

**Chapter Outline**

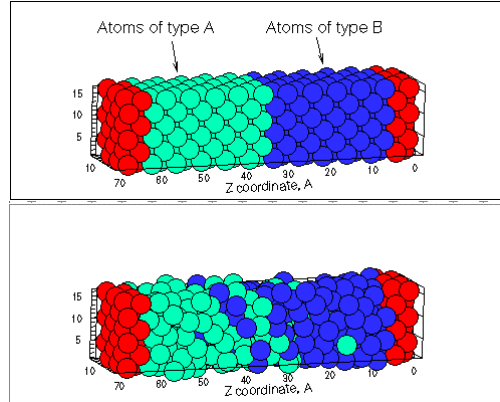
**Diffusion - how do atoms move through solids?**

- **Diffusion mechanisms**
  - Vacancy diffusion
  - Interstitial diffusion
  - Impurities
- **The mathematics of diffusion**
  - Steady-state diffusion (Fick's first law)
  - Nonsteady-State Diffusion (Fick's second law)
- **Factors that influence diffusion**
  - Diffusing species
  - Host solid
  - Temperature
  - Microstructure

5.4 Nonsteady-State Diffusion – Not Covered / Not Tested

**What is diffusion?**

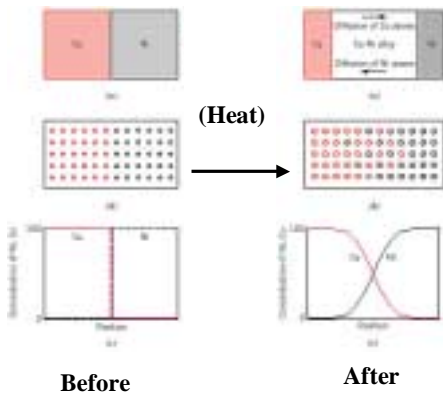
Diffusion is material transport by atomic motion.



Inhomogeneous materials can become homogeneous by diffusion. For an active diffusion to occur, the temperature should be high enough to overcome energy barriers to atomic motion.

**Interdiffusion and Self-diffusion**

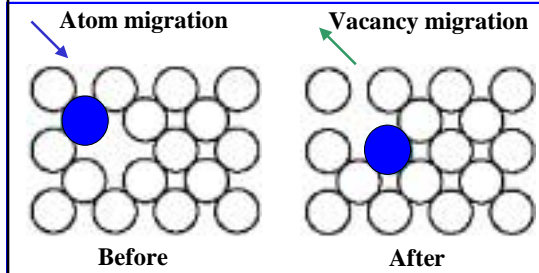
**Interdiffusion (or impurity diffusion)** occurs in response to a **concentration gradient**.



**Self-diffusion** is diffusion in one-component material, when all atoms that exchange positions are of the same type.

**Diffusion Mechanisms (I)**

**Vacancy diffusion**



To jump from lattice site to lattice site, atoms need energy to break bonds with neighbors, and to cause the necessary lattice distortions during jump. This energy comes from the thermal energy of atomic vibrations ( $E_{av} \sim kT$ )

Materials flow (the atom) is opposite the vacancy flow direction.

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### Diffusion Mechanisms (II)

**Interstitial diffusion**

Interstitial atom  
before diffusion

Interstitial atom  
after diffusion

Interstitial diffusion is generally faster than vacancy diffusion because bonding of interstitials to the surrounding atoms is normally weaker and there are many more interstitial sites than vacancy sites to jump to.

Requires small impurity atoms (e.g. C, H, O) to fit into interstices in host.

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### Diffusion Flux

**The flux of diffusing atoms, J**, is used to quantify how fast diffusion occurs. The flux is defined as either in number of atoms diffusing through unit area and per unit time (e.g., atoms/m<sup>2</sup>-second) or in terms of the mass flux - mass of atoms diffusing through unit area per unit time, (e.g., kg/m<sup>2</sup>-second).

$$J = M / At \cong (1/A) (dM/dt) \text{ (Kg m}^{-2} \text{ s}^{-1}\text{)}$$

where M is the mass of atoms diffusing through the area A during time t.

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### Steady-State Diffusion

**Steady state diffusion:** the diffusion flux does not change with time.

**Concentration profile:** concentration of atoms/molecules of interest as function of position in the sample.

**Concentration gradient: dC/dx (Kg.m<sup>-3</sup>):** the slope at a particular point on concentration profile.

(a)

$$\frac{dC}{dx} \cong \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$

(b)

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### Steady-State Diffusion: Fick's first law

**Fick's first law:** the diffusion flux along direction x is proportional to the concentration gradient

$$J = -D \frac{dC}{dx} \text{ where } D \text{ is the diffusion coefficient}$$

J = flux of atoms across plane with area, A

$$= -D \left( \frac{\partial c}{\partial x} \right)$$

The concentration gradient is often called the *driving force* in diffusion (but it is not a force in the mechanistic sense). The minus sign in the equation means that diffusion is down the concentration gradient.

