# Chapter 5: Diffusion

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Outline

- **Diffusion mechanisms**
- **Vacancy diffusion**
- **Interstitial diffusion**
- **Impurities**
- **The 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**
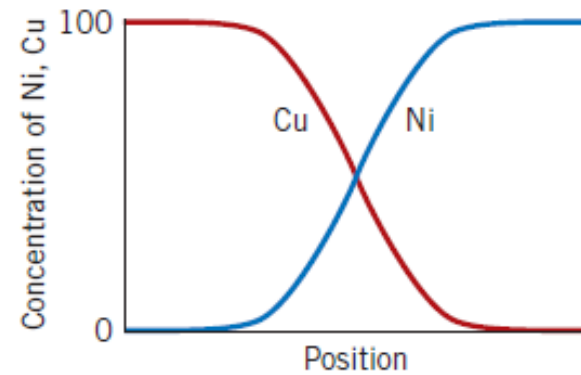
Diffusion –
How do atoms move through solids?

- Diffusion is material transport by atomic motion.

- Inhomogeneous materials can become homogeneous by diffusion. For an active diffusion to occur, the temperature should be high enough to overcome energy barriers to atomic motion.
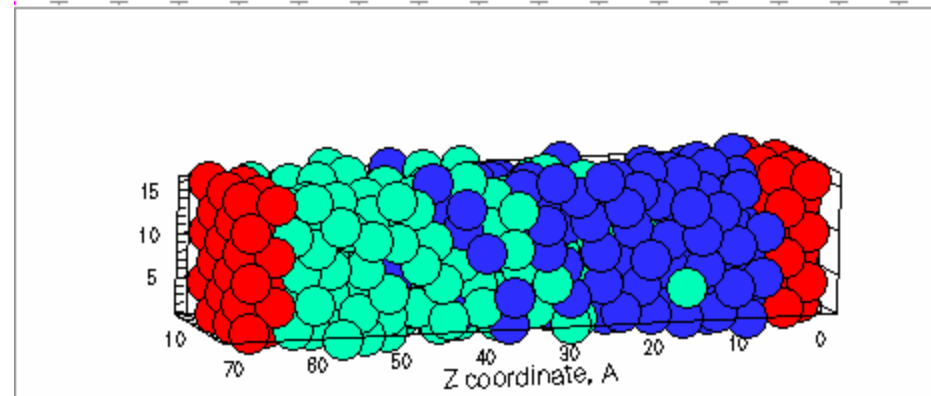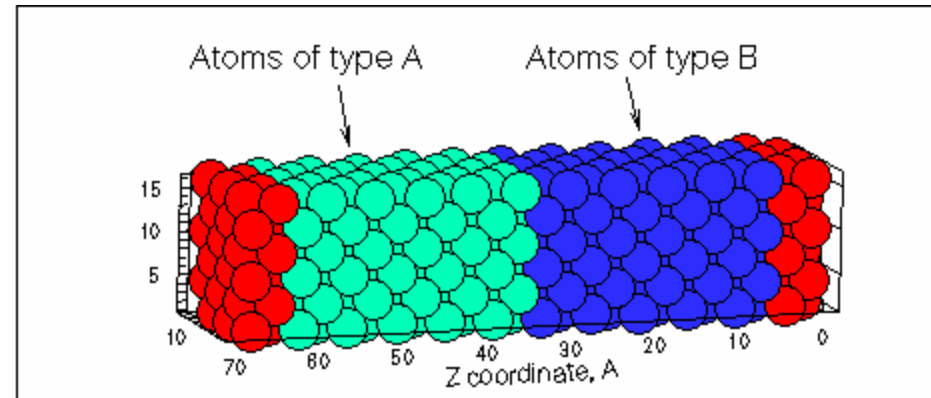
Interdiffusion and Self-diffusion

- **Interdiffusion (or impurity diffusion)** occurs in response to a **concentration gradient.**
- **Self-diffusion** is diffusion in one-component material, when all atoms that exchange positions are of the same type.

