

4 Thermodynamic potentials

4.1 Phases

We start with the definitions of the terms we will use in this section.

States of matter, solutions

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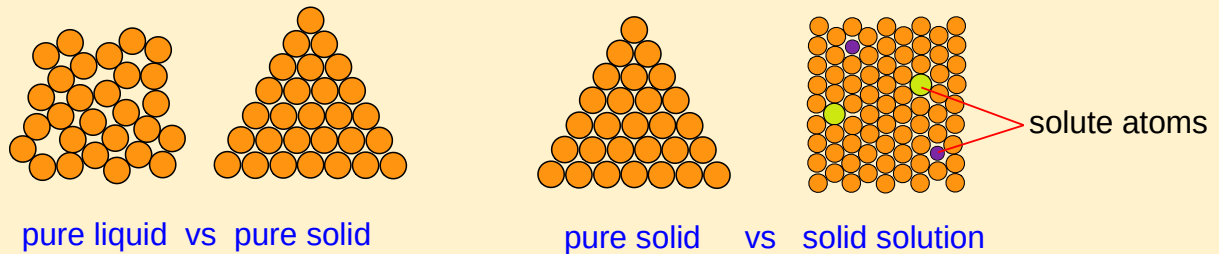


Figure 17: Typical microstructures of pure liquid and pure solid phases, as well as solid solutions.

A phase is defined by two criteria:

1. The atomic arrangement,
2. The chemical species present (although not usually their relative concentrations).

When comparing two materials, or two regions of a single material, if either 1 or 2 is different then they are a different phase.

Phases of pure materials and alloys

Pure materials: A pure material consists of only one atomic or molecular species. The phases present therefore depend only on the temperature (also pressure, but we will neglect that here).

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The major phases present in pure materials are familiar and only due to the arrangement of their constituents: **solid, liquid, gas.**

A solid can also undergo a change in phase due to a transformation from one crystal arrangement to another (FCC, BCC, HCP).

Comment: There are many other exotic phases that can be found in nature and in engineering applications. Liquid crystals are good examples, where elongated molecules are arranged in an ordered (crystal like) manner in terms of their orientation, but disordered (liquid-like) in terms of their position. These systems follow the qualitative principles introduced in this course (see examples paper/quiz).

Liquid crystals are very useful because an electric field can easily orient the elongated molecules in this phase, which in turn will affect light polarisation. So an electric signal can control light transmission, making them well suited for display applications.

Alloys: An alloy is a mixture of elements.

In this course we will be mostly concerned with **binary alloys** : mixtures of only two different components. The phases present in an alloy depend on the temperature, pressure and composition of the alloy (i.e. the proportion of each component).

The map of stable phases for each combination is the phase diagram.

Example: copper-nickel phase diagram

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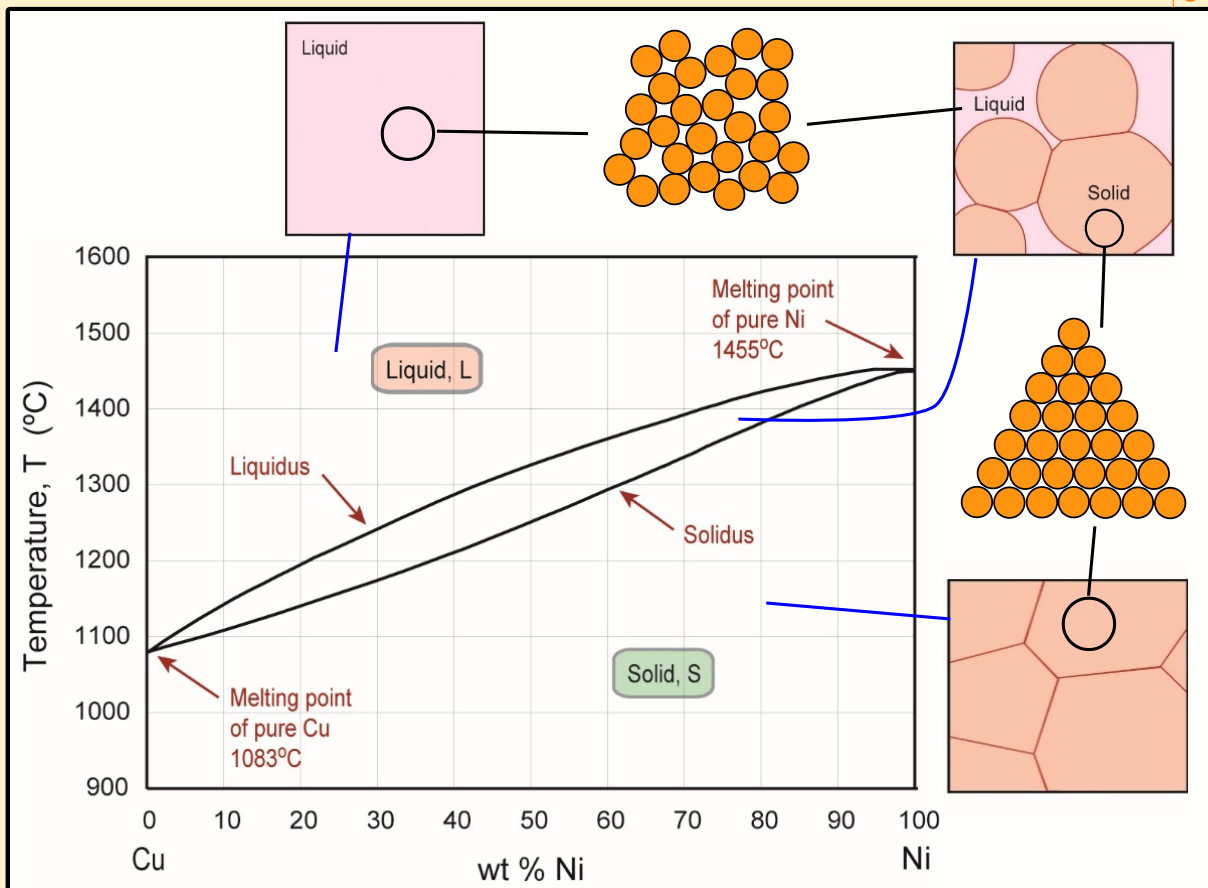


Figure 18: Copper-Nickel phase diagram and microstructures in different domains. Adapted from Ashby, Shercliff, Cebon

The Cu-Ni system has a particularly simple phase diagram, with three regions of interest:

1. At low temperatures the alloy forms a single phase solid solution of Cu in Ni (or vice versa). The material remains single phase, with one element fully dissolved in the other, at all compositions.
2. At high temperatures the material is again single phase, but now a liquid solution of one element in the other.
3. A two phase region lies in between, in which the stable state is a mixture of a liquid phase (which is a liquid solution of Cu and Ni) and a solid phase (a solid solution of Cu and Ni).

4.2 Free energy

In this section, we will study the driving force behind phase transformation, and phase equilibrium. But the approach is general and will later be applied to other forms of transformation, in the context of osmosis and even chemical reactions.

Work availability

Consider a material made of components that could transform: state change, phase separation, chemical reactions, etc.

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What do we know already?

$$dU = \delta Q - \delta W = TdS - T\delta S_{irr} - \delta W \text{ and } \delta S_{irr} \geq 0$$

The work δW may be split into a contribution from pressure forces, and other work that we may collect (or give away) $\delta W'$

$$\Rightarrow dU = TdS - T\delta S_{irr} - pdV - \delta W'$$

We could estimate how much useful work we could *at best* collect:

$$\delta W' = -dU + TdS - T\delta S_{irr} - pdV \leq -dU + TdS - pdV$$

Gibbs Free Energy

Considering the common situation where **temperature and pressure are constant**, it is convenient to introduce the function:

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$$G = U + pV - TS = H - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dG = dU + pdV - TdS \text{ if } dp = dT = 0$$

We therefore get:

$$\delta W' \leq -dG$$

The useful work available for a transformation is at best equal to the decrease of G.

