



Kwame Nkrumah University of  
Science & Technology, Kumasi, Ghana

# ENGINEERING MATERIALS I(ME 281)



## IMPERFECTIONS AND DIFFUSION IN SOLIDS

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# Outline

- **Defects and Impurities in Solids**
- Point defects
- Line defects
- Interfacial defects
- **Diffusion in Solids**
- Mechanisms of diffusion
- Diffusion under steady and unsteady states
- Factors that influence diffusion

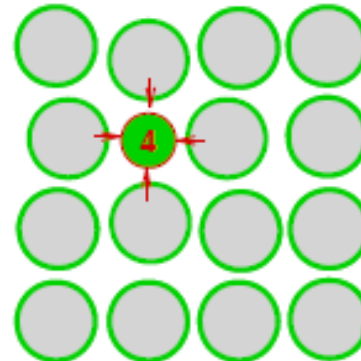
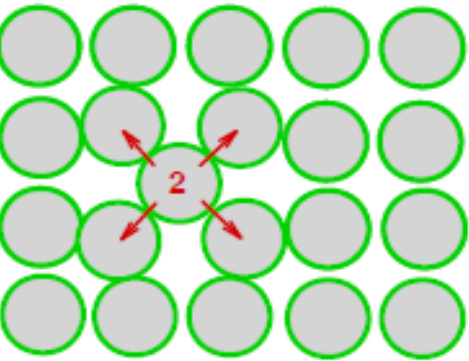
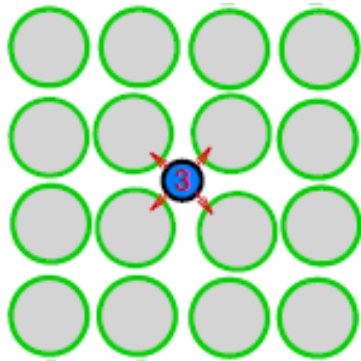
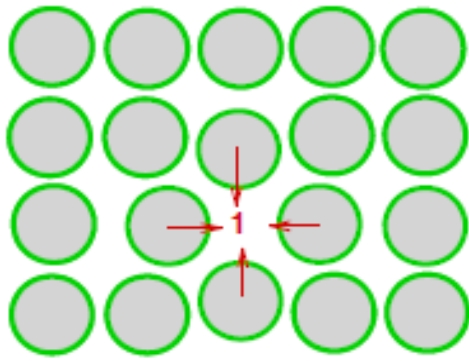
# Learning Objectives

**After studying this topic, you should be able to do the following:**

- Explain the various imperfections in solid crystals
- Describe impurities associated with solid atoms
- Determine the concentration of an alloy in terms of its constituent elements.
- Explain the diffusion mechanisms in solids
- State Fick's laws associated with steady and unsteady state diffusion
- Solve problems involving steady and unsteady state diffusion
- Explain the factors that influence diffusion in solids.

# Point Defects in Solids

- Point defects are imperfect point-like regions in the crystal. Typical size of a point defect is about 1-2 atomic diameters. The different point defects in crystals are;



(1) Vacancy

(3) Interstitial impurity

(2) Self-interstitial

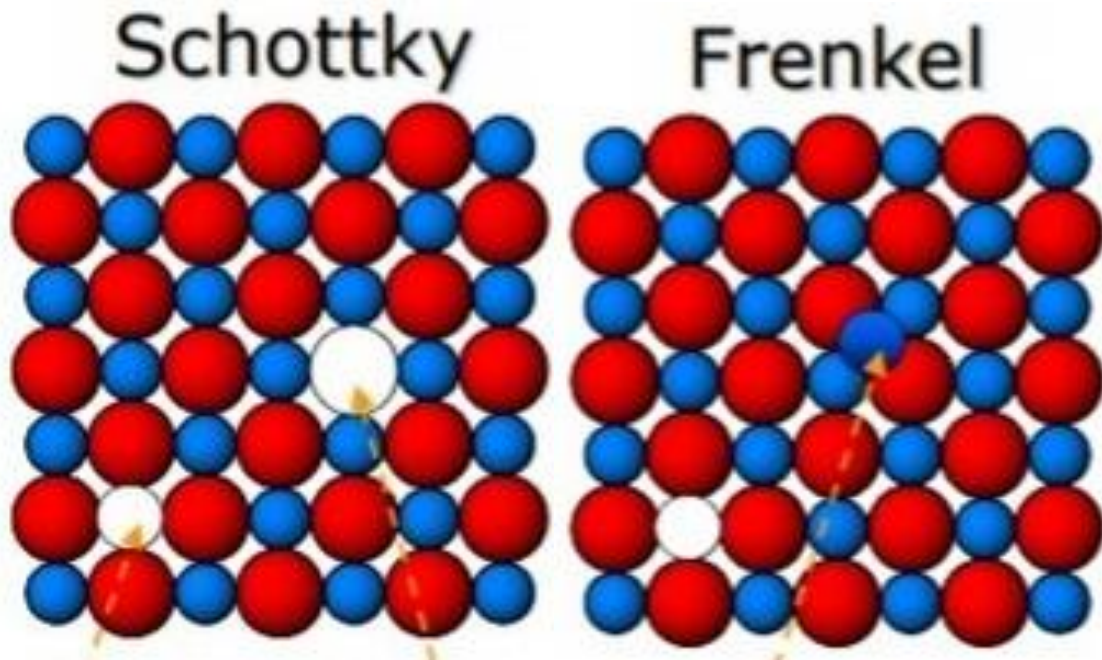
(4) Substitutional impurity

- A **vacancy** is a normal lattice position from where the atom is missing.
- An **interstitial atom** is an atom that occupies a place outside the normal lattice position.
- A **substitutional atom** is a foreign atom occupying original lattice position by displacing the parent atom.

