PY2N20
Material Properties and Phase Diagrams
Lecture 7

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Diffusion

Diffusion

- **Mass transport by atomic motion**

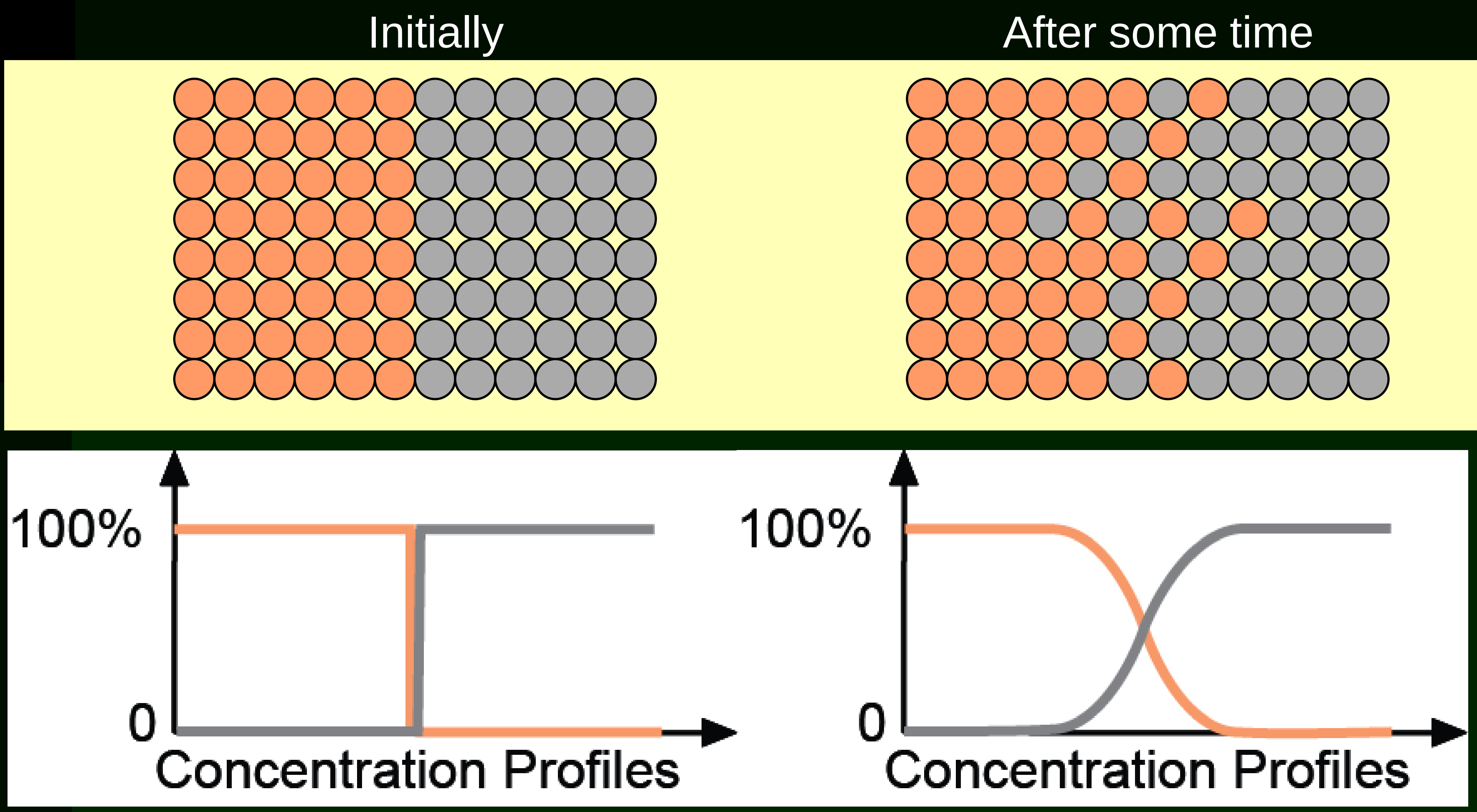
Mechanisms

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

$$D_{\text{gasses}} > D_{\text{liquids}} > D_{\text{solids}}$$

Diffusion

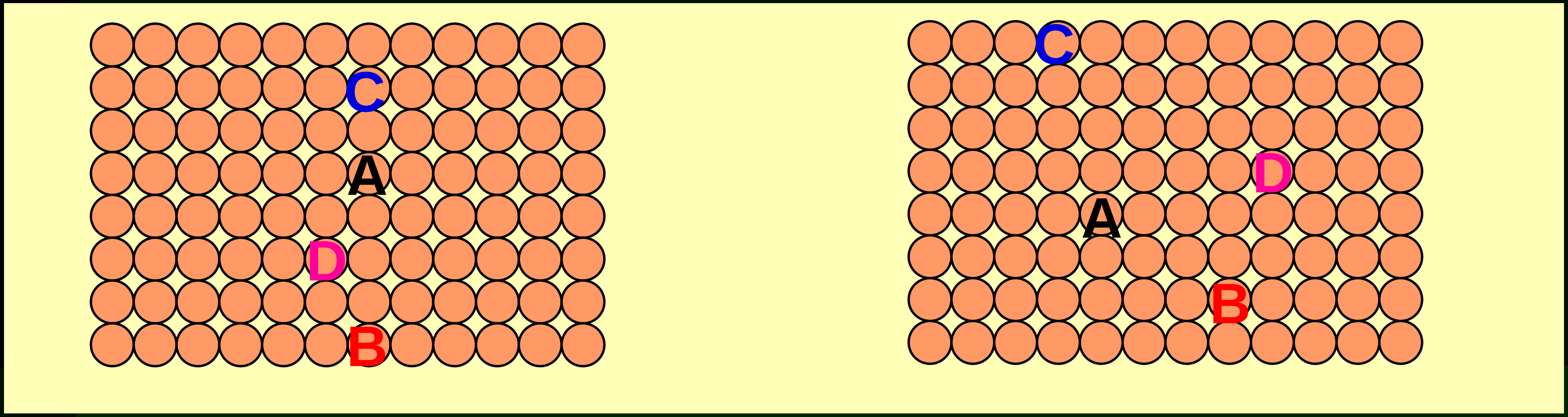
