

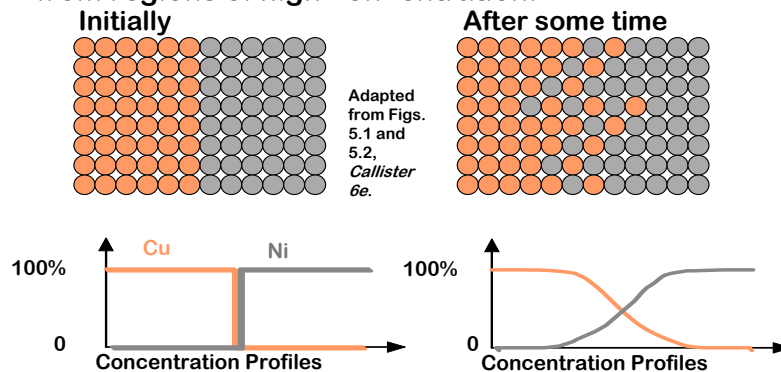
## Chapter 5: Diffusion

### Outline

- Introduction
- Diffusion mechanisms
- Steady-state diffusion
- Nonsteady-state diffusion
- Factors that influence diffusion

## Introduction

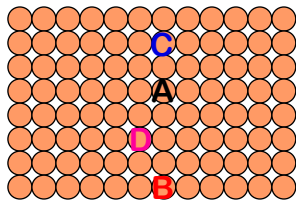
- Diffusion: the phenomenon of material transport by atomic motion
- **Interdiffusion**: In an alloy, atoms tend to migrate from regions of high concentration.



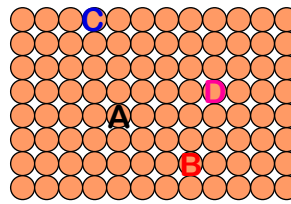
## Diffusion phenomenon (2)

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

Label some atoms



After some time

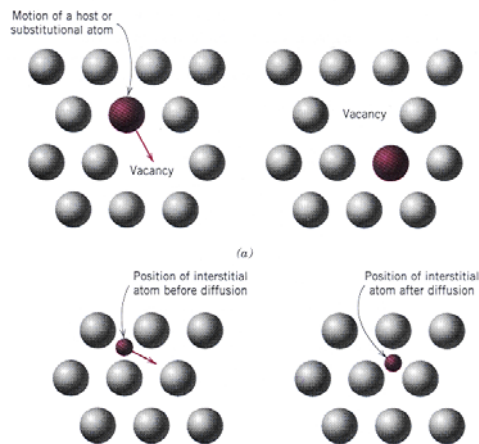


## Diffusion mechanisms

Vacancy diffusion

Interstitial diffusion

- small atoms



Interstitial is more rapid than vacancy diffusion<sup>(b)</sup>

## 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.



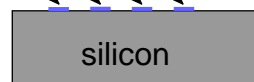
The presence of C atoms makes iron (steel) harder.

## Processing using diffusion

### □ Doping silicon with phosphorus for *n*-type semiconductors:

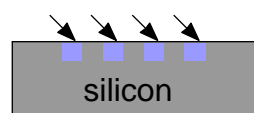
#### □ Process:

1. Deposit P rich layers on surface.

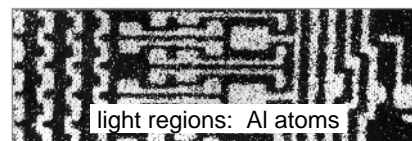
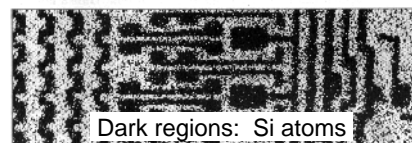
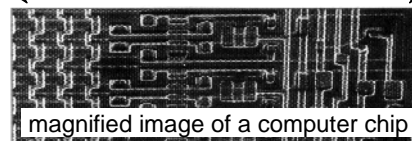


2. Heat it.

3. Result: Doped semiconductor regions.



← 0.5 mm →



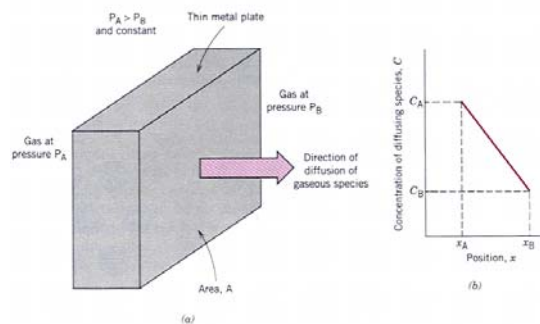
## Steady-state diffusion

- Diffusion flux

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

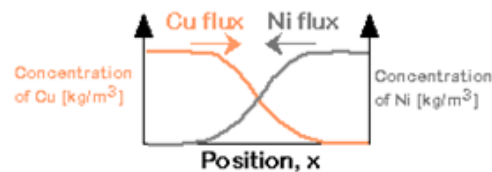
- Steady-state diffusion: the diffusion does not change with time

