



Materials Science and Engineering I

Ch. 5 Thermally activated processes and diffusion in solids

Smith and Hashemi, "Foundations of Materials Science and Engineering",
6th Ed., McGraw-Hill 2019

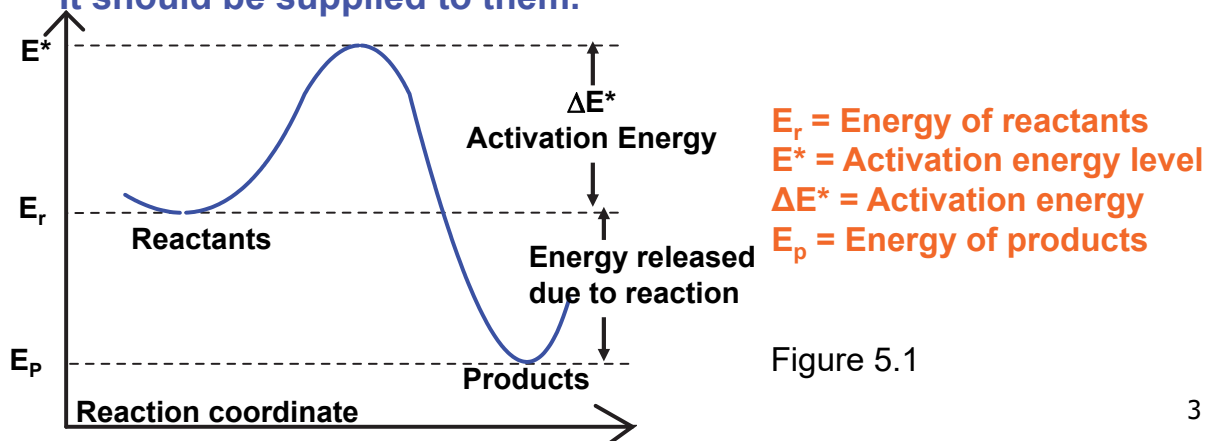


Outline

- Atomic diffusion in solids
 - Diffusion mechanism, steady-state and non-steady state diffusion, diffusion profile
- Industrial applications of diffusion processes
 - Carburizing of steel parts, dopant diffusion in Si
- Effect of temperature on diffusion in solids

Rate process in solids

- Reactions occur in solid state resulting in more **stable** atomic arrangement.
- Reacting atoms must have sufficient energy to overcome activation energy barrier.
- At a given temperature, not all atoms have activation energy E^* . It should be supplied to them.



3

Rate process in solids (Cont..)

- As **temperature** increases, more and more atoms acquire activation energy level.
- Probability** of finding an atom/molecule with energy E greater than average energy E_{ave} of all atoms/ molecules is given by

$$\alpha e^{-(E-E_{ave})/kT} \quad 1 = \int_0^\infty \alpha e^{-\frac{E-E_{ave}}{kT}} dE = \alpha e^{\frac{E_{ave}}{kT}} \left(-kT e^{-\frac{E}{kT}} \right) \Big|_0^\infty = \alpha e^{\frac{E_{ave}}{kT}} (kT)$$

$$\Rightarrow \frac{1}{kT} e^{-E/kT} \quad \alpha = \frac{1}{kT} e^{\frac{E_{ave}}{kT}}$$

k = Boltzman's constant = 1.38×10^{-23} J/(atom·K)

T = Temperature in Kelvin

4

Rate process in solids (Cont..)

- The **fraction** of atoms having energies greater than E^* in a system (when E^* is greater than average energy E_{ave}) is given by

$$\frac{n}{N_{total}} = Ce^{\frac{-E^*}{kT}} \quad P(> E^*) = \int_{E^*}^{\infty} \frac{1}{kT} e^{\frac{-E}{kT}} dE = e^{\frac{-E^*}{kT}}$$

n = Number of molecules with energy greater than E^*

N_{total} = Total number of molecules

k = Boltzmann's constant

C = Constant

T = Temperature in Kelvin.

5

Rate process in solids (Cont..)

