraction of surface sights, ϑ_i , that are occupied by i adsorbate molecules. Because the surface area is often not well known, adsorption isotherms are often reported as the amount adsorbed on the surface per gram of adsorbent. In gas adsorption, this amount is traditionally given as the volume of adsorbate at standard temperature and pressure (STP), v . This volume depends on temperature and on the pressure of the adsorbate in the gas phase. $v(T, P)$ is an equation of state for the surface and, when reported at a constant T , is known as an adsorption isotherm.

In order for the adsorbent surface to be well characterized, it must be extremely clean. Surface scientists have developed a number of techniques for producing clean surfaces. These include heating, cleaving crystals, and bombarding with high-energy ions. All of these processes must be carried out under ultrahigh-vacuum conditions, to avoid immediate contamination of the surface.

The simplest adsorption isotherm is that of Langmuir, which applies to surface coverage less than a monolayer. The isotherm assumes equilibrium

between gas-phase adsorbate molecules, **A**, and molecules adsorbed on a surface site:



S is a vacant surface site because the adsorbate cannot be adsorbed on a site **AS** that is already occupied. The activities of vacant and occupied surface sites are proportional to the fraction of the sites that are vacant, ϑ_V , and occupied by one adsorbate molecule, ϑ_1 . Because in the Langmuir isotherm, only monolayer adsorption is allowed $\vartheta_V + \vartheta_1 = 1$ and

$$K_1 = \frac{\vartheta_1}{(1 - \vartheta_1)P} \quad (55)$$

where P is the pressure of the gas-phase adsorbate. Equation (55) can be written as

$$\vartheta_1 = \frac{K_1 P}{1 + K_1 P} \quad (56)$$

For adsorption from solution, a solution concentration variable replaces the gas-phase pressure. The amount adsorbed on the surface is proportional to the fraction of the surface sites occupied, giving the following for gas adsorption:

$$v = \frac{bK_1 P}{1 + K_1 P} \quad (57)$$

where b is a proportionality constant. The Langmuir isotherm is shown in [Fig. 12](#).

At low pressure, surface coverage is proportional to pressure, whereas at high pressure, the surface coverage approaches unity, regardless of the temperature. Data are usually analyzed by plotting (or regression analysis) of v^{-1} versus P^{-1} because

$$\frac{1}{v} = \frac{1}{b} + \frac{1}{bK_1} \frac{1}{P} \quad (58)$$

An isotherm that considers multilayer adsorption was proposed by Brunauer, Emmet, and Teller in 1938 (BET isotherm). The importance of this isotherm is that, when its use is appropriate, it provides an estimate of the surface

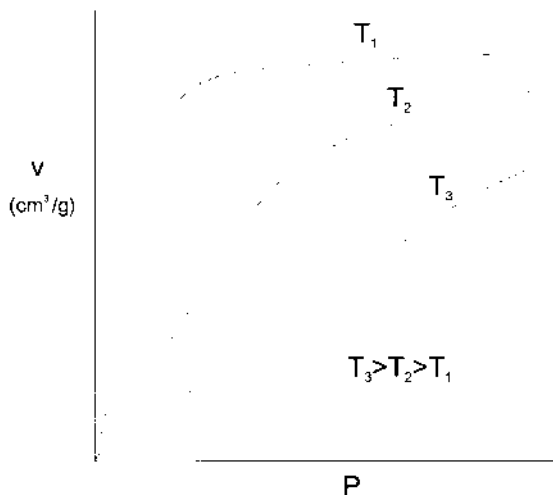
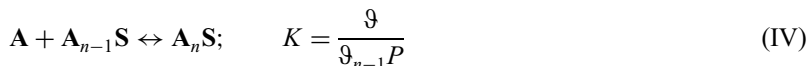
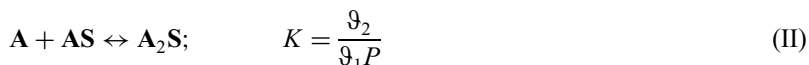


Figure 12 Langmuir isotherm.

area of an absorbent. For multilayer adsorption, we have to include the following, in addition to reaction (I):



where ϑ_n is the fraction of surface site on which there is a layer of an adsorbate n molecules thick. The justification for using the same equilibrium constant for all of these process is that, in each of them, the newly adsorbed adsorbate molecule is interacting directly with other adsorbate molecules. This interaction is taken as that for liquefaction of \mathbf{A} .



where P_{vap} is the vapor pressure of \mathbf{A} at the temperature of the isotherm.

