

# Phase Transformation of Materials

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## 2.1 Atomic mechanisms of diffusion

The mean vibrational energy is  $3kT$ , therefore increase in proportion to the absolute temperature.

If an adjacent site is vacant it can happen that a particularly violent oscillation results in the atom jumping over on to the vacancy. (Fig. 2.2)

Substitutional Diffusion

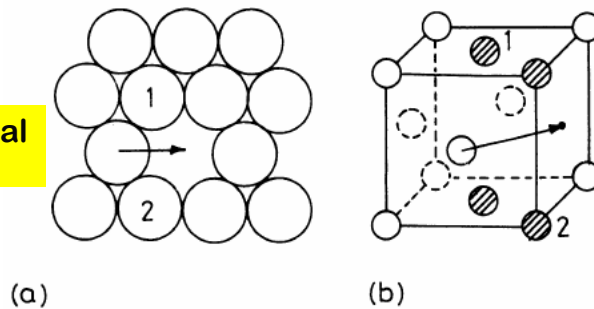


Fig. 2.2 Movement of an atom into an adjacent vacancy in an fcc lattice. (a) A close-packed plane. (b) A unit cell showing the four atoms (shaded) which must move before the jump can occur. (After P. G. Shewmon, *Diffusion in Solids*, McGraw-Hill, New York, 1963.)

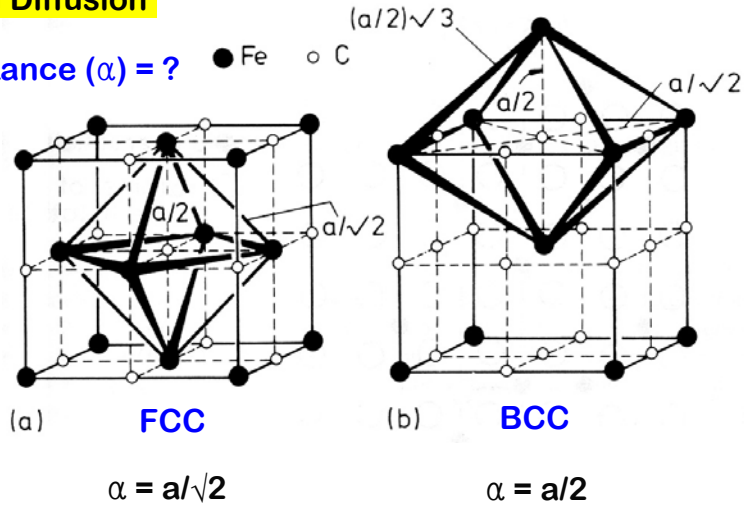


## 2.1 Atomic mechanisms of diffusion

### Interstitial Diffusion

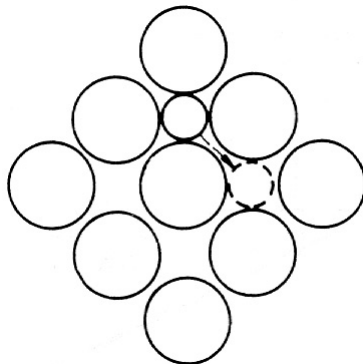
Jump distance ( $\alpha$ ) = ?

● Fe ○ C



## 2.1 Atomic mechanisms of diffusion

### Interstitial Diffusion



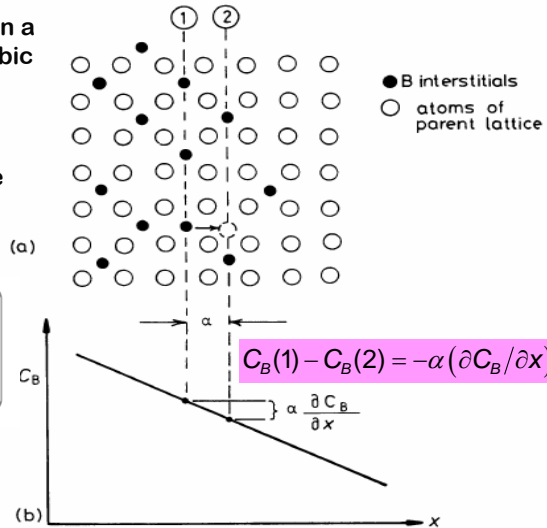
How interstitial diffusion differs from substitutional diffusion?



## 2.2 Interstitial diffusion

- Random jump of solute B atoms in a dilute solid solution of a simple cubic lattice

Assume that there is no lattice distortion and also that there are always six vacant sites around the diffusing atom.



$J_B$ : Flux of B atom  
 $\Gamma_B$ : Average jump rate of B atoms  
 $n_1$ : No. of atoms per unit area of plane 1  
 $n_2$ : No. of atoms per unit area of plane 2

$J_B?$

$$J_B = \frac{1}{6} \Gamma_B n_1 - \frac{1}{6} \Gamma_B n_2$$

Fig. 2.5 Interstitial diffusion by random jumps in a concentration gradient.



