

3 Thermodynamics of interfaces

In this chapter we introduce the basic thermodynamics of interfaces. The purpose is to present some important equations, learn to apply them, provide a broader base of understanding, and point out some of the difficulties. For a thorough understanding, further reading is certainly necessary (see for example Ref. [6]).

3.1 The surface excess

The presence of an interface influences generally all thermodynamic parameters of a system. To consider the thermodynamics of a system with an interface, we divide that system into three parts: The two bulk phases with volumes V^α and V^β , and the interface σ .

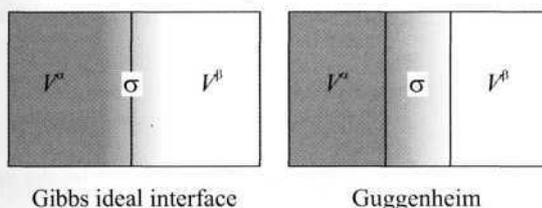


Figure 3.1: Left: In Gibbs convention the two phases α and β are separated by an ideal interface σ which is infinitely thin. Right: Guggenheim explicitly treated an extended interphase with a volume.

In this introduction we adhere to the Gibbs¹ convention [241]. In this convention the two phases α and β are thought to be separated by an infinitesimal thin boundary layer, the **Gibbs dividing plane**. This is of course an idealization and the Gibbs dividing plane is also called an ideal interface. There are alternative models. Guggenheim, for example, takes the extended interfacial region, including its volume, explicitly into account [41, 42]. We use the Gibbs model because in most applications it is more practical.

In the Gibbs model the interface is ideally thin ($V^\sigma = 0$) and the total volume is

$$V = V^\alpha + V^\beta \quad (3.1)$$

¹ Josiah Willard Gibbs, 1839–1903. American mathematician and physicist, Yale College.

All other extensive quantities can be written as a sum of three components: one of bulk phase α , one of bulk phase β , and one of the interfacial region σ . Examples are the internal energy U , the number of molecules of the i th substance N_i , and the entropy S :

$$U = U^\alpha + U^\beta + U^\sigma \quad (3.2)$$

$$N_i = N_i^\alpha + N_i^\beta + N_i^\sigma \quad (3.3)$$

$$S = S^\alpha + S^\beta + S^\sigma \quad (3.4)$$

The contributions of the two phases and of the interface are derived as follows. Let u^α and u^β be the internal energies per unit volume of the two phases. The internal energies u^α and u^β are determined from the homogeneous bulk regions of the two phases. Close to the interface they might be different. Still, we take the contribution of the volume phases to the total energy of the system as $u^\alpha V^\alpha + u^\beta V^\beta$. The internal energy of the interface is

$$U^\sigma = U - u^\alpha V^\alpha - u^\beta V^\beta \quad (3.5)$$

At an interface, the molecular constitution changes. The concentration (number of molecules per unit volume) of the i^{th} material is, in the two phases, respectively c_i^α and c_i^β . The additional quantity that is present in the system due to the interface is

$$N_i^\sigma = N_i - c_i^\alpha V^\alpha - c_i^\beta V^\beta \quad (3.6)$$

With Eq. (3.6) it is possible to define something like a surface concentration, the so called **interfacial excess**:

$$\Gamma_i = \frac{N_i^\sigma}{A} \quad (3.7)$$

A is the interfacial area. The interfacial excess is given as a number of molecules per unit area (m^{-2}) or in mol/m^2 .

In the Gibbs model of an ideal interface there is one problem: where precisely do we position the ideal interface? Let us therefore look at a liquid-vapor interface of a pure liquid more closely. The density decreases continuously from the high density of the bulk liquid to the low density of the bulk vapor (see Fig. 3.2). There could even be a density maximum in between since it should in principle be possible to have an increased density at the interface. It is natural to place the ideal interface in the middle of the interfacial region so that $\Gamma = 0$. In this case the two dotted regions, left and right from the ideal interface, are equal in size. If the ideal interface is placed more into the vapor phase the total number of molecules extrapolated from the bulk densities is higher than the real number of molecules, $N < c^\alpha V^\alpha + c^\beta V^\beta$. Therefore the surface excess is negative. Vice versa: if the ideal interface is placed more into the liquid phase, the total number of molecules extrapolated from the bulk densities is lower than the real number of molecules, $N > c^\alpha V^\alpha + c^\beta V^\beta$, and the surface excess is positive.

Let us now turn to two- or multi-component liquids such as a solvent with dissolved substances. Substituting $V^\alpha = V - V^\beta$ we can write

$$N_1^\sigma = N_1 - c_1^\alpha V + (c_1^\alpha - c_1^\beta) V^\beta \quad (3.8)$$

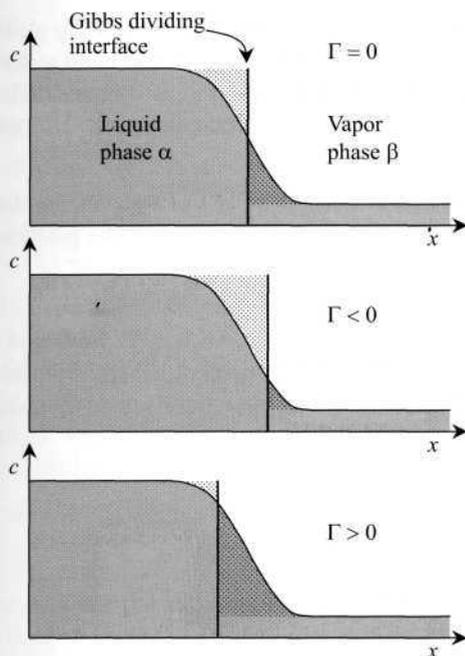


Figure 3.2: Dependence of the surface excess Γ on the position of the Gibbs dividing plane.

