Lecture 1: Atomic Diffusion

Mass transport in a gas or liquid generally involves the flow of fluid (*e.g.* convection currents) although atoms also diffuse. Solids on the other hand, can support shear stresses and hence do not flow, except by diffusion involving the jumping of atoms on a fixed network of sites.

Assume at first that such jumps can somehow be achieved in the solid state, with a frequency ν with each jump over a distance λ.

For random jumps, the mean distance is

$$\begin{aligned} \overline{x} &= \lambda\sqrt{n} \qquad \text{where } n \text{ is the number of jumps} \\ &= \lambda\sqrt{\nu t} \qquad \text{where } t \text{ is the time} \end{aligned}$$

$$\text{diffusion distance} \propto \sqrt{t}$$

Although our discussion is focused on atoms, the principles of diffusion apply also to other species such as ions and molecules.

Diffusion in a Uniform Concentration Gradient

Consider adjacent planes in a crystalline solid, as illustrated in Fig. 1.

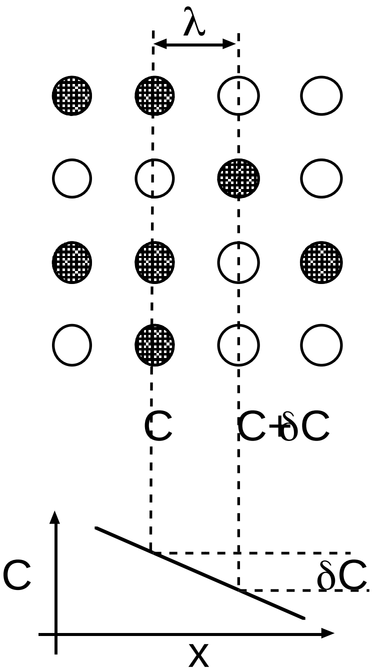

Fig. 1: Diffusion gradient in a crystalline solid. λ is the shortest jump distance between adjacent planes.

The concentration of solute, C, has units of number of atoms per unit volume (m^{-3}). Each plane therefore has $C\lambda$ atoms per unit area (m^{-2}) so that the increment of composition on traversing a distance λ is

$$\delta C = \lambda \left\{ \frac{\partial C}{\partial x} \right\}$$

Given an atomic jump frequency ν and six equally probable jump directions, it follows that the atom flux, J, atoms $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$ in the forward (x) and reverse ($-x$) directions is:

$$J_{L \rightarrow R} = \frac{1}{6}\nu C \lambda$$

$$J_{R \rightarrow L} = \frac{1}{6}\nu (C + \delta C)\lambda$$

Therefore, the net flux in the forward direction becomes

$$\begin{aligned} J = J_{L\to R} - J_{R\to L} &= -\frac{1}{6}\nu\,\delta C\,\lambda \\ &= -\frac{1}{6}\nu\,\lambda^2\left\{\frac{\partial C}{\partial x}\right\} \\ &\equiv -D\left\{\frac{\partial C}{\partial x}\right\} \end{aligned}$$

This is Fick's first law where the constant of proportionality is called the diffusion coefficient in $\mathrm{m^2\,s^{-1}}$. Fick's first law applies to steady state flux in a uniform concentration gradient. Thus, our equation for the mean diffusion distance can now be expressed in terms of the diffusivity as

$$\overline{x} = \lambda\sqrt{\nu t} \qquad \text{with} \qquad D = \frac{1}{6}\nu\lambda^2 \qquad \text{giving} \qquad \overline{x} = \sqrt{6Dt} \simeq \sqrt{Dt}$$

Non–Uniform Concentration Gradients

Suppose that the concentration gradient is not uniform (Fig. 2).

