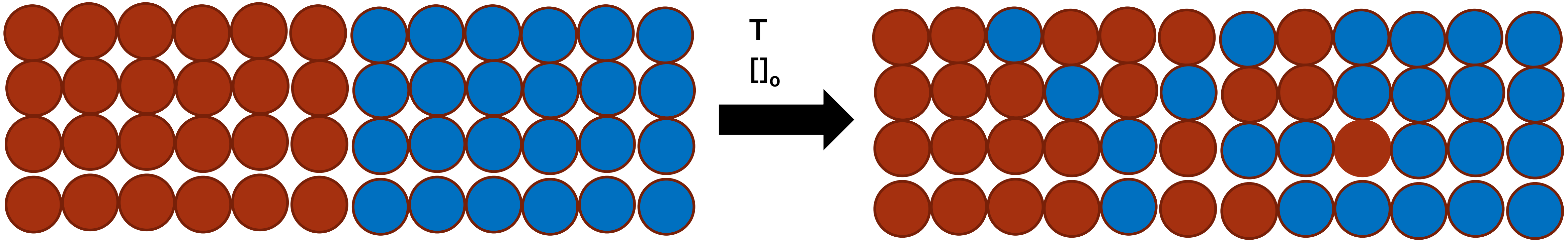
CHAPTER 5

Atomic and Ionic movements

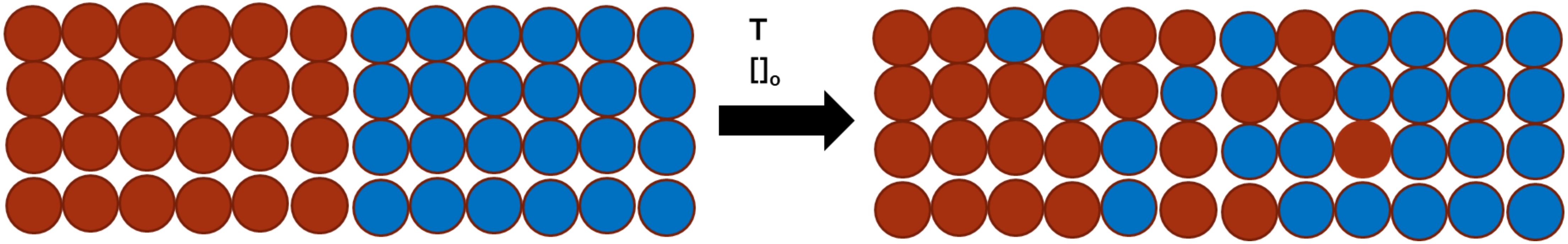
Diffusion

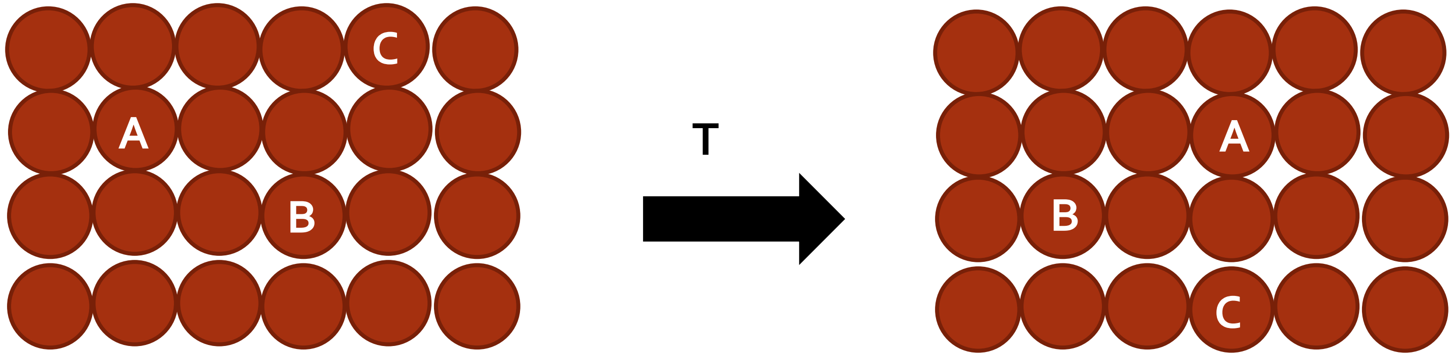
"Material transfer due to atomic motion"