We can express all of the fractions in terms of ϑ_1 :

$$\vartheta_n = \vartheta_{n-1}(KP) = \vartheta_1(KP)^{n-1} \quad (59)$$

The sum of the fractions of surface sites with all numbers of adsorbate molecules must sum to unity:

$$1 = \vartheta_v + \sum_i \vartheta_i = \vartheta_v + \sum_i \vartheta_1 (KP)^{i-1} = \vartheta_v + \frac{\vartheta_1}{1 - KP} \quad (60)$$

Since

$$\begin{aligned} 1 + KP + (KP)^2 + \dots + (KP)^n + \dots &= \sum_i (KP)^{i-1} \\ &= \frac{1}{1 - KP} \end{aligned} \quad (61)$$

The total number of molecules adsorbed on the surface per unit mass of adsorbent is

$$N = c_s \sum_i i \vartheta_i = c_s \vartheta_1 \sum_i i (KP)^{i-1} \quad (62)$$

where c_s is the number of surface sites per unit mass of adsorbent. This can be written as

$$\frac{N}{c_s} = \frac{\vartheta_1}{(1 - KP)^2} \quad (63)$$

since

$$\begin{aligned} \sum_i i (KP)^{i-1} &= \frac{d(\sum_i (KP)^i)}{d(KP)} \\ &= \frac{d[-1 + 1/(1 - KP)]}{d(KP)} \\ &= \frac{1}{(1 - KP)^2} \end{aligned} \quad (64)$$

From Eq. (60), using $\vartheta_v = \vartheta_1/K_1P$, from reaction (I),

$$\begin{aligned} 1 &= \frac{\vartheta_1}{K_1P} + \frac{\vartheta_1}{1 - KP} \\ &= \frac{\vartheta_1[1 + (K_1 - K)P]}{K_1P(1 - KP)} \end{aligned} \quad (65)$$

which when substituted into Eq. (63) gives

$$\frac{N}{c_s} = \frac{K_1P}{(1 - KP)[1 + (K_1 - K)P]} \quad (66)$$

Substituting $K = 1/P_{\text{vap}}$ from reaction (V) and rearranging gives

$$\frac{N}{c_s} = \frac{K_1 P_{\text{vap}} P}{(P_{\text{vap}} - P)[1 + (K_1 P_{\text{vap}} - 1)P/P_{\text{vap}}]} = \frac{v}{v_m} \quad (67)$$

where we have substituted the ratio of the amount of material adsorbed to the amount that would be adsorbed for a monolayer (both measured as volumes at STP) for the number of molecules adsorbed per surface site. Equation (67) is rearranged to

$$\frac{P}{v(P_{\text{vap}} - P)} = \frac{1}{K_1 P_{\text{vap}} v_m} + \frac{(K_1 P_{\text{vap}} - 1)}{K_1 P_{\text{vap}} v_m} \frac{P}{P_{\text{vap}}} \quad (68)$$

A linear plot (or regression) of $P/v(P_{\text{vap}} - P)$ versus P/P_{vap} therefore allows the determination of K_1 and v_m from the slope and intercept.

Although a number of assumptions of the derivation of the BET isotherm have been disputed, the isotherm does usually give a good fit to experimental data up to $P/P_{\text{vap}} \approx 0.35$. Obtaining the surface area of adsorbent from v_m requires a model for the size and shape of the adsorbate molecules and their arrangement on the monolayer surface. For small adsorbate molecules, such as Ar and N_2 , a spherical shape and a close-packed arrangement is assumed. A surface area for a N_2 molecule of 16.2 \AA^2 has been generally agreed upon.