G is called the **Gibbs Free Energy**.

You will see next term in Thermofluids a generalisation of this approach to estimate the availability of useful energy in more complex transformations.

Thermodynamic potentials

But here we are not interested in building machines... i.e. we are not collecting useful work. We are concerned with the transformations of materials.

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$$\delta W' = 0$$

This leads to the following statement already introduced in the Teach-yourself phase diagram paper.

- During the evolution of a material under isobaric and isothermal condition, the variation of Gibbs Free Energy must be negative:

$$dG \leq 0$$

- At the equilibrium, the Gibbs Free Energy is minimum.

The Gibbs Free Energy is an extensive quantity that depends on pressure, temperature, as well as the composition, state & microstructure of the material. Considering a system that is not necessarily at the equilibrium, one can introduce internal variables that characterise its state and eventual transformations towards equilibrium.

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$$G(P, T, \phi)$$

The variable ϕ represents any quantity affected by the evolution towards equilibrium. In the context of a phase transformation, that could be for instance the proportion of solid or liquid or the composition of the different phases. In a chemical reaction, it may be the amount of product formed, etc. We will see specific examples later and it will make more sense as we go along.

Because the system evolves towards a state that minimises G for a given P and T , the Gibbs Free Energy is called a thermodynamic potential (see figure 19).

The variable ϕ is not controlled by us in the same way as we could control the pressure and temperature. For a given pressure P and temperature T , the state observed at equilibrium is the state $\phi_{eq}(P, T)$ such that

$$\frac{\partial G}{\partial \phi}(P, T, \phi_{eq}) = 0.$$

This allows us to establish a condition for equilibrium and use this result to predict or control the equilibrium state ϕ_{eq} . It will be useful later on.

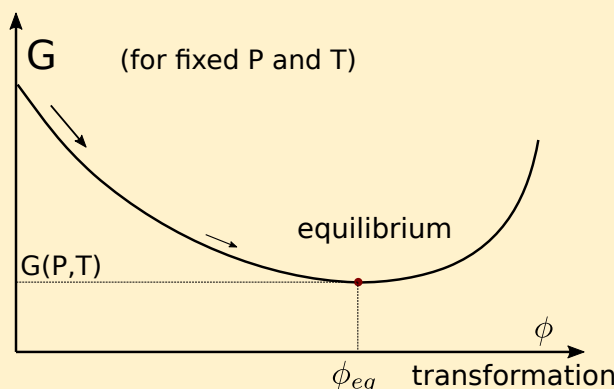


Figure 19: Sketch of the free energy evolution as a function of extent of a transformation, for constant pressure and temperature. The ϕ axis is an abstraction, and depends on the particular transformation considered. We will see a couple of examples in the course.

At the equilibrium, the Gibbs Free Energy G is a function of P and T only, defined as:

$$G(P, T) = G(P, T, \phi_{eq})$$

4.3 Phase equilibrium

4.3.1 Solid, Liquid & Gas phase transitions

A collection of molecules can be organised in different ways. They could form a regular dense packing (crystalline solid), or dense disorganised assembly (liquid), or even cover large volume at low density (gas). We know of course that temperature and pressure are important control parameters.

Could we use our understanding of free energy to determine the domains of stability of each phase?

Consider the free energy functions of a material in its three different states:

$$\text{Solid: } G_s = U_s + pV_s - TS_s$$

$$\text{Liquid: } G_l = U_l + pV_l - TS_l$$

$$\text{Gas: } G_g = U_g + pV_g - TS_g$$

Because atoms attract each other, the internal energy is lower when particles are closer to each other for a given temperature. So qualitatively we expect:

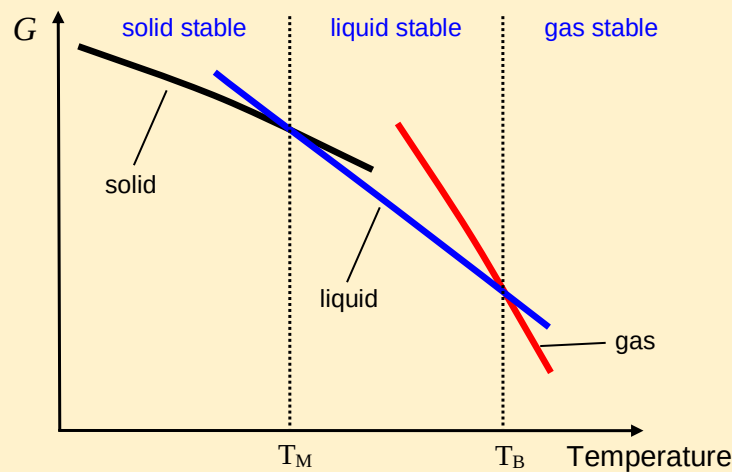
$$U_s(T) < U_l(T) < U_g(T)$$

$$V_s(T) \approx V_l(T) < V_g(T)$$

However, because entropy is a measure of disorder, we also expect that:

$$S_g(T) > S_l(T) > S_s(T)$$

As a result, the Free Energy of a gas starts higher than the free energy of a liquid at high temperature, but should decrease faster with temperature. The curves are expected to cross. The same argument can be applied for solids and liquids (see figure 20).



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Figure 20: Sketch of the free energy as a function of temperature for different states of a material.

Using the Gibbs free energy to predict the observed state

Take a mixture of solid (mole fraction ϕ_s) and liquid (mole fraction $\phi_l = 1 - \phi_s$).

The total free energy is:

$$G = \phi_s G_s + \phi_l G_l$$

$$G = \phi_s (G_s - G_l) + G_l$$

ϕ_s is an unknown, but we know that its value evolves towards a minimum of the free energy.

$$dG = (G_s - G_l)d\phi_s \leq 0$$

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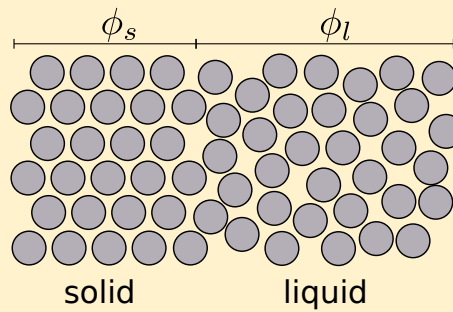


Figure 21: Microstructure of a pure material undergoing a solid-liquid transition.

- $T < T_M$: $G_s < G_l$. $d\phi_s > 0$, G minimum for $\phi_s = 1$, all solid
- $T > T_M$: $G_s > G_l$. $d\phi_s < 0$, G minimum for $\phi_s = 0$, all liquid.
- $T = T_M$: $dG/d\phi_s = 0$ for any ϕ_s . The two states happily coexist.

You will find out later in the course that in addition to the bulk free energies G_s and G_l , there is also an additional surface energy term to account for the solid/liquid interface.

4.3.2 Alloys

Free energy of a mixture

Consider now two components A and B, in proportions x_a and $x_b = 1 - x_a$. We can ask if, based on thermodynamic considerations, they should mix or not.

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Let's define G_u the free energy (per mol or per mass) of the unmixed components:

$$G_u = x_a G_a + x_b G_b = G_a + (G_b - G_a)x_b$$

The free energy of the mixed configuration contains additional terms:

$$G_m = G_u + \Delta U_m + p\Delta V - T\Delta S_m$$

- ΔU_m is the variation of internal energy due to mixing. Each A or B atom/molecule now interacts with a number of A and B, rather than their only their siblings as in the pure body case. This causes a change of internal energy.
- $p\Delta V$ is simply the work of pressure forces in case there is a change of density during mixing. It can usually be neglected for liquids and solids.
- ΔS_m is the entropy of mixing calculated in the first lecture.

Miscible materials The entropy of mixing was already calculated in the first lecture (see figure 5). It is always positive, and tends to lower the free energy of the mixture. It is often the dominant contribution to the free energy of mixing.