Gases & Liquids – random (Brownian) motion
Solids – vacancy diffusion or interstitial diffusion

Interdiffusion and self-Diffusion





Dependence of Diffusion rate on temperature

$$Rate = C_0 e^{\left(-\frac{Q}{RT}\right)}$$

$$C_0: Constant$$

$$Q: Activation\ energy\ \left(\frac{Cal}{mol}\ or\ \frac{J}{mol}\right)$$

$$T: Absolute\ temperature\ (K)$$

$$R: Gas\ constant\ (1.987\,\frac{cal}{mol{\cdot}K}\ or\ 8.315\,\frac{J}{mol{\cdot}K})$$

Example

- Atoms are found to move from one lattice position to another at the rate of 5×10^5 Jumps/s at 400°C when the activation energy for their movement is 30,000 cal/mol. Calculate the jump rate at 750°C.

Jump rate at $750°C$

Rate=$5 \times 10^5 \, \frac{Jumps}{s}$

T1=$400°C$

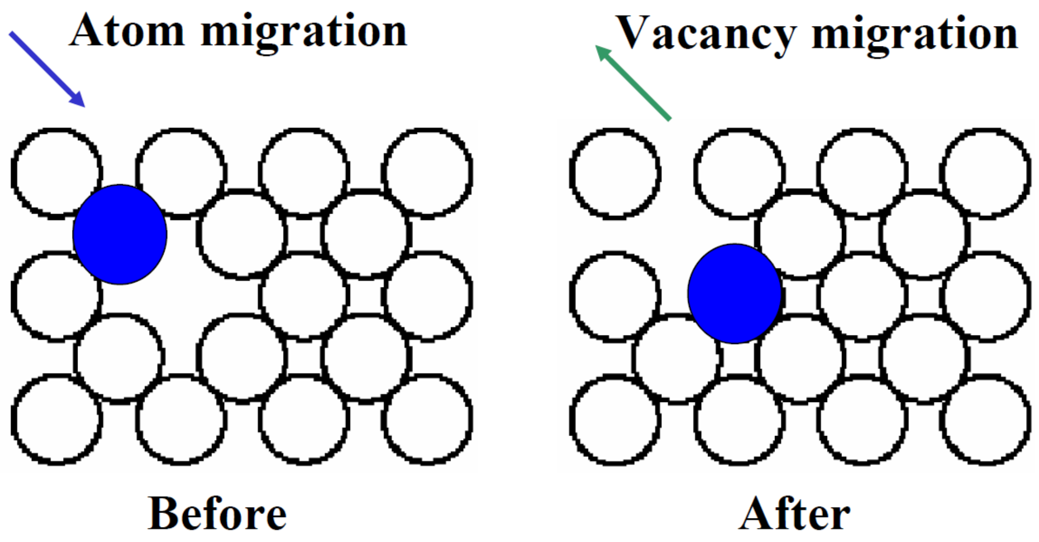
T2=$750°C$

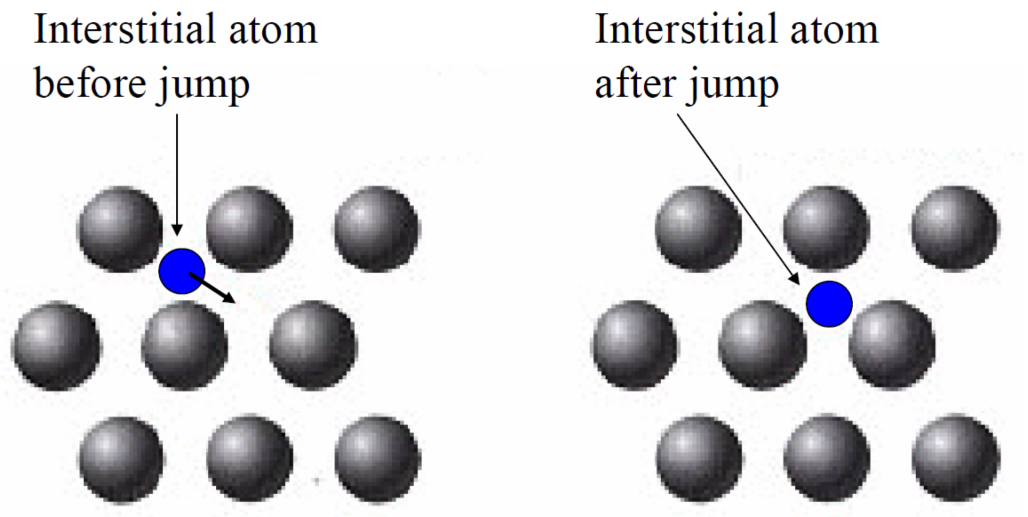
Q=$30{,}000 \, \frac{cal}{mol}$

R=$1.987 \, \frac{cal}{mol \cdot K}$

Diffusion mechanisms

- **Vacancy or substitutional diffusion**: The atoms leaves its current lattice point (Ubication) and fill the vacancy next to it.
