Why Atoms Move

Chemical Potential, Tangents and Phase Equilibrium

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Chemical potential is one of those ideas that can appear more complicated than it really is. The word "potential" can be misleading if it is treated as a vague form of energy. Its physical meaning is much more direct: chemical potential describes the thermodynamic tendency of an atom or species to move, partition, react, dissolve, precipitate, or remain where it is.

This note introduces the idea through a binary A–B solution. The central point is that diffusion and phase equilibrium are not governed by concentration alone. They are governed by chemical potential. A concentration difference may exist across an interface, but if the chemical potentials are equal, there is no thermodynamic driving force for further net diffusion.

1 Free energy as a function of composition

Consider a binary solution, Fig. 1, containing components A and B. If the mole fraction of B is

$$x_{\mathrm{B}} = x,$$

then the mole fraction of A is

$$x_{\mathrm{A}} = 1 - x.$$

At fixed temperature and pressure, the molar Gibbs free energy of the solution is written as

$$G = G(x).$$

This curve describes how the molar free energy changes as the composition changes from pure A at $x = 0$ to pure B at $x = 1$. The end points correspond to the molar free energies of the pure components:

$$\mu_A^\circ = G(0), \qquad \mu_B^\circ = G(1),$$

where μ_A° and μ_B° are the molar free energies of pure A and pure B, respectively.

The curve is usually not a straight line because the atoms do not behave as a simple mechanical mixture. They interact. Mixing may be favourable or unfavourable, atoms may prefer certain neighbours, and the solution may develop a tendency to order, cluster, or separate. These atomic interactions are expressed thermodynamically through the shape of $G(x)$.

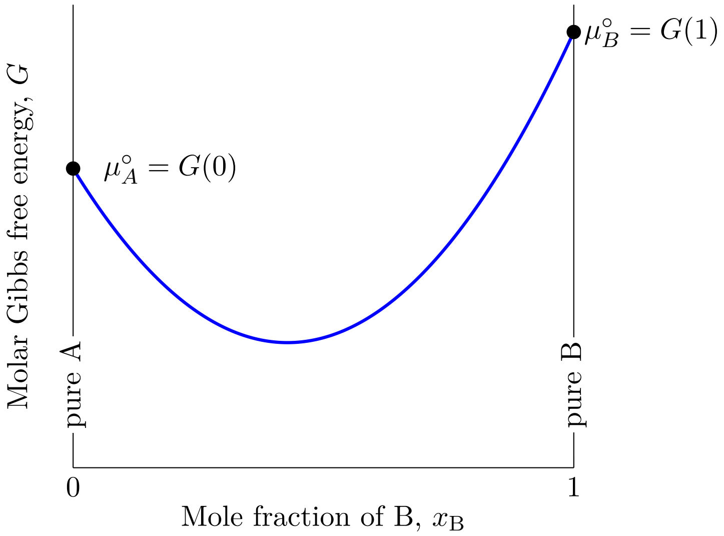

Fig. 1: Schematic molar Gibbs free-energy curve for a binary A–B solution. The curve is drawn against composition, from pure A to pure B. Its shape contains the thermodynamic information about mixing and stability.

2 Chemical potential as partial molar free energy

For a component i, the chemical potential is defined as the change in the total Gibbs free energy when a small amount of that component is added, while temperature, pressure and the amounts of all other components are fixed:

$$\mu_i = \left(\frac{\partial G_\mathrm{total}}{\partial n_i}\right)_{T,P,n_{j\neq i}}.$$

It is therefore a partial molar quantity. It is not the energy of an isolated atom. It is the free-energy contribution of that species in its actual thermodynamic environment. For example, a B atom in an A-rich matrix does not necessarily have the same chemical potential as a B atom in a B-rich matrix, because the surrounding atoms and interactions are different.

For a binary phase containing A and B, the differential change in Gibbs free energy is

$$dG = -S\,dT + V\,dP + \mu_A\,dn_A + \mu_B\,dn_B.$$

At constant temperature and pressure this reduces to

$$dG = \mu_A\,dn_A + \mu_B\,dn_B.$$

This compact expression is useful because it shows that chemical potentials are the coefficients that measure how the free energy changes when the amount of each component changes.