for the first component which is taken to be the solvent. For all other components we get similar equations.

$$N_i^\sigma = N_i - c_i^\alpha V + (c_i^\alpha - c_i^\beta) V^\beta \quad (3.9)$$

All quantities on the right side of the equations, except V^β , do not depend on the position of the dividing plane and are measurable quantities. Only V^β , depends on the choice of the dividing plane. We can eliminate V^β by multiplying Eq. (3.8) by $(c_i^\alpha - c_i^\beta)/(c_1^\alpha - c_1^\beta)$ and subtracting Eq. (3.8) from Eq. (3.9):

$$N_i^\sigma - N_1^\sigma \frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta} = N_i - c_i^\alpha V - (N_1 - c_1^\alpha V) \frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta} \quad (3.10)$$

The right side of the equation does not depend on the position of the Gibbs dividing plane and thus, also, the left side is invariant. We divide this quantity by the surface area and obtain the invariant quantity

$$\Gamma_i^{(1)} \equiv \Gamma_i^\sigma - \Gamma_1^\sigma \frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta} \quad (3.11)$$

It is called **relative adsorption** of component i with respect to component 1. This is an important quantity because it can be determined experimentally! As we shall see later it can be measured by determining the surface tension of a liquid versus the concentration of the solute.

- **Example 3.1.** To show how our choice of the position of the Gibbs dividing plane influences the surface excess, we consider an equimolar mixture of ethanol and water (p. 25 of Ref. [43]). If the position of the ideal interface is such that $\Gamma_{H_2O} = 0$, one finds experimentally that $\Gamma_{Ethanol} = 9.5 \times 10^{-7} \text{ mol/m}^2$. If the interface is placed 1 nm outward, then we obtain $\Gamma_{Ethanol} = -130 \times 10^{-7} \text{ mol/m}^2$.

For the case when component 1 is a solvent in which all other components are dissolved and thus have a much lower concentration than component 1, we choose the position of the dividing plane such that $\Gamma_1^\sigma = 0$ and from Eq. (3.11) we get

$$\Gamma_i^{(1)} = \Gamma_i^\sigma \quad (3.12)$$

In Fig. 3.3 the concentration profiles for solute 2 dissolved in liquid 1 are illustrated. We assume that the solute is enriched at the surface. The area of the dotted region corresponds to the surface excess $\Gamma_2^{(1)}$ of solute.

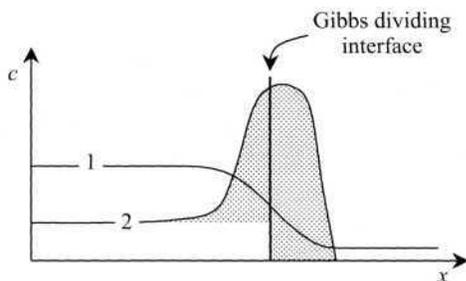


Figure 3.3: Concentration profile of a solute (2) dissolved in a liquid (1). The area of the dotted region corresponds to the surface excess $\Gamma_2^{(1)}$ of solute.

3.2 Fundamental thermodynamic relations

3.2.1 Internal energy and Helmholtz energy

Let us consider a process in a system with two phases, α and β , which are divided by an interface; we could, for instance, do work on that system. As a consequence the state quantities like the internal energy, the entropy, etc. change. How do they change and how can we describe this mathematically? In contrast to the usual “bulk” thermodynamics we have to take the interface into account.

We start the analysis with the internal energy. We first analyze the internal energy, and not the enthalpy, the Helmholtz energy, or the Gibbs energy, because the internal energy only contains extensive quantities (S, V, N_i, A) as variables. This simplifies the following calculation. A variation of the internal energy of a two-phase system is, according to the first and second principle of thermodynamics,

$$dU = TdS - PdV + \sum \mu_i dN_i + dW \quad (3.13)$$

Here, W is the work done on the system without expansion work PdV . It contains the surface work γdA . The sum runs over all components, that means over all substances that are chemically different. μ_i is the chemical potential of the i th substance.

We split the internal energy:

$$\begin{aligned} dU &= dU^\alpha + dU^\beta + dU^\sigma \\ &= TdS^\alpha + \sum \mu_i^\alpha dN_i^\alpha - P^\alpha dV^\alpha + TdS^\beta \\ &\quad + \sum \mu_i^\beta dN_i^\beta - P^\beta dV^\beta + TdS^\sigma + \sum \mu_i^\sigma dN_i^\sigma + \gamma dA \end{aligned} \quad (3.14)$$

The TdS terms stands for the change in internal energy, which is caused by an entropy change, e.g., a heat flow. The $\mu_i dN_i$ terms consider the energy change caused by a change in the composition. Both PdV terms correspond to the volume-work of the two phases. Since the interface is infinitely thin it cannot perform volume work.