- The number of **vacancies** at equilibrium at a particular temperature in a metallic crystal lattice is given by

$$\frac{n_v}{N} = Ce^{\frac{-E_v}{kT}}$$

n_v = Number of vacancies per m^3 of metal

E_v = Activation energy to form a vacancy

T = Absolute temperature

k = Boltzmann's constant

C = Constant

6

Arrhenius equation

- The rate of chemical reaction is given by **Arrhenius equation**.

$$\text{Rate of reaction} = C e^{-Q/RT}$$

Q = Activation energy J/mol

R = Molar gas constant J/mol.K

T = Temperature in Kelvin

C = Rate constant (Independent of temperature)

- Rate of reaction depends upon **number of reacting molecules**.

7

Arrhenius equation

- Arrhenius equation can also be written as

$$\ln(\text{rate}) = \ln(C) - Q/RT$$

or $\text{Log}_{10}(\text{rate}) = \text{Log}_{10}(C) - Q/2.303 RT$

Which is similar to

$$Y = b + m X$$

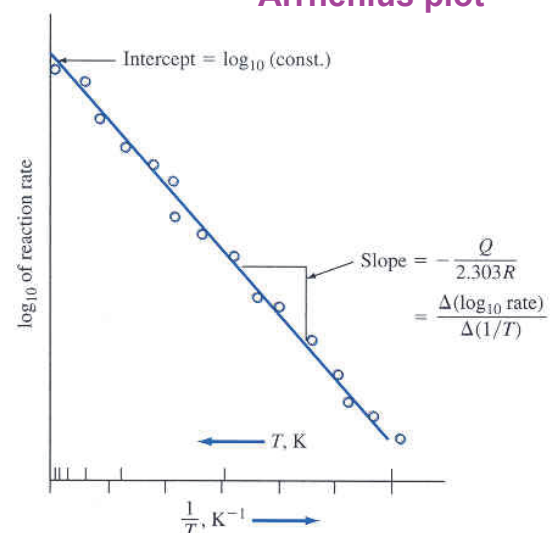
Which is equation of a **straight line**

With Y intercept as 'b' and slope 'm'.

Y	→	$\text{Log}_{10}(\text{rate})$
X	→	$(1/T)$
b	→	$\text{Log}_{10}(C)$
m	→	$Q/2.303R$

Figure 5.2

Arrhenius plot





Atomic diffusion in solids

- Diffusion is a process by which a matter is **transported** through another matter.
- **Examples:**
 - Movement of smoke particles in air : very fast.
 - Movement of dye in water : relatively slow.
 - Solid state reactions : very restricted movement due to bonding.

9



Vacancy or substitutional diffusion mechanism

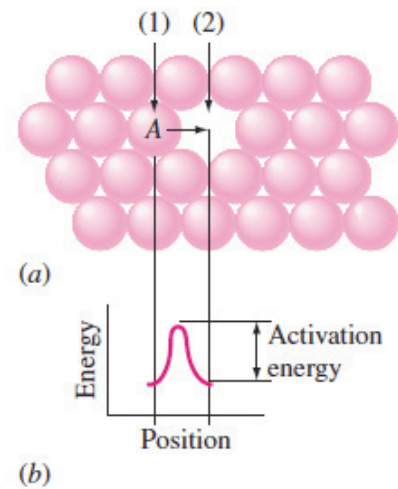
- Atoms diffuse in solids if
 - Vacancies or other crystal defects are present
 - There is enough energy to activate atomic jumping
- Atoms move into the vacancies present.
- **More vacancies are created at higher temperature.**
- Diffusion rate is higher at high temperatures.

10

Substitutional diffusion

- Example: If atom 'A' has sufficient energy, it moves into the vacancy → self diffusion.

$$\text{Activation Energy of Self diffusion} = \text{Activation Energy to form a Vacancy} + \text{Activation Energy to move a vacancy}$$



- As the melting point increases, activation energy also increases.