Ignoring $\Delta U_m + p\Delta V$, the free energy therefore takes the form of a convex function of the composition x_b , depicted on figure 22. Whatever the proportion of B is, the mixed Free energy G_m is always lower than the unmixed case.

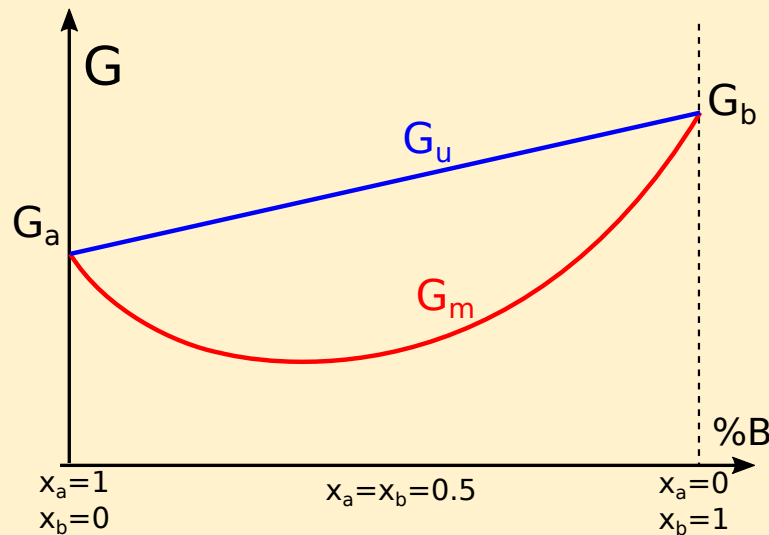


Figure 22: Free energy as a function of proportion of component B for miscible materials.

Non miscible materials Some components however don't like each other, e.g. water and oil. In this case, the energy term ΔU_m could be large and positive. This extra cost may cause the materials to be non-miscible. This effect is associated with a non-convex free energy curve as drawn on figure 23.

To understand why phases separate in this case, a graphical approach is by far the simplest. Let's look at the graph on Figure 23 and find the number of phases and their composition for a system of equal proportions of A and B.

At this point, we should bear mind that the system is not constrained to chose between a case where pure A and pure B are separated, and a case where they are fully mixed. We could also have a phase consisting of mostly A with some B in it, and another one consisting of mostly B with some A in it. As long as in average we end up with the right total proportion of A and B, the system will get there if it provides a decrease in free energy.

Let's assume that the system splits into two phases of arbitrary proportions of B x_1 and x_2 . How to choose these proportions such that the overall system's free energy is minimal? This would be achieved with the tangent construction on the figure 23. Any other choice of x_1 and x_2 would lead to a larger value of the total free energy.

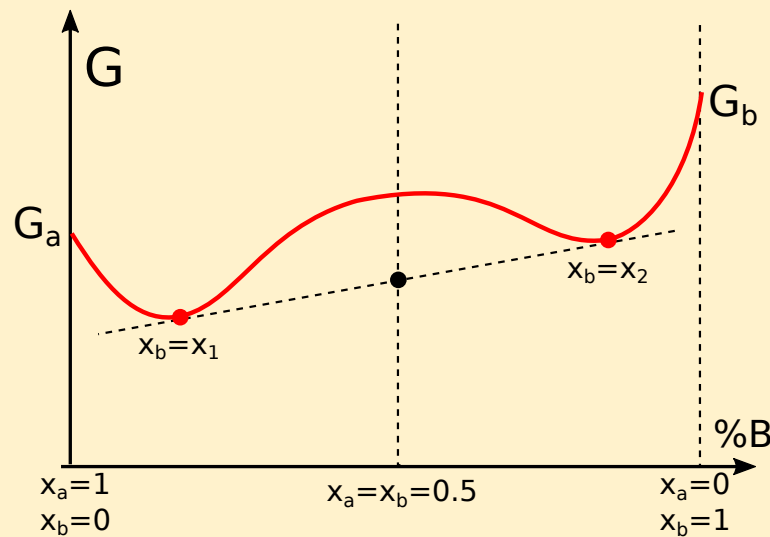


Figure 23: Free energy as a function of proportion of component B for non miscible materials.

4.3.3 Phase transitions of mixtures

We now have all the information we need to understand simple phase diagrams such as Cu-Ni. Figure 24 shows an equivalent phase diagram. Can we interpret this diagram based on free energy consideration?

- The diagram involves two phases, one solid solution, and one liquid solution. For each phase, we can introduce a specific free energy function of the composition, G_s and G_l . Each of them should look like the function G_m previously introduced (figure 22).
- As we discussed in the section on the phase transitions of pure bodies, the free energy of a solid is lower than the free energy of a liquid at low temperatures, but as temperature is increased, the free energy of the liquid decreases faster, until it becomes lower than the free energy of the solid. In the context of alloys, we expect the whole curves $G_s(x_b)$ and $G_l(x_b)$ to behave in this way.
- At low enough temperature, we anticipate that the free energy of the solid is always lower than the free energy of the liquid, $G_s < G_l$ for any x_b . We get a single phase solid solution.
- Similarly, at high temperature, we expect $G_s > G_l$ for any x_b . We get a single phase liquid solution.
- We can see however that, unless the curves happen to match exactly, they will interact in complicated ways for intermediate temperatures. Again, a

graphical method is best suited to identify the composition that minimises the total free energy, and understand when and why phase separation occurs. See Fig 24.