With $dV = dV^\alpha + dV^\beta \Rightarrow dV^\alpha = dV - dV^\beta$ and summing up the entropy terms, the equation simplifies as:

$$\begin{aligned} dU &= TdS - P^\alpha dV - (P^\beta - P^\alpha) dV^\beta \\ &\quad + \sum \mu_i^\alpha dN_i^\alpha + \sum \mu_i^\beta dN_i^\beta + \sum \mu_i^\sigma dN_i^\sigma + \gamma dA \end{aligned} \quad (3.15)$$

Now we consider the Helmholtz energy. In general, the change in Helmholtz energy of a system is $dF = -SdT - PdV + \sum \mu_i dN_i + dW$. For a two-phase system with one interface it follows that

$$\begin{aligned} dF &= dF^\alpha + dF^\beta + dF^\sigma \\ &= -SdT - P^\alpha dV - (P^\beta - P^\alpha) dV^\beta \\ &\quad + \sum \mu_i^\alpha dN_i^\alpha + \sum \mu_i^\beta dN_i^\beta + \sum \mu_i^\sigma dN_i^\sigma + \gamma dA \end{aligned} \quad (3.16)$$

When the temperature and volume are constant ($dV = 0, dT = 0$) the first two terms are zero.

3.2.2 Equilibrium conditions

In equilibrium Eq. (3.16) can be simplified even further because the chemical potentials in the three phases are equal. This can easily be demonstrated. We assume that there is no exchange of material with the outside world ($dN_i = 0$); we have a closed system. Then the three parameters $N_i^\alpha, N_i^\beta,$ and N_i^σ are not independent because $N_i = N_i^\alpha + N_i^\beta + N_i^\sigma$ is constant. Only two at a time, as an example N_i^α and N_i^β , can be varied independently. N_i^σ is then determined by the other two amounts because $dN_i^\sigma = -dN_i^\alpha - dN_i^\beta$. Therefore we can write:

$$dF = - (P^\beta - P^\alpha) dV^\beta + \gamma dA + \sum (\mu_i^\alpha - \mu_i^\sigma) dN_i^\alpha + \sum (\mu_i^\beta - \mu_i^\sigma) dN_i^\beta \quad (3.17)$$

At equilibrium, with constant volume, temperature, and constant amounts of material, the Helmholtz energy is minimal. At a minimum the derivatives with respect to all independent variables must be zero:

$$\frac{dF}{dN_i^\alpha} = \mu_i^\alpha - \mu_i^\sigma = 0, \quad \frac{dF}{dN_i^\beta} = \mu_i^\beta - \mu_i^\sigma = 0 \quad (3.18)$$

It follows that

$$\mu_i^\alpha = \mu_i^\sigma = \mu_i^\beta = \mu_i \quad (3.19)$$

Hence, in equilibrium the chemical potentials are the same everywhere in the system. With this, we can further simplify Eq. (3.17):

$$dF = - (P^\beta - P^\alpha) dV^\beta + \gamma dA \quad (3.20)$$

This equation allows us to define the surface tension based on thermodynamics:

$$\left. \frac{\partial F}{\partial A} \right|_{T, V, V^\beta, N_i} \equiv \gamma \quad (3.21)$$

The surface tension tells us how the Helmholtz energy of the system changes when increasing the surface area while keeping the temperature, the total volume, the volume of phase β and the total amounts of all components constant.

Is this a useful equation? It is not so difficult to control T , V , and N_i but V^β might be difficult to keep constant. As we shall see later, for planar surfaces (and practically those which have small curvatures) the condition that V^β has to be kept constant can be dropped.

Question: Why is it not possible, using the same argument, e. g. $dF/dA = 0$, to conclude that at equilibrium γ must be zero? Explanation: The surface area A is not an independent parameter. Surface A and the volume V^β are related. If the volume of a body changes, in general its surface area also changes. V^β and A can thus not be varied independently. In fact, a law of differential geometry says that in general $\partial V/\partial A = (1/R_1 + 1/R_2)^{-1}$.

At this point we mention a simple, alternative way of deriving the Young-Laplace equation. In equilibrium we have $dF/dA = 0$. It leads to

$$\frac{dF}{dA} = \frac{\partial F}{\partial A} + \frac{\partial F}{\partial V^\beta} \cdot \frac{\partial V^\beta}{\partial A} = \gamma - (P^\beta - P^\alpha) \cdot \frac{\partial V^\beta}{\partial A} = 0 \quad (3.22)$$

Inserting $\partial V^\beta/\partial A = (1/R_1 + 1/R_2)^{-1}$, taking $\Delta P = P^\beta - P^\alpha$, and rearranging the equation directly leads to the Young-Laplace equation.

