

Department of Manufacturing Engineering and Production

Fundamentals of Material Science

CHAPTER 5 Diffusion and Diffusion Mechanisms

Chapter 5 Outline

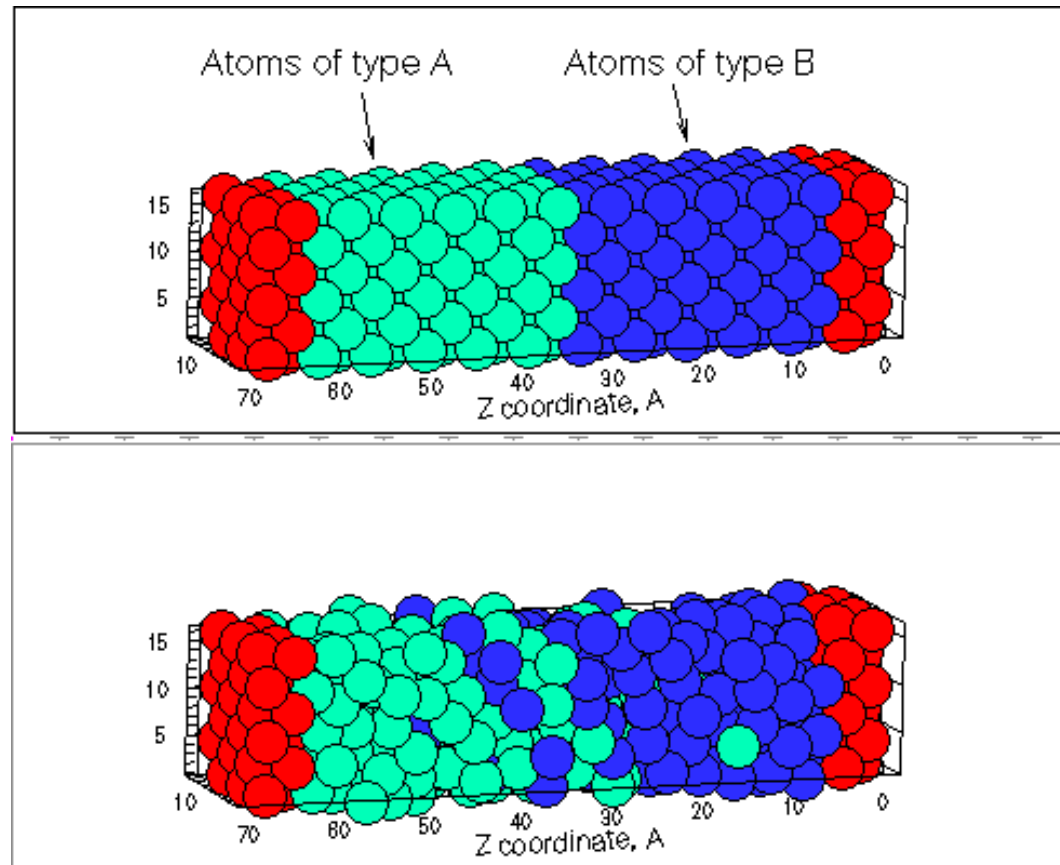
Diffusion → how atoms move in solids

Diffusion mechanisms

- Vacancy diffusion
 - Interstitial diffusion
 - Impurities
-
- **Mathematics of diffusion**
 - Steady-state diffusion (Fick's first law)
 - *Nonsteady-State Diffusion (Fick's second law)*
-
- **Factors that influence diffusion**
 - Diffusing species
 - Host solid
 - Temperature
 - Microstructure

What is diffusion?