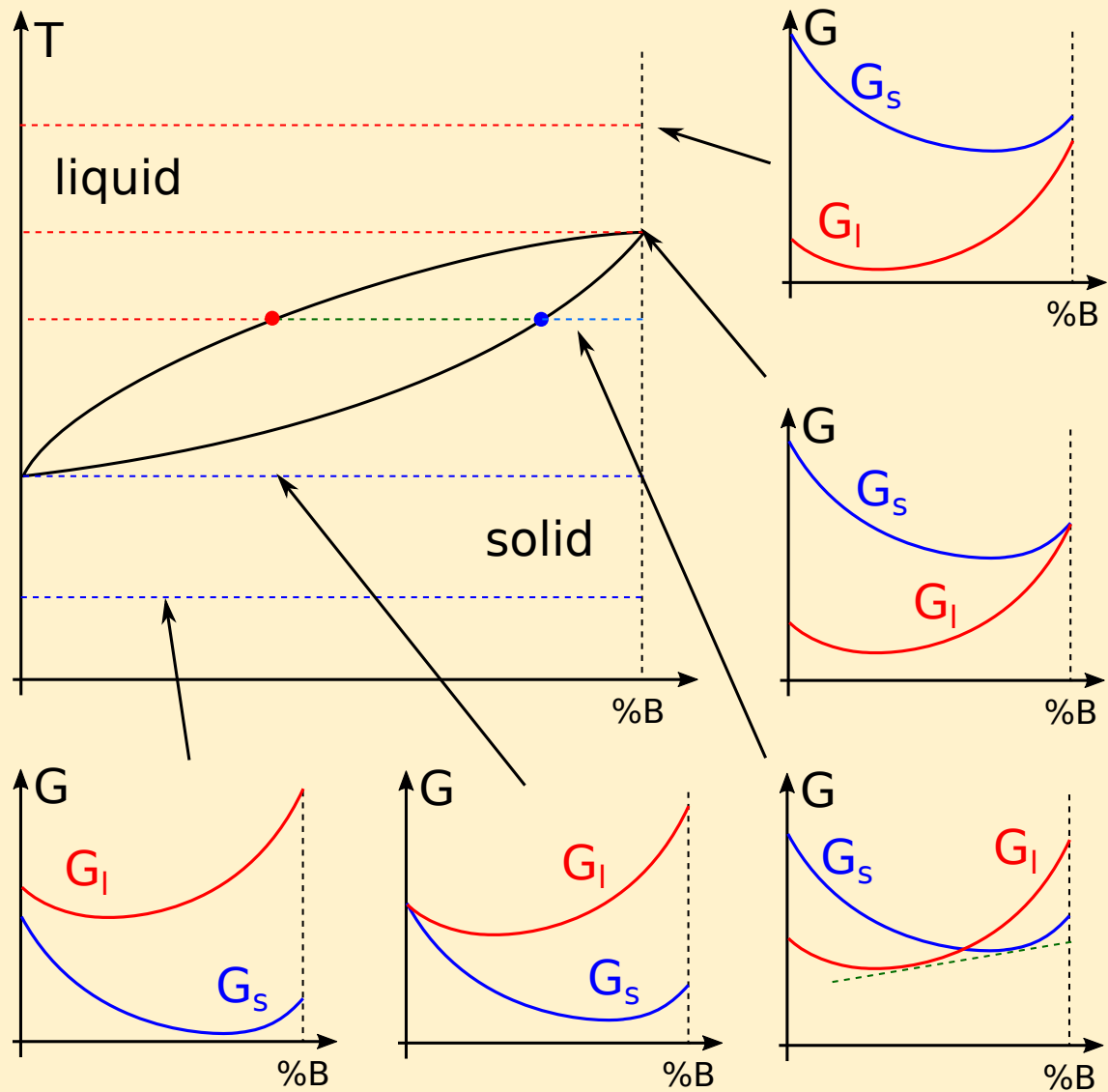


Figure 24: Interpretation of phase diagrams based on free energy curves.

Summary

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- By considering the dependence of the Gibbs free energy functions of different phases with respect to temperature, we could explain solid-liquid-gas transitions as the result of a Gibbs free energy minimisation.
- Looking at binary mixtures, and taking into account the role of the entropy of mixing and internal energy, we are able to qualitatively explain why certain materials mix and others don't.
- Phase diagrams can be qualitatively interpreted in terms of the Gibbs free energies functions of the different phases involved and their evolution with temperature.

4.4 Nucleation

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We have seen in section 4.3.1 that, for a given temperature and pressure, the equilibrium state of a material is the phase with the lowest free energy. This was derived by assuming that both phases were present and looking at the variations of the total free energy for a small transformation of some solid into some liquid, moving the interface with it.

The packing of the atoms or molecules at the interface between two phases is however different from the arrangement in the bulk of each phase. Locally, these particles are in a state of higher free energy. From the thermodynamic point of view, the interface between two phases comes with a cost and the system should minimise the area of the interface.

This is accounted for by a surface tension or surface energy γ . It is an energy per unit area, and also a force per unit length. This force is the tension along the interface that drives the system towards minimising this interface area.

If we have already a large amount of each material, the energy of the interface is insignificant. However, when a phase starts to form within another one, it starts with only a few atoms, **nucleating** a phase inside another. At this point, the surface energy plays an important role, because in a small nucleus, containing 10 to 100 atoms, a large proportion of the atoms are actually at the interface.

Would our results about phase transition and phase stability be affected by the presence of a surface energy during nucleation?

Free energy of a nucleus of solid in a fluid for $T < T_m$

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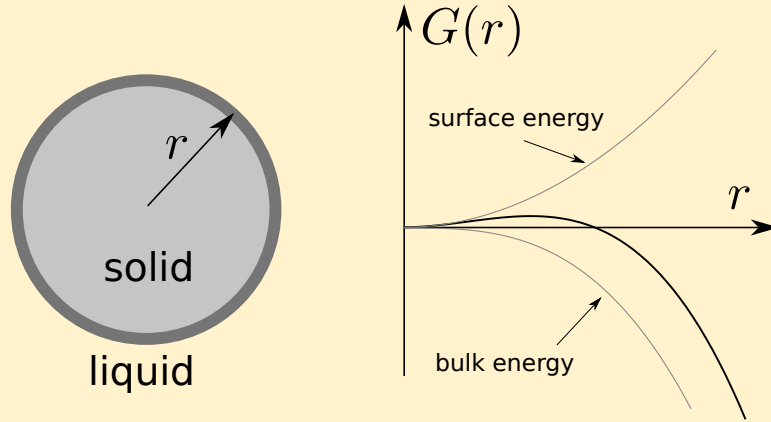


Figure 25: Spherical nucleus of radius r . Evolution of the systems Gibbs free energy G as a function of r for $T < T_m$.

Consider a spherical domain of solid, of radius r , in a liquid. To consider the stability of this nucleus, we will study how the total Gibbs free energy will evolve if r is changed (figure 25).

Let's consider the Gibbs free energy of solidification per unit volume, ΔG_v . If the temperature T is lower than the melting temperature T_m , we know that $\Delta G_v < 0$.

The total change in Gibbs free energy due to the formation of the nucleus is the sum of the bulk free energy and interfacial energy of the nucleus:

$$G(r) = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Nucleus stability

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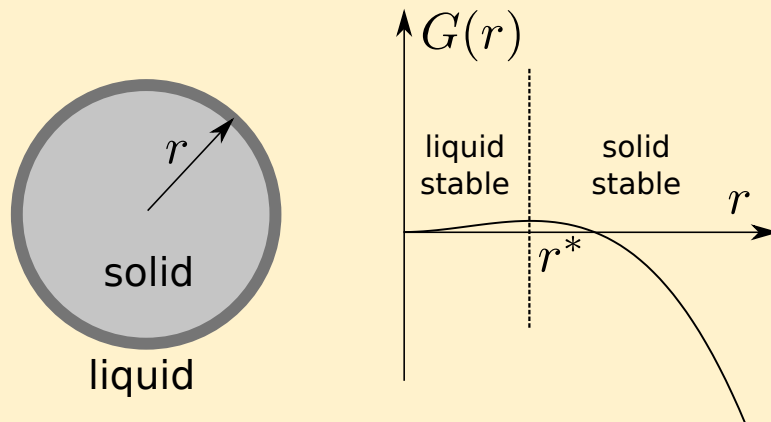


Figure 26: The Gibbs Free energy curve defines the stability domains of the liquid and solid phases.

To determine the stability of the nucleus, we consider the sign of dG/dr (figure 26). If G increases with r , the solid will not form, and instead melt back into the liquid. If G decreases with r , the nucleus will grow.

The shape of $G(r)$ shows that there is a critical radius r^* below which the nucleus is unstable. The nucleus needs to reach a certain size before it can grow.

The critical size is defined by:

$$\frac{dG}{dr}(r^*) = 0 \implies r^* = \frac{2\gamma}{|\Delta G_v|}$$

The larger r^* , the more difficult it will be to nucleate the solid.

When $T = T_m$, $\Delta G_v = 0$ and r^* is infinite. Temperatures below T_m are therefore required to nucleate the solid phase. How much smaller? We need to study how ΔG_v (and therefore r^*) varies with T .

Undercooling required for nucleation

By definition of the Gibbs free energy, we have:

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$$\Delta G = \Delta U + P\Delta V - T\Delta S = \Delta H - T\Delta S$$

It is often assumed that ΔH and ΔS do not vary too much with temperature³, i.e. that ΔH and ΔS are approximately constants, and use this to approximate the way ΔG depends on T .

At $T = T_m$ (and for a fixed pressure P), we have:

$$\Delta G(T_m) = \Delta H - T_m\Delta S = 0 \implies \Delta S = \Delta H/T_m$$

$$\Delta G(T) = \Delta H - T\Delta S = \Delta H - T\Delta H/T_m$$

$$\implies \Delta G(T) = \Delta H \cdot \left(\frac{T_m - T}{T_m} \right) \quad (21)$$

Essentially, $\Delta G(T)$ varies to the first order with $T - T_m$ and the coefficient can be related to the latent heat of the phase transformation.

In this case, r^* can be expressed as a function of T for $T < T_m$:

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$$r^* = \frac{2\gamma}{|\Delta G_v|} = \frac{2\gamma}{|\Delta H_v|} \frac{T_m}{(T_m - T)}$$

How big could a nucleus be if it were to spontaneously arise?

This is a difficult question. The trigger to nucleation would be random fluctuations of atoms which would by chance start to form a crystal. With a bit of luck, 10s to 100 atoms may transiently form a tiny crystal structure, so we could guess that a nucleus of size 1 nm may arise spontaneously.