Interdiffusion: In an alloy, atoms tend to migrate from regions of high concentration to regions of low concentration.



Diffusion

- Self-diffusion: In an elemental solid, atoms also migrate.

Label some atoms After some time

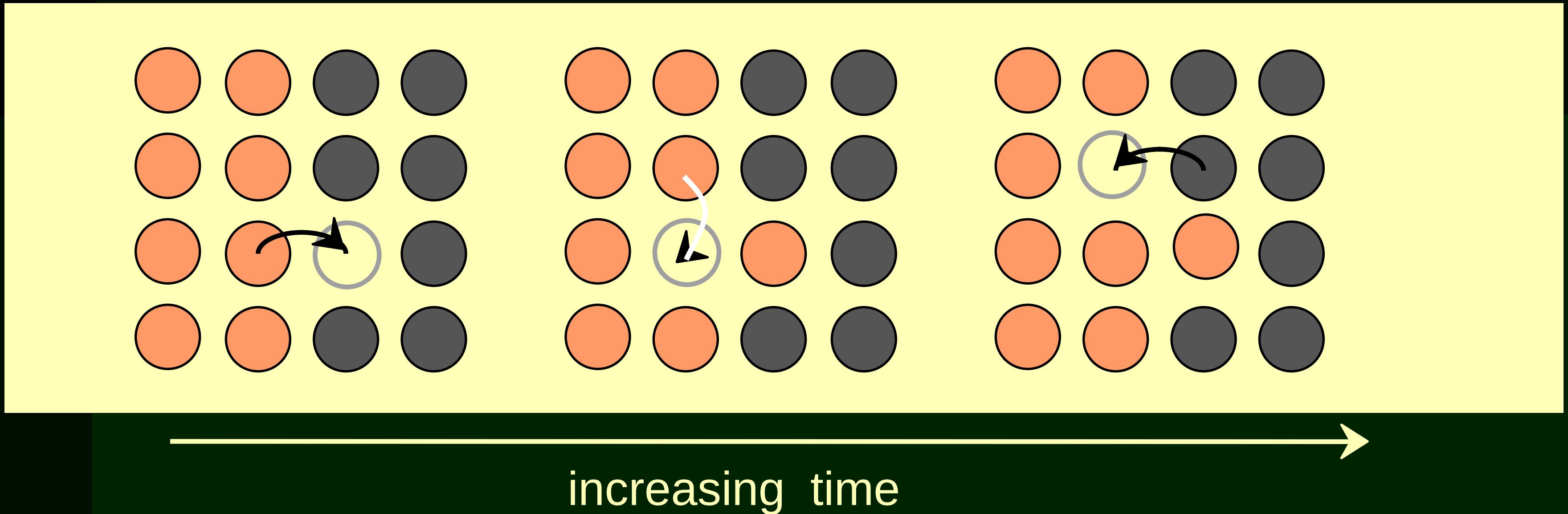


Often self-diffusion can be best characterised by radioisotope-marking, since the atoms of different isotopes are virtually identical chemically. Radiation profiles are readily traceable in macroscopic samples.