# Point Defects in Solids

- The vacancies and foreign atoms change the coordination of atoms around the defect.
- Hence, forces are not balanced in the same way as other atoms in the solid, resulting in lattice distortion around the defect.

## Point defects in ionic crystals



- **Schottky defect:** A pair of cation and anion can be missing from an ionic crystal, without violating the condition of charge neutrality when the valency of ions is equal.
- **Frenkel defect:** An ion is displaced from a regular position to an interstitial position creating a vacancy. Cations are usually smaller and thus displaced easily than anions.

# Point Defects in Solids

- At equilibrium, the fraction of lattice sites that are vacant at a given temperature (T) is given by the expression;

$$\frac{n}{N} = e^{(-Q/kT)}$$

- n is the number of vacant sites
- T is absolute temperature in Kelvin,
- Q is the energy required to move an atom from the interior of a crystal to its surface.
- k is the gas or Boltzmann's constant ( $1.38 \times 10^{-23}$  J/atom K, or  $8.62 \times 10^{-5}$  eV/atom K).

- The number of atomic sites, N, is determined by the expression;

$$N = \frac{N_A \cdot \rho}{A}$$

- Where A is atomic weight and  $\rho$  is density.
- From the equation, there is an **exponential increase in number of vacancies with temperature.**
- When the density of vacancies becomes relatively large, there is a possibility for them to cluster together and form voids.

# Point Defects in Solids

## Determining the equilibrium number of vacant sites: Example Question

Calculate the equilibrium number of vacancies per cubic meter for copper at 1000 °C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density (at 1000 °C) for copper are 63.5 g/mol and 8.4 g/cm<sup>3</sup>, respectively.

### • Solution

$$N = \frac{N_A \cdot \rho}{A_{cu}} = \frac{(6.022 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}}$$

$$N = 8.0 \times 10^{28} \text{ atoms/m}^3$$

$$n = N \cdot \exp\left(\frac{-Q}{kT}\right) = 8.0 \times 10^{28} \text{ atoms/m}^3 \cdot \exp\left(\frac{-(0.9 \text{ eV/atom})}{(8.62 \times 10^{-5} \text{ eV/atom} \cdot \text{K})(1273 \text{ K})}\right)$$

$$n = 2.2 \times 10^{25} \text{ vacancies/m}^3$$



# Point Defects in Solids

## Impurities in Solids

- Impurity atoms are intentionally added to pure metals to impart specific characteristics to the material.
- Adding impurity atoms to a metal result in the **formation of a solid solution** and/or a new second phase, depending on the type of impurity, their concentrations, and the temperature of the alloy.
- For alloys, **solute** and **solvent** are commonly used terms. Solvent and solute represents the element or compound that is present in major and minor concentrations, respectively. On occasion, **solvent atoms are also called host atoms**.
- **A solid solution is formed as the solute atoms being added to the host material maintains the crystal structure with no new structures.**
- A solid solution is compositionally homogeneous; the impurity atoms are randomly and uniformly dispersed.



# Point Defects in Solids

## Specification of Alloy Composition

- The composition (or concentration) of an alloy is expressed in terms of its constituent elements.
- The two most common ways to specify composition are weight (or mass) percent and atom percent.

## Concentration in weight percent (wt%)

$$C_x = \frac{m_x}{m_x + m_y} \times 100\%$$

- Where  $m_x$  and  $m_y$  represent the weight or mass of elements x and y, respectively.
- The concentration of y would be determined in an analogous manner.

# Point Defects in Solids

## Specification of Alloy Composition

### Concentration in atom percent (at%)

$$C'_x = \frac{(m_x/A_x)}{[(m_x/A_x) + (m_y/A_y)]} \times 100\% = \frac{n_x}{n_x + n_y} \times 100\%$$

- Where  $m_x$  and  $m_y$  represent the weight or mass,  $A_x$  and  $A_y$  represent the atomic weight and  $n_x$  and  $n_y$  represent number of moles of the elements x and y, respectively.
- **Concentration in (at%) given concentration in (wt%) and vice versa**

$$C'_x = \frac{C_x A_y}{C_x A_y + C_y A_x} \times 100\%$$

$$C'_y = \frac{C_y A_x}{C_y A_x + C_x A_y} \times 100\%$$

# Point Defects in Solids

## Specification of Alloy Composition: Example

### Question

- Determine the composition, in atom percent, of an alloy that consists of 97 wt% aluminum and 3 wt% copper. The atomic weight (molar mass) of copper and aluminum are 63.55 g/mol and 26.98 g/mol respectively.

### Solution

$$C'_{Al} = \frac{C_{Al}A_{Cu}}{C_{Al}A_{Cu} + C_{Cu}A_{Al}} \times 100\% = \frac{97 \times 63.55 \text{ g/mol}}{(97 \times 63.55 \text{ g/mol}) + (3 \times 26.98 \text{ g/mol})} \times 100\%$$

$$C'_{Al} = 98.7 \text{ at\%}$$

$$C'_{Cu} = \frac{C_{Cu}A_{Al}}{C_{Cu}A_{Al} + C_{Al}A_{Cu}} \times 100\% = \frac{3 \times 26.98 \text{ g/mol}}{(3 \times 26.98 \text{ g/mol}) + (97 \times 63.55 \text{ g/mol})} \times 100\%$$