Data for the adsorption of N_2 on 45.6 g of copper at 90 K are shown in Fig. 13a. In Fig. 13b, these data are plotted in the form of Eq. (68). Linear regression gives a slope of 0.227 and an intercept of 2.338×10^{-3} , both in units of $(\text{cm}^3 \text{ at STP})^{-1}$.

Example 4. Use the plot of Fig. 13b to estimate the surface area per gram of the copper sample used in the experiment. The vapor pressure of N_2 at 90 K is 2710 torr.

Solution: From the slope and intercept of Eq. (68),

$$\begin{aligned} K_1 P_{\text{vap}} &= 1 + \frac{\text{Slope}}{\text{Intercept}} = 1 + \frac{0.227}{2.338 \times 10^{-3}} = 98 \\ v_m &= \frac{1}{K_1 P_{\text{vap}} \text{intercept}} = \frac{1}{98} \frac{\text{cm}^3 \text{ at STP}}{2.338 \times 10^{-3}} = 4.36 \text{ cm}^3 \text{ at STP} \\ &= \frac{4.36 \text{ cm}^3 \text{ at STP}}{45.6 \text{ g Cu}} \frac{6.02 \times 10^{23} \text{ molec}}{22,400 \text{ cm}^3 \text{ at STP}} \frac{16.2 \times 10^{-20} \text{ m}^2}{\text{molec}} \\ &= 0.416 \frac{\text{m}^2}{\text{g Cu}} \end{aligned}$$

It should be noted that the “surface area of a solid” is not a very well-defined quantity. Much like the “length of the coastline of Maine,” it depends on

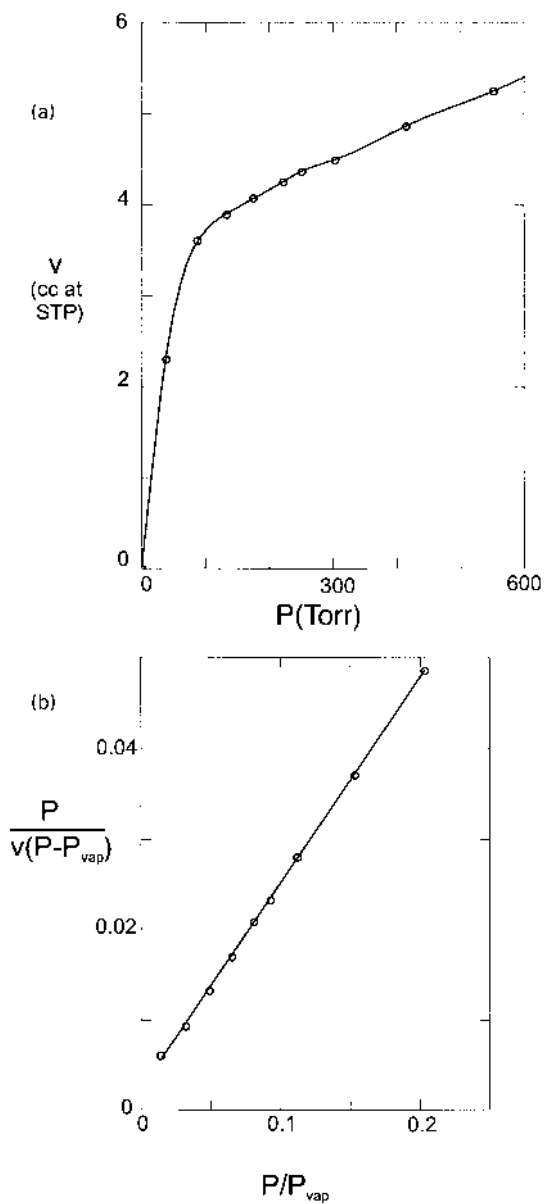


Figure 13 (a) Adsorption of N_2 on copper (data from S Brunauer, PV Emmett. Determination of the surface area of adsorbents. J Am Chem Soc 59:2683, 1972); (b) Adsorption of N_2 on copper; BET plot.

the scale of the measuring device used for the measurement. In Example 4, that scale was that of the N_2 molecule (i.e., approximately 4 Å). If the area of the same solid had been measured using a much larger molecule, whose size precluded it coating the finer details of the surface, a somewhat smaller surface area would have been found.