## Fick's First Law of Diffusion

$$J_B = \frac{1}{6} \Gamma_B n_1 - \frac{1}{6} \Gamma_B n_2 = \frac{1}{6} \Gamma_B (n_1 - n_2)$$

$\alpha$ : Jump distance       $C_B(1) = n_1/\alpha$ ,  $C_B(2) = n_2/\alpha$

$(n_1 - n_2) = \alpha (C_B(1) - C_B(2))$        $C_B(1) - C_B(2) = -\alpha \left( \frac{\partial C_B}{\partial x} \right)$

$$J_B = \frac{1}{6} \Gamma_B (n_1 - n_2) = - \left( \frac{1}{6} \Gamma_B \alpha^2 \right) \frac{\partial C_B}{\partial x} = -D_B \frac{\partial C_B}{\partial x}$$

(atoms  $\text{m}^{-2} \text{s}^{-1}$ )

$D_B$ : Intrinsic diffusivity or Diffusion coefficient of B



$$D_B = \frac{1}{6} \Gamma_B \alpha^2$$

Estimate the jump frequency of a carbon atom in  $\gamma$ -Fe at 1000°C.

lattice parameter of  $\gamma$ -Fe :  $\sim 0.37 \text{ nm}$   $D = 2.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$

$\alpha = 0.37 / \sqrt{2} = 0.26 \text{ nm}$   $\Gamma = 2 \times 10^9 \text{ jumps s}^{-1}$

the vibration frequency of carbon :  $\sim 10^{13}$

For random walk in 3 dimensions,  
after n steps of length  $\alpha$

$$\rightarrow \alpha \sqrt{n}$$

What would be  $\alpha \sqrt{n}$  of a carbon atom in  $\gamma$ -Fe at 1000°C after 1 s?

During random walk, an atom will move in  
time (t) a radial distance (r) from the origin

$$r = \alpha \sqrt{(\Gamma t)} = f(D) = 2.4 \sqrt{Dt} \because \Gamma = \frac{6D}{\alpha^2} \rightarrow r = \sqrt{6} \sqrt{Dt}$$

In 1 s, each carbon atom will move a total distance of  $\sim 0.5 \text{ m}$

$\rightarrow$  a net displacement :  $\sim 10 \text{ } \mu\text{m}$ .



## 2.2.2 EFFECT OF TEMPERATURE on Diffusivity

### Thermal Activation

How D varies  
with T?

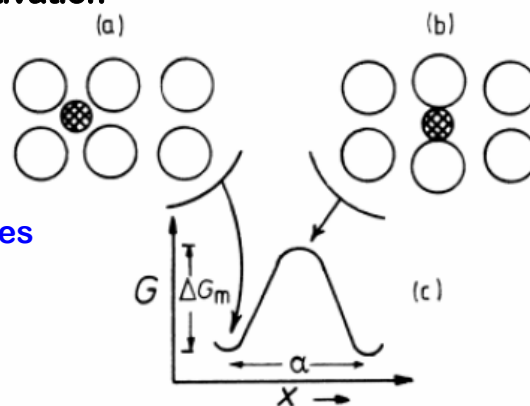


Fig. 2.6 Interstitial atom, (a) in equilibrium position, (b) at the position of maximum lattice distortion. (c) Variation of the free energy of the lattice as a function of the position of interstitial. (After P.G. Shewmon, in *physical Metallurgy*, 2<sup>nd</sup> edn., R.W. Cahn (Ed.), North-Holland, Amsterdam, 1974.)



$$\Gamma_B = z \nu \exp(-\Delta G_m / RT) \quad \text{jump frequency} \quad \Gamma_B ?$$

$\left\{ \begin{array}{l} z : \text{Nearest neighbor sites} \\ \nu : \text{Vibration frequency} \\ \Delta G_m : \text{Activation energy for moving} \end{array} \right\}$

$$\left\{ \Delta G_m = \Delta H_m - T \Delta S_m, D_B = \frac{1}{6} \Gamma_B \alpha^2 \right\}$$

$$D_B = \left[ \frac{1}{6} \alpha^2 z \nu \exp(\Delta S_m / R) \right] \exp(-\Delta H_m / RT)$$

$$\Delta H_m \equiv Q_{ID}$$

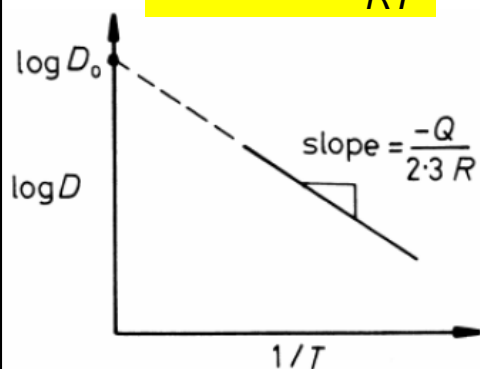
$$D_B = D_{B0} \exp \frac{-Q_{ID}}{RT} \quad (\text{Arrhenius-type equation})$$



## Temperature Dependence of Diffusion

$$D_B = D_{B0} \exp \frac{-Q_{ID}}{RT}$$

How to determine  $Q_{ID}$  experimentally?



$$\log D = \log D_0 - \frac{Q}{2.3R} \left( \frac{1}{T} \right)$$

**Therefore, from the slope of the  $D$ -curve in an  $\log D$  vs  $1/T$  coordinate, the activation energy may be found.**

Fig. 2.7 The slope of  $\log D$  v.  $1/T$  gives the activation energy for diffusion  $Q$ .