3.2.3 Location of the interface

At this point we should note that, fixing the bending radii, we define the location of the interface. A possible choice for the ideal interface is the one that is defined by the Young-Laplace equation. If the choice for the interface is different, the value for the surface tension must be changed accordingly. Otherwise the Young-Laplace equation would no longer be valid. All this can be illustrated with the example of a spherical drop [44]. We can, for instance, consider the evaporation or the condensation of liquid from, or to, a drop of radius r . There we have

$$V^\beta = \frac{4\pi}{3} r^3, \quad A = 4\pi r^2 \quad \Rightarrow \quad V^\beta = \frac{4\pi}{3} \left(\frac{A}{4\pi} \right)^{3/2} \quad \Rightarrow \quad \frac{\partial V^\beta}{\partial A} = \frac{r}{2} \quad (3.23)$$

If the interface is chosen to be at a radius r' , then the corresponding value for $\partial V^\beta/\partial A$ is $r'/2$. The pressure difference $P^\beta - P^\alpha$ can in principle be measured. This implies that

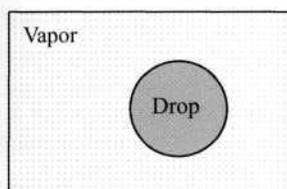


Figure 3.4: A drop in its vapor phase.

$P^\beta - P^\alpha = 2\gamma/r$ and $P^\beta - P^\alpha = 2\gamma'/r'$ are both valid at the same time. This is only possible if, dependent on the radius, one accepts a different interfacial tension. Therefore we used γ' in the second equation. In the case of a curved surface, the interfacial tension depends on the location of the Gibbs dividing plane! In the case of flat surfaces this problem does not occur. There, the pressure difference is zero and the surface tension is independent of the location of the ideal interface.

A possible objection could be that the surface tension is measurable and thus the Laplace equation assigns the location of the ideal interface. But this is not true. The only quantity that can be measured is mechanical work and the forces acting during the process. For curved surfaces it is not possible to divide volume and surface work. Therefore, it is not possible to measure *only* the surface tension.

3.2.4 Gibbs energy and definition of the surface tension

In this chapter we introduce a more useful equation for the surface tension. This we do in two steps. First, we seek an equation for the change in the Gibbs energy. The Gibbs energy G is usually more important than F because its natural variables, T and P , are constant in most applications. Second, we have just learned that, for curved surfaces, the surface tension is not uniquely defined and depends on where precisely we choose to position the interface. Therefore we concentrate on planar surfaces from now on.

For the Gibbs energy we write

$$dG = -SdT + V^\alpha dP^\alpha + V^\beta dP^\beta + \sum \mu_i dN_i + \gamma dA \quad (3.24)$$

Assuming that the interface is flat (planar) we have the same pressure in both phases $P^\alpha = P^\beta = P$ and we get

$$dG = -SdT + VdP + \sum \mu_i dN_i + \gamma dA \quad (3.25)$$

With the help of this equation it is also possible to give a definition of the interfacial tension, which is equivalent to the previous definition:

$$\left. \frac{\partial G}{\partial A} \right|_{T, P, N_i} \equiv \gamma \quad (3.26)$$

The surface tension is the increase in the Gibbs free energy per increase in surface area at constant T , P , and N_i .

3.2.5 Helmholtz surface energy, interfacial enthalpy, and Gibbs surface energy

Until now we have considered the total energy quantities of the system. Now we turn to the interfacial excess quantities. We start with the internal interfacial or internal surface energy

$$dU^\sigma = TdS^\sigma + \sum \mu_i dN_i^\sigma + \gamma dA \quad (3.27)$$

The term PdV^σ disappears, because the ideal interface has no volume.

In Eq. (3.27) U^σ is a homogeneous, linear function of the extensive properties S^σ , A , and all N_i^σ 's of the system. It may therefore be integrated, keeping the intensive properties T , γ , and all μ_i 's constant. Physically this means that it is possible to increase the "size" of the system by increasing the surface area and in proportion adding matter to the surface in such a way that the ratio $dN_1^\sigma : dN_2^\sigma : dN_3^\sigma : \dots$ is the same as in the original (and final) system. This can be realized by, for instance, tilting a sealed test tube which is partially filled with a liquid (Fig. 3.5). Mathematically, the integration is possible because of Euler's theorem. Euler's theorem states that if $f(x, y)$ is a homogeneous, linear function of the variables x and y , then $f = x \cdot \partial f / \partial x|_y + y \cdot \partial f / \partial y|_x$. Application of Euler's theorem to U^σ in Eq. (3.27) with S^σ , A , and N_i^σ 's as variables leads to

$$U^\sigma = TS^\sigma + \sum \mu_i N_i^\sigma + \gamma A \quad (3.28)$$

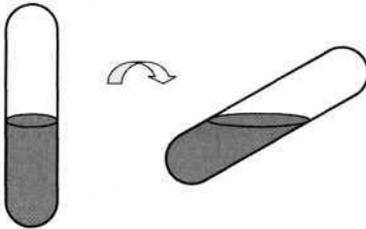


Figure 3.5: Increasing the surface area size by tilting a test tube.