11.11 Statistical Mechanics of Adsorption

11.11.1 Statistical Approach for the Langmuir Isotherm

Physical understanding of the assumptions underlying the various isotherms can be increased by deriving them by statistical mechanics. This will be done only for the Langmuir isotherm. At equilibrium, the chemical potential of the adsorbate in the gas phase and on the surface must be equal:

$$\mu_g = \mu_{\text{surf}} \quad (69)$$

For μ_g , we use Eq. (38) of Chapter 5 with U_0 as the desorption energy and the molecular partition function written as a product of a translational partition function [Eq. (72) of Chapter 5] and q_{int} , which accounts for the internal degrees of freedom of the molecule:

$$\begin{aligned} \mu_g &= U_0 - RT \ln q_{\text{int}} \frac{V_m}{N_A h^3} (2\pi m k T)^{3/2} \\ &= RT \ln \left[q_{\text{int}} \frac{V_m}{N_A h^3} (2\pi m k T)^{3/2} \exp\left(-\frac{U_0}{RT}\right) \right] \end{aligned} \quad (70)$$

For the surface, we calculate the Helmholtz free energy from Eq. (45) of Chapter 5: $A = -RT \ln Q$. We assume that surface molecules are distinguishable (by their position) and noninteracting, so that the system partition function is a product of N molecular partition functions. However, because we are not interested in which of the N out of a total of M surface sites are occupied, we must include a degeneracy factor of $M!/N!(M-N)!$. The energy of a molecule on the surface is taken as zero.

$$Q_{\text{surf}} = \frac{M!}{N!(M-N)!} q_{\text{surf}}^N \quad (71)$$

Using Stirling's approximation and making the assumption that

$$q_{\text{surf}} = q_{\text{int}} \quad (72)$$

(i.e. that the molecules on the surface have all of their internal degrees of freedom identical to gas-phase molecules, but have lost their translational degrees of freedom), for the adsorbed molecules we get

$$A = -kT[M \ln M - M - N \ln N + N - (M - N) \ln (M - N) + (M - N) + N \ln q_{\text{int}}] \quad (73)$$

The chemical potential on the surface is obtained from

$$\mu_{\text{surf}} = \left(\frac{\partial A}{\partial n} \right)_{M,T} = N_A \left(\frac{\partial A}{\partial N} \right)_{M,T} \quad (74)$$

Note that here M is the number of surface sites, which takes the place of volume, the usual natural variable for A .

Inserting Eq. (73) into Eq. (74) gives

$$\begin{aligned} \mu_{\text{surf}} &= RT[\ln N - \ln(M - N) + \ln q_{\text{int}}] \\ &= RT \ln \left(\frac{Nq_{\text{int}}}{(M - N)} \right) \end{aligned} \quad (75)$$

Equating Eqs. (70) and (75) and cancelling q_{int} gives

$$\frac{N}{M - N} = \frac{N_A h^3}{V_m (2\pi m k T)^{3/2}} \exp \left(\frac{U_0}{RT} \right) \quad (76)$$

Because $\vartheta = N/M$, Eq. (76) becomes

$$\frac{\vartheta}{1 - \vartheta} = \frac{h^3 P}{k T (2\pi m k T)^{3/2}} \exp \left(\frac{U_0}{RT} \right) = b(T)P \quad (77)$$

Equation (77) may be written as

$$\vartheta = \frac{bP}{1 + bP} \quad (78)$$

which is identical in form to Eq. (56).