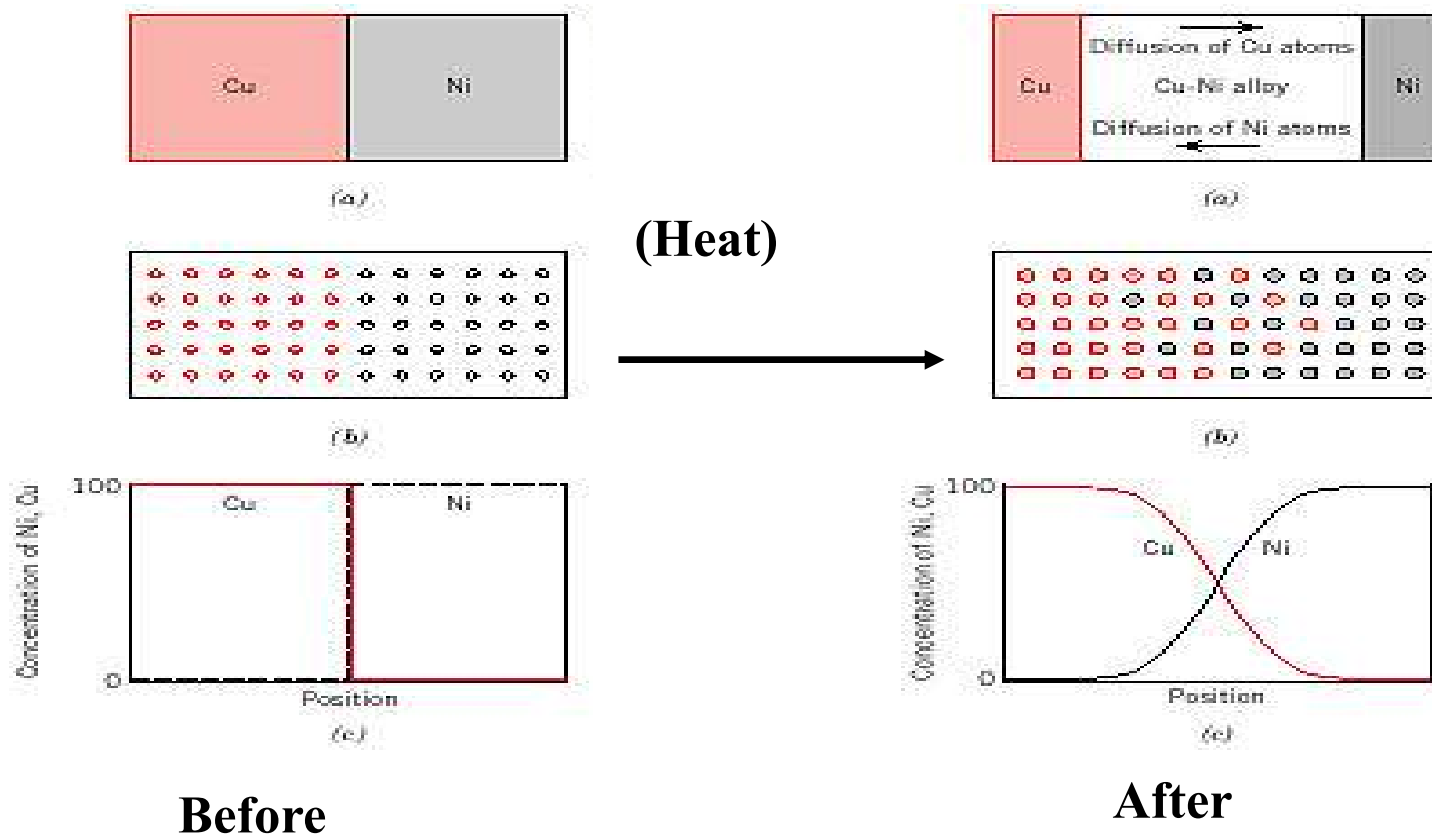
Diffusion → transport by atomic motion.



Inhomogeneous material can become homogeneous by diffusion. Temperature should be high enough to overcome energy barrier.

Inter-diffusion vs. Self-diffusion

Concentration Gradient \rightarrow Interdiffusion (or Impurity Diffusion).

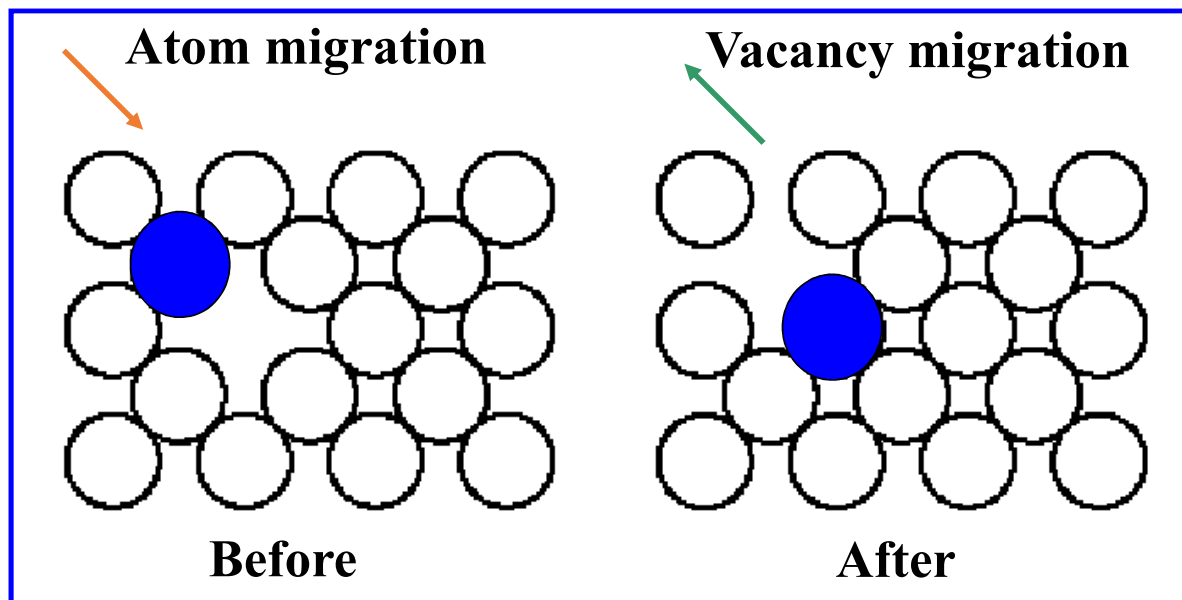


Self-diffusion:

one-component material, atoms are of same type.