For the free energy of the surface we use $F^\sigma = U^\sigma - TS^\sigma$ and get

$$F^\sigma = \gamma A + \sum \mu_i N_i^\sigma \Rightarrow \frac{F^\sigma}{A} = \gamma + \sum \mu_i \Gamma_i \quad (3.29)$$

The differential of F^σ is:

$$dF^\sigma = -S^\sigma dT + \sum \mu_i dN_i^\sigma + \gamma dA \quad (3.30)$$

Before turning to the surface enthalpy we would like to derive an important relationship between the surface entropy and the temperature dependence of the surface tension. The interfacial Helmholtz energy is a state function. Therefore we can use the Maxwell relations and obtain directly an important equation for the surface entropy:

$$-\left. \frac{\partial S^\sigma}{\partial A} \right|_{T, N_i^\sigma} = \left. \frac{\partial \gamma}{\partial T} \right|_{A, N_i^\sigma} \quad (3.31)$$

There are two common and widely used definitions of the interfacial excess enthalpy. We can argue that enthalpy is equal to the internal energy minus the total mechanical work $\gamma A - PV^\sigma$. Since in the Gibbs convention $PV^\sigma = 0$ we define

$$H^\sigma \equiv U^\sigma - \gamma A \quad (3.32)$$

This definition is recommended by the IUPAC [45]. One consequence is that $H = H^\alpha + H^\beta + H^\sigma + \gamma A$. The differential is again easily obtained to be

$$dH^\sigma = TdS^\sigma + \sum \mu_i dN_i^\sigma - Ad\gamma \quad (3.33)$$

Alternatively, one could argue that the enthalpy is equal to the internal energy minus the volume work PV^σ . Since the volume work is zero in the Gibbs convention we simply get

$$H'^\sigma \equiv U^\sigma \quad (3.34)$$

What is the interfacial excess Gibbs energy? The difference between U^σ and F^σ should be the same as the one between H^σ and G^σ . Therefore we define

$$G^\sigma \equiv H^\sigma - TS^\sigma = F^\sigma - \gamma A = \sum \mu_i N_i^\sigma \quad (3.35)$$

One consequence is that $G = G^\alpha + G^\beta + G^\sigma + \gamma A$. The differential is

$$dG^\sigma = -S^\sigma dT + \sum \mu_i dN_i^\sigma - Ad\gamma \quad (3.36)$$

With the alternative definition of H'^σ we obtain

$$G'^\sigma \equiv H'^\sigma - TS^\sigma = F^\sigma \quad (3.37)$$

and $G = G^\alpha + G^\beta + G'^\sigma$.

3.3 The surface tension of pure liquids

For pure liquids the description becomes much simpler. We start by asking, how is the surface tension related to the surface excess quantities, in particular to the internal surface energy and the surface entropy?

One important relationship can be derived directly from Eq. (3.29). For pure liquids we choose the Gibbs dividing plane such that $\Gamma = 0$. Then the surface tension is equal to the free surface energy per unit area:

$$f^\sigma = \frac{F^\sigma}{A} = \gamma \quad (3.38)$$

Let us turn to the entropy. We start with Eq. (3.31). For pure liquids the position of the interface is chosen such that $N^\sigma = 0$. For homogeneous systems we also know that $s^\sigma \equiv S^\sigma/A = \partial S^\sigma/\partial A$. Putting everything together we find

$$s^\sigma = - \left. \frac{\partial \gamma}{\partial T} \right|_{P,A} \quad (3.39)$$

The surface entropy per unit area is given by the change in the surface tension with temperature. In order to determine the surface entropy one needs to measure how the surface tension changes with temperature.

Question: If the volume of the interface is zero, why is the condition important that it is constant? Reason: A change in pressure may change the structure of the interface. Since in the Gibbs approach we view the surface as being "collapsed" to an ideal plane, its entropy may change, even though its volume is zero. Eq. (3.39) is generally valid, not only within Gibbs formalism.

For the majority of liquids, the surface tension decreases with increasing temperature. This behavior was already observed by Eötvös, Ramsay & Shields at the end of the 19th century [46,47]. The entropy on the surface is thus increased, which implies that the molecules at the surface are less ordered than in the bulk liquid phase.

What about the internal energy? For a pure liquid we have $U^\sigma = TS^\sigma + \gamma A$. Division by A and, assuming that we have a homogeneous system, leads to

$$u^\sigma \equiv \frac{U^\sigma}{A} = Ts^\sigma + \gamma \quad (3.40)$$

or

$$u^\sigma = \gamma - T \cdot \left. \frac{\partial \gamma}{\partial T} \right|_{P,A} \quad (3.41)$$

It is thus possible to determine the internal surface energy and the surface entropy by measuring the dependence of the surface tension on the temperature.

□ **Example 3.2.** The surface tension of water decreases with increasing temperature from 74.23 mNm⁻¹ at 10°C, to 71.99 at 25°C, and 67.94 mNm⁻¹ at 50°C. Calculate f^σ , s^σ and u^σ at 25°C.

The first one is easy to answer: $f^\sigma = \gamma = 71.99$ mNm⁻¹. Using the other two values for the surface tension we can estimate that $\partial\gamma/\partial T = -157.3 \times 10^{-6}$ Nm⁻¹K⁻¹ at 25°C. Thus, the surface entropy is $s^\sigma = 157.3 \times 10^{-6}$ mNm⁻¹K⁻¹. Using Eq. (3.41) the surface energy is obtained to be $u^\sigma = 71.99 + 293.2 \cdot 0.1573$ mNm⁻¹ = 118.09 mNm⁻¹.