> *Chemical potential is the free-energy price, or benefit, of adding a little more of a species to the system.*

If that price is high in one region and lower in another, the species has a thermodynamic reason to move. That is why chemical potential is more fundamental than concentration when describing diffusion.

3 Activity, ideality and real solutions

For a component B in solution, the chemical potential is commonly written as

$$\mu_B = \mu_B^\circ + RT \ln a_B,$$

where a_B is the activity of B. The activity is related to composition through

$$a_B = \gamma_B x_B,$$

where γ_B is the activity coefficient. If $\gamma_B = 1$, the solution behaves ideally and

$$\mu_B = \mu_B^\circ + RT \ln x_B.$$

For a real solution,

$$\mu_B = \mu_B^\circ + RT \ln(\gamma_B x_B).$$

This distinction is important. In an ideal solution, composition is often a good guide to chemical potential. In a real alloy, however, interactions between atoms change γ_B, so a concentration gradient and a chemical-potential gradient need not tell the same story.

This is the thermodynamic origin of many behaviours that look surprising if concentration alone is used: partitioning, uphill diffusion, clustering, ordering and phase separation are all controlled by how the free energy changes with composition, not simply by how many atoms are present.

4 Reading chemical potentials from a tangent

At a chosen composition x, draw the tangent to the molar free-energy curve, Fig. 2. The tangent can be written as

$$G\{x\} = \mu_A(1 - x) + \mu_B x.$$

This equation has a direct interpretation. The molar free energy at that composition is written as the weighted contribution of A atoms and B atoms:

$$\text{A contribution} = \mu_A(1 - x), \qquad \text{B contribution} = \mu_B x.$$

The tangent intercept at $x = 0$ gives μ_A, and the tangent intercept at $x = 1$ gives μ_B. The tangent therefore provides a graphical way of reading the chemical potentials of both components at the selected composition.

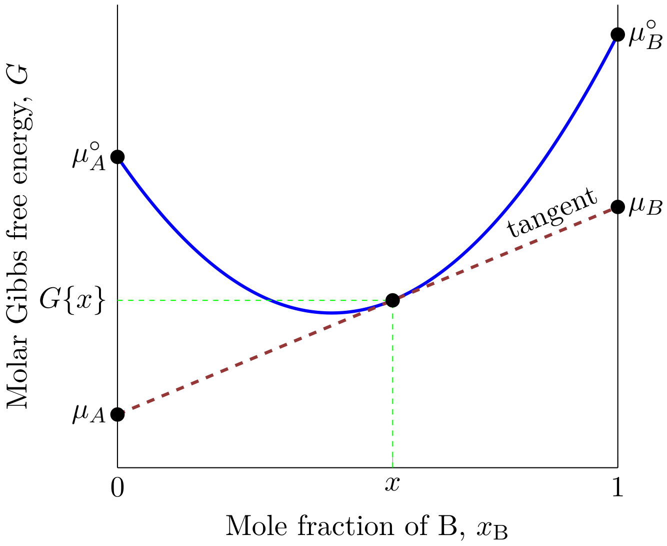

Fig. 2: At composition x, the tangent touches the free-energy curve. The left intercept gives μ_A, the right intercept gives μ_B, and the ordinate at the touching point is the free energy of the solution, $G\{x\}$.

5 Why chemical potential is not the slope

A common mistake is to say that chemical potential is the slope of the tangent. This is not correct for a binary molar free-energy curve plotted against x_B.

The tangent has the form

$$G(x) = \mu_A(1 - x) + \mu_B x.$$

Expanding the right-hand side gives

$$G(x) = \mu_A + x(\mu_B - \mu_A).$$

The slope of the tangent is therefore

$$\frac{dG}{dx} = \mu_B - \mu_A.$$

So the slope gives the *difference* between the chemical potentials of B and A, not either chemical potential by itself. The individual chemical potentials are the tangent intercepts. Fig. 3 makes this point directly.