Diffusion Mechanisms (I)

Vacancy diffusion



To jump from lattice site to lattice site, atoms need energy to break bonds with neighbors, and to cause the necessary lattice distortions during jump.

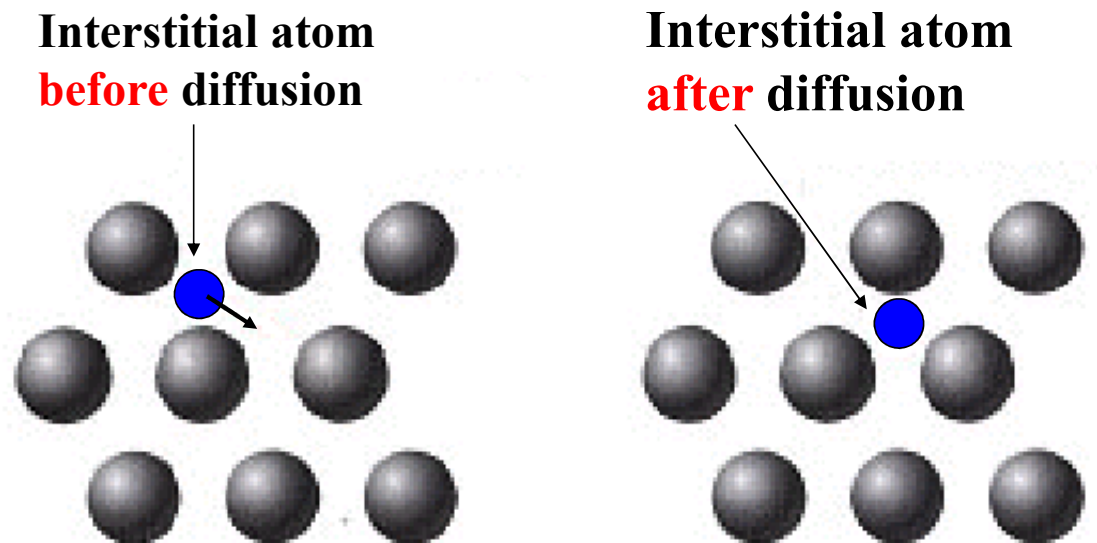
Therefore, there is **an energy barrier**.

Energy comes from thermal energy of atomic vibrations $(E_{av} \sim kT)$

Atom flow is opposite to vacancy flow direction.

Diffusion Mechanisms (II)

Interstitial diffusion



Generally faster than vacancy diffusion because bonding of interstitials to surrounding atoms is normally weaker and there are more interstitial sites than vacancy sites to jump to.

Smaller energy barrier

Only small impurity atoms (e.g. C, H, O) fit into interstitial sites.

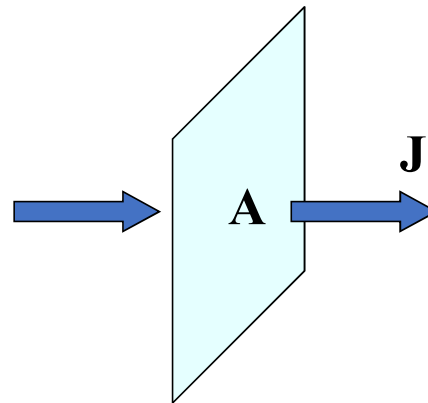
Flux of diffusing atoms, J .