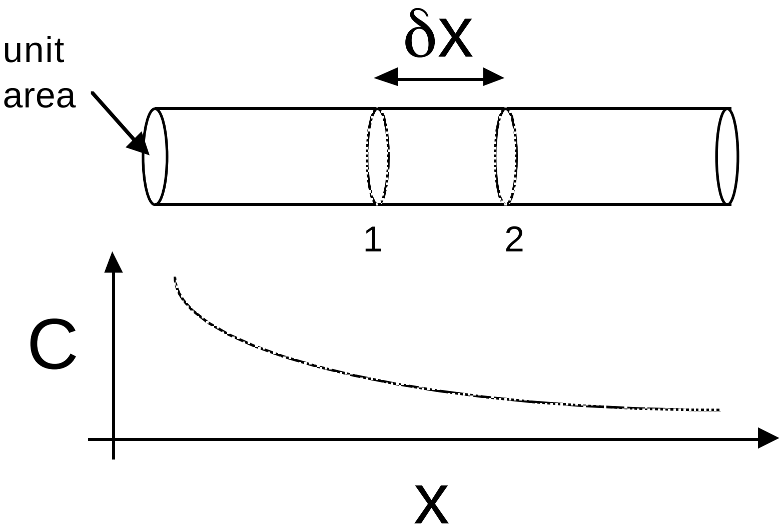

Fig. 2: Non–uniform concentration gradient

$$\begin{aligned}\text{Flux in} \qquad &= -D\left\{\frac{\partial C}{\partial x}\right\}_1 \\ \text{Flux out} \qquad &= -D\left\{\frac{\partial C}{\partial x}\right\}_2 \\ &= -D\left[\left\{\frac{\partial C}{\partial x}\right\}_1 + \delta x\left\{\frac{\partial^2 C}{\partial x^2}\right\}\right]\end{aligned}$$

In the time interval δt, the concentration changes δC

$$\delta C \delta x = (\text{Flux in} - \text{Flux out})\delta t$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

assuming that the diffusivity is independent of the concentration. This is Fick's second law of diffusion.

This is amenable to numerical solutions for the general case but there are a couple of interesting analytical solutions for particular boundary conditions. For a case where a fixed quantity of solute is plated onto a semi–infinite bar (Fig. 3),

$$\text{boundary conditions:} \qquad \int_0^\infty C\{x,t\}dx = B$$

$$\text{and} \qquad C\{x, t=0\} = 0$$

$$C\{x,t\} = \frac{B}{\sqrt{\pi D t}}\exp\left\{\frac{-x^2}{4Dt}\right\}$$

Now imagine that we create the diffusion couple illustrated in Fig. 4, by stacking an infinite set of thin sources on the end of one of the bars. Diffusion can thus be treated by taking a whole set of the exponential functions obtained above, each slightly displaced along the x axis, and summing (integrating) up their individual effects. The integral is in fact the error function

$$\text{erf}\{x\} = \frac{2}{\sqrt{\pi}}\int_0^x \exp\{-u^2\}du$$

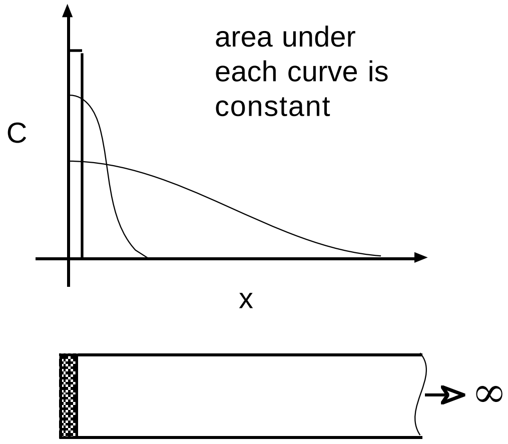

Fig. 3: Exponential solution. Note how the curvature changes with time.

so the solution to the diffusion equation is

$$\text{boundary conditions:} \qquad C\{x=0,t\} = C_s$$

$$\text{and} \qquad C\{x,t=0\} = C_0$$

$$C\{x,t\} = C_s - (C_s - C_0)\text{erf}\left\{\frac{x}{2\sqrt{Dt}}\right\}$$

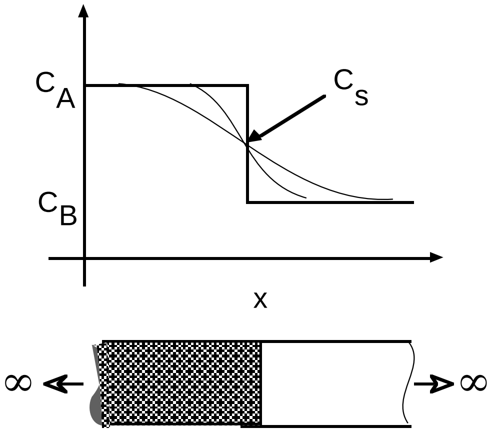

Fig. 4: The error function solution. Notice that the "surface" concentration remains fixed.

This solution can be used in many circumstances where the surface concentration is maintained constant, for example in the carburisation or decarburisation processes (the concentration profiles would be the same as in Fig. 4, but with only one half of the couple illustrated). The solutions described here apply also to the diffusion of heat.