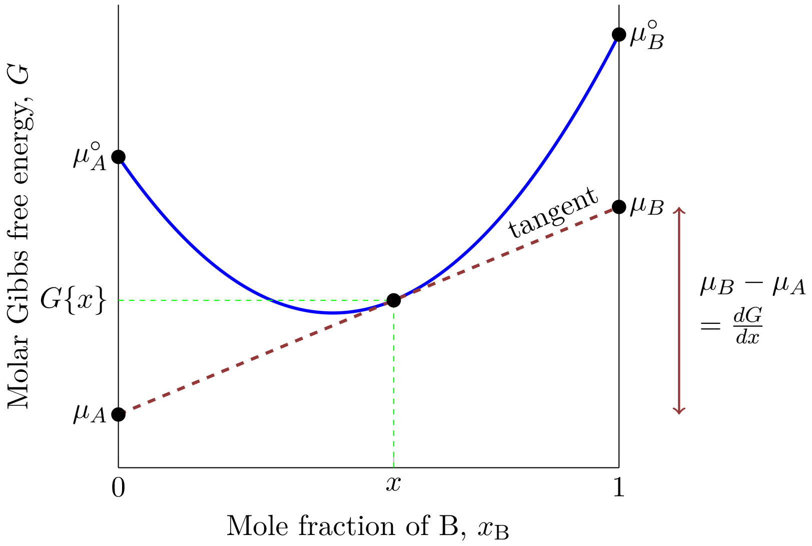

Fig. 3: For a binary molar free-energy curve, the tangent slope is $dG/dx = \mu_B - \mu_A$. The chemical potentials themselves are still obtained from the tangent intercepts.

6 A numerical check

Suppose an A–B solution contains 30% B:

$$x_B = 0.30, \qquad x_A = 0.70.$$

If the tangent to the free-energy curve at this composition gives

$$\mu_A = -20 \text{ kJ mol}^{-1}, \qquad \mu_B = -5 \text{ kJ mol}^{-1},$$

then the molar Gibbs free energy of the solution is

$$G = (0.70)(-20) + (0.30)(-5) = -15.5 \text{ kJ mol}^{-1}.$$

The slope of the tangent is

$$\frac{dG}{dx} = \mu_B - \mu_A = -5 - (-20) = 15 \text{ kJ mol}^{-1}.$$

The chemical potentials are -20 and -5 kJ mol^{-1}; the slope is 15 kJ mol^{-1}. The slope is therefore not the chemical potential of A or B. It is the difference between them.

7 Diffusion: the true driving force

Diffusion is often described as movement from high concentration to low concentration. That is a useful first approximation, but it is not the full thermodynamic statement. More precisely,

Diffusion is driven by gradients in chemical potential.

For species i, the driving force is associated with

$$\nabla \mu_i.$$

If μ_i is high in one region and low in another, atoms of species i can lower the total free energy by moving towards the lower chemical potential. In an ideal solution, this often looks like ordinary diffusion down a concentration gradient. In real alloys, concentration alone can be misleading because the chemical potential also depends on atomistic interactions, phase constitution, elastic stress, defects and temperature.

This is particularly important in metallic systems. Carbon, nitrogen, hydrogen and substitutional alloying elements do not move merely because their concentration is different from one place to another. They move because their chemical potential is different.

In some alloys, a species can move from a region of lower concentration to a region of higher concentration, provided that direction lowers its chemical potential. This is uphill diffusion. It looks impossible if concentration alone is treated as the driving force. It becomes natural once chemical potential is used as the true driving force.