³This assumption, often found in text books, is not necessarily correct and is discussed further at the end of this section. The result is robust nonetheless because even if they are not constant, their contributions cancel out.

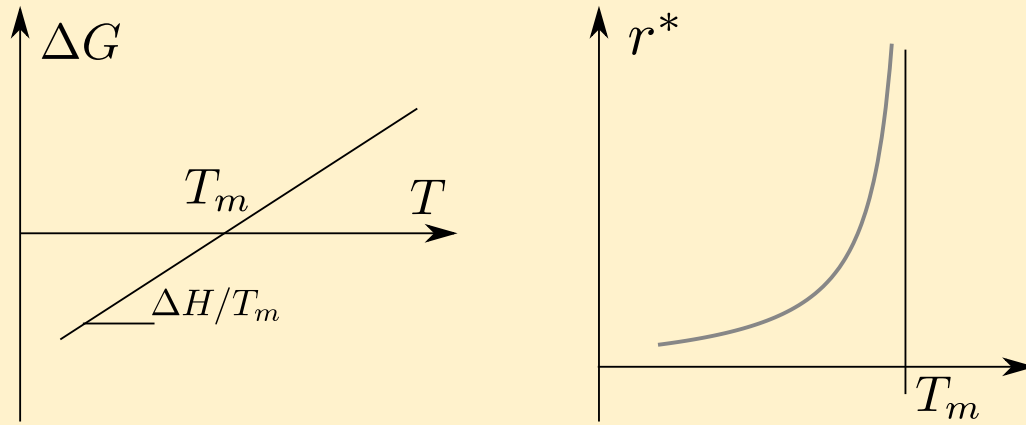


Figure 27:

This would lead to undercooling ($T_m - T$) of the order of 10s to 100 degrees, which we do not see in practice. Therefore, another mechanism must be responsible for the nucleation of crystals.

Heterogeneous nucleation

The reason why in practice solidification occurs fairly close to T_m is because crystals will start to form around defects or dirt particles that will provide an anchoring point for the growth. This is called **heterogeneous nucleation**, by contrast with the previous case of a spherical crystal suspended in the fluid, called **homogeneous nucleation**.

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We can model this situation by considering a spherical cap (radius r and contact angle θ) of solid at the surface of a catalyst that would promote the nucleation process. The volume of solid is V_S , the area of contact between the solid and the catalyst is A_{CS} , the area of the spherical cap between solid and liquid is A_{SL} .

We can write the Gibbs free energy of the system:

$$G = V_S(r)\Delta G_v + A_{SL}(r)\gamma_{SL} + A_{CS}(r)(\gamma_{CS} - \gamma_{CL})$$

The geometry of the cap is controlled by the surface energies of the different interfaces, γ_{SL} , γ_{CS} and γ_{CL} . Because these surface energies are also forces per unit length along the rim of the cap, force balance along the rim gives:

$$\gamma_{CL} = \gamma_{CS} + \gamma_{SL} \cos \theta$$

θ is therefore fixed by the surface energies. The cap would grow or shrink without changing shape.

Skiping here the algebra (see book reference Ashby & Jones), finding the extremum of G with respect to r gives the same result as before:

$$r^* = \frac{2\gamma_{SL}}{|\Delta G_v|} = \frac{2\gamma_{SL}}{|\Delta H_v|} \frac{T_m}{(T_m - T)}$$

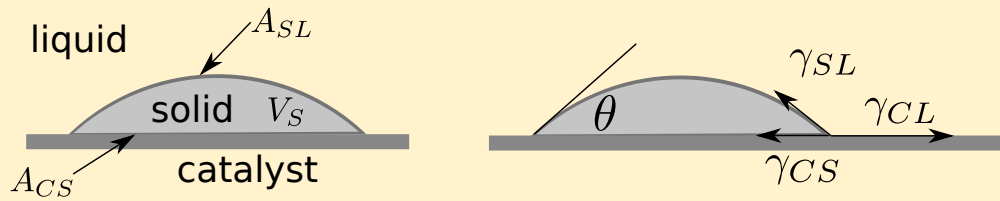


Figure 28: Geometry of a spherical cap of solid at the surface of a catalyst.

Role of the contact angle θ

This may seem to be disappointing at first that the catalyst doesn't help reduce the radius of nucleation. But the radius is not what matters - it is the number of atoms (i.e. the volume of solid V_S) required to reach that radius.

The smaller the contact angle θ , the smaller the volume V_S and the more likely it is that thermal fluctuations would trigger the growth of the solid phase.

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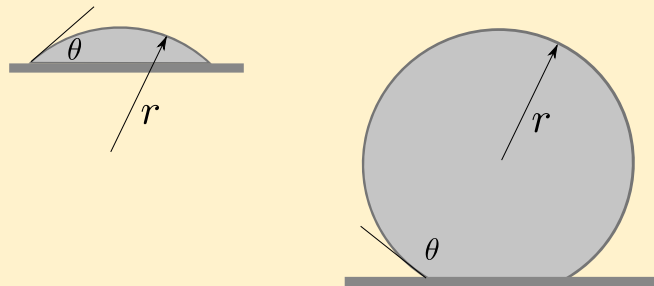


Figure 29: Effect of θ on the cap geometry. For the same radius r , a large θ leads to a large volume of solid V_S , and hence low probability of forming the stable nucleus.

Summary

- Interfaces between phases of materials have an energetic cost, that can be expressed as a surface energy.
- Considering the role of this energy on the stability of phases, we find that a crystal needs to reach a finite size before it can grow macroscopically.
- Homogeneous nucleation is difficult to trigger as it requires large radii of nucleation.
- Heterogeneous nucleation is much easier on substrates that have a small contact angle with the solid phase.

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To go further: how ΔG varies with temperature near a phase transition.

Although the equation 21 is correct, the assumption that ΔH and ΔS do not vary too much with temperature can be challenged in practice. In fact, these terms would in general have first order variations with the temperature, and therefore it is not mathematically appropriate to assume that they are constant to derive a first order approximation for ΔG .

You may remember from classical thermodynamics that $\partial H/\partial T$ would represent the heat capacity at constant pressure, say $C_{p,s}$ and $C_{p,l}$ for the solid and liquid phases respectively. We can therefore write first order approximations for the enthalpy of the solid and liquid around T_m :

$$\begin{aligned} H_s(T) &= H_s(T_m) + c_{p,s}(T - T_m) \\ H_l(T) &= H_l(T_m) + c_{p,l}(T - T_m) \\ \implies \Delta H(T) &= \Delta H(T_m) + (c_{p,l} - c_{p,s})(T - T_m) \end{aligned}$$

So unless $c_{p,l} \approx c_{p,s}$, $\Delta H(T)$ would indeed have first order variations with the temperature.

An alternative, more robust approach, to get the first order approximation of $\Delta G(T)$ would involve using the “ TdS ” equation for the Gibbs Free Energy in both the solid and liquid phases. This can be fairly easily obtained from classical thermodynamics:

$$G = U - TS + pV \implies dG = dU - TdS - SdT + pdV + Vdp$$

but since $dU = TdS - pdV$ (your standard TdS equation), we get:

$$dG = -SdT + Vdp$$

At constant pressure, $\partial G/\partial T = -S$. Considering now the difference between the liquid and solid phases, we get $\partial \Delta G/\partial T = -\Delta S$.

$$\Delta G(T) = \Delta G(T_m) + \partial \Delta G/\partial T \cdot (T - T_m) = -\Delta S(T) \cdot (T - T_m)$$

To get $\Delta G(T)$ to the first order, we only need $\Delta S(T)$ at the order 0 in the expression above, which corresponds to $\Delta S(T_m)$. Since at T_m , $\Delta G(T_m) = 0$, we also have $\Delta S(T_m) = \Delta H(T_m)/T_m$, returning the same result as equation 21.