Number of atoms diffusing through unit area per unit time **[atoms/(m²s)]**

or

Mass of atoms diffusing through unit area per unit time **[kg/(m² s)]**

$$\text{Mass: } J = M / (A t) \cong (1/A) (dM/dt)$$



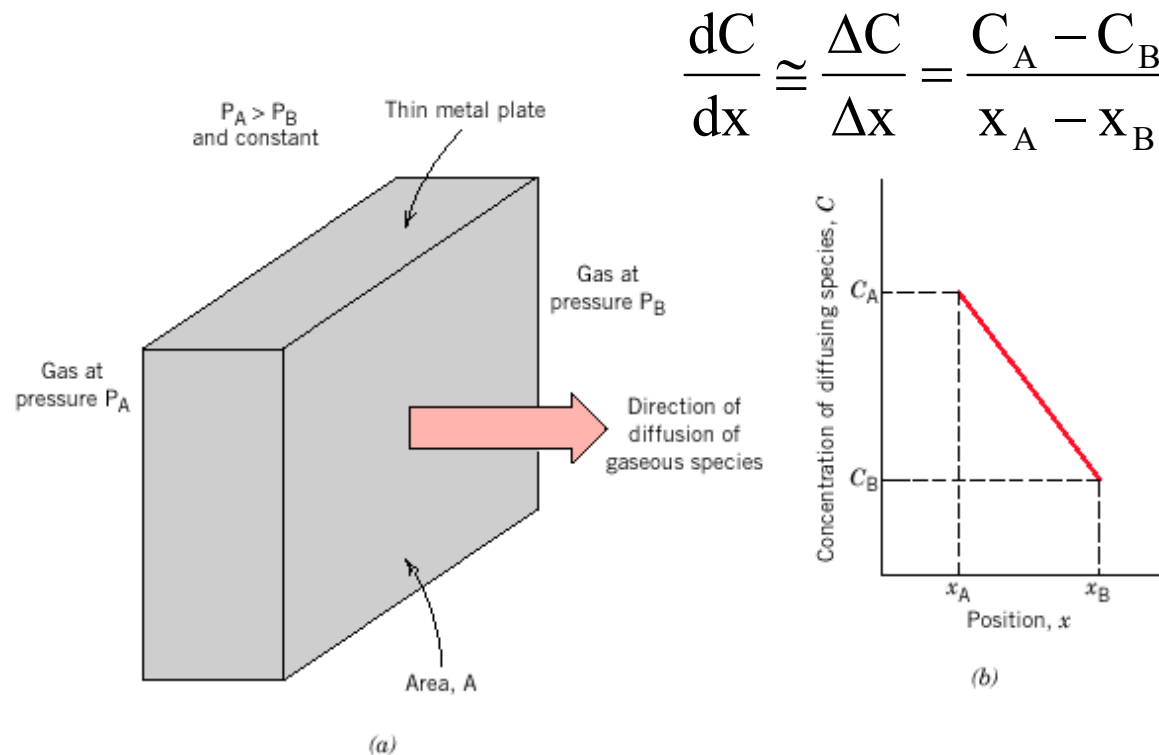
Steady-State Diffusion

Diffusion flux does not change with time

Concentration profile:

Concentration (kg/m³) vs. position

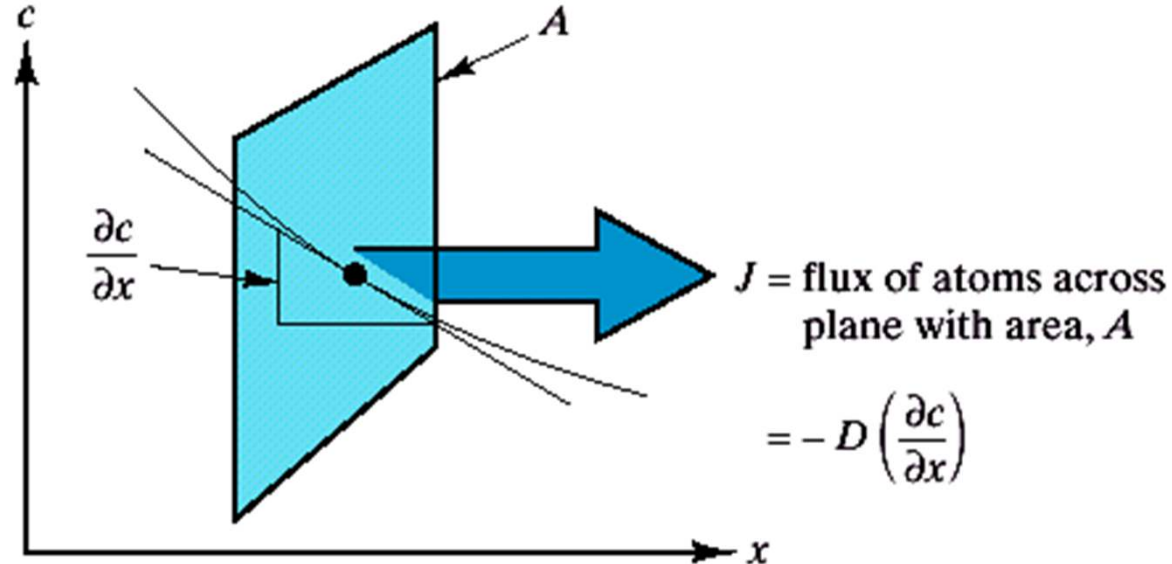
Concentration gradient: dC/dx (kg / m⁴)



Steady-State Diffusion

Fick's first law: **J** proportion to **dC/dx**

$$J = -D \frac{dC}{dx} \quad \mathbf{D} = \text{diffusion coefficient}$$



Concentration gradient is '*driving force*'