- **Interstitial diffusion**: A interstitial atom or ion moves between interstitial sites, without affection the lattice points.





Rate of diffusion: Fick's Law

$$J = -D\frac{dc}{dx}$$

J (**flux of diffusing atoms**): How fast diffusion occurs $(\frac{atoms}{m^2 \cdot s})$ or $(\frac{kg}{m^2 \cdot s})$.

D: Diffusion coefficient $\left(\frac{cm^2}{s}\right)$ $\qquad D = D_0 e^{(-\frac{Q}{RT})}$

dc/dx: Concentration gradient $(\frac{atoms}{cm^3 \cdot cm})$

The concentration normally goes form High to low

Example

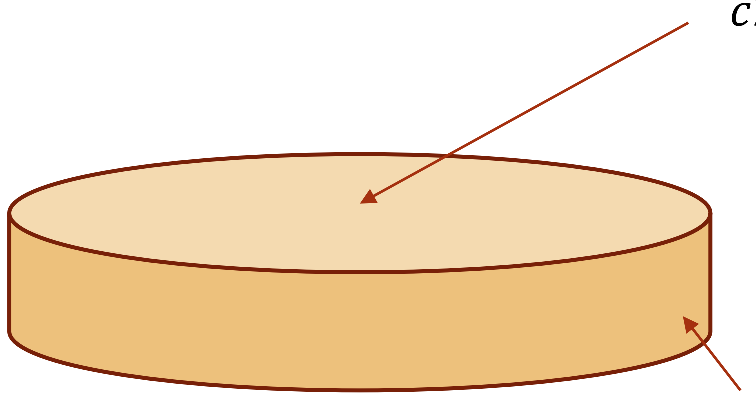
- Silicon wafer of 0.1 cm thick originally containing 1 atoms of P for every 10^7 atoms of Si, is treated so that the surface contains 400 atoms of P for every 10^7 atoms of Si. Consider that silicon has a diamond structure (8 atoms/unit cell.) Calculate the concentration gradient in:

a) atoms/cm

b) P atoms/ cm^3 cm

$$c2 = \frac{4 \times 10^2 \ P \ atoms}{10^7 Si \ atoms}$$

Δx



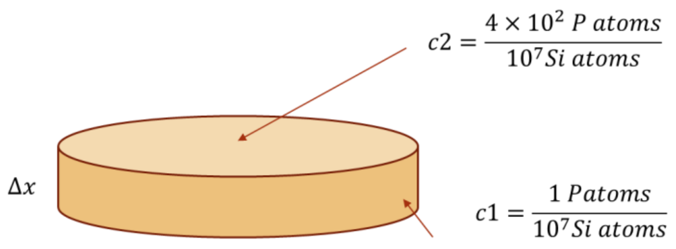
$$c1 = \frac{1 \ Patoms}{10^7 Si \ atoms}$$