8 Equilibrium across an interface

Now consider two phases, α and γ, in the same binary system. Suppose that a small amount of component A is transferred from γ to α at constant temperature and pressure. The corresponding change in Gibbs free energy is

$$dG = dG^{\alpha} + dG^{\gamma} = \mu_A^{\alpha} dn_A^{\alpha} + \mu_A^{\gamma} dn_A^{\gamma}.$$

The amount added to α is equal to the amount removed from γ, so

$$dn_A^{\gamma} = -dn_A^{\alpha}.$$

Therefore,

$$dG = (\mu_A^{\alpha} - \mu_A^{\gamma}) dn_A^{\alpha}.$$

This equation contains both the condition for equilibrium and the direction of transfer. If $\mu_A^{\gamma} > \mu_A^{\alpha}$, moving A from γ to α gives $dn_A^{\alpha} > 0$ and lowers the free energy. Transfer will continue until the chemical potential of A is the same in both phases. At equilibrium, no infinitesimal transfer of A can reduce the free energy, so $dG = 0$ for arbitrary small transfer, and therefore

$$\mu_A^{\alpha} = \mu_A^{\gamma}.$$

The same argument applies to component B:

$$\mu_B^{\alpha} = \mu_B^{\gamma}.$$

This is the compact thermodynamic condition for phase equilibrium: every component that can exchange between phases must have the same chemical potential in those phases.

The important point is that equilibrium does not require the two phases to have the same composition. A phase α of composition x_α and a phase γ of composition x_γ may coexist even when

$$x_\alpha \neq x_\gamma.$$

What must be equal are the chemical potentials:

$$\mu_A^{\alpha} = \mu_A^{\gamma}, \qquad \mu_B^{\alpha} = \mu_B^{\gamma}.$$

Once these equalities are satisfied, transferring A or B from one phase to the other cannot lower the total free energy. The phases may therefore remain chemically different, but the thermodynamic driving force for further net diffusion has vanished.

This is why a concentration jump can exist across a phase boundary at equilibrium. The interface does not require equal concentration on both sides; it requires equality of chemical potential for each exchangeable species.

9 Common tangent and phase coexistence

Each phase has its own molar free-energy curve:

$$G^\alpha(x), \qquad G^\gamma(x).$$

At a given temperature, the system may lower its free energy by separating into an α phase of composition x_α and a γ phase of composition x_γ. These two equilibrium compositions are found using the common tangent construction.

A common tangent is a single straight line that touches both free-energy curves, Fig. 4. The point where it touches the α curve gives x_α; the point where it touches the γ curve gives x_γ. Because the same tangent touches both curves, the tangent intercepts are the same for both phases. Therefore,

$$\mu_A^\alpha = \mu_A^\gamma, \qquad \mu_B^\alpha = \mu_B^\gamma.$$

These equalities are the condition for two-phase equilibrium in a binary system.

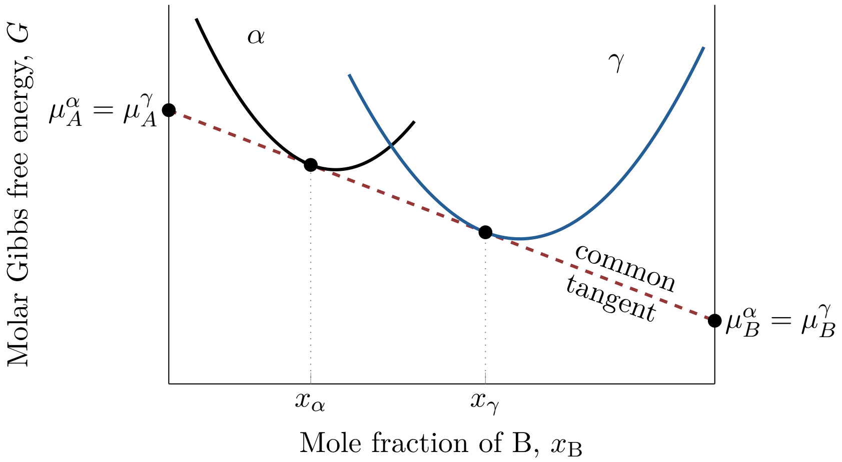

Fig. 4: Common tangent construction for two-phase equilibrium. The two tangent points define the equilibrium phase compositions x_α and x_γ along the x_B composition axis. The phase compositions are different, but the chemical potential of each component is identical in both phases.