Figure 5.3

11

Self-diffusion activation energy vs melting point

Table 5.1 Self-diffusion activation energies for some pure metals

Metal	Melting point (°C)	Crystal structure	Temperature range studied (°C)	Activation energy	
				kJ/mol	kcal/mol
Zinc	419	HCP	240–418	91.6	21.9
Aluminum	660	FCC	400–610	165	39.5
Copper	1083	FCC	700–990	196	46.9
Nickel	1452	FCC	900–1200	293	70.1
α iron	1530	BCC	808–884	240	57.5
Molybdenum	2600	BCC	2155–2540	460	110

12

Kirkendall effect

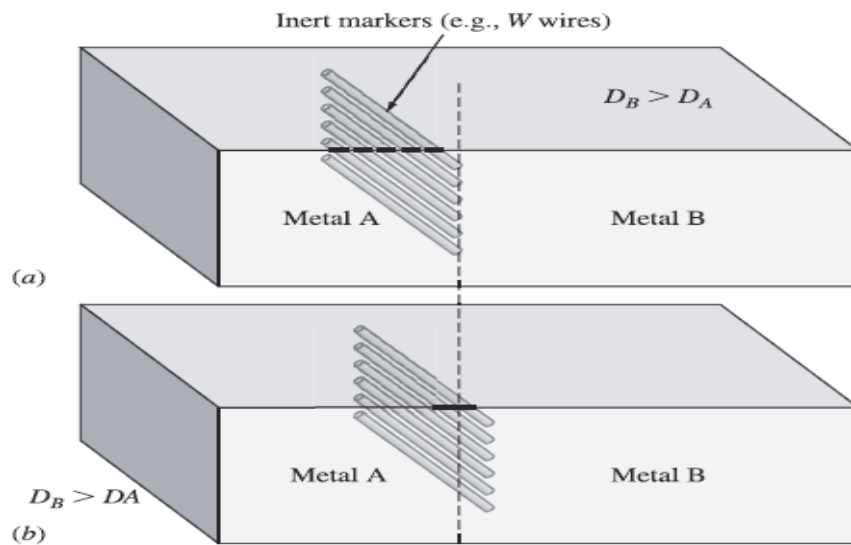


Figure 5.4

Experiment to illustrate the Kirkendall effect. (a) At start of diffusion experiment ($t = 0$). (b) After time t , markers move in the direction opposite the most rapidly diffusing species, B .

13

Interstitial diffusion mechanism

- Atoms move from one interstitial site to another.
- The atoms that move must be much **smaller** than the matrix atom.
- Example:
Carbon interstitially diffuses into BCC α or FCC γ iron.

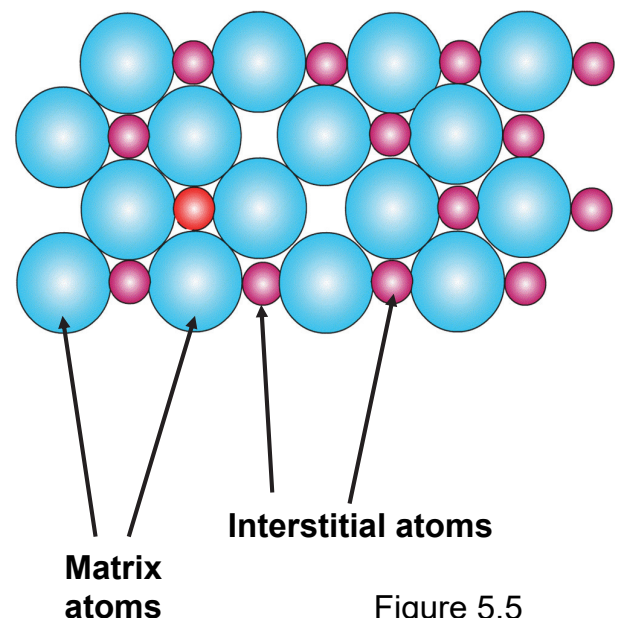
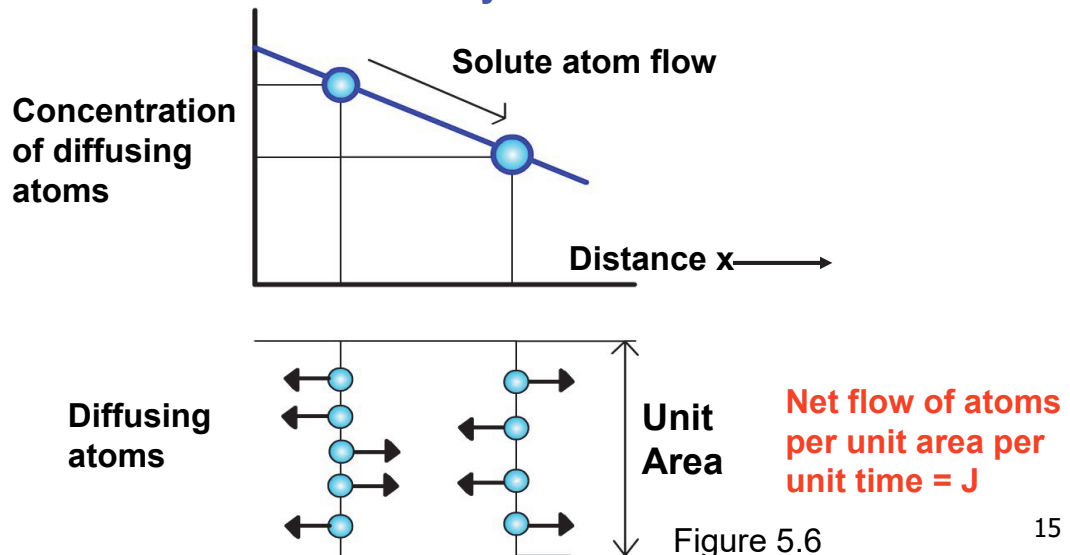


