

## Worked Examples

### 1. Question

Explain, in the context of binary solutions, what is meant by the term ‘chemical potential’. Hence justify the fact that the common tangent construction, on a free energy versus concentration plot, gives the equilibrium compositions of the phases.

Distinguish between an *ideal*, a *regular* and a *quasichemical* solution thermodynamic model. Explain qualitatively why none of these models are used in their exact forms in the computer calculation of phase diagrams.

### 1. Answer

Consider an alloy consisting of two components  $A$  and  $B$ . For the phase  $\alpha$ , the free energy will in general be a function of the mole fractions  $(1 - X)$  and  $X$  of  $A$  and  $B$  respectively:

$$G^\alpha = (1 - X)\mu_A + X\mu_B \quad (1)$$

where  $\mu_A$  represents the mean free energy of a mole of  $A$  atoms in  $\alpha$ . The term  $\mu$  is called the *chemical potential* of  $A$ , and is illustrated in Fig. 1a. 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. 1.

Consider now the coexistence of two phases  $\alpha$  and  $\gamma$  in our binary alloy. They will only be in equilibrium with each other if the  $A$  atoms in  $\gamma$  have the same free energy as the  $A$  atoms in  $\alpha$ , 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  $\alpha$  which is in equilibrium with phase  $\gamma$  etc.

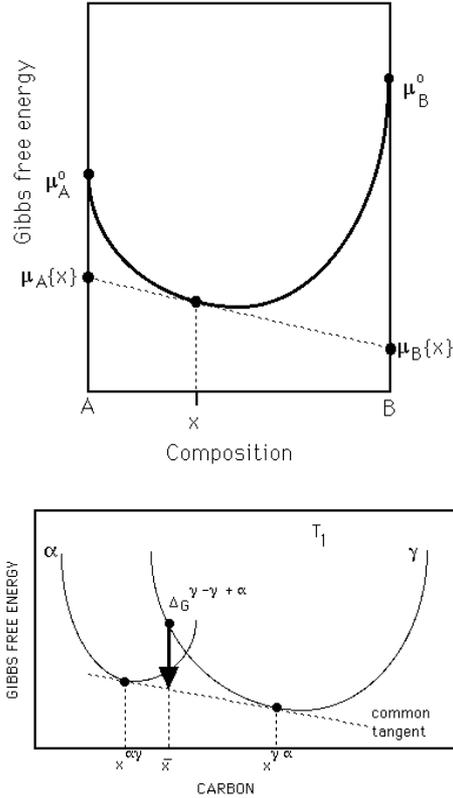


Fig. 1: (a) Diagram illustrating the meaning of a chemical potential  $\mu$ . (b) The common tangent construction giving the equilibrium compositions of the two phases at a fixed temperature.

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. 1b.

An ideal solution is one where the atoms mix at random because there is no enthalpy change on mixing ( $\Delta H_M$ ) the components (Table 1). The configurational entropy of mixing is ( $\Delta S_M$ ) is easily derived because the probabilities can be estimated assuming a random distribution of atoms. The enthalpy of mixing is finite for a regular solution, so that the atoms at low temperatures may not be randomly mixed. Nevertheless, as a convenient approximation, the entropy of mixing is assumed to be ideal. A quasichemical model avoids this latter approximation. Note that the regular solution may be considered as a zeroth approximation quasichemical model.

The models describe above help in the understanding of phase equilibria and in the behaviour of solutions. The theories are, nevertheless, too complicated for general application in phase diagram calculations. Computer methods are designed to enable the calculations to be implemented over the entire periodic table, for any concentration, and in a seamless manner. The thermodynamic functions have to be constructed in such a way that the modification of one set of data does not entail the recreation of the entire dataset.

Type	$\Delta S_M$	$\Delta H_M$
Ideal	Random	0
Regular	Random	$\neq 0$
Quasichemical	Not random	$\neq 0$

Table 1: Elementary thermodynamic properties of solutions

## 2. Question

Give three examples of cases where the rate of energy dissipation is given by the product of the “flux” ( $J$ ) and a corresponding “force”, ( $X$ ), *i.e.*

$$T\sigma = JX$$

where  $T$  is the absolute temperature and  $\sigma$  is the rate of entropy production. How could this relationship be generalised for multiple dissipation processes?

Using the concept of forces and fluxes in the theory of irreversible thermodynamics, deduce the relationship between the velocity  $V$  of a grain boundary and the free energy change  $\Delta G$  accompanying its motion. State any assumptions involved in this derivation.

Prove that the general relation between  $V$  and  $\Delta G$  should in fact be as follows:

$$V \propto \exp\{-Q/kT\}[1 - \exp\{-\Delta G/kT\}]$$

where  $Q$  is the activation energy for the transfer of atoms across the grain boundary,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature.

Is it possible to reconcile this equation with the relationship deduced from irreversible thermodynamics?

## 2. Answer

Force	Flux
Electromotive force (e.m.f.) = $\frac{\partial\phi}{\partial z}$	Electrical Current
$-\frac{1}{T} \frac{\partial T}{\partial z}$	Heat flux
$-\frac{\partial\mu_i}{\partial z}$	Diffusion flux

Table 2: Examples of forces and their conjugate fluxes.  $z$  is distance,  $\phi$  is the electrical potential in Volts, and  $\mu$  is a chemical potential.

We have seen that in an irreversible process, the product of the force  $Z$  and the flux  $J$  gives the rate of energy dissipation:

$$T\sigma = JZ$$

where  $T$  is the temperature,  $\sigma$  is the rate of entropy production.  $T\sigma$  is therefore the rate of energy dissipation. In many cases, it is found experimentally that  $J \propto Z$ .

When there is more than one dissipative process, the total energy dissipation rate can still be written

$$T\sigma = \sum_i J_i X_i. \quad (2)$$

In the case of grain boundary motion, the rate of energy dissipation is simply  $V\Delta G$  so that we immediately get

$$V \propto \Delta G$$

An alternative is to consider the transfer of atoms across a grain boundary (a barrier of height  $Q$ ). The probability of forward jumps (*i.e.* jumps which lead to a reduction in free energy) is given by

$$\exp\{-Q/kT\}$$

whereas that of reverse jumps is given by

$$\exp\{-(Q + \Delta G)/kT\} = \exp\{-Q/kT\} \exp\{-\Delta G/kT\}$$

.

The rate at which an interface moves is therefore given by

$$V \propto \exp\{-Q/kT\}[1 - \exp\{-\Delta G/kT\}]$$

Note that this relation is hardly that predicted from irreversible thermodynamics. However, they become identical when  $\Delta G$  is small, *i.e.* there is not a great deviation from equilibrium. Note that for small  $x$ ,  $\exp\{x\} \simeq 1 + x$ . Thus, at small driving forces,

$$V_i \propto \exp\{-Q/kT\}[\Delta G/kT]$$

The three parts of the question carry equal marks.