Diffusion Mechanisms

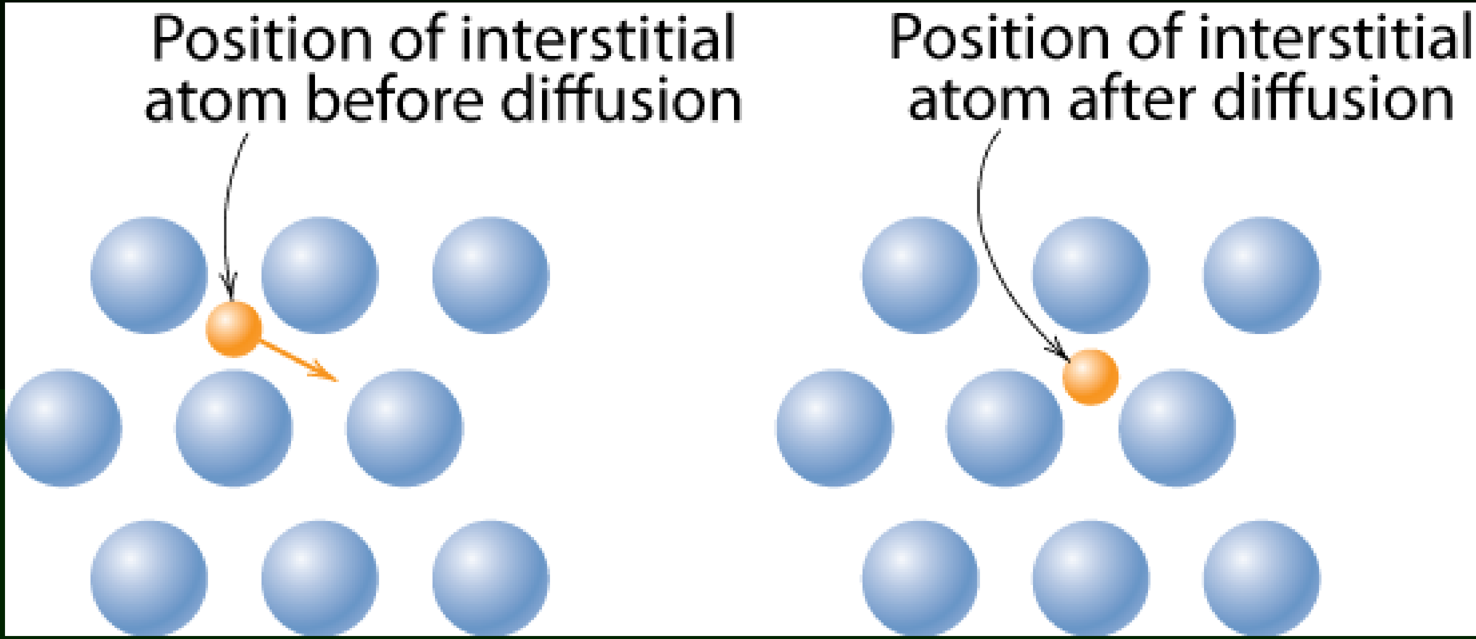
Vacancy Diffusion:

- atoms exchange with vacancies
- applies to substitutional impurities atoms
- rate depends on:
  - number of vacancies
  - activation energy to exchange.



Diffusion Mechanisms

- **Interstitial diffusion – smaller atoms can diffuse between atoms.**



More rapid than vacancy diffusion !