How does the heat flow during an increase in the surface area? In a reversible process TdS is the heat δQ that the system absorbs. The heat absorption is proportional to the surface area increase and we can write $\delta Q = qdA$. Here, q is the heat per unit area that is taken up by the system. With $dS = s^\sigma dA$ and $s^\sigma = -\partial\gamma/\partial T$ we get

$$qdA = \delta Q = TdS = Ts^\sigma dA = -T \cdot \frac{\partial \gamma}{\partial T} \cdot dA \quad (3.42)$$

or

$$q = -T \cdot \frac{\partial \gamma}{\partial T} \quad (3.43)$$

This is the heat per unit area absorbed by the system during an isothermal increase in the surface. Since $\partial\gamma/\partial T$ is mostly negative the system usually takes up heat when the surface area is increased. Table 3.1 lists the surface tension, surface entropy, and internal surface energy of some liquids at 25°C.

Table 3.1: Surface tension, surface entropy, and internal surface energy of some liquids at 25°C.

	$\gamma = f^\sigma (\text{mNm}^{-1})$	$T \cdot s^\sigma (\text{mNm}^{-1})$	$u^\sigma (\text{mNm}^{-1})$
Mercury	485.48	61.1	549.6
Water	71.99	46.9	121.1
<i>n</i> -hexane	17.89	30.5	49.9
<i>n</i> -heptane	19.65	29.2	50.3
<i>n</i> -octane	21.14	28.3	50.9
<i>n</i> -nonane	22.38	27.9	51.7
<i>n</i> -decane	23.37	27.4	52.2
Methanol	22.07	23.0	46.3
Ethanol	21.97	24.8	48.0
1-propanol	23.32	23.1	47.6
1-butanol	24.93	26.8	53.0
1-hexanol	23.81	29.8	55.6
Toluene	27.93	35.4	65.1

3.4 Gibbs adsorption isotherm

It is well known that the surface tension of water decreases when a detergent is added. Detergents are strongly enriched at the surface, which lowers the surface tension. This change of surface tension upon adsorption of substances to the interface, is described by the Gibbs adsorption isotherm.

3.4.1 Derivation

The Gibbs adsorption isotherm is a relationship between the surface tension and the excess concentrations. To derive it we start with Eq. (3.28). Differentiation of Eq. (3.28) leads to

$$dU^\sigma = TdS^\sigma + S^\sigma dT + \sum \mu_i dN_i^\sigma + \sum N_i^\sigma d\mu_i + \gamma dA + Ad\gamma \quad (3.44)$$

Equating this to expression (3.27) results in

$$0 = S^\sigma dT + \sum N_i^\sigma d\mu_i + Ad\gamma \quad (3.45)$$

At constant temperature it can be simplified to

$$d\gamma = - \sum \Gamma_i d\mu_i \quad (3.46)$$

Equations (3.45) and (3.46) are called **Gibbs adsorption isotherms**. In general, "isotherms" are state functions plotted versus pressure, concentration, etc. at constant temperature.

One word of caution: The given equation is only valid for those surfaces whose deformation is reversible and plastic, i. e., liquid surfaces. In solids, changes of the surface are usually accompanied by elastic processes [48, 49]. In order to consider elastic tensions an additional term has to be added to Eq. (3.45). This will be discussed in Section 8.4.1.

3.4.2 System of two components

The simplest application of the Gibbs adsorption isotherm is a system of two components, e. g., a solvent 1 and a solute 2. In this case we have

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \quad (3.47)$$

The ideal interface is conveniently defined such that $\Gamma_1 = 0$. Then we get

$$d\gamma = -\Gamma_2^{(1)} d\mu_2 \quad (3.48)$$

The superscript “(1)” should remind us of the special choice of the interface. The chemical potential of the solute is described by the equation

$$\mu_2 = \mu_2^0 + RT \cdot \ln \frac{a}{a_0} \quad (3.49)$$

Here, a is the activity and a_0 is a standard activity (1 mol/L). Differentiating with respect to a/a_0 at constant temperature leads to

$$d\mu_2 = RT \cdot \frac{d(a/a_0)}{a/a_0} = RT \cdot \frac{da}{a} \quad (3.50)$$

Substituting this into Eq. (3.48) leads to

$$\Gamma_2^{(1)} = -\frac{a}{RT} \cdot \left. \frac{\partial \gamma}{\partial a} \right|_T \quad (3.51)$$

This is a very important equation. It directly tells us that when a solute is enriched at the interface ($\Gamma_2^{(1)} > 0$), the surface tension decreases when the solution concentration is increased. Such solutes are said to be surface active and they are called **surfactants** or surface active agents. Often the term amphiphilic molecule or simply amphiphile is used. An amphiphilic molecule consist of two well-defined regions: One which is oil-soluble (lyophilic or hydrophobic) and one which is water-soluble (hydrophilic).

When a solute avoids the interface ($\Gamma_2^{(1)} < 0$), the surface tension increases by adding the substance. Experimentally Equation (3.51) can be used to determine the surface excess by measuring the surface tension versus the bulk concentration. If a decrease in the surface tension is observed, the solute is enriched in the interface. If the surface tension increases upon addition of solute, then the solute is depleted in the interface.

□ **Example 3.3.** You add 0.5 mM SDS (sodium dodecylsulfate, $\text{NaSO}_4(\text{CH}_2)_{11}\text{CH}_3$) to pure water at 25°C. This leads to a decrease in the surface tension from 71.99 mJ/m² to 69.09 mJ/m². What is the surface excess of SDS?