5 Osmosis

5.1 Osmotic pressure

One important aspect of the ideal gas law derivation is that it is not specific to a particular gas. We simply counted the number of ways to distribute particles in the volume available to them. A thermodynamic approach can be applied to other systems with similar microscopic configuration, for instance a solute dispersed in a solvent. 74

Consider a piston separating two compartments as illustrated in the top panel of figure 30. Entropy controls gas pressure and drives the system towards equilibrium where gas pressures are equal on either side of the piston, i.e. gas density on either side should be the same if temperature is uniform. This is in principle analogous to the case in the bottom panel of figure 30, where each compartment now contains solvent with some solute in it, assuming the piston is semi-permeable, i.e. that it lets the solvent through but not the solute. The system should evolve towards a situation solute concentrations are the same on either side.

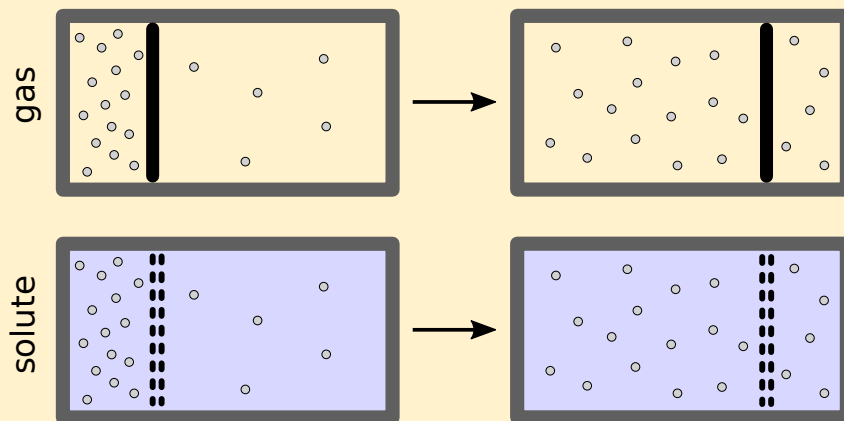


Figure 30: Sketches illustrating the analogy between pressure equilibrium between two gas compartments (top), and the osmotic equilibrium between two solute solutions free to exchange solvent (bottom).

In this section, we will focus on the mechanical impact of the entropy of mixing of solutes in solutions, called the **osmotic pressure**. Osmosis plays an important role in the context of biomaterials.

Empirical evidence

There are many illustrations of osmosis available in chemistry and biology text books. The video below is a typical example of osmosis in action, and shows that semi-permeable membranes do exist. 75

Online Resource 4: Osmosis through dialysis tubing

Copyright: NCSSMDistanceEd

<http://frama.link/1BMat-Dialysis>**Osmotic pressure**

The traditional setup to illustrate osmotic pressure is a U-shaped tube with a semi-permeable membrane in the middle that lets the solvent go through but not the solute. In this case, n_s solute molecules are placed on one side only. See figure 31.

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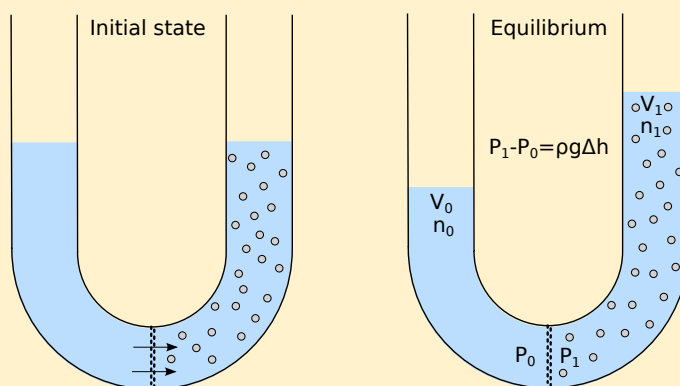


Figure 31: U-tube experiment illustrating osmosis and introducing the system used in the derivation.

As the system evolves towards equilibrium, water flows through the semi-permeable membrane, setting a difference of hydrostatic pressure $P_1 > P_0$ across the membrane.

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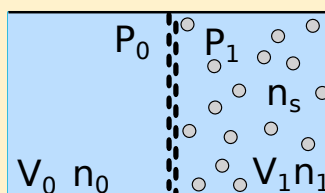


Figure 32: Zoom of the semi-permeable membrane region

By analogy with the case of ideal gases, the osmotic pressure π of a solution with n_s solute molecules is:

$$(P_1 - P_0) = \pi = \frac{n_s}{V_1} k_B T$$

Using moles and the Gas Constant $R = k_B \mathcal{N}_A$, we get:

$$\pi = RTc \quad (22)$$

where c is the solute concentration, expressed in **moles per m³**.

As for ideal gases, this is valid for low concentrations, typically less the 1 mol/L.

Example: Osmotic pressure of a teaspoon of sugar in a cup of tea

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Mass of a teaspoon of sugar (sucrose): $m \approx 4$ g

Molar mass of sucrose $C_{12}H_{22}O_{11}$: 342 g/mol.

⇒ we have about 0.01 mol of sugar, say in a cup, 250 mL = $2.5 \cdot 10^{-4}$ m³.

⇒ the sucrose concentration is about 40 mol/m³.

At room temperature, $RT \approx 2500$ J/mol.

Hence $\pi \approx 10^5$ Pa, i.e. about 1 atm !

How to derive this relationship?

It is all about defining the relevant free energy function, and minimising it!

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The system of interest consists of two compartments, one with pure water and the other with a solute, of free energy G_0 and G_1 respectively. Compartments can exchange solvent molecules through a semi-permeable membrane, as in figure 31.

$$G(n_0, P_0, n_1, n_s, P_1, T) = G_0(n_0, P_0, T) + G_1(n_1, n_s, P_1, T)$$

How to construct these free energy functions?

G_0 is the free energy of pure water - it must be proportional to the amount of water:

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$$G_0 = \mathbf{n}_0 \mathbf{g}_w(\mathbf{P}_0, \mathbf{T})$$

where g_w is the free energy per molecule of pure water.

G_1 is the free energy of a solution containing a solute. We can build this function by considering how the system was formed. We start with n_1 pure water molecules and n_s pure solute, and mix them. During mixing, there will be a change of internal energy, and a term of entropy of mixing, as seen in the context of binary mixtures.

$$G_1 = \mathbf{n}_1 \mathbf{g}_w(\mathbf{P}_1, \mathbf{T}) + \mathbf{n}_s \mathbf{g}_s(\mathbf{P}_1, \mathbf{T}) + \Delta U_d - T \Delta S_{\text{mix}}$$

where g_s is the free energy per molecule of solute, ΔU_d is the change of internal energy due to dissolving the solute in water, and ΔS_{mix} is the mixing entropy, i.e. the configurational entropy due to solutes in the available volume of the water.

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At the equilibrium, G must be minimum with respect to water transfer across the membrane:

$$\frac{\partial G}{\partial n_1} = 0 \text{ with } n_0 + n_1 = \text{constant} \quad (23)$$

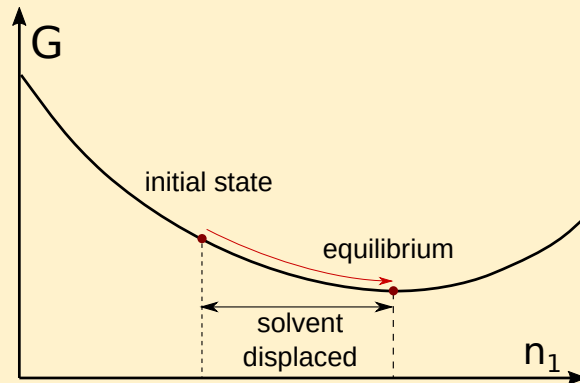


Figure 33: Evolution towards equilibrium

We could with a bit of effort identify all the terms of interest in the limit of small solute concentration, and mathematically derive the expression of the osmotic pressure from the equilibrium condition above (see section 5.3).