Concentration gradient:

- $c1 = 10^{-7} \frac{P\ atoms}{Si\ atoms}$
- $c2 = 4 \times 10^{-5} \frac{P\ atoms}{Si\ atoms}$
- $\Delta x = 0.1\ cm$
- $a_0(Si) = 5.431 \times 10^{-8} cm$
- $Dimond = 8\ at/uc$

a) atoms/cm

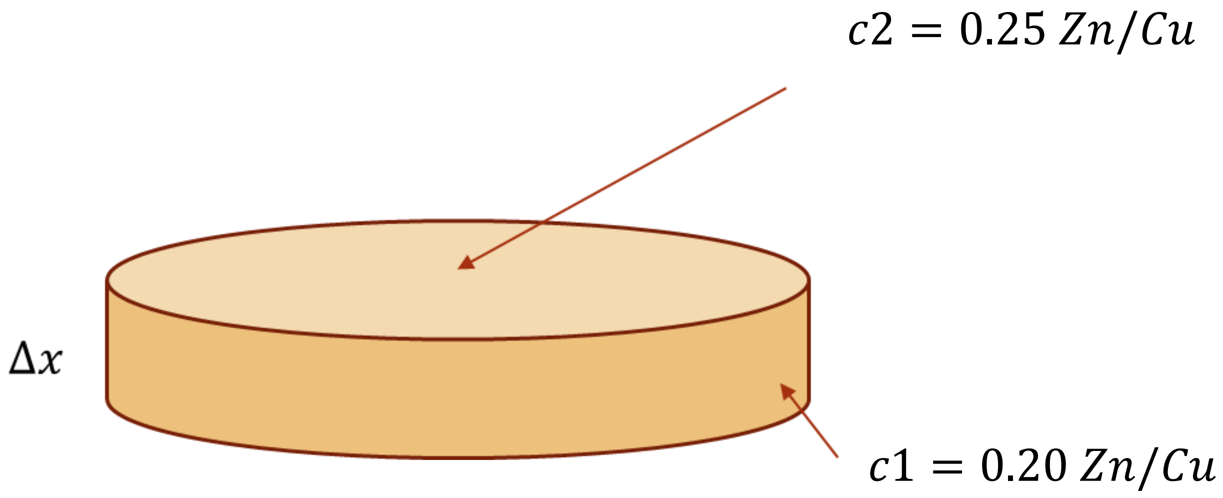
b) $P \frac{atoms}{cm^3 \cdot cm}$



Example

When a Cu-Zn alloy solidifies, one portion of the structure contains 25 atomic percent zinc and another portion 0.025 mm away contains 20 atomic percent zinc. The lattice parameter for the FCC alloy is about $3.63 * 10^{-8}$ cm. Determine the concentration gradient in

- (a) atomic percent Zn per cm;
- (b) weight percent Zn per cm;
- (c) Zn atoms /(cm3 cm)



Concentration gradient:

- $c1 = 0.2 \frac{Zn\ atoms}{Cu\ atoms}$
- $c2 = 0.25 \frac{Zn\ atoms}{Cu\ atoms}$
- $\Delta x = 2.5 \times 10^{-3} cm$
- $a_0 = 3.63 \times 10^{-8} cm$
- $FCC = 4\ at/uc$
- Ar (Cu)=63.5
- Ar (Zn)=65.4

a) atoms/cm

b)weight percent Zn per cm

Concentration gradient:

- $c1 = 0.2 \frac{Zn\ atoms}{Cu\ atoms}$
- $c2 = 0.25 \frac{Zn\ atoms}{Cu\ atoms}$
- $\Delta x = 2.5 \times 10^{-3} cm$
- $a_0 = 3.63 \times 10^{-8} cm$
- $FCC = 4\ at/uc$
- Ar (Cu)=63.5
- Ar (Zn)=65.4