Mechanism of Diffusion

We have so far considered diffusion in a phenomenological manner, neglecting the details of the atomic mechanisms. Atoms in the solid–state migrate by jumping into vacancies (Fig. 5). The vacancies may be interstitial or in substitutional sites. There is, nevertheless, a barrier to the motion of the atoms because the motion is associated with a transient distortion of the lattice.

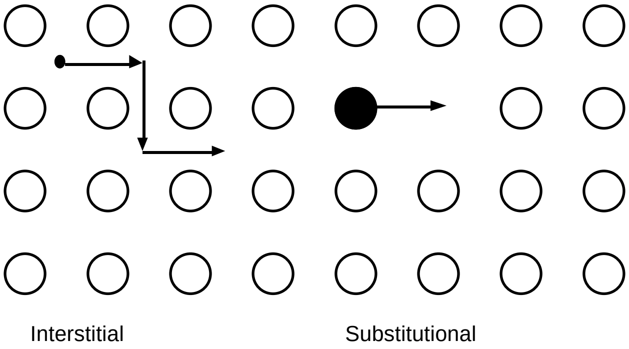

Fig. 5: Mechanism of interstitial and substitutional diffusion.

Assuming that the atom attempts jumps at a frequency ν_0, the frequency of successful jumps is given by

$$\begin{aligned}\nu &= \nu_0 \exp\left\{-\frac{G^*}{kT}\right\} \\ &\equiv \underbrace{\nu_0 \exp\left\{\frac{S^*}{k}\right\}}_{\text{independent of } T} \times \exp\left\{-\frac{H^*}{kT}\right\}\end{aligned}$$

where k and T are the Boltzmann constant and the absolute temperature respectively, and H^* and S^* the activation enthalpy and activation entropy respectively. Since

$$D \propto \nu \qquad \text{we find} \qquad D = D_0 \exp\left\{-\frac{H^*}{kT}\right\}$$

A plot of the logarithm of D versus $1/T$ should therefore give a straight line (Fig. 6), the slope of which is $-H^*/k$. Note that H^* is frequently called the activation energy for diffusion and is often designated Q.

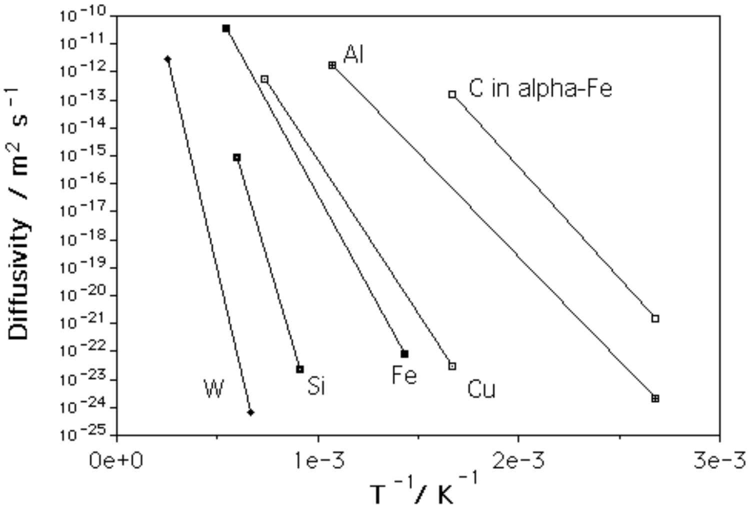

Fig. 6: Typical self–diffusion coefficients for pure metals and for carbon in ferritic iron. The uppermost diffusivity for each metal is at its melting temperature.

The activation enthalpy of diffusion can be separated into two components, one the enthalpy of migration (due to distortions) and the enthalpy of formation of a vacancy in an adjacent site. After all, for the atom to jump it is necessary to have a vacant site; the equilibrium concentration of vacancies can be very small in solids. Since there are many more interstitial vacancies, and since most interstitial sites are vacant, interstitial atoms diffuse far more rapidly than substitutional solutes.

Additional Information

1. R.–E. Reed Hill and R. Abbaschian, Physical Metallurgy Principles, 3rd edition, published by Wadsworth.
2. A. H. Cottrell, Introduction to Metallurgy, 2nd edition, published by The Institute of Materials.
3. Diffusion bonding, one example of the application of diffusion theory, http://www.msm.cam.ac.uk/phase-trans/2005/Amir/bond.html
4. Hardening of gears, another application of diffusion, http://www.msm.cam.ac.uk/
trans/2001/diffusion.html

Lecture 2: Atomic Diffusion

Diffusion is at first sight difficult to appreciate for the solid state. A number of mechanisms have been proposed historically. This includes a variety of ring mechanisms where atoms simply swap positions, but controversy remained because the strain energies associated with such swaps made the theories uncertain. One possibility is that diffusion occurs by atoms jumping into vacancies. But the equilibrium concentration of vacancies is typically 10^{-6}, which is very small. The theory was therefore not generally accepted until an elegant experiment by Smigelskas and Kirkendall (Fig. 7).