Degree of interstitialcy – obvious definition…

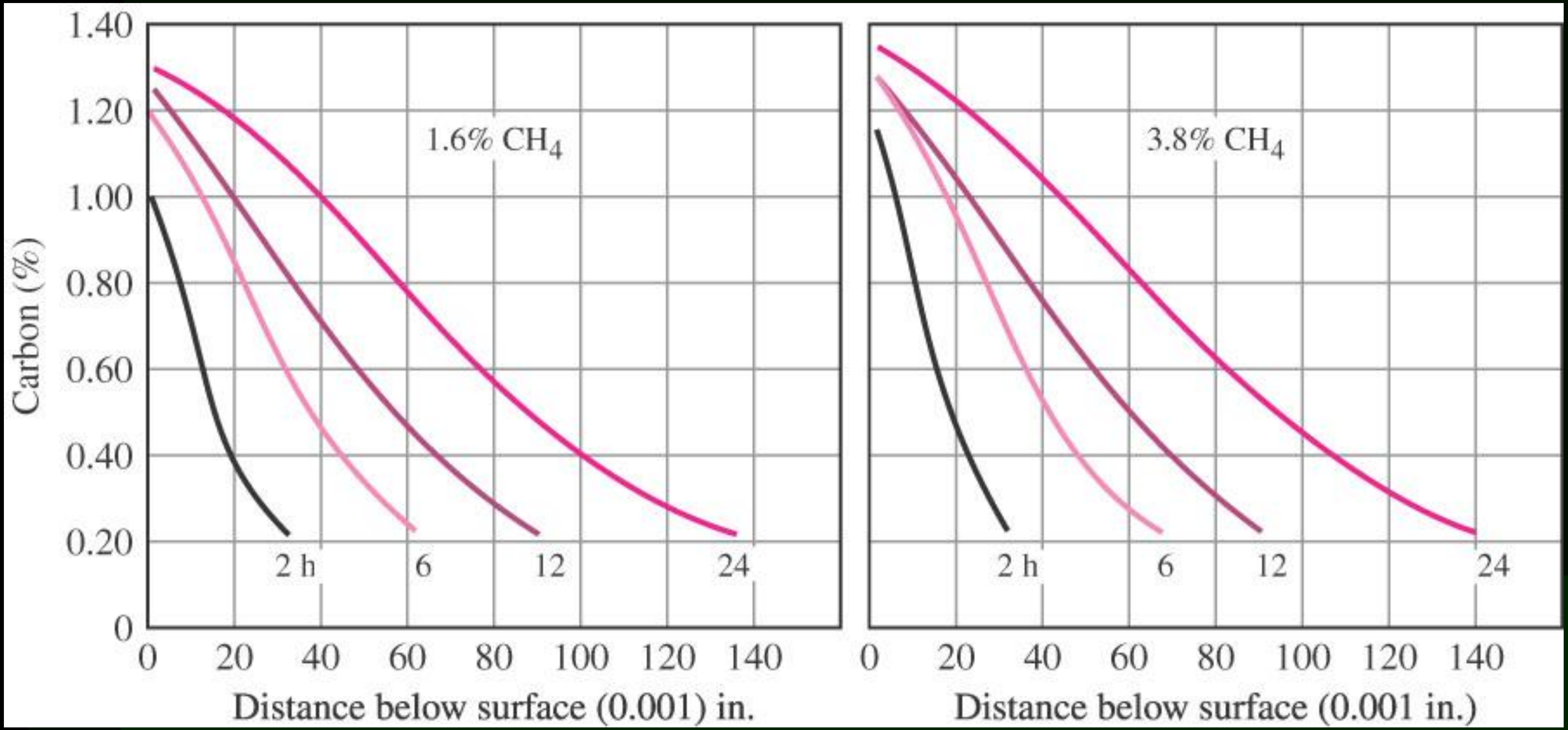
Processing Using Diffusion

- Case Hardening:
  - Diffuse carbon atoms into the host iron atoms at the surface.
  - Example of interstitial diffusion is a case hardened gear.

- Result:

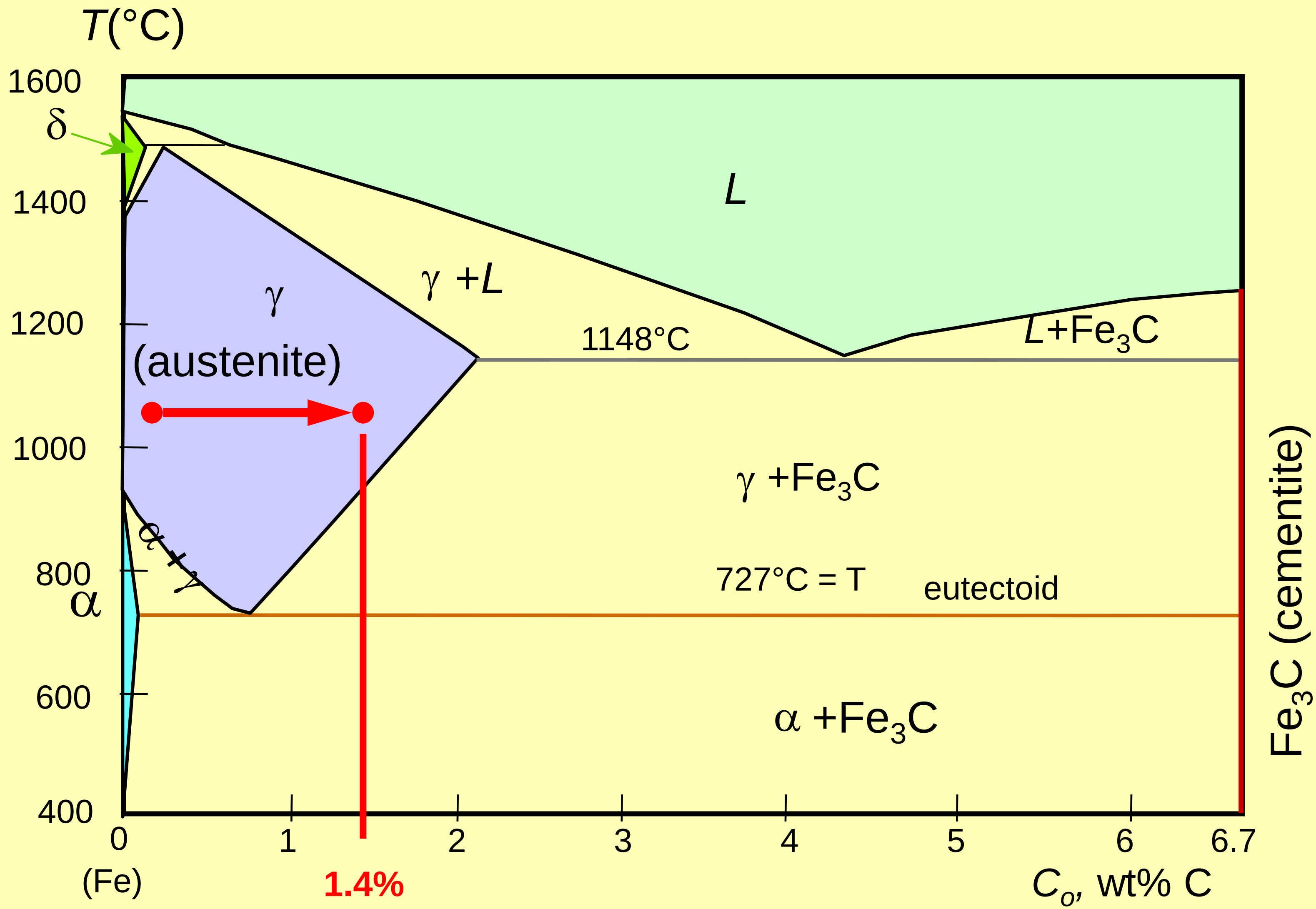
The presence of C atoms makes iron (steel) harder.

Carburising of steel



Note: Distances in thousands of inch. Times in hours.