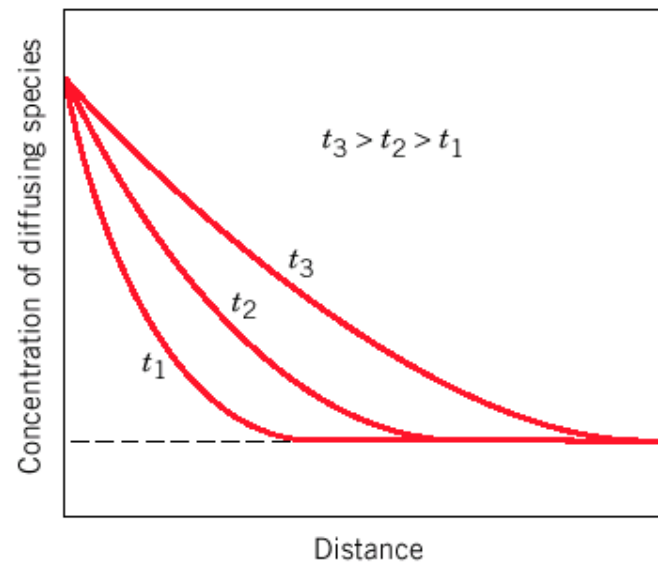
Minus sign means diffusion is 'downhill':
toward lower concentrations

Nonsteady-State Diffusion (not tested)

Concentration changing with time
Fick's second law

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

Find $C(x,t)$



Atom needs enough thermal energy to break bonds and squeeze through its neighbors.

Energy needed → energy barrier →

Called the activation energy E_m (like Q)

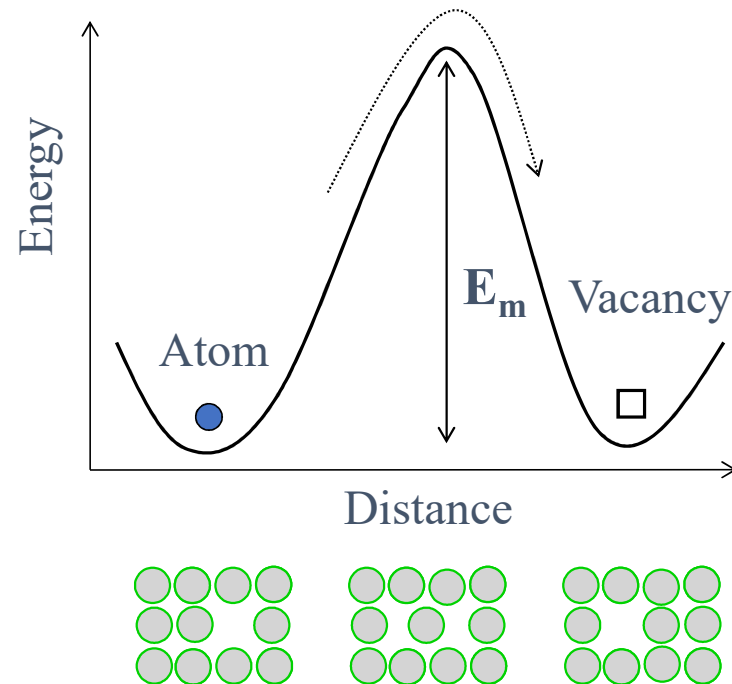


Diagram for Vacancy Diffusion

Diffusion → Thermally Activated Process

Diffusion – Thermally Activated Process

Room temperature ($k_B T = 0.026 \text{ eV}$)

Typical activation energy E_m ($\sim 1 \text{ eV/atom}$) (like Q_v)

Therefore, a **large fluctuation** in energy is needed for a jump.

Probability of a fluctuation or frequency of jump, $R_j \rightarrow$

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

R_0 = attempt frequency proportional to vibration frequency
Swedish chemist Arrhenius

Calculate Activated Diffusion

1. Probability of finding a vacancy in an adjacent lattice site (Chap. 4):

times $P = Const. \exp\left(-\frac{Q_v}{k_B T}\right)$

2. Probability of thermal fluctuation

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

The diffusion coefficient = Multiply

$$D = Const. \exp\left(-\frac{E_m}{k_B T}\right) \exp\left(-\frac{Q_v}{k_B T}\right)$$

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

Arrhenius dependence.

Diffusion – Temperature Dependence

$J = -D \frac{dC}{dx}$ Diffusion coefficient is the measure of mobility of diffusing species.