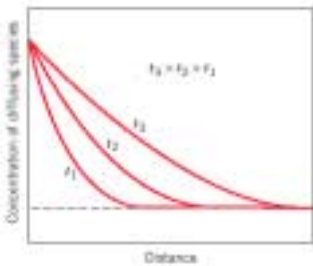
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### Nonsteady-State Diffusion: Fick's second law (not tested)

In most real situations the concentration profile and the concentration gradient are changing with time. The changes of the concentration profile is given in this case by a differential equation, *Fick's second law*.

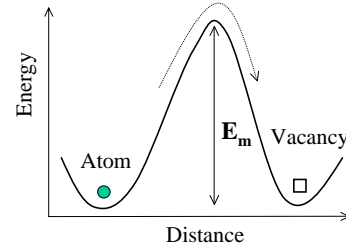
$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2}$$

Solution of this equation is concentration profile as function of time,  $C(x,t)$ :



### Diffusion – Thermally Activated Process (I) (not tested)

In order for atom to jump into a vacancy site, it needs to possess enough energy (thermal energy) to break the bonds and squeeze through its neighbors. The energy necessary for motion,  $E_m$ , is called **the activation energy** for vacancy motion.



Schematic representation of the diffusion of an atom from its original position into a vacant lattice site. At activation energy  $E_m$  has to be supplied to the atom so that it could break inter-atomic bonds and to move into the new position.

### Diffusion – Thermally Activated Process (II) (not tested)

The average thermal energy of an atom ( $k_B T = 0.026$  eV for room temperature) is usually much smaller than the activation energy  $E_m$  ( $\sim 1$  eV/atom) and a large fluctuation in energy (when the energy is “pooled together” in a small volume) is needed for a jump.

The probability of such fluctuation or frequency of jumps,  $R_j$ , depends exponentially from temperature and can be described by equation that is attributed to Swedish chemist **Arrhenius** :

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

where  $R_0$  is an attempt frequency proportional to the frequency of atomic vibrations.

### Diffusion – Thermally Activated Process (III) (not tested)

For the vacancy diffusion mechanism the probability for any atom in a solid to move is the product of

the probability of finding a vacancy in an adjacent lattice site (see Chapter 4):

$$P = C.N.\exp\left(-\frac{Q_v}{k_B T}\right)$$

and the probability of thermal fluctuation needed to overcome the energy barrier for vacancy motion

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

The diffusion coefficient, therefore, can be estimated as

$$\begin{aligned} D &\approx C.N.R_0 a^2 \exp\left(-\frac{E_m}{k_B T}\right) \exp\left(-\frac{Q_v}{k_B T}\right) = \\ &= D_0 \exp\left(-\frac{(E_m + Q_v)}{k_B T}\right) = D_0 \exp\left(-\frac{Q_d}{k_B T}\right) \end{aligned}$$

Temperature dependence of the diffusion coefficient, follows the Arrhenius dependence.

**Diffusion – Temperature Dependence (I)**

$J = -D \frac{dC}{dx}$  Diffusion coefficient is the measure of mobility of diffusing species.

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

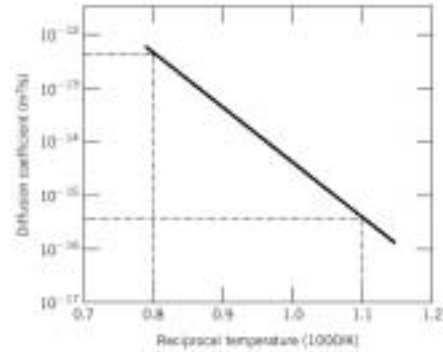
$D_0$  – temperature-independent preexponential ( $m^2/s$ )  
 $Q_d$  – the activation energy for diffusion (J/mol or eV/atom)  
 $R$  – the gas constant (8.31 J/mol-K or  $8.62 \times 10^{-5}$  eV/atom-K)  
 $T$  – absolute temperature (K)

The above equation can be rewritten as

$$\ln D = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T}\right) \text{ or } \log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T}\right)$$

The activation energy  $Q_d$  and preexponential  $D_0$ , therefore, can be estimated by plotting  $\ln D$  versus  $1/T$  or  $\log D$  versus  $1/T$ . Such plots are Arrhenius plots.

**Diffusion – Temperature Dependence (II)**

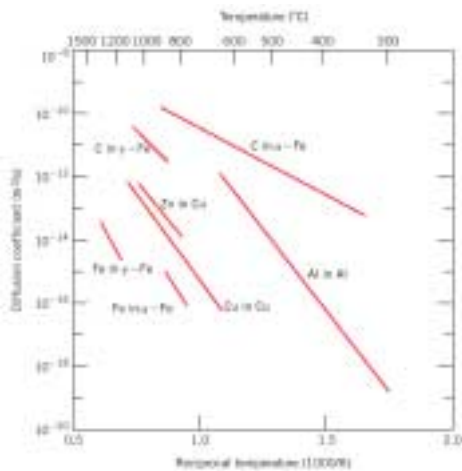


Graph of  $\log D$  vs.  $1/T$  has slope of  $-Q_d/2.3R$ , intercept of  $\ln D_0$