11.11.2 Statistical Approach to the Thermodynamics of Adsorption

In analogy to what we did for solutions, we define the change in a thermodynamic function upon adsorption as

$$\Delta_{\text{ads}} X = X - \sum_i n_i X_{m,i}^* = \sum_i n_i (\bar{X}_i - X_{m,i}^*) \quad (79)$$

$X_{m,i}^*$ is the molar thermodynamic property of a pure component (adsorbate or adsorbent) and \bar{X}_i is the partial molar property of the component, defined as

$$\bar{X}_i \equiv \left(\frac{\partial X}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial X}{\partial n_i} \right)_{T,P,\theta} \quad (80)$$

$\Delta_{\text{ads}}X$ is an integral change and involves contributions as the fractional coverage varies from $0 \rightarrow \theta$. Usually, we are interested in how thermodynamic properties vary with coverage and want the differential change

$$\Delta_{\text{ads,dif}}X_i \equiv \left(\frac{\partial \Delta_{\text{ads}}X}{\partial n_i} \right)_{T,P,\theta} = \bar{X}_i - X_{m,i}^* \quad (81)$$

We will illustrate the method by outlining the calculation of the (differential) entropy of adsorption. For S_m^* , we use the Sackur–Tetrode expression, Eq. (76) of Chapter 5, with a term added for the internal degrees of freedom:

$$S_m^* = R \ln q_{\text{int}} + \frac{5}{2}R + R \ln \left(\frac{(2\pi M)^{3/2} R^{5/2} T^{5/2}}{N_A^4 h^3 P} \right) \quad (82)$$

Assuming that the adsorbed molecules have lost their three translational degrees of freedom, we calculate S from Eq. (32) of Chapter 5, taking the energy term as zero. The partition function for the molecules on the surface is given by Eqs. (71) and (72):

$$S = k \ln \left(\frac{M!}{(M-N)!N!} q_{\text{int}}^N \right) \quad (83)$$

Using Sterling's approximation for the factorials,

$$S = k[M \ln M - (M-N) \ln(M-N) - N \ln N + N \ln q_{\text{int}}] \quad (84)$$

From Eq. (80), the partial molar entropy of the adsorbate is

$$\bar{S} = \left(\frac{\partial S}{\partial n} \right)_{T,P} = N_A \left(\frac{\partial S}{\partial N} \right)_{T,P} = R[\ln(M-N) - \ln N + \ln q_{\text{int}}] \quad (85)$$

Combining the first two terms and writing them in terms of $\theta = N/M$, gives

$$\bar{S} = R \ln \left(\frac{1-\theta}{\theta} \right) + R \ln q_{\text{int}} \quad (86)$$

The entropy of adsorption then becomes

$$\Delta_{\text{ads}}S = R \ln \left(\frac{1-\theta}{\theta} \right) - \frac{5}{2}R - R \ln \left(\frac{(2\pi M)^{3/2} R^{5/2} T^{5/2}}{N_A^4 h^3 P} \right) \quad (87)$$

The first term, called the (differential) *configurational entropy*, results from the different possible ways the adsorbed molecules can occupy the surface sites. The last two terms, which are negative, are the Sackur–Tetrode entropy due to the lost translational degrees of freedom of the gaseous molecules.

11.12 Colloids

Colloids are systems with size intermediate between the microscopic and macroscopic realms. They have been defined as particles with a characteristic dimension between a micron and a few nanometers or, alternatively, as entities containing between 10^3 and 10^9 atoms. With their small size, colloids have a very large surface-to-volume ratio and surface interactions are dominant in determining their stability. Some properties of systems in the colloidal size range are as follows:

1. They cannot be removed from solution by filters, but they can by semipermeable membranes.
2. They do not rapidly sediment (settle out) from solution under the influence of gravity,⁸ but they often do in an ultracentrifuge.⁹
3. While individual dispersed particles are not visible, the suspensions can scatter light (the Tyndall effect).

Colloidal suspensions are everywhere around us. We encounter them in everything from washing our clothes to painting our homes to eating our morning cereal (Question 12). A large fraction of our bodies are colloidal materials. Colloids are used extensively in a variety of industrial processes. Their importance is illustrated by the original name of the *Journal of Physical Chemistry* being the *Journal of Physical and Colloid Chemistry*.

Colloidal suspensions can be classified in a number of ways. Most obvious is by the phase of the homogeneous *dispersing medium* and that of the *dispersed particles*, as shown in Table 2.