At such low activities and as an approximation we replace the activity a by the concentration c and get

$$\frac{\partial \gamma}{\partial a} \approx \frac{\Delta \gamma}{\Delta c} = \frac{(0.06909 - 0.07199)\text{Nm}^{-2}}{(0.0005 - 0)\text{molL}^{-1}} = -5.80 \frac{\text{NL}}{\text{mol m}} \quad (3.52)$$

In water SDS dissociates into a negatively charged surfactant and Na^+ . For each adsorbed surfactant we in addition have one Na^+ ion in the electric double layer. This has to be counted in the Gibbs adsorption isotherm [50]. It follows that

$$\Gamma = -\frac{a}{2RT} \cdot \frac{\partial \gamma}{\partial a} = \frac{0.0005 \text{ mol L}^{-1}}{8.31 \cdot 298 \text{ J mol}^{-1}} \cdot 5.80 \frac{\text{N L}}{\text{mol m}} = 5.85 \times 10^{-7} \frac{\text{mol}}{\text{m}^2} \quad (3.53)$$

Every molecule occupies an average surface area of 2.84 nm^2 .

The choice of the ideal interface in the Gibbs adsorption isotherm (3.51) for a two-component system is, in a certain view, arbitrary. It is, however, convenient. There are two reasons: First, on the right side there are physically measurable quantities (a, γ, T), which are related in a simple way to the interfacial excess. Any other choice of the interface would lead to a more complicated expression. Second, the choice of the interface is intuitively evident, at least for $c_1 \gg c_2$. One should, however, keep in mind that different spatial distributions of the solute can lead to the same $\Gamma_2^{(1)}$. Figure 3.6 shows two examples of the same interfacial excess concentration $\Gamma_2^{(1)}$. In the first case the distribution of molecules 2 stretches out beyond the interface, but the concentration is nowhere increased. In the second case, the concentration of the molecules 2 is actually increased.

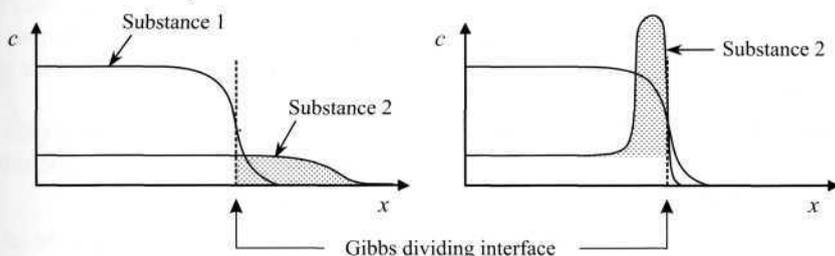


Figure 3.6: Examples of two different concentration profiles leading to the same interfacial excess concentration $\Gamma_2^{(1)}$.

3.4.3 Experimental aspects

How can Eq. (3.51) be verified? For verification, the two variables — concentration and surface tension — need to be determined independently. One way is to use radioactively labeled dissolved substances. The radioactivity close to the surface is measured. β -emitters (^3H , ^{14}C , ^{35}S) are suitable because electrons only travel a short range, i.e., any recorded radioactivity comes from molecules from the interface, or close below [51].

Plots of surface tension versus concentration for *n*-pentanol [52], LiCl (based on Ref. [53]), and SDS in an aqueous medium at room temperature are shown in Fig. 3.7. The three curves are typical for three different types of adsorption. The SDS adsorption isotherm is typical for amphiphilic substances. In many cases, above a certain critical concentration defined aggregates called micelles are formed (see Section 12.1). This concentration is called the critical micellar concentration (CMC). In the case of SDS at 25°C this is at 8.9 mM . Above the CMC the surface tension does not change significantly any further because any added substance goes into micelles not to the liquid–gas interface.

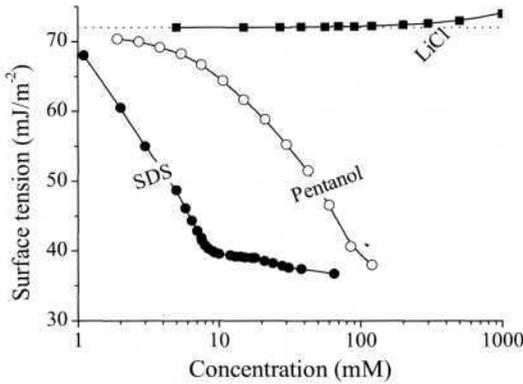


Figure 3.7: Plots of surface tension versus concentration for *n*-pentanol [52], LiCl (based on Ref. [53]), and SDS in an aqueous medium at room temperature.

The adsorption isotherm for pentanol is typical for lyophobic substances, i. e., substances which do not like to stay in solution, and for weakly amphiphilic substances. They become enriched in the interface and decrease the surface tension. If water is the solvent, most organic substances show such a behavior. The LiCl adsorption isotherm is characteristic for lyophilic substances. Most ions in water show such behavior.

In order to describe the influence of a substance on the surface tension, one could specify the gradient of the adsorption isotherm for $c \rightarrow 0$. A list of these values for some substances dissolved in water at room temperature is shown in Table 3.2.