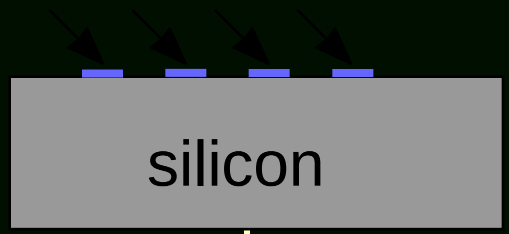
Carburising of steel



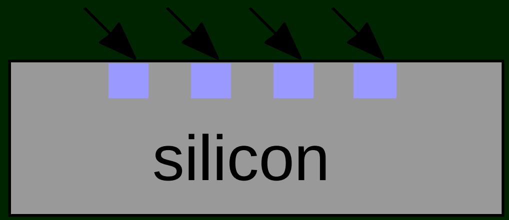
Processing Using Diffusion

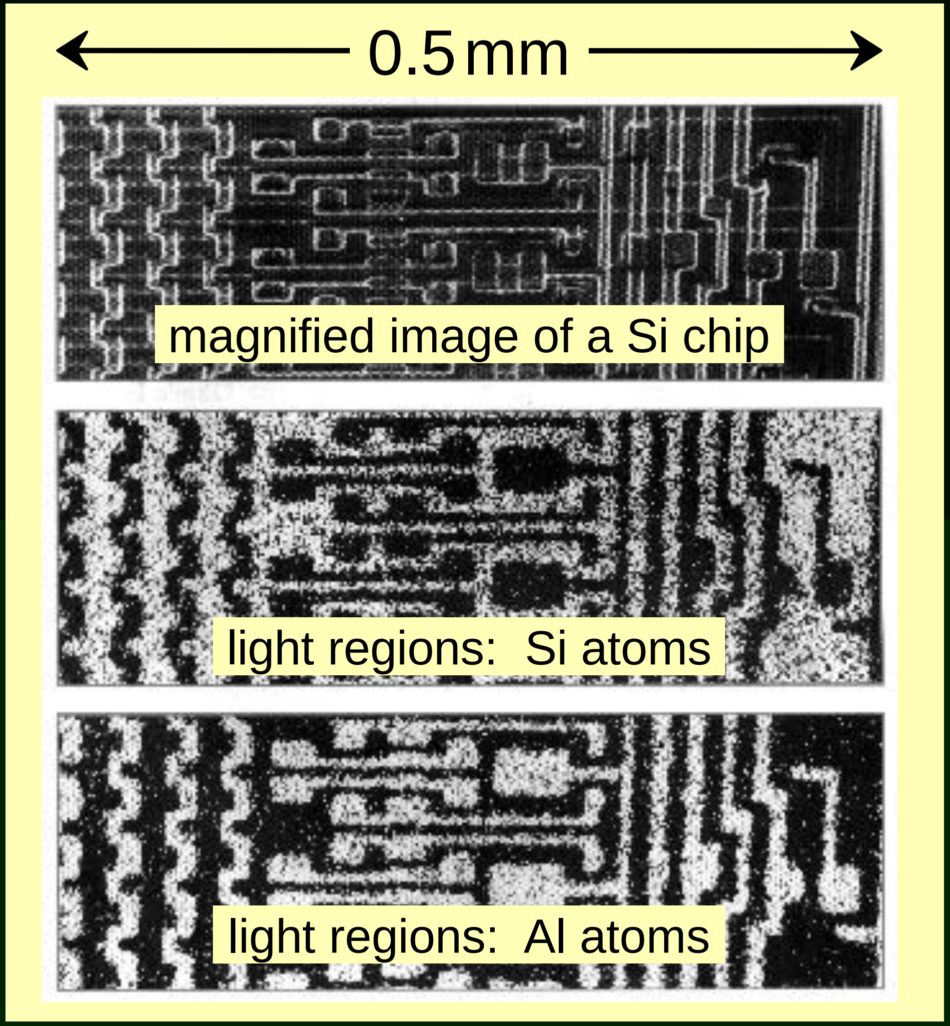
- Doping silicon with phosphorus for *n*-type regions:
- Process:

1. Deposit P rich layers on surface.



2. Heat it.
3. Result: Doped semiconductor regions.





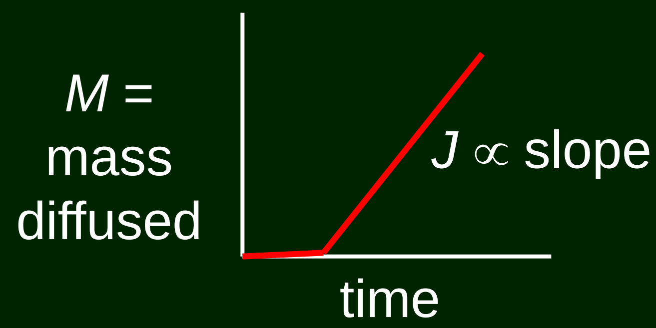
Diffusion

- **How do we quantify the amount or rate of diffusion?**

$$J \equiv \text{Flux} \equiv \frac{\text{moles (or mass) diffusing}}{(\text{surface area})(\text{time})} = \frac{\text{mol}}{\text{cm}^2\text{s}} \text{ or } \frac{\text{kg}}{\text{m}^2\text{s}}$$

- **Measured empirically**
  - **Make thin film (membrane) of known surface area**
  - **Impose concentration gradient**
  - **Measure how fast atoms or molecules diffuse through the membrane**