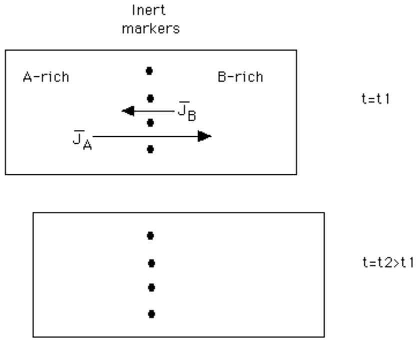

Fig. 7: Diffusion couple with markers

The experiment applies to solids as well as immiscible liquids. Consider a couple made from A and B. If the diffusion fluxes of the two elements are different ($|J_A| > |J_B|$) then there will be a net flow of matter past the inert markers, causing the couple to shift bodily relative to the markers. This can only happen if diffusion is by a vacancy mechanism.

An observer located at the markers will see not only a change in concentration due to intrinsic diffusion, but also because of the Kirkendall flow of matter past the markers. The net effect is described by the usual Fick's laws, but with an interdiffusion coefficient $\overline{D}$ which is a weighted average of the two intrinsic diffusion coefficients:

$$\overline{D} = X_B D_A + X_A D_B$$

where X represents a mole fraction. It is the interdiffusion coefficient that is measured in most experiments.

Structure Sensitive Diffusion

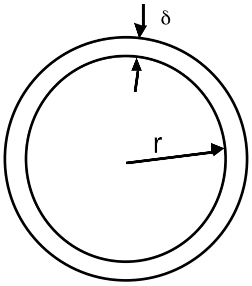

Fig. 8: Idealised grain

Crystals may contain nonequilibrium concentrations of defects such as vacancies, dislocations and grain boundaries. These may provide easy diffusion paths through an otherwise perfect structure. Thus, the grain boundary diffusion coefficient D_{gb} is expected to be much greater than the diffusion coefficient associated with the perfect structure, D_P.

Assume a cylindrical grain. On a cross section, the area presented by a boundary is $2\pi r\delta$ where δ is the thickness of the boundary. Note that the boundary is shared between two adjacent grains so the thickness associated with one grain is $\frac{1}{2}\delta$. The ratio of the areas of grain boundary to grain is therefore

$$\text{ratio of areas} = \frac{1}{2} \times \frac{2\pi r\delta}{\pi r^2} = \frac{\delta}{r} = \frac{2\delta}{d}$$

where d is the grain diameter (Fig. 8).

For a unit area, the overall flux is the sum of that through the lattice and that through the boundary:

$$J \simeq J_P + J_{gb}\frac{2\delta}{d}$$

$$\text{so that} \qquad D_{measured} = D_P + D_{gb}\frac{2\delta}{d}$$

Note that although diffusion through the boundary is much faster, the fraction of the sample which is the grain boundary phase is small. Consequently, grain boundary or defect diffusion in general is only of importance at low temperatures where $D_P \ll D_{gb}$ (Fig. 9).

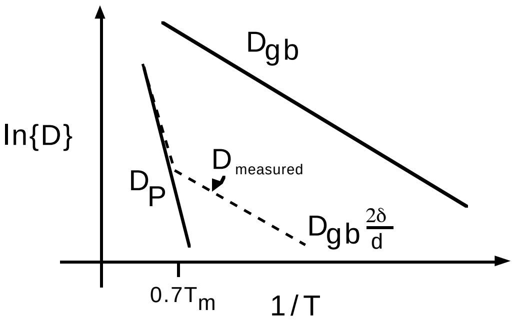

Fig. 9: Structure sensitive diffusion. The dashed line will in practice be curved.

Some solids, particularly polymers, relax under the influence of solutes which penetrate them. Alternatively, they react with the solute. For example, the structure of an assembly of polymeric molecules may change when penetrated by a solute, and indeed may undergo a change in volume. Some of these phenomena can be exploited in the design of delivery systems for medicines, where a slow release of chemicals may be advantageous in contrast to immediate dissolution of tablets.