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

D_0 – temperature-independent (m^2/s)

Q_d – the activation energy (J/mol or eV/atom)

R – the gas constant (8.31 J/mol-K)

or

k_B - Boltzman constant ($8.62 \times 10^{-5} \text{ eV/atom-K}$)

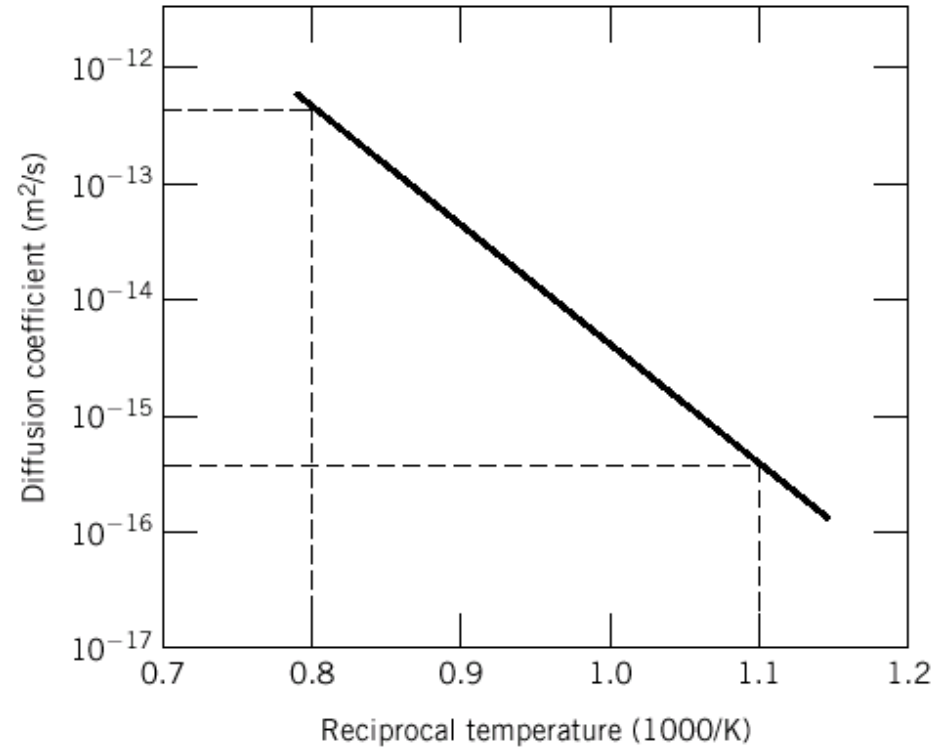
T – absolute temperature (K)

$$\ln D = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T}\right) \quad \text{or} \quad \log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T}\right)$$

Arrhenius Plots

($\ln D$) vs. ($1/T$) or ($\log D$) vs. ($1/T$)

Diffusion – Temperature Dependence (II)