5.2 Applications

5.2.1 Cellular mechanics

Effect of osmotic forces on red blood cells

Most living cells can only function properly in a certain range of osmotic forces in their environment. This is well illustrated by the effect of changes in medium composition on red blood cell morphologies (see figure 34).

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This sets constraints on treatments injected intravenously. The solution injected must match the osmotic pressure of blood plasma, the fluid surrounding red blood cells.

Osmotic forces and plant mechanics

Plant cells also respond to osmotic pressure, however cells are trapped in a cell wall made of cellulose (see figure 35 and online resource 5). Osmosis does not change much the volume of plant tissue, but can control its **rigidity**.

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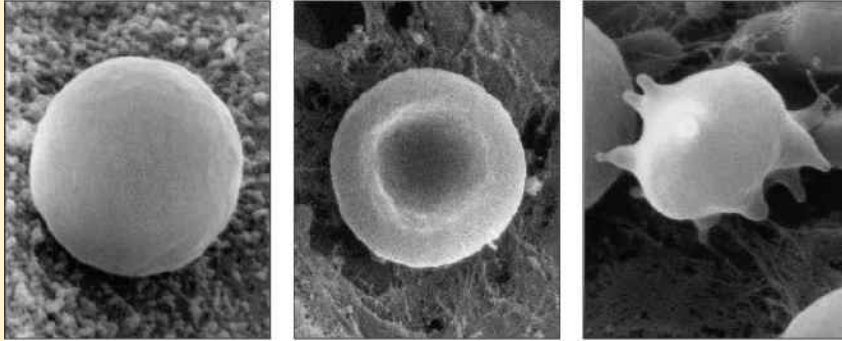


Figure 34: Effect of osmotic pressure on red blood cells. In the middle image, the cell is in an environment where the internal and external osmotic pressures are balanced (isotonic). On the left, the osmotic pressure of the media is insufficient and the red blood cell fills with water (hypotonic). On the right, the osmotic pressure is too high and the red blood cell shrinks (hypertonic). Source: www.rrnursingschool.biz

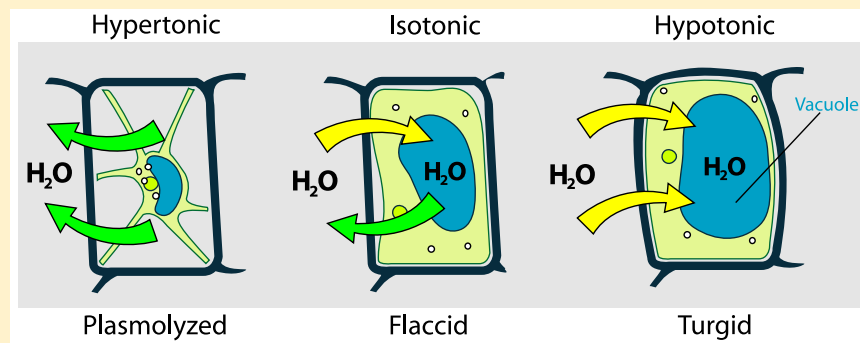


Figure 35: Effect of osmotic forces on a plant cell. Source: Wikimedia

Online Resource 5: Hydration and dehydration through osmosis

Red onion cells in salty water

Youtube video, A-level Biology

<https://frama.link/1BMat-Plasmolysis>



Turgid tissues are stiff, but placid tissues are compliant (see figure 36). Plants can control their stiffness and geometry by controlling their osmotic pressure. This is in particular the case for most circadian movements, as well as the initiation of the closure of the Venus fly-trap.

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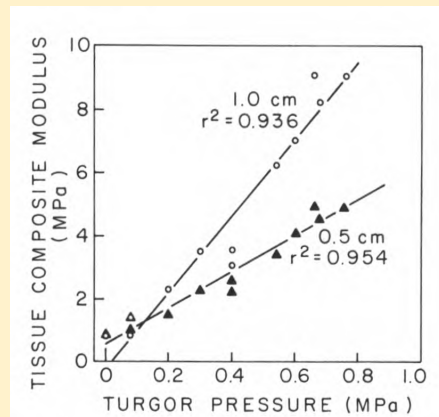


Figure 36: Relation between the tissue composite modulus (the elastic modulus of a tissue) and the turgor (osmotic) pressure of two plugs of non-woody tissues (differing in cross-sectional diameter, 0.5 and 1.0 cm) isolated from potato tubers. As the turgor pressure of the tissue increases, the elastic modulus of the tissue samples increases linearly. Source: K Niklas, 1992. Plant Biomechanics. University of Chicago Press.

5.2.2 Depletion forces

Depletion forces between particles in suspension

Consider the simple case of two plates of surface area A separated by a small gap d in a suspension of colloids or large polymers of diameter a , concentration c .

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If $d > a$, then colloids are present all around the plates and there is **no net force**.

If $d < a$, then colloids are excluded from the space between the plates and osmotic pressure creates an **attractive** force between the plate.

$$F = RTcA$$

This is called a **depletion force**.

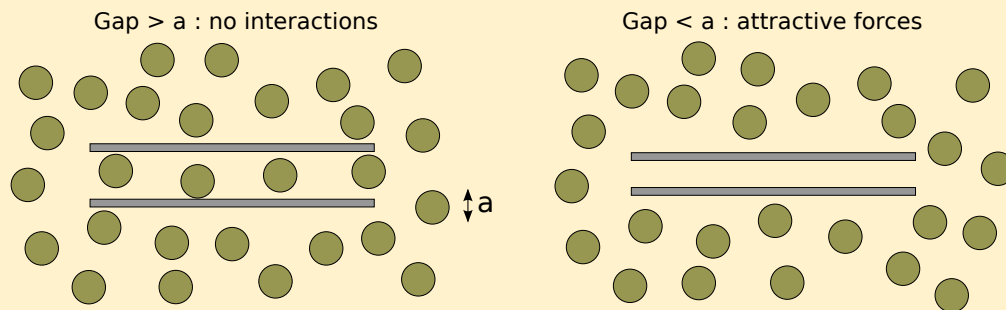


Figure 37: Depletion interactions between plates.

Application to water purification

Depletion interactions are used to facilitate the aggregation of large size (1-10 μm) suspended contaminants in water purification. A suspension of non toxic polymers or small colloids are typically added to dirty water to create aggregates large enough to sink.

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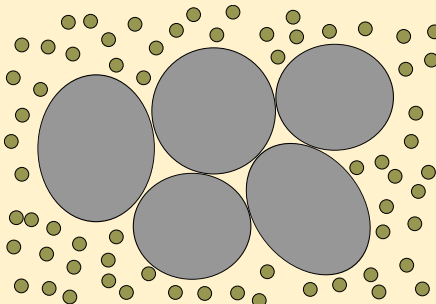


Figure 38: Aggregates of large particles resulting from depletion interactions.

Hydrogels

Hydrogels are polymer networks in food products and biomaterials.

The mass fraction of polymer is only a few per cents.

Common examples include agarose and gelatin.

These materials are more compliant (10-100 kPa) than rubber because the polymer density is much lower.

The reason why hydrogels are swollen with water is **osmosis**.

The properties of the polymer and solvent are therefore key to understand the structure and behaviour of hydrogels.

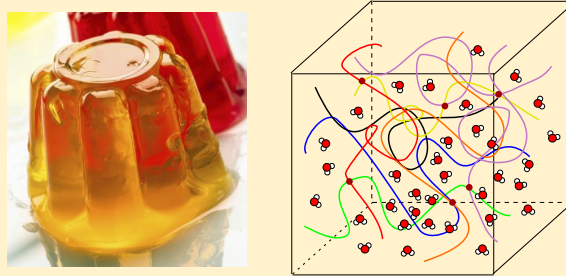


Figure 39: Jell-o (left) is a typical hydrogel based on gelatin (derived from collagen). The polymer network absorbs a lot of water through osmosis.