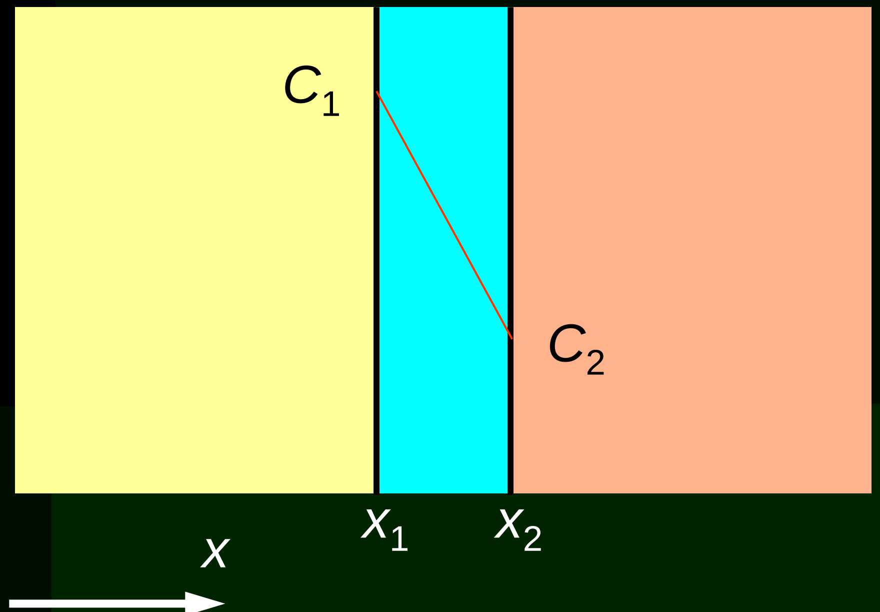
$$J = \frac{M}{At} = \frac{1}{A}\frac{dM}{dt}$$



Steady-State Diffusion

Rate of diffusion independent of time

Flux proportional to concentration gradient = $\frac{dC}{dx}$



Fick's first law of diffusion

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

$D \equiv$ diffusion coefficient

$[D]$ = m^2/s

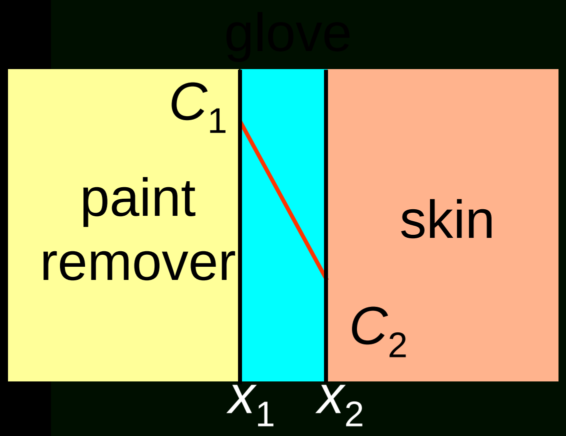
$$\text{if linear } \frac{dC}{dx} \cong \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1}$$

Example: Chemical Protective Clothing (CPC)

- Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using this paint remover, protective gloves should be worn.
- If butyl rubber gloves (0.04 cm thick) are used, what is the diffusive flux of methylene chloride through the glove?
- Data:
  - diffusion coefficient in butyl rubber: $D = 110 \times 10^{-8}$ cm^2/s
  - surface concentrations: $C_1 = 0.44$ g/cm^3, $C_2 = 0.02$ g/cm^3

Example (cont).

- Solution – assuming linear conc. gradient



$$J = -D\frac{dC}{dx} \cong -D\frac{C_2 - C_1}{x_2 - x_1}$$

Data:
$D = 110 \times 10^{-8}\ cm^2/s$
$C_1 = 0.44\ g/cm^3$
$C_2 = 0.02\ g/cm^3$
$x_2 - x_1 = 0.04\ cm$

$$J = -(110 \times 10^{-8}\ cm^2/s)\frac{(0.02\ g/cm^3 - 0.44\ g/cm^3)}{(0.04\ cm)} = 1.16 \times 10^{-5}\ \frac{g}{cm^2 s}$$

Diffusion and Temperature

- Diffusion coefficient increases with increasing *T*.

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

D = diffusion coefficient [m^2/s]

D_o = pre-exponential [m^2/s]