- Concentration profile



## Flux vs concentration profile

- Concentration profile,  $C$ :  $[\text{kg}/\text{m}^3]$



- Fick's First Law:

$$\text{flux in } x\text{-dir.} \quad [\text{kg}/\text{m}^2\text{-s}] \quad \rightarrow \quad J_x = -D \frac{dC}{dx}$$

Diffusion coefficient  $[m^2/s]$ 
concentration gradient  $[kg/m^4]$

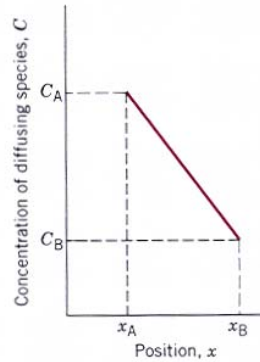
The steeper the concentration profile, the greater the flux!

## Steady-state diffusion (continue)

□ Concentration gradient =  $dC/dx$

□ Linear concentration gradient

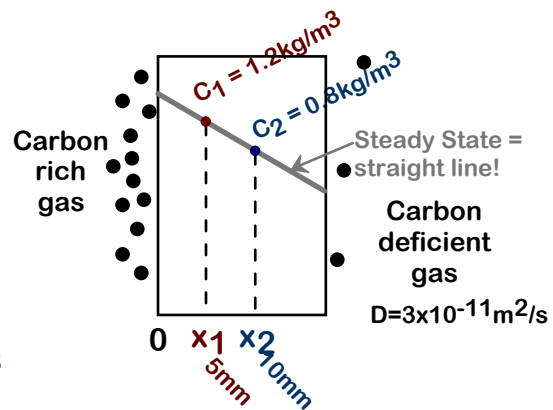
□ Driving force =  $\frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$



(b)

## Examples (steady state)

- Steel plate at 700°C with geometry shown:



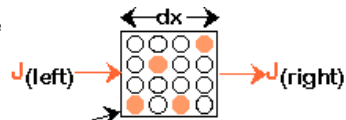
- Q: How much carbon transfers from the rich to the deficient side?

$$J = -D \frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9} \frac{\text{kg}}{\text{m}^2 \text{s}}$$

## Nonsteady-state diffusion

### □ Fick's second law

- C changes with time



Concentration, C, in the box

- To conserve matter:

$$\frac{J(\text{right}) - J(\text{left})}{dx} = -\frac{dC}{dt}$$

$$\frac{dJ}{dx} = -\frac{dC}{dt}$$

- Fick's First Law:

$$J = -D \frac{dC}{dx} \quad \text{or}$$

$$\frac{dJ}{dx} = -D \frac{d^2C}{dx^2}$$

- Governing Eqn.:  $\Rightarrow$

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2}$$

## Non-steady state diffusion

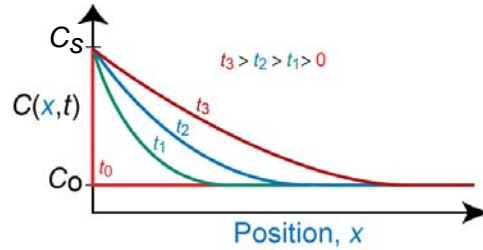
- The concentration of diffusing species is a function of both time and position  $C = C(x, t)$
- In this case Fick's Second Law is used

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

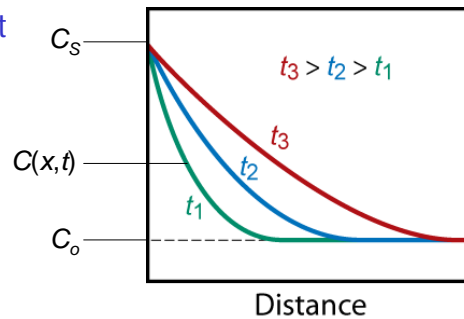
$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

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

$\operatorname{erf}(z)$  = error function

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

$\operatorname{erf}(z)$  values are given in Table 5.1



## Nonsteady-state diffusion

**Table 5.1** Tabulation of Error Function Values

$z$	$erf(z)$	$z$	$erf(z)$	$z$	$erf(z)$
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

## Examples (non-steady state)

- **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 Eqn. 5.5

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



## Solution (cont.)

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

- $t = 49.5 \text{ h}$
- $C_x = 0.35 \text{ wt\%}$
- $C_o = 0.20 \text{ wt\%}$
- $x = 4 \times 10^{-3} \text{ m}$
- $C_s = 1.0 \text{ wt\%}$