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

$$Q_d = -2.3R \left[ \frac{\log D_1 - \log D_2}{1/T_1 - 1/T_2} \right]$$

**Diffusion – Temperature Dependence (III)**



Arrhenius plot of diffusivity data for some metallic systems

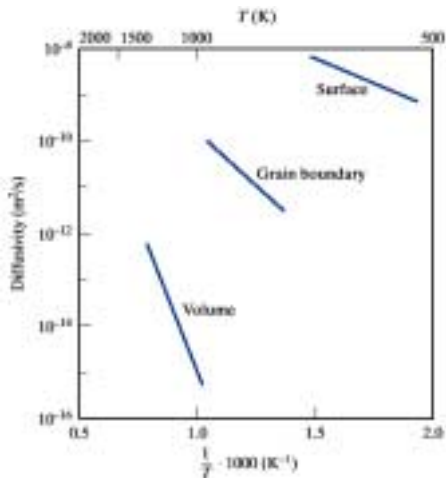
**Diffusion of different species**

Table 5.2 A Tabulation of Diffusion Data

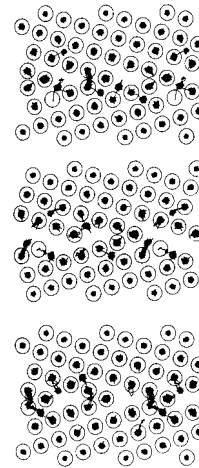
Diffusion Species	Host Metal	$D_0$ ( $m^2/s$ )	$Q_d$ (kJ/mol)	$Q_d$ (eV/atom)	$T$ ( $^\circ C$ )	$D$ ( $m^2/s$ )
Fe	$\alpha$ -Fe (BCC)	$1.0 \times 10^4$	24	2.8	500	$1.6 \times 10^{-13}$
	$\gamma$ -Fe (FCC)	$5.0 \times 10^4$	26	2.9	600	$1.1 \times 10^{-12}$
C	$\alpha$ -Fe	$6.2 \times 10^7$	81	9.8	600	$2.4 \times 10^{-11}$
	$\gamma$ -Fe	$2.3 \times 10^8$	148	17.8	600	$1.7 \times 10^{-10}$
Cu	Cu	$7.8 \times 10^4$	211	25.4	600	$4.2 \times 10^{-13}$
	Zn	$2.4 \times 10^4$	185	22.4	500	$4.0 \times 10^{-13}$
Al	Al	$2.3 \times 10^4$	146	17.6	500	$4.2 \times 10^{-13}$
	Ni	$6.5 \times 10^4$	136	16.3	500	$4.1 \times 10^{-13}$
Mg	Al	$1.2 \times 10^4$	131	15.8	500	$1.9 \times 10^{-13}$
	Ni	$2.7 \times 10^4$	200	24.1	500	$1.1 \times 10^{-13}$

Source: E. A. Brindley and G. B. Brook (Editors), *Materials Science Reference Series*, 7th Edition, Butterworth-Heinemann, Oxford, 1992.

Smaller atoms diffuse more readily than big ones, and diffusion is faster in open lattices or in open directions

**Diffusion: Role of the microstructure (I)**

Self-diffusion coefficients for Ag depend on the diffusion path. In general the diffusivity is greater through less restrictive structural regions – grain boundaries, dislocation cores, external surfaces.

**Diffusion: Role of the microstructure (II)**

The plots below are from the computer simulation by T. Kwok, P. S. Ho, and S. Yip. Initial atomic positions are shown by the circles, trajectories of atoms are shown by lines. We can see the difference between atomic mobility in the bulk crystal and in the grain boundary region.

**Factors that Influence Diffusion: Summary**

- **Temperature** - diffusion rate increases very rapidly with increasing temperature
- **Diffusion mechanism** - interstitial is usually faster than vacancy
- **Diffusing and host species** -  $D_o$ ,  $Q_d$  is different for every solute, solvent pair
- **Microstructure** - diffusion faster in polycrystalline vs. single crystal materials because of the accelerated diffusion along grain boundaries and dislocation cores.

**Summary**

Make sure you understand language and concepts:

- Activation energy
- Concentration gradient
- Diffusion
- Diffusion coefficient
- Diffusion flux
- Driving force
- Fick's first and second laws
- Interdiffusion
- Interstitial diffusion
- Self-diffusion
- Steady-state diffusion
- Vacancy diffusion

**Reading for next class:**

**Chapter 6: Mechanical Properties of Metals**

➤ **Stress and Strain**

- ✓ Tension
- ✓ Compression
- ✓ Shear
- ✓ Torsion

➤ **Elastic deformation**

➤ **Plastic Deformation**

- ✓ Yield Strength
- ✓ Tensile Strength
- ✓ Ductility
- ✓ Resilience
- ✓ Toughness
- ✓ Hardness