

## Part I : Preliminaries (Thermodynamics and Kinetics)

### Module 6: Diffusivity

#### 7.1 Motivation

Atomic fluxes can be set up in material not only due to concentration gradients; stresses, magnetic field (in magnetic materials), and electric fields (in ionic materials) can also set up atomic fluxes. What is the relevant constitutive law in these cases? How is the diffusivity related to such constitutive laws?

#### 7.2 Diffusivity: mechanism and thermal activation

Typical diffusivities in materials is given by giving the pre-exponential constant (typically denoted as  $D_0$ ) and the activation energy for diffusion  $Q$ . The temperature dependence of diffusivity, then, is given by

$$D(T) = D_0 \exp \left[ -\frac{Q}{RT} \right] \quad (11)$$

It is possible to rationalise the temperature dependence of diffusivity given in the expression above. Typically, diffusion takes place via a vacancy mediated process. In such cases, as the temperature increases, the number of vacancies increase exponentially, leading to an exponential relationship. Even in cases where diffusion is not mediated by vacancies, the movement of atoms from one point to another is a process in which the atoms have to overcome a barrier. This barrier to atomic movement exists because during such movement the atoms have to go through a configuration of high energy. Since overcoming such a barrier is a thermally activated process, there is an Arrhenius type of relationship between diffusivity and temperature.

Typically, diffusion through lattice is very slow as compared to diffusion through dislocations (known as pipe diffusion) and diffusion through grain boundaries. Such fast diffusion processes have a strong say in the development of microstructures as well as in determining the kinetics of processes.

#### 7.3 Diffusivity and mobility

Diffusivity is the flux of atoms to per unit concentration gradient that gives rise to it. However, there is a more fundamental quantity with reference to the movement of atoms, namely, mobility. Mobility is defined as the velocity of atoms per unit chemical potential gradient:

$$v = -M \frac{\partial \mu}{\partial x} \quad (12)$$

Note the negative sign which indicates that the movement of atoms brings down the gradients in chemical potential. Such a drift velocity can give rise to its own flux, which is then given by

$$J = cv = -Mc \frac{\partial \mu}{\partial x} \quad (13)$$

Comparing this expression with the Fick's first law, one obtains the relationship between diffusivity and mobility as follows:

$$D = Mc \frac{\partial \mu}{\partial c} \quad (14)$$

Note that in the case of binary alloys [Porter],

$$D = MRT \left\{ 1 + \frac{d \ln \gamma}{d \ln c} \right\} \quad (15)$$

#### 7.4 Tutorial problems and questions

1. Given  $D_0 = 190 \times 10^{-6} \text{ms}^{-2}$  and  $Q = 179.7 \text{ kJ/mol}$  for self-diffusion in pure nickel, calculate the self-diffusivity in pure nickel at 300, 700 and 1200 K.

**Answer**

Using Eq. 11, we obtain

$$D(300) = 3.8 \times 10^{-57} \text{ m}^2/\text{sec}$$

$$D(700) = 2.6 \times 10^{-25} \text{ m}^2/\text{sec}$$

$$D(1200) = 1.3 \times 10^{-16} \text{ m}^2/\text{sec}$$

Thus, we can see that diffusional processes are extremely slow at room temperature in Nickel.

2. The following is the data on melting temperature,  $D_0$  and  $Q$  (for self-diffusivity) for a few fcc metals. Calculate the self-diffusivity in these metals at their respective melting temperatures.

Nickel: 1726 K,  $190 \times 10^{-6} \text{ m}^2\text{s}^{-1}$ , 279.7 kJ/mol

Copper: 1356 K,  $31 \times 10^{-6} \text{ m}^2\text{s}^{-1}$ , 200.3 kJ/mol

Silver: 1234 K,  $40 \times 10^{-6} \text{ m}^2\text{s}^{-1}$ , 184.6 kJ/mol

Answer

Again using Eq. 11, we obtain

$$D(T_m) \text{ of nickel: } 6.5 \times 10^{-13} \text{ m}^2/\text{sec}$$

$$D(T_m) \text{ of copper: } 6.0 \times 10^{-13} \text{ m}^2/\text{sec}$$

$$D(T_m) \text{ of silver: } 6.1 \times 10^{-13} \text{ m}^2/\text{sec}$$

Thus, we can see that the diffusivities become more or less a constant at the melting temperature for these metals.

### Supplementary information

The exponential dependence of vacancy concentration can be derived from a regular solution model assuming that the atoms and vacancy form a binary solution; see Porter, Easterling and Sherif [2].

### References

1. David R Gaskell, Introduction to the thermodynamics of materials, Fourth edition (Special Indian edition), Taylor & Francis, 2010.
2. David A Porter, Kenneth E Easterling, Mohamed Y Sherif, Phase transformations in metals and alloys, Third edition (Special Indian edition), C R C press, 2009.