Interdiffusion

Diffusion of Cu atoms

Cu-Ni alloy

Diffusion of Ni atoms
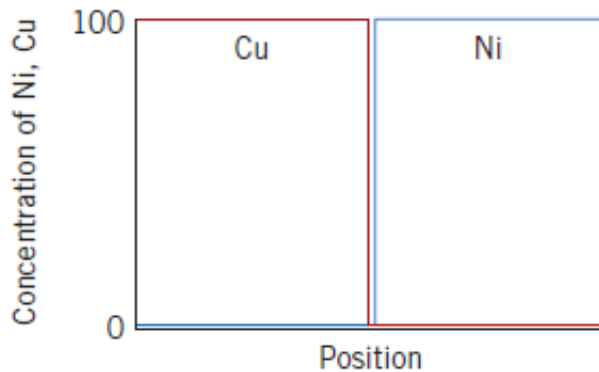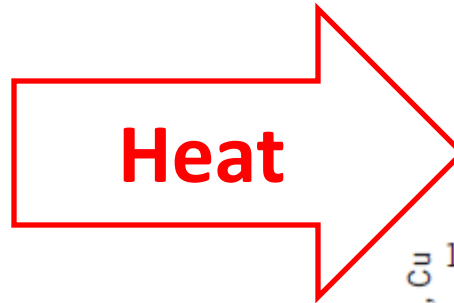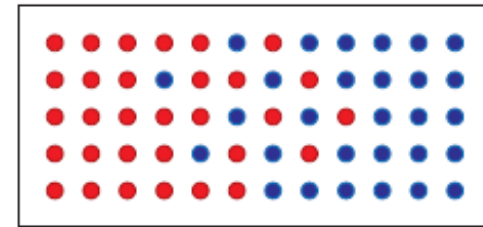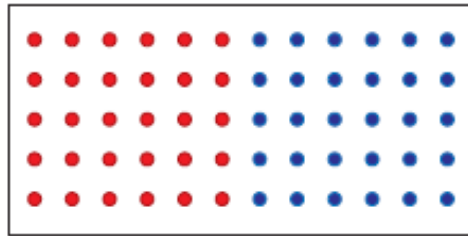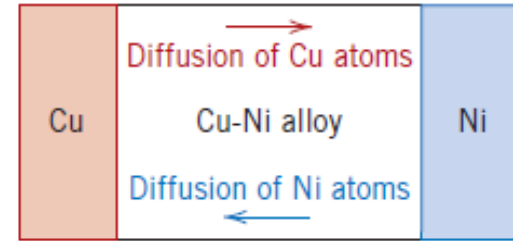
Heat

Diffusion Mechanisms

- From an atomic perspective, diffusion is just the stepwise migration of atoms from lattice site to lattice site. In fact, the atoms in solid materials are in constant motion, rapidly changing positions. For an atom to make such a move, two conditions must be met:

(1) there must be an empty adjacent site, and

(2) the atom must have sufficient energy to break bonds with its neighbor atoms and then cause some lattice distortion during the displacement.

Diffusion Mechanism Types

1. Vacancy Diffusion

2. Interstitial Diffusion

1- Vacancy diffusion mechanism

Before

After
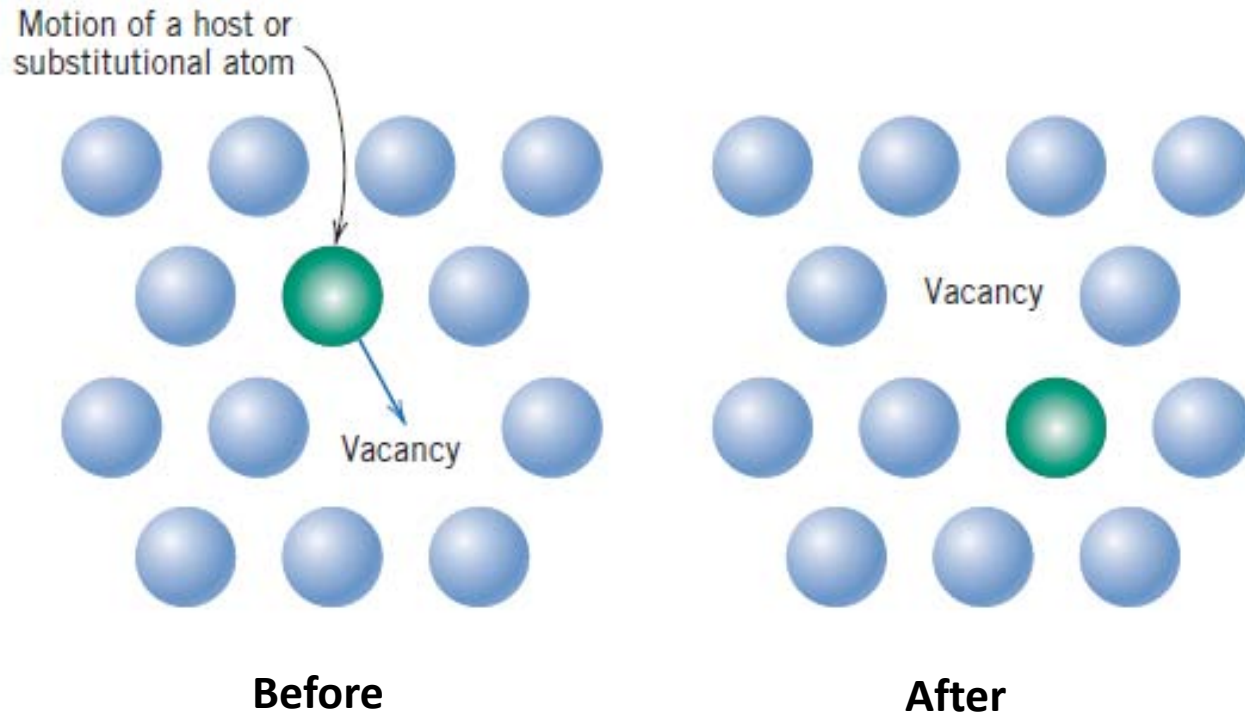
The direction of flow of atoms is opposite the vacancy flow direction.