Colloids can also be classified by the nature of the interaction between the dispersed particles and the homogeneous dispersing medium. If this interaction is attractive, the system is known as a *lyophilic colloid*. If the interaction is repulsive, it is called a *lyophobic colloid*. Because water is the most common dispersing medium, these terms usually become *hydrophilic* and *hydrophobic*. If all the dispersed particles are roughly the same size, the colloid is called *monodispersed*; if they cover a range of sizes, it is called *polydispersed*. The dispersed particles may be *macromolecules* or *aggregates* and their shape may be *globular* (roughly spherical) or *fibrous*. The function of biological macromolecules is intimately related to their dispersed shape. Determining the relationship

TABLE 2 Classification of Colloidal Systems

Medium	Particle	Name	Example
Gas	Liquid	Fog	Fog
Gas	Solid	Smoke	Smoke
Liquid	Gas	Foam	Beer foam
Liquid	Liquid	Emulsion	Milk
Liquid	Solid	Sol	White paint
Solid	Liquid	Gel	Skin
Solid	Solid	Suspension	Metallic alloy

between macromolecular structure, shape and function is a very active field of biochemical research.

Because in lyophilic colloids there is an attractive interaction between the particles and the medium, the interface between these two phases has a low surface energy and the particles are solvated. There is little reason for particles to clump together under these circumstances; thus, the dispersed particles are usually individual macromolecules. The shape of the macromolecule depends on the relative magnitude of the forces within the molecule to those between the molecule and the medium. If the former is larger, the particle will be globular, if the latter is larger, the particles will be extended. In the latter case, there may be some interactions between different dispersed molecules, producing semisolid properties (a gel).

Lyophobic colloids (sols) may be prepared by grinding crystalline materials or running an electric arc between metallic electrodes, both in the dispersing medium. More commonly, they are prepared by precipitating the solid from a strongly supersaturated solution, which produces a large number of precipitation nuclei. Because there is little attractive interaction between the particles and the medium, attractive forces between the particles would soon lead to their aggregation (*flocculation*). This tendency, however, is counterbalanced by repulsive electrical forces between the particles.

The origin of the electrical forces between colloidal particles is the difference in chemical potentials for some charged species at the particle–medium interface. As shown in Eq. (36) of [Chapter 10](#), this results in charge transfer, which produces an electric potential difference between the particle and the medium. The net charge on the colloidal particle influences the distribution of ions in the surrounding medium, much as we have discussed for the Debye–Huckel theory of ionic activities. Thus, if the particle has a net positive surface charge, there will be a predominance of negative charge in its vicinity in the medium. This produces what is commonly called an *electrical double layer*.

Because the charge distributions around similar particles have the same sign, they will repel each other, counteracting the influence of the attractive interactions. The Debye length, a measure of the distance from the charged particle over which electrical imbalances persist, is, by Eq. (18) of [Chapter 10](#), inversely proportional to the square root of the ionic strength of the medium. Adding electrolytes to the medium thus reduces the influence of the repulsive electrical forces and often flocculates the colloid. To increase the stability of colloids, they can be dialyzed after their formation to remove excess electrolyte. Some observations require for their explanation a tightly held layer of adsorbed ions on the particle, called the *Stern layer*, as well as the diffuse cloud of ions in the medium.

Surfactant molecules in solution can form *association colloids* (called *micelles*) when the concentration of the surfactant is above a *critical micelle concentration*. This behavior only occurs above a given temperature, called the *Kraft temperature*. Below this temperature, the surfactant shows normal solubility behavior. In Fig. 14, a two-dimensional cut through a micelle, according to the most popular model, is shown.

This micelle is comprised of surfactant molecules consisting of long hydrocarbon tails attached to an anionic lyophilic group. Typically, there are 50–100 molecules in the micelle. Some counterions in the medium are adsorbed on the aggregate, whereas others form the diffuse ionic environment. Some workers believe that there is considerable penetration of the medium into the micelle. Micelles are important for detergent action, with oily dirt particles dissolved in the hydrocarbon interior of the micelle.