$$C'_{Cu} = 1.30 \text{ at\%}$$

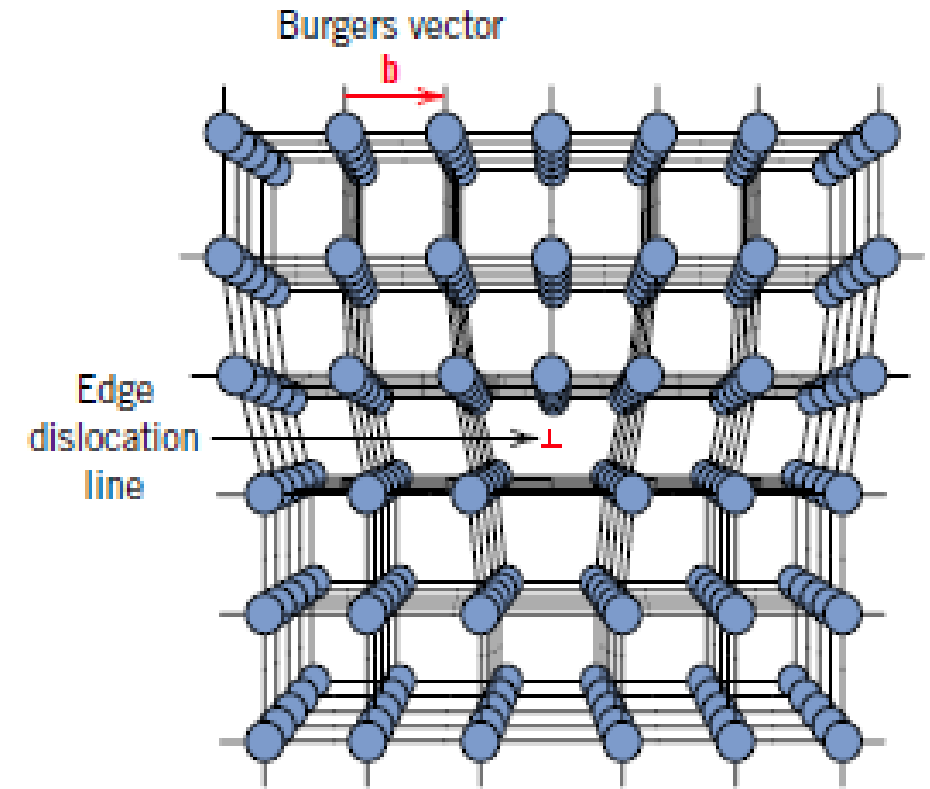
# Line Defects in Solids

- **Line defects (one-dimensional defects) are also called dislocations.** They are abrupt changes in the regular ordering of atoms along a line (dislocation line) in the solid.
- They occur in high densities and strongly influence the mechanical properties of material.
- They are characterized by the Burgers vector ( $b$ ), whose direction and magnitude can be determined by constructing a loop around the disrupted region and noticing the extra inter-atomic spacing needed to close the loop.
- Dislocations occur when an extra incomplete plane is inserted. The dislocation line is at the end of the plane.
- **Two limiting cases - Edge dislocation and Screw dislocation.**

# Line Defects in Solids

## Edge Dislocation

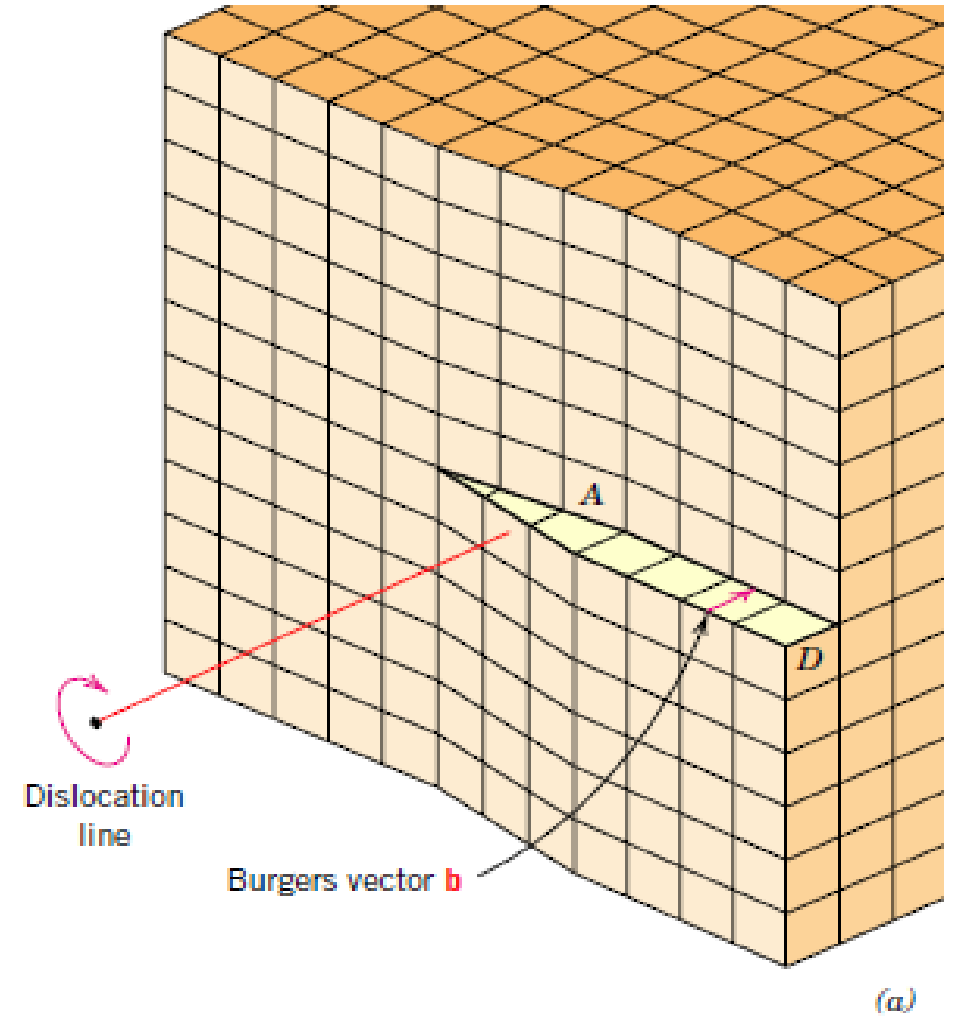
- It is described as edge of an extra (half) plane of atoms within a crystal structure.
- The Burger's vector (measure of distortion caused by line defect) is perpendicular to the dislocation line.
- The atoms above the dislocation line are squeezed together (compressive stresses) whereas atoms below are pulled apart and experience tensile stresses.
- Edge dislocation is considered positive when compressive stresses are above the dislocation line, and is represented by  $\perp$



# Line Defects in Solids

## Screw Dislocation

- A partial slip of a crystal on one side of the dislocation line.
- The Burger's vector is parallel to the dislocation line.
- It is formed by a shear stress that is applied to produce the distortion.
- All crystalline materials contain some dislocations.
- Any dislocation in a crystal is a combination of edge and screw types, having varying degrees.