Figure 5.5

14

Steady state diffusion

- There is no change in **concentration** of solute atoms at different planes in a system, over a period of time.
- No chemical reaction occurs. Only net flow of atoms.



15

Fick's First Law

- The flux or flow of atoms is given by

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

J = Flux or net flow of atoms

D = Diffusion coefficient

$\frac{dc}{dx}$ = **Concentration gradient.**

i.e. for **steady state** diffusion condition, the net flow of atoms by atomic diffusion is equal to diffusivity D times the diffusion gradient dc/dx .

- Example: Diffusivity of FCC iron at 500 °C is $5 \times 10^{-15} \text{ m}^2/\text{s}$ and at 1000°C is $3 \times 10^{-11} \text{ m}^2/\text{s}$

16



Diffusivity

■ Diffusivity depends upon

- **Type of diffusion** : Whether the diffusion is interstitial or substitutional.
- **Temperature**: As the temperature increases diffusivity increases.
- **Type of crystal structure**: BCC crystal has lower APF than FCC and hence has higher diffusivity.
- **Type of crystal imperfection**: More open structures (grain boundaries) increases diffusion.
- **The concentration of diffusing species**: Higher concentrations of diffusing solute atoms will affect diffusivity.

17



Diffusivity data for some metals

Table 5.2 Diffusivities at 500°C and 1000°C for selected solute-solvent diffusion systems

Solute	Solvent (host structure)	Diffusivity (m ² /s)	
		500°C (930°F)	1000°C (1830°F)
1. Carbon	FCC iron	$(5 \times 10^{-15})^*$	3×10^{-11}
2. Carbon	BCC iron	10^{-12}	(2×10^{-9})
3. Iron	FCC iron	(2×10^{-23})	2×10^{-16}
4. Iron	BCC iron	10^{-20}	(3×10^{-14})
5. Nickel	FCC iron	10^{-23}	2×10^{-16}
6. Manganese	FCC iron	(3×10^{-24})	10^{-16}
7. Zinc	Copper	4×10^{-18}	5×10^{-13}
8. Copper	Aluminum	4×10^{-14}	$10^{-10} \text{ M}^\dagger$
9. Copper	Copper	10^{-18}	2×10^{-13}
10. Silver	Silver (crystal)	10^{-17}	10^{-12} M
11. Silver	Silver (grain boundary)	10^{-11}	
12. Carbon	HCP titanium	3×10^{-16}	(2×10^{-11})

18

Temperature-dependent diffusivity

TABLE I. Melting point and diffusivities of Cu, Al, and eutectic SnPb.