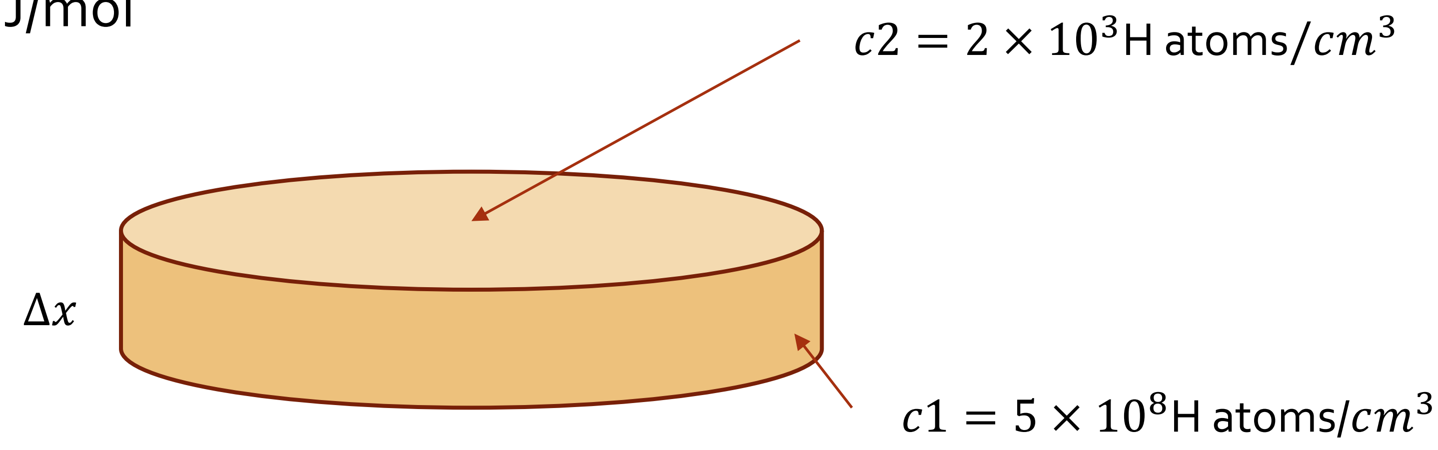
c) Zn atoms /(cm3 cm)

Recap

DIFFUSION RATE	RATE OF DIFFUSION
Jumps of 1 atom from lattice point to another in a second	number of atoms diffusing through unit area per unit time or the mass of atoms diffusing through unit area per unit time
$Rate = C_0 e^{\left(-\frac{Q}{RT}\right)}$ Unit=jumps/s	$J = -D\,\frac{dc}{dx} \quad \left[\frac{atoms}{cm^2 \cdot s}\right] \text{ Or } \left[\frac{kg}{cm^2 \cdot s}\right]$ $D = D_0 e^{\left(-\frac{Q}{RT}\right)} \quad \left[\frac{cm^2}{s}\right]$

Example

- A 0.001 in. BCC iron foil is used to separate a high hydrogen content gas from a low hydrogen content gas at 650°C. 5×10^8 H atoms/cm^3 are in equilibrium on one side of the foil, and 2×10^3 H atoms/cm^3 are in equilibrium with the other side. Determine (a) the concentration gradient of hydrogen and (b) the flux of hydrogen through the foil if the initial diffusion coefficient is 0.0012 $\frac{cm^2}{s}$ and activation energy of 15062.4 J/mol



- $c1 = 5 \times 10^8$ H atoms$/cm^3$
- $c2 = 2 \times 10^3$ H atoms$/cm^3$
- $\Delta x = 0.00254\ cm$
- $BCC = 2\ at/uc$
- $D_0 = 0.0012\ cm^2/s$
- $Q = 15062.4$ J/mol
- $T = 650°\text{C} + 273 = 923K$

a) Concentration gradient:

b) $J\ (flux)$ through foil

Factors influencing diffusion: Temperature

$$D = D_0 e^{\left(-\frac{Q}{RT}\right)}$$

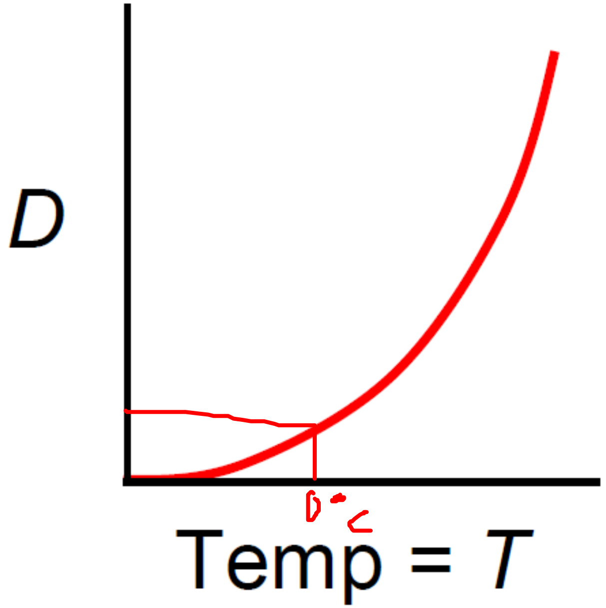
D: Diffusion coefficient $\left(\frac{cm^2}{s}\right)$

Do: Initial Diffusion coefficient $\left(\frac{cm^2}{s}\right)$

Q: Activation energy $\left(\frac{Cal}{mol} \; or \; \frac{J}{mol}\right)$

T:Absolute temperature (K)

R:Gas constant (1.987cal/(mol·K) or 8.315J/(mol·K))



Factors influencing diffusion: Time

Fick's Second Law

$$\frac{c_s - c_x}{c_s - c_0} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