# Interfacial (Planar) Defects in Solids

- Interfacial defects are boundaries that have two dimensional imperfections in crystalline solids.
- They refer to the regions of distortions that lie about a surface having thickness of a few atomic diameters.
- These defects include external surfaces and grain boundaries. They arise from the clustering of line defects into a plane.

## External surfaces:

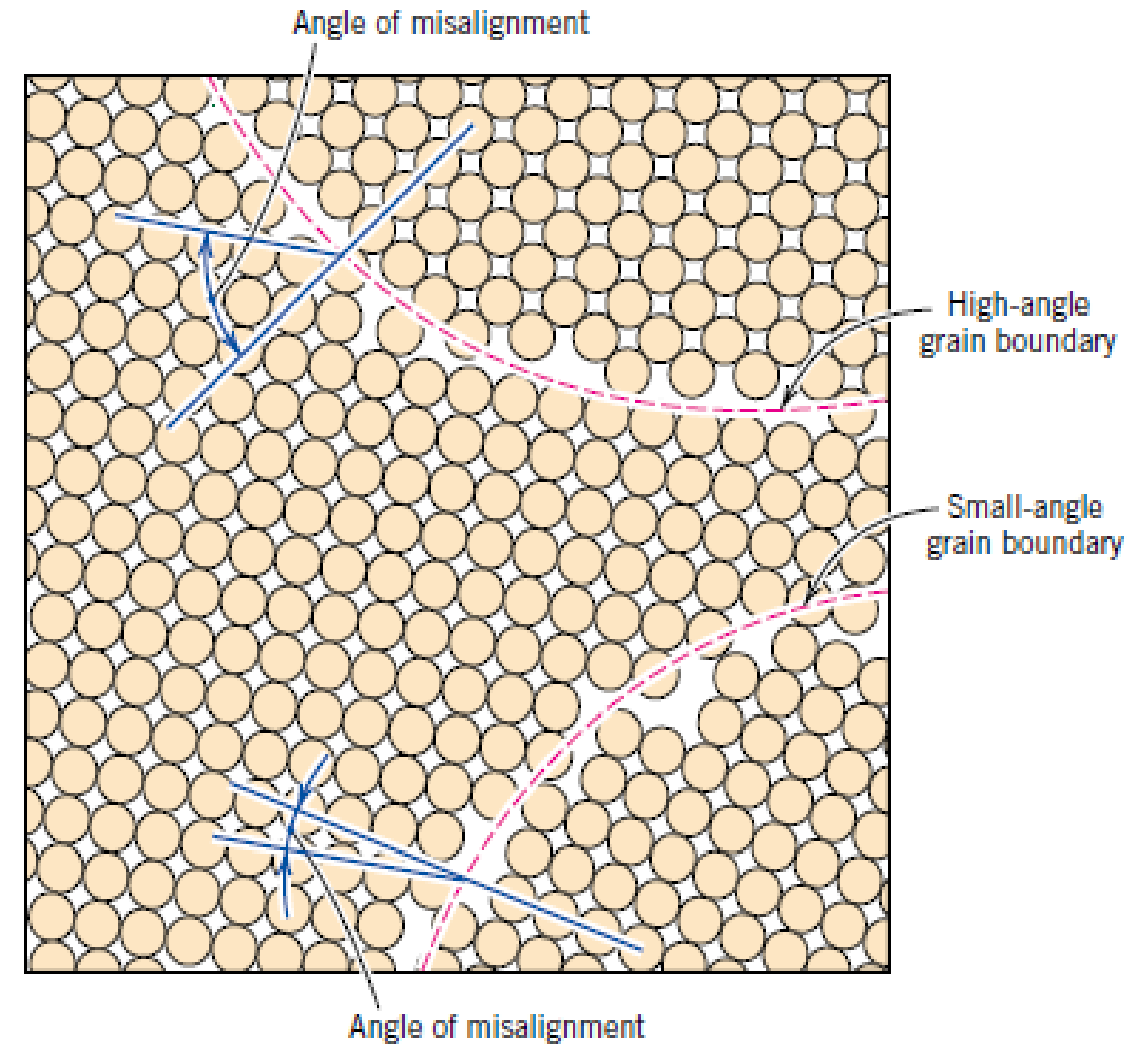
- Surface atoms are not bonded to the maximum number of closest atoms, and are in a higher energy state than the atoms at interior positions.
- Bonds of these surface atoms give rise to a surface energy, expressed in units of energy per unit area ( $\text{J/m}^2$  or  $\text{erg/cm}^2$ ).
- To reduce energy, materials tend to minimize the total surface area against surface tension