Solute	$d(\Delta\gamma)/dc(10^{-3} \text{ Nm}^{-1} \text{ M}^{-1})$
HCl	-0.28
LiCl	1.81
NaCl	1.82
CsCl	1.54
CH ₃ COOH	-38

Table 3.2: Gradient of the adsorption isotherm for $c \rightarrow 0$ of different solutes in water at 25°C.

- **Example 3.4.** Adding 1 mM NaCl in water results in a slight increase of the surface tension of $\Delta\gamma = 1.82 \times 10^{-3} \text{ N/m} \cdot 0.001 = 1.82 \times 10^{-6} \text{ N/m}$. Upon addition of 1 mM CH₃COOH the surface tension decreases by $3.8 \times 10^{-5} \text{ N/m}$.

3.4.4 The Marangoni effect

Local variations in the surface concentration of solutes will give rise to local differences in the surface tension. Such a gradient in surface tension will result in a net transport of liquid from the region of lower surface tension towards regions with higher surface tension. This so-called Marangoni effect was first described by James Thompson (brother of Lord Kelvin) and studied in detail by Carlo Marangoni² [56]. A famous example of the Marangoni effect are

² Carlo Marangoni, 1840-1925. Italian physicist, professor at a lyceum in Florence.

“tears of wine”. This term denotes a special flow pattern that is formed if a mixture of water and ethanol (e.g. red wine) is filled in a wine glass or a watch dish [54, 55]. The liquid wets the surface of the glass and is pulled up a certain distance along the walls by capillary forces. Since ethanol has a higher vapor pressure, it will evaporate faster from the thin film than water. At the rim, where the liquid film is thinnest, the ethanol concentration will decrease fastest. Since the surface tension of ethanol is much smaller than that of water, the reduced ethanol concentration at the rim leads to a higher surface tension at the rim compared to the bulk liquid. This drives the flow of more liquid up the wall towards the rim. At some point the accumulation of liquid at the rim will become instable and lead to the formation of droplets that start flow down again due to gravity, resulting in “tears” or fingerlike structures (Fig. 3.8). An example of a technical application of the Marangoni effect is the drying of silicon wafers in the semiconductor industry after wet cleaning processes in aqueous media. By blowing ethanol vapor over the wet surface through a moving nozzle efficiently drives the water film off the wafer.

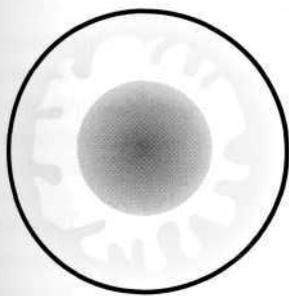


Figure 3.8: Schematic of the flow pattern for tears of wine.

3.5 Summary

- To apply the thermodynamic formalism to surfaces, Gibbs defined the ideal dividing plane which is infinitely thin. Excess quantities are defined with respect to a particular position of the dividing plane. The most important quantity is the interfacial excess which is the amount of substance enriched or depleted at an interface per unit area.
- For a pure liquid the Gibbs dividing plane is conveniently positioned so that the surface excess is zero. Then the surface tension is equal to the surface Helmholtz energy and the interfacial Gibbs energy: $f^\sigma = g^\sigma = \gamma$.
- For solutions the Gibbs dividing plane is conveniently positioned so that the surface excess of the solvent is zero. Then the Gibbs adsorption isotherm (Eq. 3.51) relates the surface tension to the amount of solute adsorbed at the interface:

$$\Gamma = -\frac{a}{RT} \cdot \frac{\partial \gamma}{\partial a}$$

When the solute is enriched at the interface, the surface tension decreases upon addition of a solute. When a solute avoids the interface, the surface tension increases when adding the substance.

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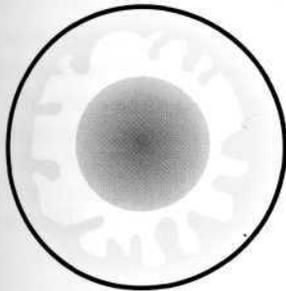


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3.6 Exercises

1. The surface tensions (in mN/m) of methanol and octane are

	10°C	25°C	50°C
Methanol	23.23	22.07	20.14
Octane	22.57	21.14	18.77

Calculate the surface entropy and the internal surface energy at 25°C.

2. The surface tension of water with a mole fraction of 0.001, 0.002, 0.003, ..., 0.007 of *n*-propanol is 67.4, 64.4, 61.9, 59.7, 57.7, 55.8, and 54.1 mN/m at 25°C, respectively. Estimate the surface excess of propanol at mole fractions of 0.002, 0.004, and 0.006. Does the surface excess increase linearly with the mole fraction?
3. Soap bubbles: To stabilize a bubble, surfactants are usually added to water. Assume we add a surfactant to a concentration of 2 mM. At this concentration we have a positive surface excess. As an average, each surfactant molecule occupies a surface area of 0.7 nm². Estimate the change in pressure inside a soap bubble with a radius of 1 cm compared to a hypothetical bubble formed from pure water.
4. Eq. (3.51) can be used to describe the adsorption of gases to surfaces. Then it can be written as

$$\Gamma = -\frac{1}{RT} \cdot \frac{d\gamma}{d \ln P}, \quad (3.54)$$

with P being the partial pressure of the adsorbing gas. Derive Eq. (3.54) from Eq. (3.51).