## 2.2.3 Steady-state diffusion

*The simplest type of diffusion to deal with is when the concentration at every point does not change with time.*

The case of thin-walled pressure vessel containing hydrogen gas: a steady state is reached when the hydrogen concentration is constant.

Provided  $D_H$  is independent of concentration there will be a single concentration gradient in the wall.

$l$ : Thickness of the container wall

$$J = -D \frac{\partial C}{\partial x}$$

independent of  $t$

$$\frac{\partial C}{\partial x} = ?$$

$$\frac{\partial C}{\partial x} = \frac{0 - C_H}{l}$$

$$J_H = D_H \frac{C_H}{l}$$



## 2.2.4 Nonsteady-state diffusion

*In most practical situations steady-state conditions are not established, i.e. concentration varies with both distance and time, and Fick's 1st law can no longer be used.*

How do we know the variation of  $C_B$  with time?

→ Fick's 2nd law

• Derive Fick's 2nd law.

hint 1

The flux will depend on  $D_B$  and  $\partial C_B / \partial x$ .

hint 3

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} \left( D_B \frac{\partial C_B}{\partial x} \right)$$

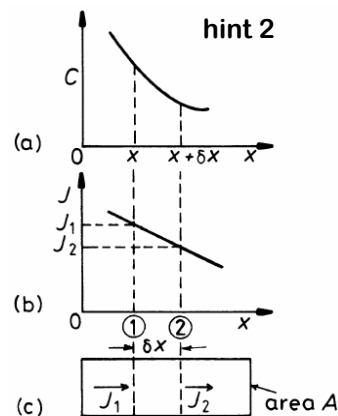


Fig 2.8 The derivation of Fick's second law.



## Fick's Second Law

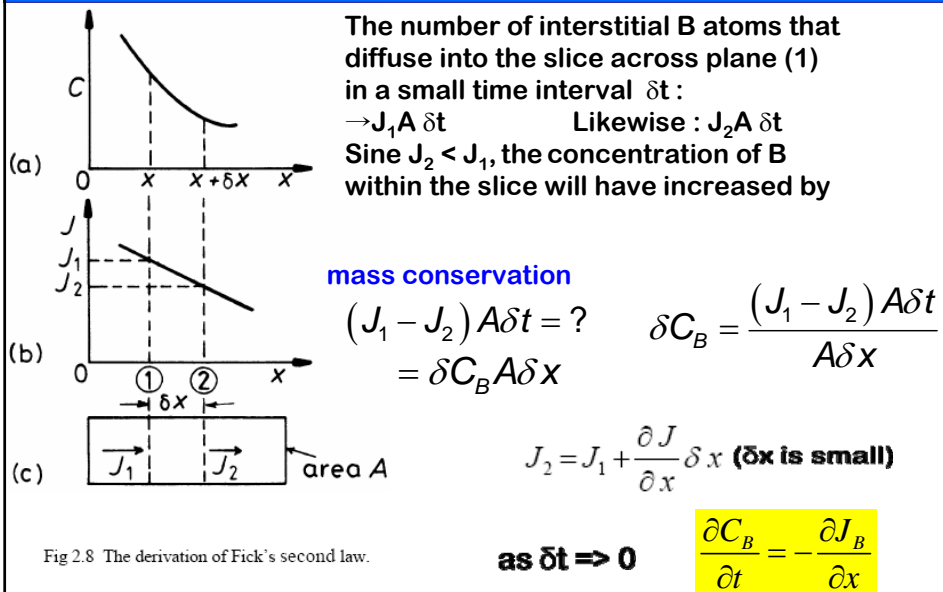


Fig 2.8 The derivation of Fick's second law.

as  $\delta t \Rightarrow 0$

$$\frac{\partial C_B}{\partial t} = - \frac{\partial J_B}{\partial x}$$



## Fick's Second Law

$$\frac{\partial C_B}{\partial t} = - \frac{\partial J_B}{\partial x} \quad J_B = -D \frac{\partial C_B}{\partial x}$$

substituting Fick's 1st law gives

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} \left( D_B \frac{\partial C_B}{\partial x} \right)$$

If variation of D with concentration can be ignored

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} \quad \text{(Fick's 2nd law)}$$