	Melting point (K)	Temperature ratio 373 K/T m	Diffusivities at 100 °C (cm ² /s)	Diffusivities at 350 °C (cm ² /s)
Cu	1356	0.275	Lattice $D_l = 7 \times 10^{-28}$	$D_l = 5 \times 10^{-17}$
			Grain boundary $D_{gb} = 3 \times 10^{-15}$	$D_{gb} = 1.2 \times 10^{-9}$
			Surface $D_s = 10^{-12}$	$D_s = 10^{-8}$
Al	933	0.4	Lattice $D_l = 1.5 \times 10^{-19}$	$D_l = 10^{-11}$
			Grain boundary $D_{gb} = 6 \times 10^{-11}$	$D_{gb} = 5 \times 10^{-7}$
Eutectic SnPb	456	0.82	Lattice $D_l = 2 \times 10^{-9} - 2 \times 10^{-10}$	Molten state $D_l > 10^{-5}$

K. N. Tu, *JAP*, **94**, 5451 (2003)

19

Non-steady state diffusion

- Concentration of solute atoms at any point in metal **changes with time** in this case.
- **Ficks second law**: Rate of compositional change is equal to diffusivity times the rate of change of concentration gradient.

$$\frac{dC_x}{dt} = \frac{d}{dx} \left(D \frac{dc_x}{dx} \right)$$

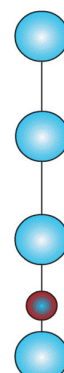
$$= D \frac{dc_x^2}{d^2x} \quad \text{If D is constant}$$

Change of concentration of solute atoms with change in time in different planes

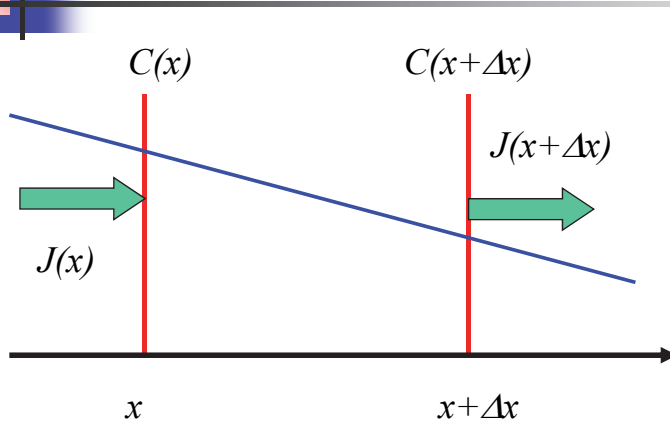
Plane 1



Plane 2



Fick's second law - continuity equation



$$J(x) = -D \frac{dC(x)}{dx}$$

$$C(x + \Delta x) = C(x) + \frac{dC(x)}{dx} \Delta x$$

$$J(x + \Delta x) = -D \frac{dC(x + \Delta x)}{dx}$$

$$= -D \frac{dC(x)}{dx} - D \frac{d^2C(x)}{dx^2} \Delta x$$

$$C(t + \Delta t) - C(t) = \frac{[J(x) - J(x + \Delta x)]A\Delta t}{A\Delta x} = D \frac{d^2C(x)}{dx^2} \Delta t$$

$$\Rightarrow \frac{dC}{dt} = D \frac{d^2C(x)}{dx^2}$$

21

Fick's Second Law – Solution

$$\frac{C_s - C(x, t)}{C_s - C_0} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-z^2} dz$$

C_s = Surface concentration of element in gas diffusing into the surface.

C_0 = Initial uniform concentration of element in solid.