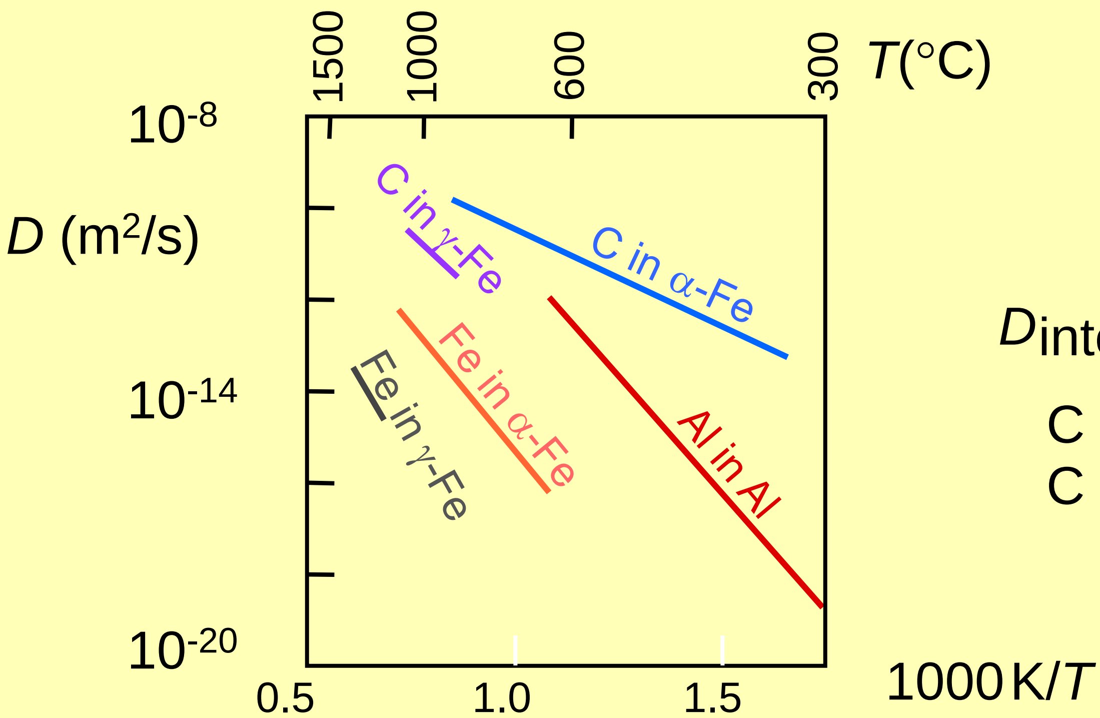
Q_d = activation energy [J/mol or eV/atom]

R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

Diffusion and Temperature

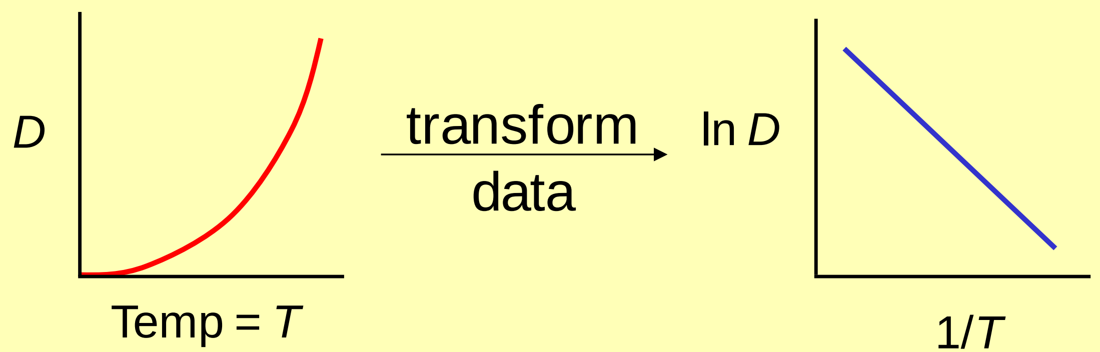
D has exponential dependence on *T*



$D_{interstitial}$ >> $D_{substitutional}$

C in α-Fe
C in γ-Fe

Al in Al
Fe in α-Fe
Fe in γ-Fe



Example

Example: At 300ºC the diffusion coefficient and activation energy for Cu in Si are

$D(300ºC) = 7.8 \times 10^{-11}$ m²/s
$Q_d = 41.5$ kJ/mol

What is the diffusion coefficient at 350ºC?

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\therefore \quad \ln D_2 - \ln D_1 = \ln\frac{D_2}{D_1} = -\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Example (cont.)

$$D_2 = D_1 \exp\left[-\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$$D_2 = (7.8 \text{ x } 10^{-11} \text{ m}^2/\text{s}) \exp\left[\frac{-41{,}500 \text{ J/mol}}{8.314 \text{ J/mol-K}}\left(\frac{1}{623 \text{ K}} - \frac{1}{573 \text{ K}}\right)\right]$$

$$D_2 = 15.7 \text{ x } 10^{-11} \text{ m}^2/\text{s}$$

Non-steady State Diffusion

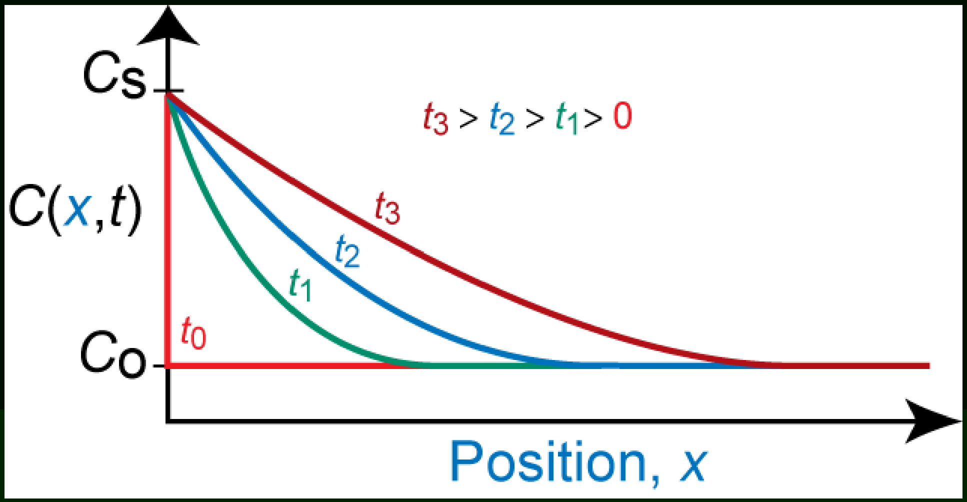
- The concentration of diffusing species is a function of both time and position $C = C(x,t)$
- In this case ***Fick's Second Law*** is used

Fick's Second Law

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.