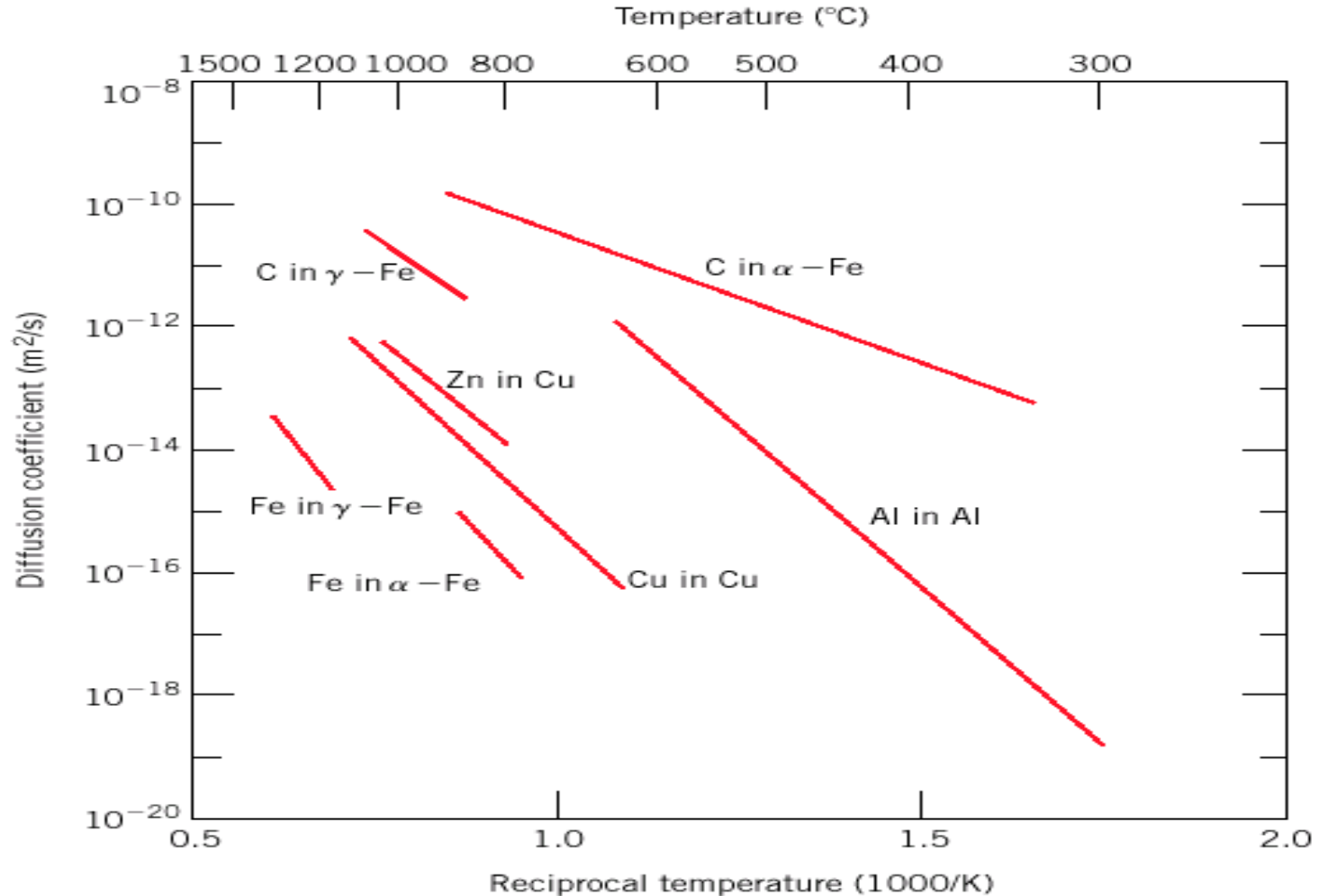


Graph of $\log D$ vs. $1/T$ has slope of $-Q_d/2.3R$,
intercept of $\ln D_0$

$$\log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T} \right)$$

$$Q_d = -2.3R \left[\frac{\log D_1 - \log D_2}{1/T_1 - 1/T_2} \right]$$

Diffusion – Temperature Dependence (III)



**Arrhenius plot:
Diffusivity for metallic systems**

Diffusion of different species

Table 5.2 A Tabulation of Diffusion Data

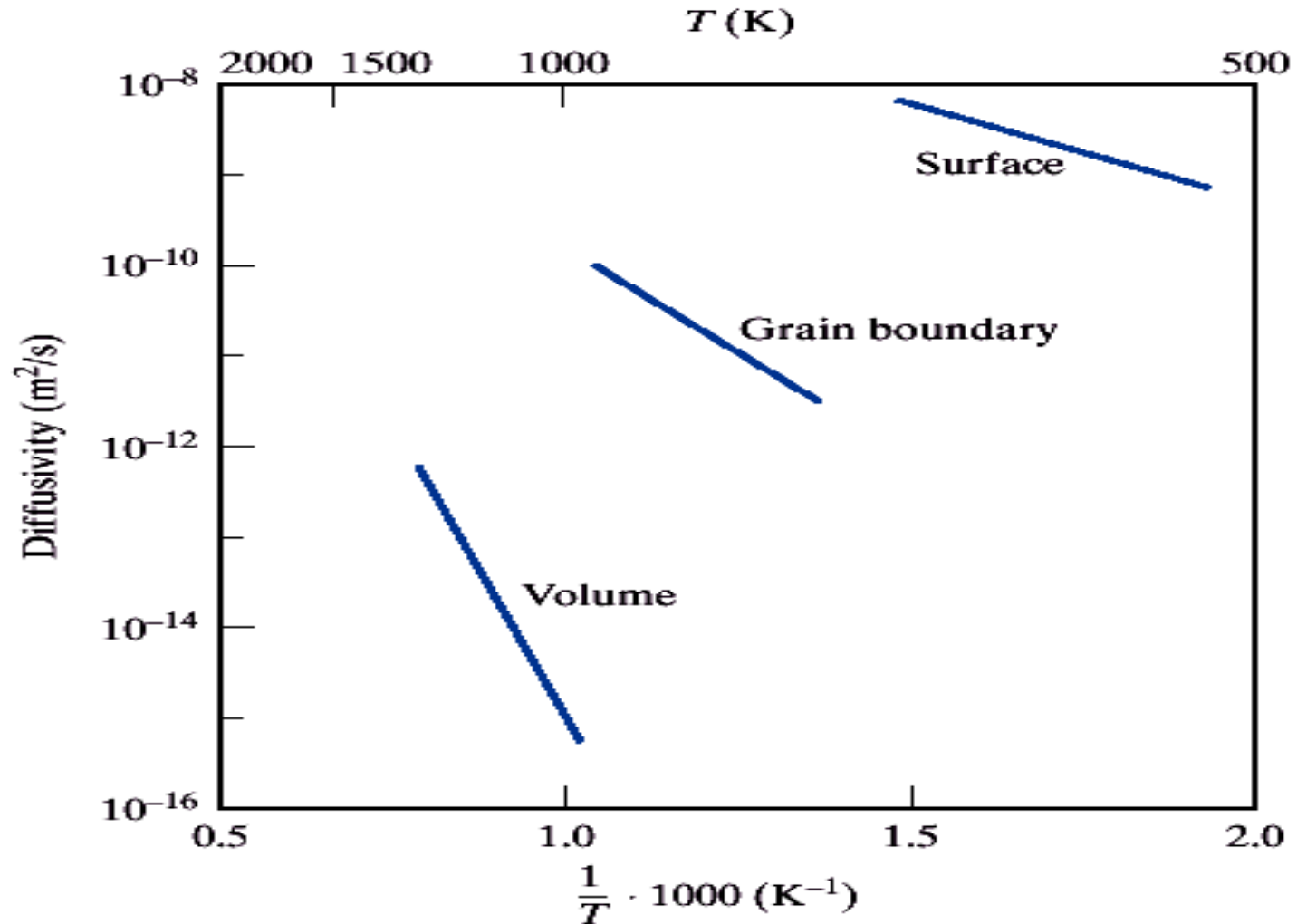
Diffusing Species	Host Metal	D_0 (m^2/s)	Activation Energy Q_d		Calculated Values	
			kJ/mol	$eV/atom$	T ($^{\circ}C$)	D (m^2/s)
Fe	α -Fe (BCC)	2.8×10^{-4}	251	2.60	500	3.0×10^{-21}
					900	1.8×10^{-15}
Fe	γ -Fe (FCC)	5.0×10^{-6}	284	2.94	900	1.1×10^{-17}
					1100	7.8×10^{-16}
C	α -Fe	6.2×10^{-7}	80	0.83	500	2.4×10^{-12}
					900	1.7×10^{-10}
C	γ -Fe	2.3×10^{-8}	148	1.53	900	5.9×10^{-12}
					1100	5.3×10^{-11}
Cu	Cu	7.8×10^{-6}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-6}	189	1.96	500	4.0×10^{-15}
Al	Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Cu	Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Mg	Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-15}
Cu	Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}