# Interfacial (Planar) Defects in Solids

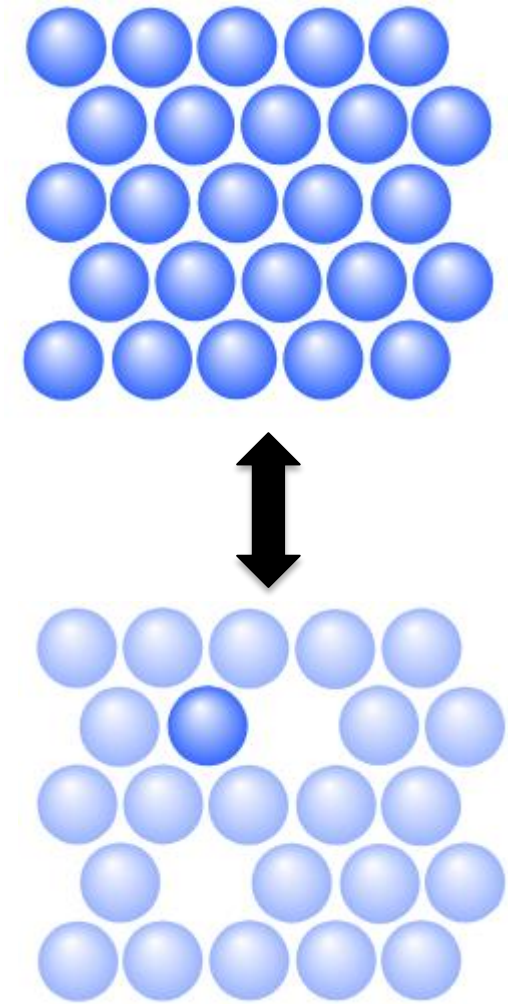
## Grain boundaries

- Crystalline solids usually consist of number of grains separated by boundaries.
- Grain boundaries are regions formed between two adjacent grains.
- There is a disorder (mismatch of orientation of grains) on either side of the boundary.
- For slight disorder ( $< 10^\circ$ ), it is called low angle grain boundary.
- If low grain boundary is formed by edge dislocations, it is called **tilt boundary**, and if formed by screw dislocations, it is called **twist boundary**.



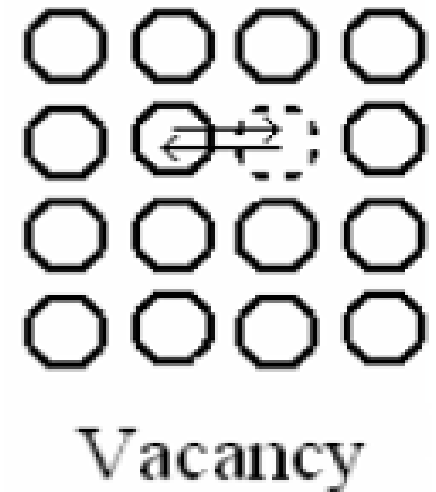
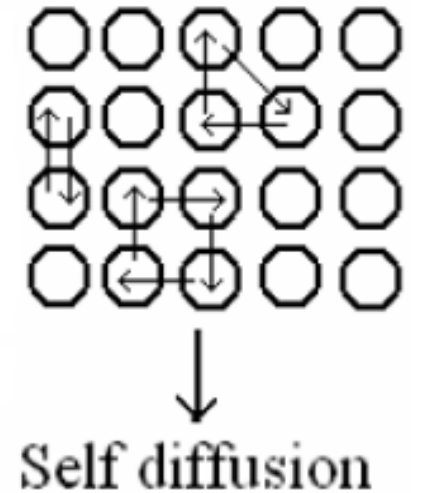
# Diffusions in Solids

- **Diffusion** is the process by which atoms move in a material. Many reactions in solids and liquids are diffusion dependent.
- Atoms are able to move throughout solids because they are not stationary but execute rapid, vibrations about their equilibrium positions.
- Such vibrations increase with temperature and at any temperature a very small fraction of atoms has sufficient amplitude to move from one atomic position to an adjacent one.
- Defects especially vacancies affect the diffusion process based on the type and number of defects that are present, as well as the thermal vibrations of atoms.
- Diffusion can be defined as the mass flow process in which atoms change their positions relative to neighbors in a given phase under the influence of temperature and a gradient.



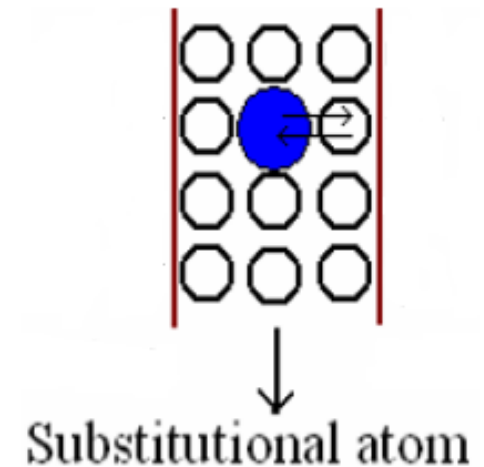
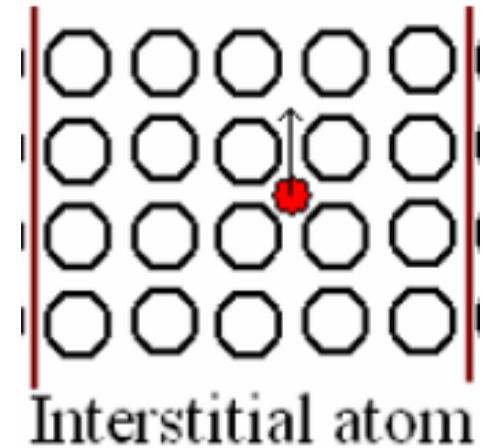
# Mechanisms of Diffusions in Solids

- **Self-Diffusion** occurs in pure metals where there is no net mass transport, but atoms migrate in a random manner throughout the crystal.
- ✓ In self-diffusion atoms in the form of a ring move simultaneously round the ring, thereby interchanging their positions. High activation energy would be required.
- In alloys, **inter-diffusion** takes place where the mass transport almost always occurs so as to minimize compositional differences.
- **Vacancy diffusion** involves the interchange of an atom from a normal lattice position to an adjacent vacant lattice site or vacancy.
- This process demands not only the motion of vacancies, but also the presence of vacancies.
- The unit step involves an atom breaking its bonds and jumping into a neighboring vacant site.