10 A metallurgical example: ferrite and austenite

A familiar example in steels is carbon partitioning between ferrite and austenite. Ferrite and austenite have very different capacities for dissolving carbon. Austenite can usually contain much more carbon than ferrite, so at equilibrium the carbon concentration in austenite can be much higher than in ferrite.

This does not mean that carbon must continue to move until the carbon contents are equal. At equilibrium, the condition is

$$\mu_C^\alpha = \mu_C^\gamma,$$

where α represents ferrite and γ represents austenite. The carbon contents can be different, yet the chemical potential of carbon can be the same. Once that balance is reached, there is no net thermodynamic drive for carbon transfer across the interface.

This idea is central to phase transformations in steels, including austenite decomposition, bainite formation, partitioning treatments and tempering. In these cases, the key question is not only “how much carbon is present?”, but also “what is the chemical potential of carbon in each phase?”

11 Phase diagrams and the lever rule

Phase diagrams are often read as maps of temperature and composition. Beneath every two-phase field, however, is the same thermodynamic condition. At a fixed temperature, the ends of a tie-line correspond to phase compositions that satisfy equality of chemical potentials.

For an overall alloy composition X_0 lying between the two equilibrium phase compositions,

$$X_\alpha < X_0 < X_\gamma,$$

the alloy is a mixture of α and γ. The phase fractions follow from the lever rule:

$$f_\alpha = \frac{X_\gamma - X_0}{X_\gamma - X_\alpha}, \qquad f_\gamma = \frac{X_0 - X_\alpha}{X_\gamma - X_\alpha}.$$

If $0 < X_0 < X_\alpha$, the stable state is single-phase α. If $X_\gamma < X_0 < 1$, the stable state is single-phase γ. Between X_α and X_γ, the stable state is a two-phase mixture, not because the individual phase free-energy curves are separately minimal at X_0, but because the total free energy of the mixture lies on the common tangent and is lower.

For a multicomponent alloy, the same idea applies to every independent component:

$$\mu_i^\alpha = \mu_i^\gamma \qquad \text{for each component } i.$$

This is the thermodynamic foundation of CALPHAD calculations, Thermo-Calc predictions and phase-equilibrium modelling. The calculation may be numerical and high-dimensional, but the principle is still the same: stable phase coexistence requires balanced chemical potentials.

12 Essential equations

Concept	**Equation**
Binary composition	$x_A = 1 - x_B$
Molar free energy	$G = G(x_B)$
Chemical potential	$\mu_i = \left(\frac{\partial G_{\text{total}}}{\partial n_i}\right)_{T,P,n_{j\neq i}}$
Constant T, P free-energy change	$dG = \mu_A dn_A + \mu_B dn_B$
Activity form	$\mu_B = \mu_B^\circ + RT \ln a_B$
Real solution	$a_B = \gamma_B x_B$
Tangent representation	$G = (1 - x)\mu_A + x\mu_B$
Slope of tangent	$\frac{dG}{dx} = \mu_B - \mu_A$
Two-phase equilibrium	$\mu_i^\alpha = \mu_i^\gamma$ for each species i
Lever rule	$f_\alpha = \frac{X_\gamma - X_0}{X_\gamma - X_\alpha}, \quad f_\gamma = \frac{X_0 - X_\alpha}{X_\gamma - X_\alpha}$
Diffusion driving force	gradient in chemical potential, $\nabla \mu_i$

13 Closing remarks

Chemical potential is the thermodynamic tendency of a species to move or change its state. In a binary solution, it can be read graphically from the tangent to the molar Gibbs free-energy curve. The tangent intercepts give μ_A and μ_B, while the slope gives only their difference, $\mu_B - \mu_A$.

For two phases in equilibrium, the common tangent construction gives the two equilibrium phase compositions. The phases do not need to have the same composition. They need to have the same chemical potential for each component. That is why a concentration jump can exist across a phase boundary at equilibrium, and why diffusion is properly understood as being driven by chemical-potential gradients, not concentration gradients alone.

All figures are schematic. They are drawn to show the thermodynamic construction clearly rather than to represent a specific experimental alloy system.