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

Smaller atoms diffuse more readily

Diffusion faster in open lattices or in open directions

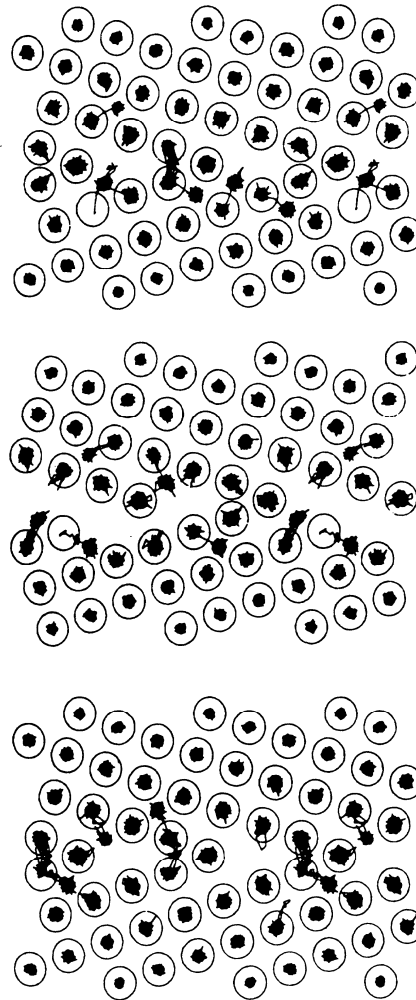
Diffusion: Role of the microstructure (I)



**Self-diffusion coefficients for Ag
Depends on diffusion path**

Grain boundaries and surfaces less restrictive

Diffusion: Role of the microstructure (II)



Plots are from computer simulations

Initial positions are shown by the circles, paths are shown by lines. See difference between mobility in the bulk and in the grain boundary.

Factors that Influence Diffusion

- **Temperature** - diffusion rate increases very rapidly with increasing temperature
- **Diffusion mechanism** - interstitial is usually faster than vacancy
- **Diffusing and host species** - D_0 , Q_d is different for every solute, solvent pair
- **Microstructure** - diffusion faster in polycrystalline vs. single crystal materials because of the rapid diffusion along grain boundaries and dislocation cores.

Quiz

1. What is diffusion?
2. What are the two necessary conditions for diffusion to occur?
3. What are the mechanisms of diffusion?
4. What is self-diffusion?
5. What is steady state diffusion? Describe Fick's first law of diffusion.
6. What is Fick's second law of diffusion?
7. What is the effect of temperature on diffusion? How is the activation energy obtained?
8. What other factors affect diffusion rate in metals?
9. Give an example of an industrial process which uses diffusion.
10. Calculate the diffusivity of carbon in γ -Fe at 927 °C.
 $D_0 = 2 \times 10^{-5} \text{ m}^2/\text{s}$ and $Q = 142 \text{ kJ/mol}$