# Mechanisms of Diffusions in Solids

- In **interstitial diffusion**, solute atoms which are small enough to occupy interstitial sites diffuse by jumping from one interstitial site to another.
- The unit step involves jump of the diffusing atom from one interstitial site to a neighboring site.
- H, C, N and O diffuse interstitially in most metals.
- In self-interstitial diffusion only small activation energy is required for atom to move to an equilibrium atomic position and simultaneously displace the neighboring atom into an interstitial site.
- **Substitutional diffusion** occurs by the movement of atoms from one atomic site to another.
- It generally proceeds vacancy mechanism but interstitial diffusion is faster than substitutional diffusion.

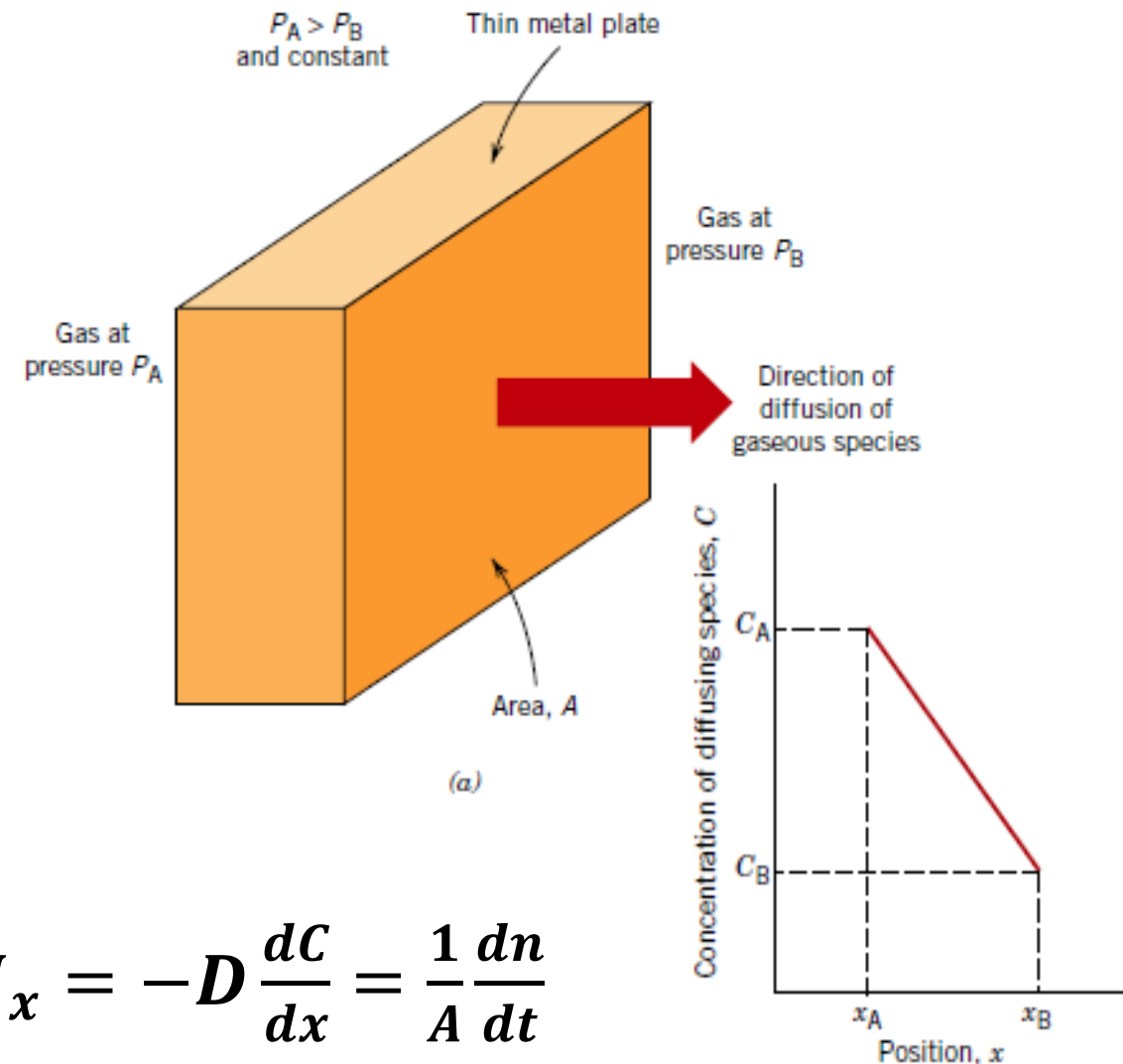


# Diffusions in Ionic Solids

- **Diffusion in most ionic solids occurs by a vacancy mechanism.** In ionic crystals, Schottky and Frenkel defects assist the diffusion process.
- When Frenkel defects (pair of vacancy-interstitial) are dominant in an ionic crystal, the cation interstitial of the Frenkel defect carries the diffusion flux.
- If Schottky defects (pair of vacant sites) dominate, the cation vacancy carries the diffusion flux.
- Imperfections in ionic materials that influence diffusion arise in two ways:
  - ✓ Intrinsic point defects such as Frenkel and Schottky defects whose number depends on temperature, and
  - ✓ Extrinsic point defects whose presence is due to impurity ions of different valance than the host ions.