$C(x, t)$ = Concentration of element at distance x from surface at time t

x = distance from surface

D = diffusivity of solute

t = time

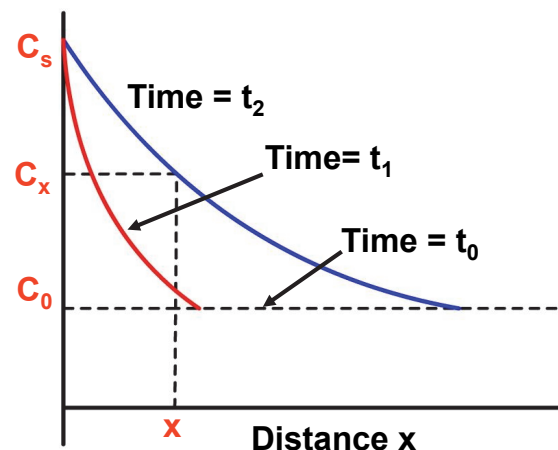


Figure 5.7

22

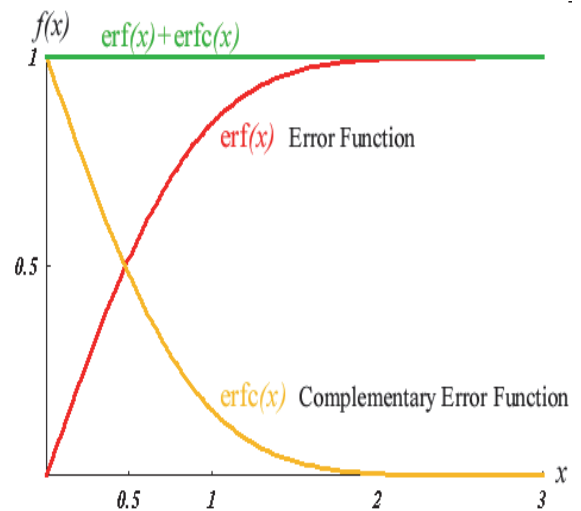
Error function

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-w^2} dw$$

$$\text{erfc}(x) = 1 - \text{erf}(x)$$

Table 5.3 Table of the error function

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



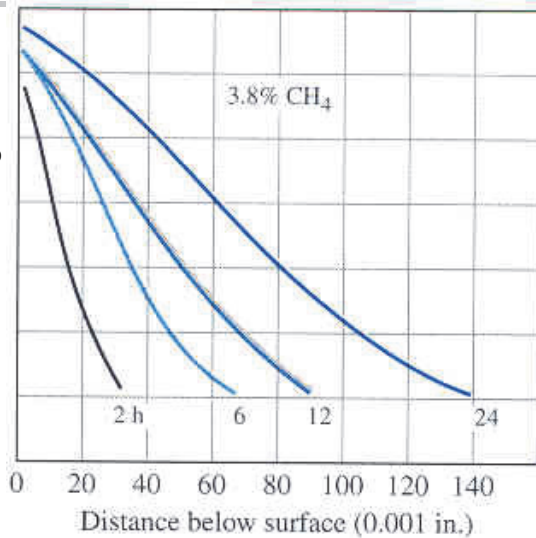
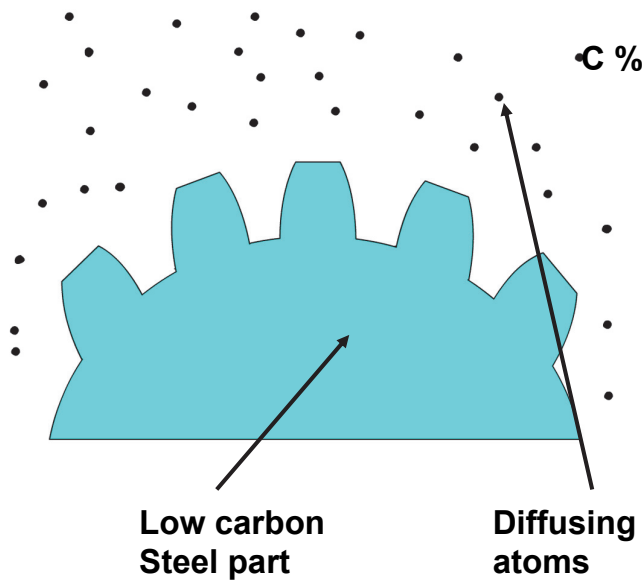
23

Industrial applications of diffusion – Case hardening

- Sliding and rotating parts need to have **hard surfaces**.
- These parts are usually machined with low carbon steel as they are easy to machine.
- Their surface is then hardened by **carburizing**.
- Steel parts are placed at elevated temperature (927°C) in an atmosphere of hydrocarbon gas (CH₄).
- Carbon **diffuses** into iron surface and fills interstitial space to make it harder.