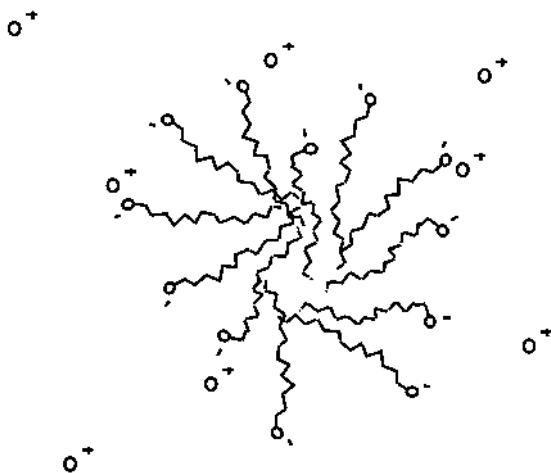


Figure 14 A micelle.

Questions

1. Explain how certain insects are able to walk on water, when their density is greater than that of water.
2. Arrange the following liquids in order of increasing surface tension: ether, water, and mercury.
3. Tables of surface tension often list values in dynes per centimeter, millinewtons per meter, or grams per second squared. How is each of these related to the units used in [Table 1](#)?
4. Equation (32) predicts that the larger the γ , the higher up into a capillary a liquid will be drawn. However, it is found that liquids with very high surface tension will not be drawn into capillaries at all. Rationalize this in light of the derived equation. (Hint: The surface tension is a measure of the cohesive energy of a liquid.)
5. Show that Young's equation [Eq. (24)] can be derived by requiring that the net horizontal component of force on the interface is zero.
6. Two bubbles, one of radius 1 cm and the other of radius 2 cm, stick together. In which direction does the interface between the two bubbles curve?
7. Devise a method to accurately use two Wilhelmy plates (see [Fig. 6](#)) to measure the surface tension of a Langmuir film. Do not forget about the gravitational and buoyancy forces. Such a device is called a Wilhelmy balance.
8. How would you expect the solubility of a solid to depend on crystal size? What happens as a newly formed precipitate ages in contact with its supernatant liquid?
9. Consider the physical assumptions used to derive the BET isotherm. List three ways in which these assumptions might be in error.
10. The Langmuir isotherm describes chemisorption, whereas the BET isotherm describes physisorption. Why is more appropriate to estimate surface areas using the latter isotherm?
11. Sketch the dependence of the differential and integral configurational entropies on the fraction of a monolayer covered.
12. How do colloids play a role in washing our clothes, painting our homes, and eating our morning cereal?
13. To make Jello, powder containing gelatin (a protein), sugar and flavoring is dissolved in hot water and then placed in the refrigerator to cool. Describe, from a microscopic perspective, what happens in this process.
14. If a 0.1 M mixture of AgI is prepared in colloidal form, no measurable osmotic pressure is observed even though the colloidal particles do not pass through a semipermeable membrane. Explain.
15. Explain why detergent does not clean very well below their Kraft temperatures.

16. For 1% by mass of each of the following in water: sugar, starch, and colloidal gold, which has the largest osmotic pressure?