# Steady State Diffusion

- **Diffusion is a time-dependent process.**
- It is necessary to know how fast diffusion occurs which is characterized by a parameter known as flux.
- The diffusion flux ( $J$ ), is defined as the net number of atoms crossing a unit area perpendicular to a given direction per unit time.
- For steady-state diffusion, the flux is constant with time.
- Steady-state diffusion is described by **Fick's first law** which states that the diffusion flux,  $J$ , is proportional to the concentration gradient.
- The constant of proportionality is called diffusion coefficient (diffusivity),  $D$  ( $\text{cm}^2/\text{sec}$ ).



$$J_x = -D \frac{dC}{dx} = \frac{1}{A} \frac{dn}{dt}$$



# Steady state diffusion: Example

## Question

- A plate of iron is exposed to a carburizing atmosphere on one side and a decarburizing atmosphere on the other side at 700 °C (1300 °F). If a condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of 5 and 10 mm beneath the carburizing surface are 1.2 and 0.8 kg/m<sup>3</sup>, respectively. Assume diffusion coefficient of  $3 \times 10^{-11} \text{ m}^2/\text{s}$  at this temperature.

## Solution

$$\begin{aligned} J_x &= -D \frac{C_A - C_B}{x_A - x_B} = -(3 \times 10^{-11} \text{ m}^2/\text{s}) \frac{(1.2 - 0.8) \text{ kg/m}^3}{(5 \times 10^{-3} - 10^{-2}) \text{ m}} \\ &= 2.4 \times 10^{-9} \text{ kg/m}^2 \cdot \text{s} \end{aligned}$$

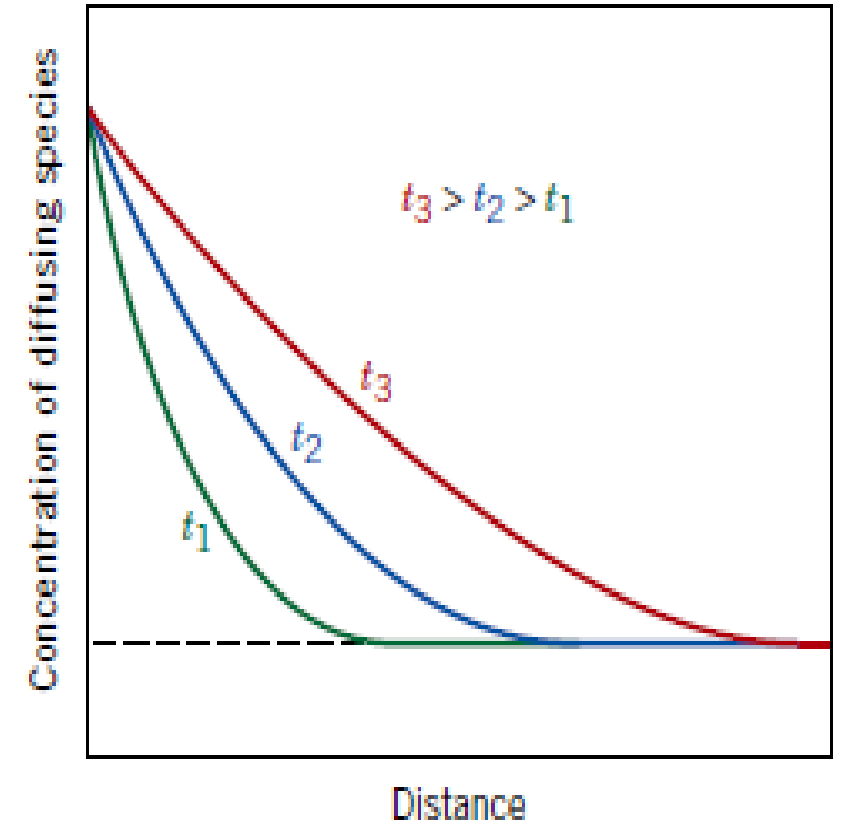


# Unsteady State Diffusion

- In **unsteady-state diffusion**, the concentration at a given position changes with time.
- This is the case when the diffusion flux depends on time, which means that a type of atoms accumulates in a region or depleted from a region.
- **Fick's second law** characterizes these processes, which is expressed as:

$$\frac{\partial C}{\partial t} = -\frac{\partial J_x}{\partial x} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right)$$

Where  $\partial C/\partial t$  is the time rate of change of concentration at a particular position, x.



# Unsteady State Diffusion

- If  $D$  is assumed to be a constant, then 
$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

- **Solution based on boundary conditions**

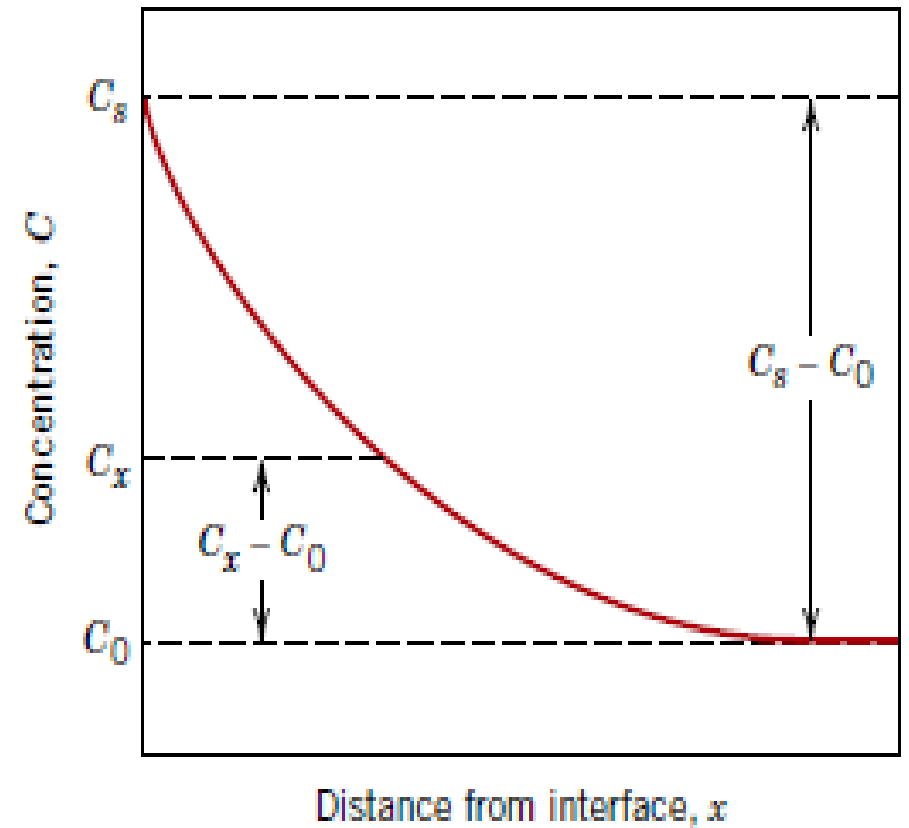
*For  $t = 0$ ,  $C = C_o$  at  $0 \leq x \leq \infty$*