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

$$\therefore \operatorname{erf}(z) = 0.8125$$

## Solution (cont.)

We must now determine from Table 5.1 the value of  $z$  for which the error function is 0.8125. An interpolation is necessary as follows

$z$	$\operatorname{erf}(z)$	$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$
0.90	0.7970	
$z$	0.8125	$z = 0.93$
0.95	0.8209	

Now solve for  $D$

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

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

## Factors that influence diffusion

### □ Diffusing species

Table 5.2 A Tabulation of Diffusion Data

Diffusing Species	Host Metal	$D_0(m^2/s)$	Activation Energy $Q_d$		Calculated Values	
			$kJ/mol$	$eV/atom$	$T(^{\circ}C)$	$D(m^2/s)$
Fe	$\alpha$ -Fe (BCC)	$2.8 \times 10^{-4}$	251	2.60	500	$3.0 \times 10^{-23}$
					900	$1.8 \times 10^{-5}$
Fe	$\gamma$ -Fe (FCC)	$5.0 \times 10^{-5}$	284	2.94	900	$1.1 \times 10^{-7}$
					1100	$7.8 \times 10^{-9}$
C	$\alpha$ -Fe	$6.2 \times 10^{-7}$	80	0.83	500	$2.4 \times 10^{-12}$
					900	$1.7 \times 10^{-9}$
C	$\gamma$ -Fe	$2.3 \times 10^{-5}$	148	1.53	900	$5.9 \times 10^{-2}$
					1100	$5.3 \times 10^{-11}$
Cu	Cu	$7.8 \times 10^{-5}$	211	2.19	500	$4.2 \times 10^{-9}$
Zn	Cu	$2.4 \times 10^{-5}$	189	1.96	500	$4.0 \times 10^{-9}$
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	$1.9 \times 10^{-9}$
Cu	Ni	$2.7 \times 10^{-5}$	256	2.65	500	$1.3 \times 10^{-22}$

Source: E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1992

## Diffusion and temperature

### □ Diffusion coefficient increases with increasing $T$

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

$D$  = diffusion coefficient [ $m^2/s$ ]

$D_0$  = pre-exponential [ $m^2/s$ ]

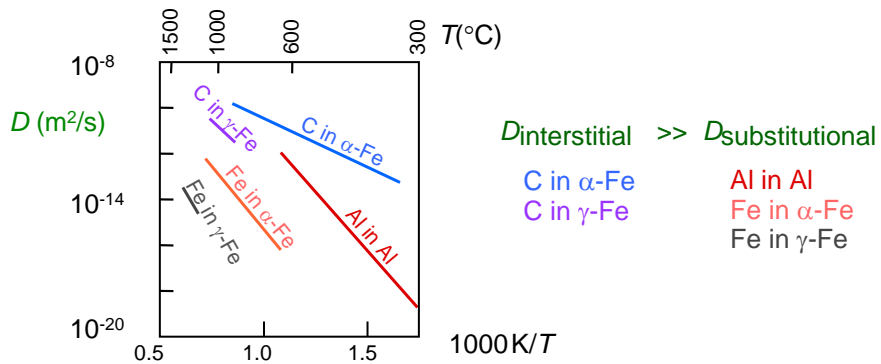
$Q_d$  = activation energy [J/mol or eV/atom]

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

$T$  = absolute temperature [K]

## Diffusion and temperature

□  $D$  has exponential dependence on  $T$

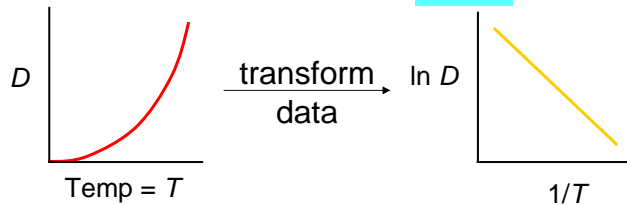


**Example:** At  $300^\circ\text{C}$  the diffusion coefficient and activation energy for Cu in Si are

$$D(300^\circ\text{C}) = 7.8 \times 10^{-11} \text{ m}^2/\text{s}$$

$$Q_d = 41.5 \text{ kJ/mol}$$

What is the diffusion coefficient at  $350^\circ\text{C}$ ?



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

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

### Example (cont.)

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

$$T_1 = 273 + 300 = 573 \text{ K}$$

$$T_2 = 273 + 350 = 623 \text{ K}$$

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

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

### Summary

#### Diffusion **FASTER** for...

- open crystal structures
- materials w/secondary bonding
- smaller diffusing atoms
- lower density materials

#### Diffusion **SLOWER** for...

- close-packed structures
- materials w/covalent bonding
- larger diffusing atoms
- higher density materials