Thermodynamics of diffusion

Fick's first law is empirical in that it assumes a proportionality between the diffusion flux and the concentration gradient. However, diffusion occurs so as to minimise the free energy. It should therefore be driven by a gradient of free energy. But how do we represent the gradient in the free energy of a particular solute?

The Chemical Potential

We first examine equilibrium for an allotropic transition (*i.e.* when the structure changes but not the composition). Two phases α and γ are said to be in equilibrium when they have equal free energies:

$$G^{\alpha} = G^{\gamma} \tag{1}$$

When temperature is a variable, the transition temperature is also fixed by the above equation (Fig. 10).

A different approach is needed when chemical composition is also a variable. Consider an alloy consisting of two components A and B. For the phase α, the free energy will in general be a function of the mole

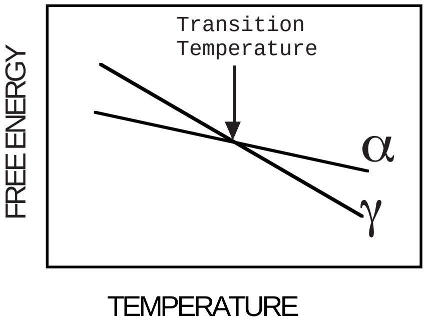

Fig. 10: The transition temperature for an allotropic transformation.

fractions $(1 - X)$ and X of A and B respectively:

$$G^{\alpha} = (1 - X)\mu_A + X\mu_B \tag{2}$$

where μ_A represents the mean free energy of a mole of A atoms in α. The term μ is called the *chemical potential* of A, and is illustrated in Fig. 11a. Thus the free energy of a phase is simply the weighted mean of the free energies of its component atoms. Of course, the latter varies with concentration according to the slope of the tangent to the free energy curve, as shown in Fig. 11.

Consider now the coexistence of two phases α and γ in our binary alloy. They will only be in equilibrium with each other if the A atoms in γ have the same free energy as the A atoms in α, and if the same is true for the B atoms:

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

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

If the atoms of a particular species have the same free energy in both the phases, then there is no tendency for them to migrate, and the system will be in stable equilibrium if this condition applies to all species of atoms. Since the way in which the free energy of a phase varies with concentration is unique to that phase, the *concentration* of a particular species of atom need not be identical in phases which are at equilibrium. Thus, in general we may write:

$$X_A^{\alpha\gamma} \neq X_A^{\gamma\alpha}$$

$$X_B^{\alpha\gamma} \neq X_B^{\gamma\alpha}$$

where $X_i^{\alpha\gamma}$ describes the mole fraction of element i in phase α which is in equilibrium with phase γ *etc.*

The condition the chemical potential of each species of atom must be the same in all phases at equilibrium is quite general and obviously justifies the common tangent construction illustrated in Fig. 11b.

Diffusion in a Chemical Potential Gradient

The concept of a chemical potential is powerful indeed. Thus, it is proper to say that diffusion is driven by gradients of free energy rather than chemical concentration:

$$J_A = -C_A M_A \frac{\partial \mu_A}{\partial x} \qquad \text{so that} \qquad D_A = C_A M_A \frac{\partial \mu_A}{\partial C_A}$$

where the proportionality constant M_A is known as the mobility of A. In this equation, the diffusion coefficient is related to the mobility by comparison with Fick's first law.

The relationship is remarkable: if $\partial \mu_A / \partial C_A > 0$ as for the solution illustrated in Fig. 11a, then the diffusion coefficient is positive and the