*For  $t > 0$ ,  $C = C_s$  at  $x = 0$*

*For  $t > 0$ ,  $C = C_o$  at  $x = \infty$*

And the solution is

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$



# Unsteady State Diffusion: Error Function Table

$z$	$erf(z)$	$z$	$erf(z)$	$z$	$erf(z)$
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

# Unsteady state diffusion: Example

## Question

- Consider one such alloy that initially has a uniform carbon concentration of 0.25 wt% and is to be treated at 950 °C (1750 °F). If the concentration of carbon at the surface is suddenly brought to and maintained at 1.20 wt%, how long will it take to achieve a carbon content of 0.80 wt% at a position 0.5 mm below the surface? The diffusion coefficient for carbon in iron at this temperature is  $1.6 \times 10^{-11} \text{ m}^2/\text{s}$ ; assume that the steel piece is semi-infinite.

## Solution

Values for all the parameters in this expression except time  $t$  are specified in the problem as follows:

$$C_o = 0.25 \text{ wt\%}; C_s = 1.2 \text{ wt\%}; C_x = 0.8 \text{ wt\%}; x = 0.5 \text{ mm};$$
$$D = 1.6 \times 10^{-11} \text{ m}^2/\text{s}$$

# Unsteady state diffusion: Example

## Solution

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \Rightarrow \frac{0.8 - 0.25}{1.2 - 0.25} = 1 - \operatorname{erf}\left[\frac{5 \times 10^{-4} \text{ m}}{2\sqrt{(1.6 \times 10^{-11} \text{ m}^2/\text{s})(t)}}\right]$$

$$0.4210 = \operatorname{erf}\left(\frac{62.5 \cdot s^{1/2}}{\sqrt{t}}\right)$$

Determine the value of  $z$  from Tables which the error function is 0.4210. An interpolation may be necessary as

$$\frac{z - 0.35}{0.40 - 0.35} = \frac{0.4210 - 0.3794}{0.4284 - 0.3794} \Rightarrow z = 0.3920$$

$$\frac{62.5 s^{1/2}}{\sqrt{t}} = 0.932 \Rightarrow t = \left(\frac{62.5 s^{1/2}}{0.3920}\right)^2 = 25,400 \text{ s} = 7.1 \text{ h}$$

# Factors that Influence Diffusion

- **Diffusing species:** If the diffusing species is able to occupy interstitial sites, then it can easily diffuse through the parent matrix. On the other hand, if the size of substitutional species is almost equal to that of parent atomic size, substitutional diffusion would be easier. Thus size of diffusing species will have great influence on diffusivity of the system.
- **Temperature:** Temperature has a most profound influence on the diffusivity and diffusion rates. Atomic vibrations created by temperature assist diffusion.
- ✓ Empirical analysis of the system resulted in Arrhenius type of relationship between diffusivity and temperature.
$$D = D_o \cdot \exp\left(\frac{-Q_d}{RT}\right)$$
- **Lattice structure:** Diffusion is faster in open lattices or in open directions than in closed directions.
- **Presence of defects**

# Diffusion data

<i>Diffusing Species</i>	<i>Host Metal</i>	$D_0(m^2/s)$	<i>Activation Energy <math>Q_d</math></i>		<i>Calculated Value</i>	
			<i>kJ/mol</i>	<i>eV/atom</i>	<i>T(°C)</i>	$D(m^2/s)$
Fe	$\alpha$ -Fe (BCC)	$2.8 \times 10^{-4}$	251	2.60	500	$3.0 \times 10^{-21}$
					900	$1.8 \times 10^{-15}$
Fe	$\gamma$ -Fe (FCC)	$5.0 \times 10^{-5}$	284	2.94	900	$1.1 \times 10^{-17}$
					1100	$7.8 \times 10^{-16}$
C	$\alpha$ -Fe	$6.2 \times 10^{-7}$	80	0.83	500	$2.4 \times 10^{-12}$
					900	$1.7 \times 10^{-10}$
C	$\gamma$ -Fe	$2.3 \times 10^{-5}$	148	1.53	900	$5.9 \times 10^{-12}$
					1100	$5.3 \times 10^{-11}$
Cu	Cu	$7.8 \times 10^{-5}$	211	2.19	500	$4.2 \times 10^{-19}$
Zn	Cu	$2.4 \times 10^{-5}$	189	1.96	500	$4.0 \times 10^{-18}$
Al	Al	$2.3 \times 10^{-4}$	144	1.49	500	$4.2 \times 10^{-14}$
Cu	Al	$6.5 \times 10^{-5}$	136	1.41	500	$4.1 \times 10^{-14}$
Mg	Al	$1.2 \times 10^{-4}$	131	1.35	500	$1.9 \times 10^{-13}$
Cu	Ni	$2.7 \times 10^{-5}$	256	2.65	500	$1.3 \times 10^{-22}$