Summary

- Solute molecules in a solvent are analogous to gas molecules as far as their configuration entropy is concerned.
- A solute in a solution generates an entropic pressure, called osmotic pressure π :

$$\pi = RTc \text{ where the concentration } c \text{ is in mol/m}^3$$

where c is the solute concentration, valid at low solute concentration $c < 1 \text{ mol/L}$.

- This pressure is effective across a semi-permeable membrane such that the solvent can go through, but not the solute.
- The process of osmosis controls flow of water and equilibrium states in many natural materials, and often influences their mechanical properties.

5.3 To go further: derivation of the osmotic pressure expression

This section demonstrates how to use the thermodynamic principles introduced in this course to derive the expression of the osmotic pressure.

Free energy of a solvent+solute solution

Let's calculate the free energy of the whole system involved in the previous experiment. 89

$$G = n_0 g_w(P_0, T) + n_1 g_w(P_1, T) + n_s g_s(P_1, T) + \Delta U_d - T \Delta S_{mix} \quad (24)$$

where:

- n_0 and n_1 are the numbers of water molecules in the pure water side and solute side respectively,
- g_w is the free energy per molecule of pure water,
- g_s is the free energy per molecule of solute,
- ΔU_d is the change of internal energy due to dissolving the solute in water,
- ΔS_{mix} is the mixing entropy, i.e. the configurational entropy due to solutes in the available volume of the water.

We will work in the limit of very dilute solutes, i.e. $n_s \ll n_1$.

Thermodynamic equilibrium

At the equilibrium, G must be minimum with respect to water transfer across the membrane: 90

$$\frac{\partial G}{\partial n_1} = 0 \quad (25)$$

$$\frac{\partial G}{\partial n_1} = \frac{\partial n_0}{\partial n_1} g_w(P_0, T) + g_w(P_1, T) + \frac{\partial \Delta U_d}{\partial n_1} - T \frac{\partial \Delta S_{mix}}{\partial n_1} \quad (26)$$

Considering that $n_0 + n_1$ remains constant ($dn_0 = -dn_1$), we get:

$$\frac{\partial G}{\partial n_1} = -g_w(P_0, T) + g_w(P_1, T) + \frac{\partial \Delta U_d}{\partial n_1} - T \frac{\partial \Delta S_{mix}}{\partial n_1} \quad (27)$$

Internal energy term: ΔU_d

ΔU_d is due to the fact that molecules of the solute have some energy of interaction (usually attractive) with solvent molecules. 91

If the concentration of solute is low enough, each solute molecule is already surrounded by water molecules, so adding/removing a bit of water to the solution has no effect on this term.

$$\frac{\partial \Delta U_d}{\partial n_1} = 0 \quad (28)$$

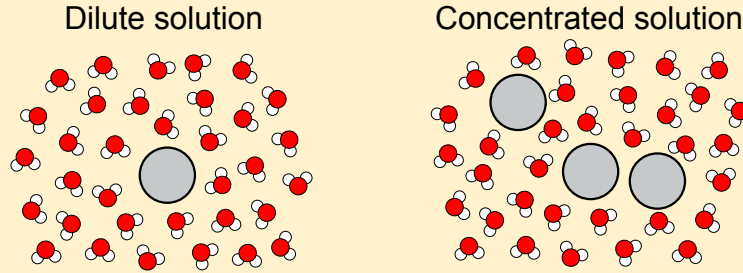


Figure 40: At low solute concentrations, solute molecules only interact with water, while at larger concentrations, solute-solute interactions cannot be ignored.

Mixing entropy: ΔS_{mix}

This term has essentially been already calculated in previous lectures on binary solutions. Here, we will consider that the solute has a very low concentration $n_s \ll n_1$. 92

Let's count the number of ways to place n_s solute molecules in a volume V_1 water molecules. By analogy with the ideal gas calculation, we have $\Omega_c = KV_1^{n_s}$, where K is an unspecified constant. Hence:

$$\Delta S_{mix} = k_B \ln (KV_1^{n_s}) \quad (29)$$

$$\frac{\partial \Delta S_{mix}}{\partial n_1} = \frac{\partial V_1}{\partial n_1} \frac{\partial}{\partial V_1} (k_B \ln (KV_1^{n_s})) \quad (30)$$

$$\frac{\partial \Delta S_{mix}}{\partial n_1} = \frac{V_1}{n_1} \frac{k_B n_s}{V_1} = \frac{k_B n_s}{n_1} \quad (31)$$

Back to the equilibrium condition: $\partial G / \partial n_1 = 0$

$$\frac{\partial G}{\partial n_1} = \frac{\partial n_0}{\partial n_1} g_w(P_0, T) + g_w(P_1, T) + \frac{\partial \Delta U_d}{\partial n_1} - T \frac{\partial \Delta S_{mix}}{\partial n_1} \quad (32)$$

$$\frac{\partial G}{\partial n_1} = -g_w(P_0, T) + g_w(P_1, T) - T \frac{k_B n_s}{n_1} = 0 \quad (33)$$

Using a Taylor expansion for $g_w(P)$: $g_w(P_1) \approx g_w(P_0) + (P_1 - P_0) \frac{\partial g_w(P, T)}{\partial P}$

$$(P_1 - P_0) \frac{\partial g_w(P, T)}{\partial P} = T \frac{k_B n_s}{n_1} \quad (34)$$

Maxwell relationship

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We need to understand what $\frac{\partial g_w(P, T)}{\partial P}$ represents. g_w is the free energy per molecule of pure solvent. Consider pure water. The free energy G_w of a system made of n water molecules is $G_w = n g_w(P, T)$, i.e.

$$g_w = \frac{\partial G_w}{\partial n}$$

Therefore:

$$\frac{\partial g_w(P, T)}{\partial P} = \frac{\partial^2 G_w}{\partial P \partial n}$$

G_w is almost certainly a nice mathematical function, continuous and smooth. The order of differentiation can be inverted.

$$\frac{\partial g_w(P, T)}{\partial P} = \frac{\partial}{\partial P} \frac{\partial G_w}{\partial n} = \frac{\partial}{\partial n} \frac{\partial G_w}{\partial P}$$

But, since $dG_w = V dP - S dT$, we have $\frac{\partial G_w}{\partial P} = V$.

Hence:

$$\frac{\partial g_w(P, T)}{\partial P} = \frac{\partial V}{\partial n} = \text{volume of a water molecule} \quad (35)$$

Back to the equilibrium condition, again...

Combining equations 34 and 35:

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$$(P_1 - P_0) \frac{\partial g_w(P, T)}{\partial P} = T \frac{k_B n_s}{n_1}$$

with

$$\frac{\partial g_w(P, T)}{\partial P} = \frac{\partial V}{\partial n} \approx \frac{V_1}{n_1}$$

leads to:

$$(P_1 - P_0) \frac{V_1}{n_1} = T \frac{k_B n_s}{n_1} \quad (36)$$

$$(P_1 - P_0) V_1 = n_s k_B T \quad (37)$$

also known as the Ideal Gas Law.

quod erat demonstrandum!

Intended Learning Outcomes

The intended learning outcomes of this section are:

- Apply the second principle of thermodynamics to systems evolving at constant pressure and temperature, and establish the relevance of Gibbs free energy in the context of materials transformations.
- Qualitatively use the idea of Gibbs free energy minimisation to interpret phase transformations and phase equilibrium.
- Qualitatively justify why solids are more likely to be observed at low temperature, and fluids at higher temperatures, based on internal energy and entropy considerations
- Qualitatively justify why certain materials mix and others don't, based on Gibbs free energy considerations
- Qualitatively explain why a surface energy is associated with the interface between two materials and why it plays a role in the context of nucleation.
- Derive an expression for the critical radius of a nucleus for solidification to happen.
- Calculate the osmotic pressure of a very dilute solute in the relevant conditions, and explain the origin of this force based on entropy and free energy considerations.

You can test yourself against these to make sure you have covered the relevant content, and return to your notes if necessary. The week 2 quiz and examples paper questions may now be fully attempted and will also cover most of these learning outcomes.