24

Carburizing



Carbon Gradients
In Carburized metals

Figure 5.10

(After "Metals handbook," vol.2: "Heat Treating," 8th ed, American Society of Metals, 1964, p.100)

25

Example

Consider the gas carburizing of a gear of 1018 steel (0.18 wt %) at 927°C. Calculate the time necessary to increase the carbon content to 0.35 wt % at 0.40 mm below the surface of the gear. Assume the carbon content at the surface to be 1.15 wt % and that the nominal carbon content of the steel gear before carburizing is 0.18 wt %. Diffusivity of C in γ iron at 927°C = $1.28 \times 10^{-11} \text{ m}^2/\text{s}$.

The solution of the diffusion equation is

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

where: $C_s = 1.15\%$ $C_o = 0.18\%$ $C_x = 0.35\%$
 $x = 0.40 \text{ mm} = 4 \times 10^{-4} \text{ m}$ $D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$

Substituting $\frac{1.15 - 0.35}{1.15 - 0.18} = \text{erf} \left[\frac{4 \times 10^{-4} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})t}} \right]$
 $0.8247 = \text{erf} \left[\frac{55.90}{\sqrt{t}} \right] = \text{erf } z$

$$\frac{0.8247 - 0.8209}{0.8427 - 0.8209} = \frac{x - 0.95}{1.0 - 0.95} \quad x = 0.959$$

erf z	z
0.8209	0.95
0.8247	x
0.8427	1.0

Thus,

$$z = \frac{55.90}{\sqrt{t}} = 0.959$$

$$t = 3397.7 \text{ s} = 56.6 \text{ min.}$$

26

Impurity diffusion into silicon wafer

- Impurities are made to diffuse into silicon wafer to change its electrical characteristics.
- Used in integrated circuits.
- Silicon wafer is exposed to **vapor of impurity** at 1100°C in a quartz tube furnace.
- The concentration of impurity at any point depends on **depth** and **time** of exposure.

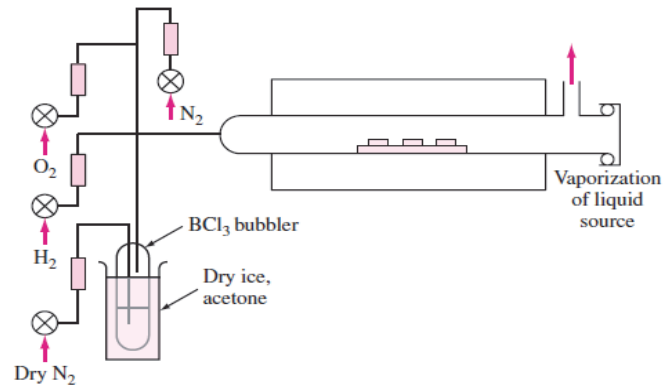


Figure 5.11

(After W.R. Runyan, "Silicon Semiconductor Technology," McGraw-Hill, 1965.)

27

Diffusion in Si wafer



Figure 5.12

Loading a rack of silicon wafers into a tube furnace for impurity diffusion.
(Getty/RF)

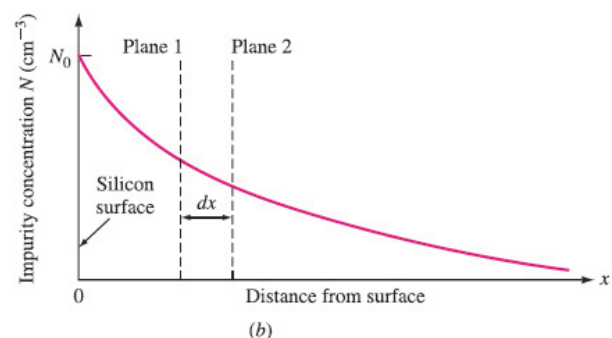
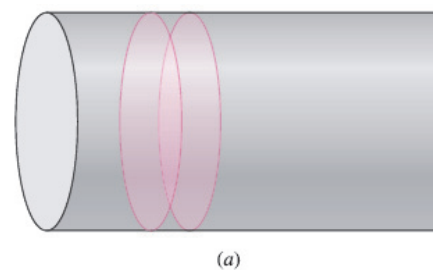