D: Diffusion coefficient $\left(\frac{cm^2}{s}\right)$

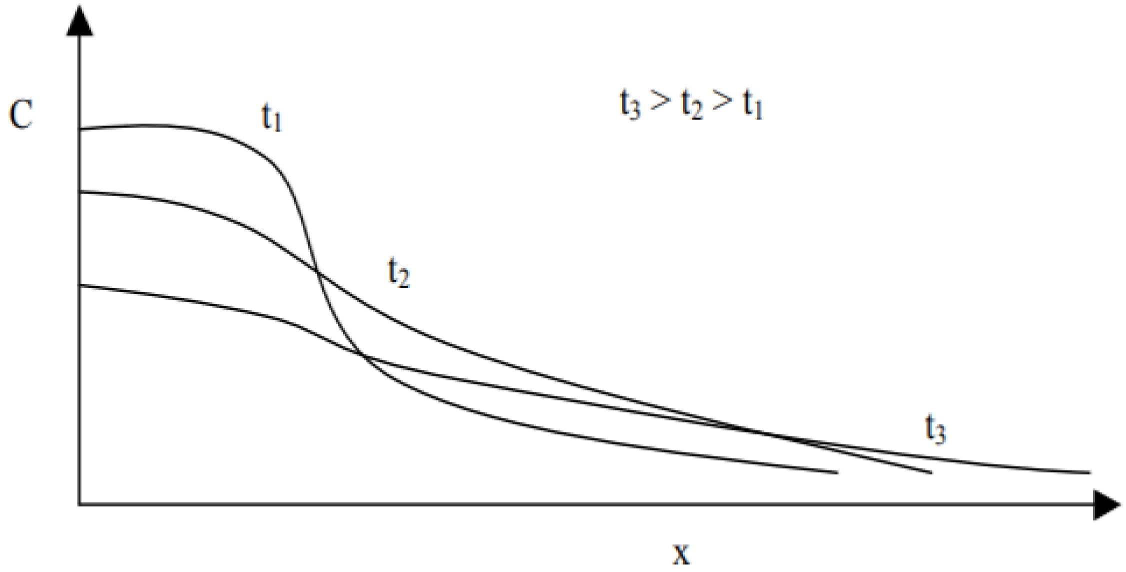
c_0: *Initial concentration*

c_s: *Surface concentration*

c_x: *Bulk concentration* or concentration at x distance

Erf: error function

x: thickness or distance

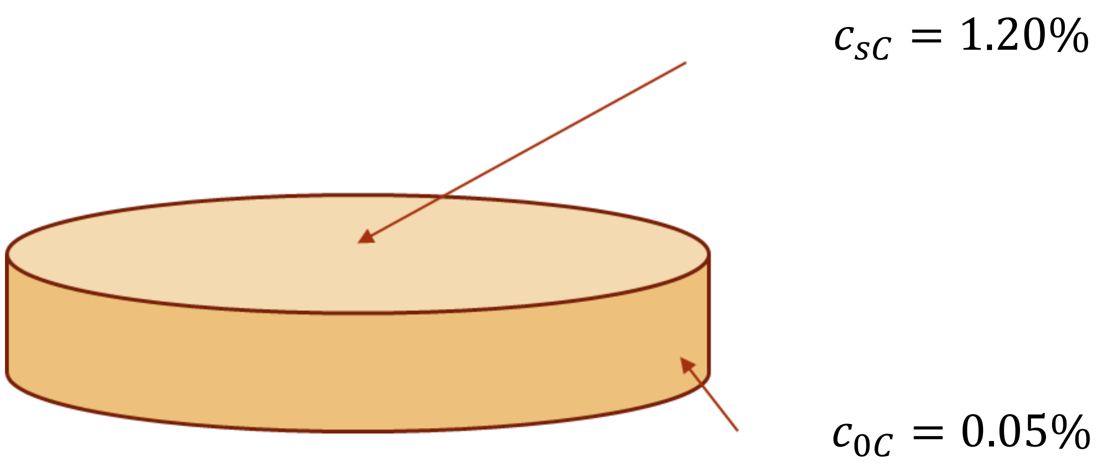


Example

- Iron containing 0.05% C is heated to 912°C in an atmosphere that produces 1.20% C at the surface and is held for 24 h. Calculate the carbon content at 0.05 cm beneath the surface if (a) the iron is BCC and (b) the iron is FCC. Explain the difference.

- BCC
- Q=$20900 \frac{cal}{mo}$
- Do=$0.011 \frac{cm^2}{s}$

- FCC
- Q=32900 cal/mol
- Do=0.23 $\frac{cm^2}{s}$



Carbon content beneath the surface if the Fe is BCC. Cx?

- $c_{sC} = 0.012 \text{ C atoms}/cm^3$
- $c_0 = 0.0005 \text{ C atoms}/cm^3$
- $x = 0.05\ cm$
- $D_0 = 0.011\ cm^2/s$
- $Q = 20900 \frac{cal}{mo}$
- R=1.987 $\frac{cal}{mol\ K}$
- $T = 912°\text{C} + 273 = 1185K$
- t= 24 h=86400 s

Carbon content beneath the surface if the Fe is FCC. Cx?

- $c_{sC} = 0.012$ C atoms$/cm^3$
- $c_0 = 0.0005$ C atoms$/cm^3$
- $x = 0.05\ cm$
- $D_0 = 0.23\ cm^2/s$
- $Q = 32900 \frac{cal}{mo}$
- R=1.987 $\frac{cal}{mol\ K}$
- $T = 912°\text{C} + 273 = 1185K$
- t= 24 h=86400 s

Factors influencing diffusion

- Time
- Diffusion mechanism
- Microstructure

Recap

DIFFUSION RATE	RATE OF DIFFUSION (First Law)	TIME EFFECT (Secodn Law)
Jumps of 1 atoms from lattice point to another in a second	number of atoms diffusing through unit area per unit time or the mass of atoms diffusing through unit area per unit time	Dynamics in a non steady state of diffusion of atoms
$Rate = C_0 e^{(-\frac{Q}{RT})}$ Unit=jumps/s	$J = -D\frac{dc}{dx} \quad \left[\frac{atoms}{cm^2 \cdot s}\right] \text{Or} \left[\frac{kg}{cm^2 \cdot s}\right]$ $D = D_0 e^{(-\frac{Q}{RT})} \quad \left[\frac{cm^2}{s}\right]$	$\frac{c_s - c_x}{c_s - c_0} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$