Problems

1. Calculate the diameter of circular plates that a 150-lb. man would have to wear on his feet in order to walk on water. You can assume that the plates are perfectly nonwettable.
2. We add 1.0 nmol of an organic substance to 1 L of water in a 15-cm-diameter container. The substance concentrates in the top 2.0-nm layer of the solution. What is its concentration in this layer?
3. Show that if $n = 1$ in Eq. (15), the surface energy is temperature independent.
4. Show that if $(\partial\gamma/\partial P)_T = 0$, then $(\partial\gamma/\partial T)_V = (\partial\gamma/\partial T)_P$.
5. For a metal plate, 1 cm \times 3 cm \times 10 cm with density 7.0 g/cm³, suspended 5 cm. deep in water and making a contact angle of 30° with the water surface, compare the gravitational force, buoyancy force, and the vertical component of the surface tension force on the plate.
6. Show that in the case that a liquid makes a contact angle θ with the wall of a capillary tube of radius R , the capillary rise in the tube is $h = (2\gamma \cos \theta)/\rho g R$.
7. Calculate the height to which water is raised in capillary tubes of diameters of 1.0 mm and 0.1 mm, assuming that the water completely wets the surface of the tube.
8. What pressure above atmospheric must be applied in a tube of diameter 1.0 mm, placed 3.0 cm below the surface of water at 25°C in order to blow a bubble? (Assume perfect wetting of the tube.)
9. What would the radius of a water droplet have to be at 25°C in order for it to have a vapor pressure of 25 torr?
10. Find an expression for the surface entropy, $s_\sigma \equiv (\partial S/\partial \sigma)_T$, for a substance whose surface tension follows the temperature dependence of Eq. (15). You can assume $(\partial S/\partial \sigma)_{T,V} \approx (\partial S/\partial \sigma)_{T,P}$. Comment on the sign of s_σ .
- 11.* For the case in which, in the absence of gravity, a liquid droplet adsorbs onto a surface as a hemispherical droplet, what is the ratio of the adhesive energy to the cohesive energy?
12. The surfactant molecule hexadecanol, C₁₆H₃₃OH, has been used to retard evaporation from water reservoirs. If the cross-sectional area of this molecule is 0.25 nm², what mass of hexadecanol would have to be added to a reservoir of area 10⁴ m² in order to completely cover the surface and retard the evaporation of water?
13. Derive the Langmuir isotherm by equating the rate of desorption of adsorbate from the surface (proportional to the fraction of surface sites occupied) to the rate of adsorption (proportion to the pressure of adsorbate in the gas phase).

14. For a gas–solid system following the Langmuir isotherm, how would you plot $\vartheta(P)$ so that a fit to a straight line would provide $b(T)$? From Eq. (77), how would you plot $b(T)$ so that a fit to a straight line would provide U_0 ?

15. From Eq. (75), sketch the chemical potential of adsorbed molecules as a function of ϑ , the fraction of surface sites occupied. What values does μ_{surf} approach as $\vartheta \rightarrow 0$ and $\vartheta \rightarrow 1$? Is μ_{surf} an “escaping tendency” from the surface phase in the sense that it is just related to the rate that molecules escape from the surface?

16. Show that, following the derivation of the Langmuir isotherm, for the case of two different species competing for monolayer adsorption sites,

$$\vartheta_1 = \frac{b_1 P_1}{1 + b_1 P_1 + b_2 P_2}, \quad \vartheta_2 = \frac{b_2 P_2}{1 + b_1 P_1 + b_2 P_2}$$

17. Show that Eq. (55) can be written in the form of Eq. (56).

18.* Monodispersed colloidal gold particles allowed to sit in perfectly quiescent aqueous suspension at 25°C form a sedimentation equilibrium in which their number density decreases by a factor of 2 in 10 cm of elevation. What is the average number of gold atoms in each colloidal particle?

19.^M On the same surface as used in Example 4, Brunauer and Emmett also obtained the following data for adsorption of CO₂ at –78°C:

P (torr)	65	122	175	212	260	305	420	522	600	710
v (cm ³)	1.70	2.55	3.15	3.50	3.78	4.05	4.60	5.22	5.78	6.65

The sublimation pressure of CO₂ at –78°C is 780 torr. What area should be assigned to solid CO₂ on the Cu surface in order to obtain the same surface area as calculated in Example 4.

Notes

1. The derivative at constant V and σ means at constant surface-to-volume ratio.
2. Note that the energy of vaporization also goes to zero at the critical point.
3. AW Adamson. *Physical Chemistry of Surfaces*. New York, Interscience, 1960, pp 4–6.
4. After Irving Langmuir (1881–1957), Nobel laureate in chemistry, 1932.
5. After Agnes Pockels, an amateur scientist, who did many of the early experiments on surface tension in her kitchen.
6. Of course, 40 kJ/mol is an arbitrary cutoff. For particular purposes, we might decide to modify this cutoff between physisorption and chemisorption.
7. See Example 4 of [Chapter 1](#).
8. Suspensions of colloidal gold prepared by Michael Faraday (1791–1867) are still on exhibit at the British Museum.
9. An ultracentrifuge typically provides an acceleration 10^5 times that of gravity.