Figure 5.13

28

Effect of temperature on diffusion

- Dependence of rate of diffusion on temperature is given by

$$D = D_0 e^{\frac{-Q}{RT}}$$

or $\ln D = \ln D_0 - \frac{Q}{RT}$

or $\log_{10} D = \log_{10} D_0 - \frac{Q}{2.303RT}$

D = Diffusivity m²/s

D₀ = Proportionality constant m²/s

Q = Activation energy of diffusing species J/mol

R = Molar gas constant = 8.314 J/mol.K

T = Temperature (K)

29

Effect of temperature on diffusion

- If diffusivity at two temperatures are determined, two equations can be solved for **Q** and **D₀**
- Example: The diffusivity of silver atoms in silver is 1×10^{-17} at 500 °C and 7×10^{-13} at 1000 °C.

Therefore,

$$\frac{D_{1000}}{D_{500}} = \frac{\exp(-Q/RT_2)}{\exp(-Q/RT_1)} = \exp\left(\frac{-Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$$\frac{7 \times 10^{-13}}{1 \times 10^{-17}} = \exp\left(-\frac{Q}{R}\left(\frac{1}{1273} - \frac{1}{773}\right)\right)$$

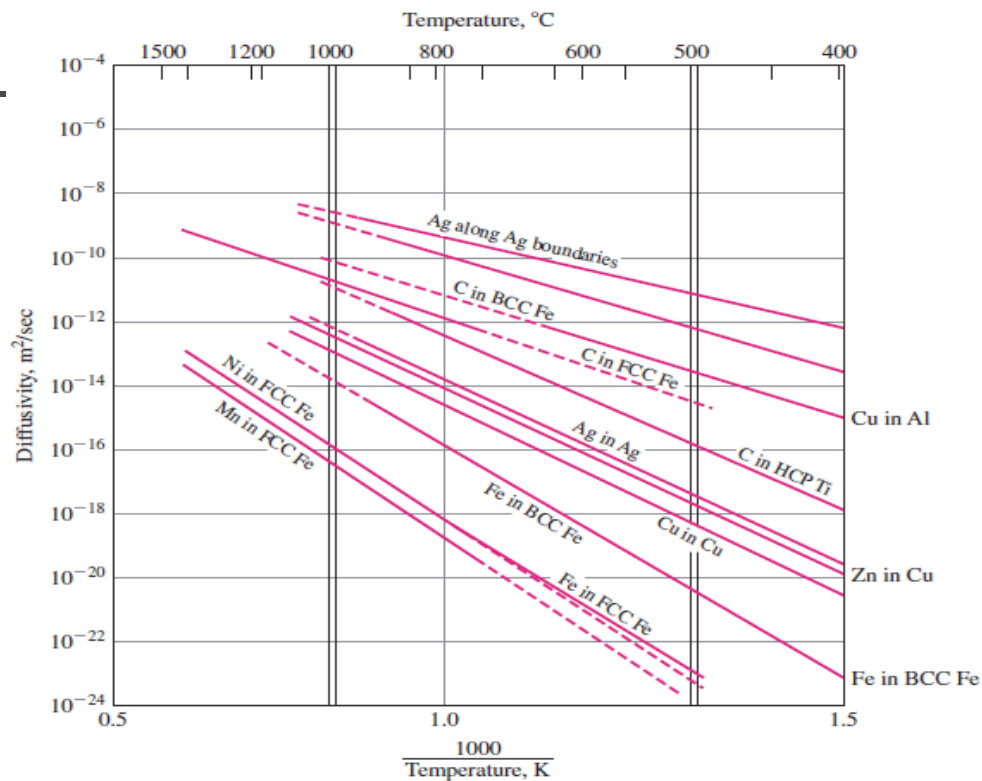
Solving for activation energy Q

$$Q = 183 \text{ KJ / mol}$$

30



Diffusivity data for some metals



(After L.H. Van Vlack. "Elements of Materials Science and Engineering." 5th ed., Addison-Wesley, 1985. P.137.)

31



Summary

- Atomic diffusion mechanism
- Diffusion profile for steady-state and non-steady state diffusion processes
- Industrial applications of diffusion processes
- Temperature-dependent diffusivity

32