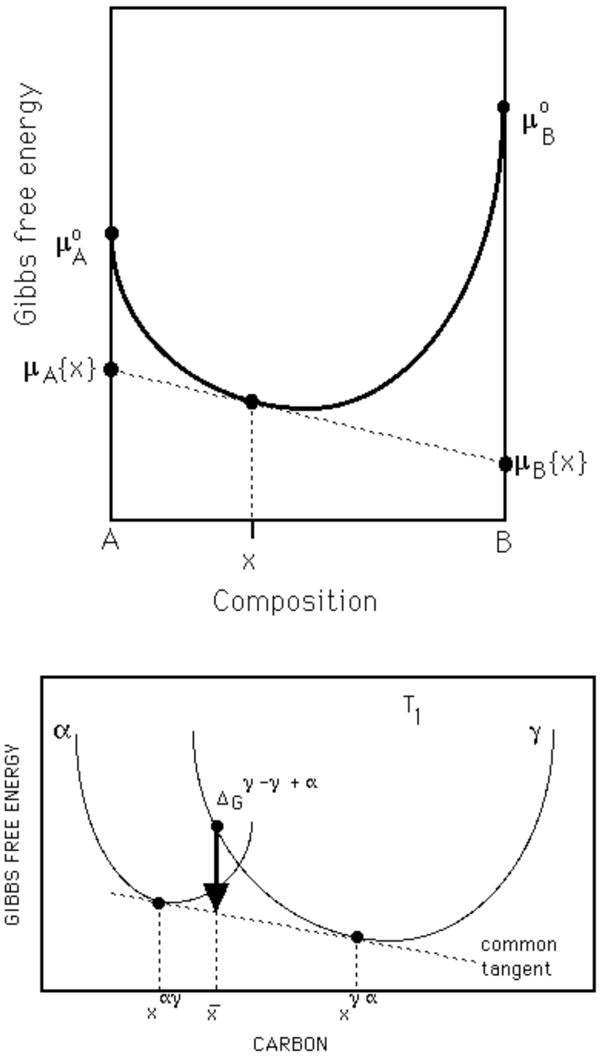

Fig. 11: (a) Diagram illustrating the meaning of a chemical potential μ. (b) The common tangent construction giving the equilibrium compositions of the two phases at a fixed temperature.

chemical potential gradient is along the same direction as the concentration gradient. However, if $\partial\mu_A/\partial C_A < 0$ then the diffusion will occur against a concentration gradient! This can only happen in a solution where the free energy curve has the form illustrated in Fig. 12.

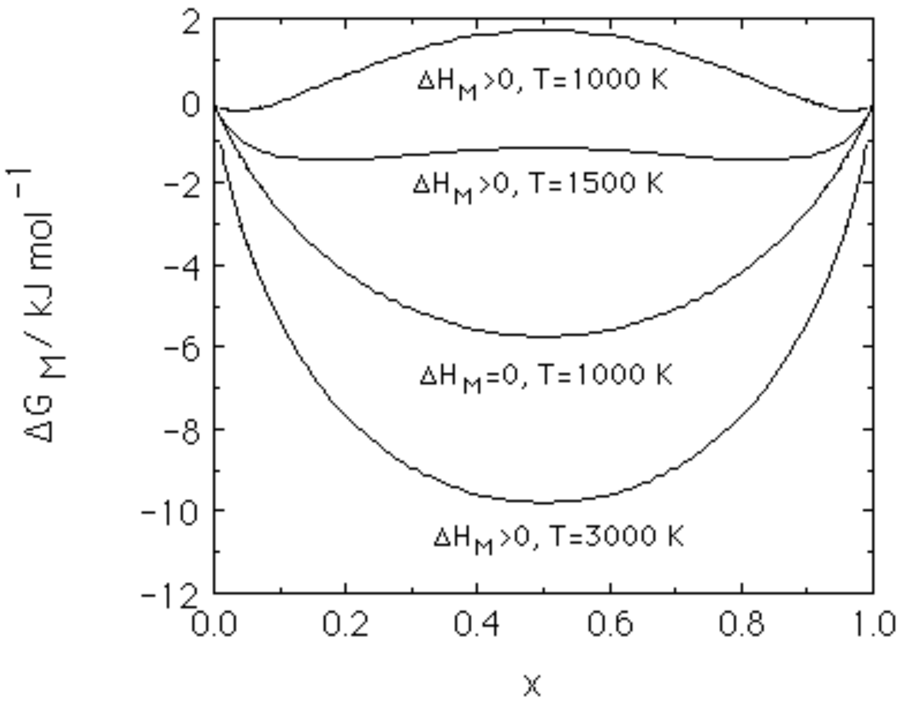

Fig. 12: Free energy of mixing plotted as a function of temperature and of the enthalpy ΔH_M of mixing. $\Delta H_M = 0$ corresponds to an ideal solution where the atoms of different species always tend to mix at random and it is always the case that $\partial \mu_A / \partial C_A > 0$. When $\Delta H_M < 0$ the atoms prefer unlike neighbours and it is always the case that $\partial \mu_A / \partial C_A > 0$. When $\Delta H_M > 0$ the atoms prefer like neighbours so for low temperatures and for certain composition ranges $\partial \mu_A / \partial C_A < 0$ giving rise to the possibility of uphill diffusion.

Additional Information

1. Kirkendall effect,

   http://www.msm.cam.ac.uk/phase-trans/kirkendall.html

2. Comprehensive resources on thermodynamics,

   http://www.msm.cam.ac.uk/phase-trans/thermodynamics.html