B.C. at $t = 0$, $C = C_o$ for $0 \leq x \leq \infty$

at $t > 0$, $C = C_S$ for $x = 0$ (const. surf. conc.)

$C = C_o$ for $x = \infty$

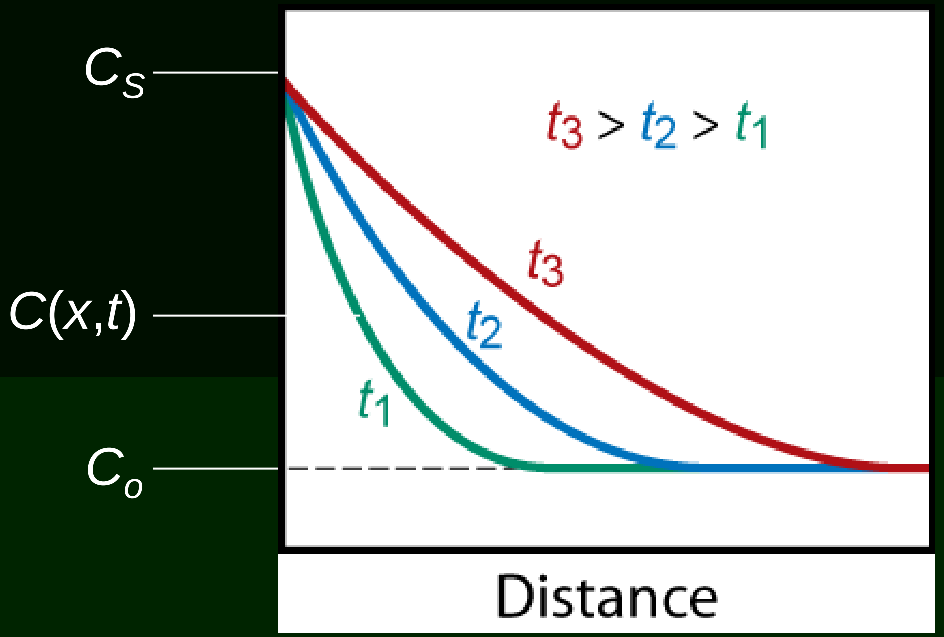
Solution:

$$\frac{C(x,t)-C_o}{C_s-C_o}=1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$C(x,t)$ = Conc. at point x at time t

erf (z) = Gaussian error function

$$=\frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}dy$$



$$\tau=\frac{(\Delta x)^2}{16D}$$

Characteristic diffusion time necessary to penetrate an infinite slab of thickness Δx, for about 0.5% concentration threshold.

Non-steady State Diffusion

- **Sample Problem: An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface carbon concentration constant at 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.**

- **Solution: use equation**

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

Example

Solution (cont.):

$$\frac{C(x,t)-C_o}{C_s-C_o}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

- t = 49.5 h
- C_x = 0.35 wt%
- C_o = 0.20 wt%

x = 4 x 10^{-3} m

C_s = 1.0 wt%

$$\frac{C(x,t)-C_o}{C_s-C_o}=\frac{0.35-0.20}{1.0-0.20}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)=1-\text{erf}(z)$$

$\therefore$ erf(z) = 0.8125

Example (cont.)

We must now determine from table the value of *z* for which the error function is 0.8125.

z	erf(*z*)
0.90	0.7970
z	**0.8125**
0.95	0.8209

$$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

$$z = 0.93$$

Now solve for *D*

$$z = \frac{x}{2\sqrt{Dt}} \Rightarrow D = \frac{x^2}{4z^2 t}$$

$$\therefore D = \left(\frac{x^2}{4z^2 t}\right) = \frac{(4 \times 10^{-3}\,\text{m})^2}{(4)(0.93)^2(49.5\,\text{h})} \frac{1\,\text{h}}{3600\,\text{s}} = 2.6 \times 10^{-11}\,\text{m}^2/\text{s}$$

- **To solve for the temperature at which *D* has above value, we use a rearranged form of**

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

$$T = \frac{Q_d}{R(\ln D_o - \ln D)}$$

for diffusion of C in FCC Fe

D_o = 2.3 x 10^{-5} m^2/s Q_d = 148,000 J/mol

$$T = \frac{148{,}000 \text{ J/mol}}{(8.314 \text{ J/mol-K})(\ln 2.3\text{x}10^{-5} \text{ m}^2/\text{s} - \ln 2.6\text{x}10^{-11} \text{ m}^2/\text{s})}$$

T = 1300 K = 1027°C