2- Interstitial diffusion mechanism

Position of interstitial
atom before diffusion

Position of interstitial
atom after diffusion

Before   **After**
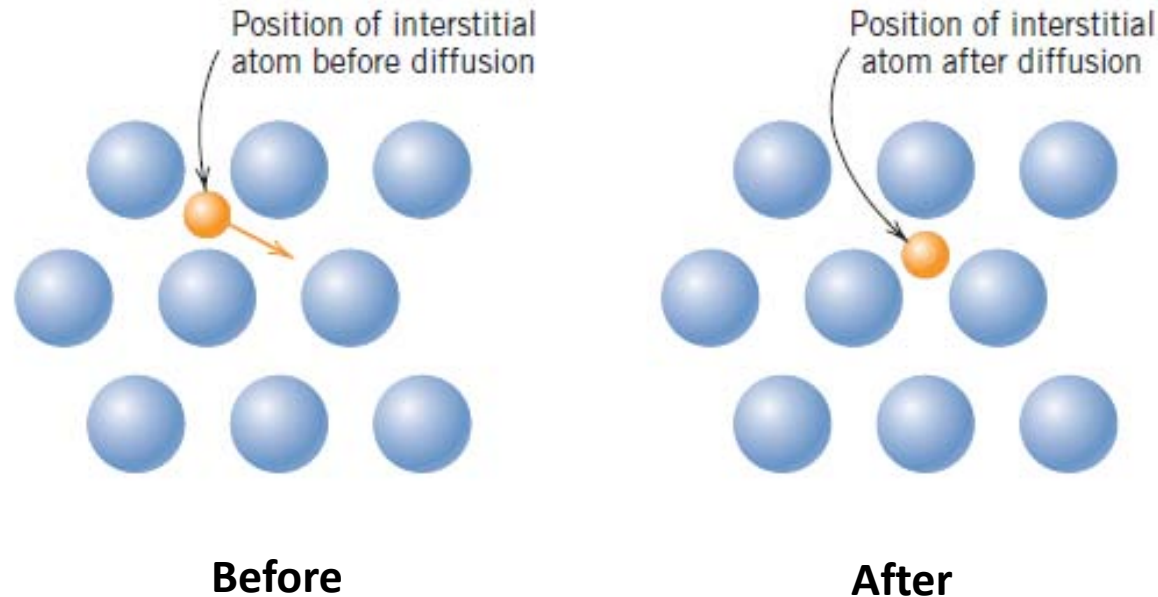
Interstitial diffusion is generally faster than vacancy diffusion because bonding of interstitials to the surrounding atoms is normally weaker and there are many more interstitial sites than vacancy sites to jump to.
Requires small impurity atoms (e.g. C, H, O) to fit into interstices in host.

Diffusion Flux

- The flux of diffusing atoms, J, is used to quantify how fast diffusion occurs. The flux is defined as either the number of atoms diffusing through unit area (A) per unit time (t) (atoms/m²-second) or the mass of atoms (M) diffusing through unit area per unit time, (kg/m²- second).

- For example, for the mass flux we can write

$$J = \frac{M}{At} \quad \textbf{Or} \approx \quad J = \frac{1}{A}\frac{dM}{dt}$$

Steady-State Diffusion
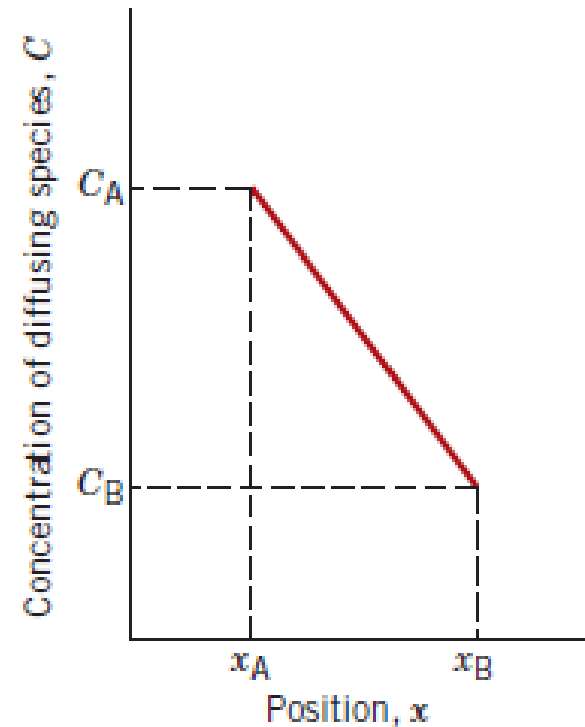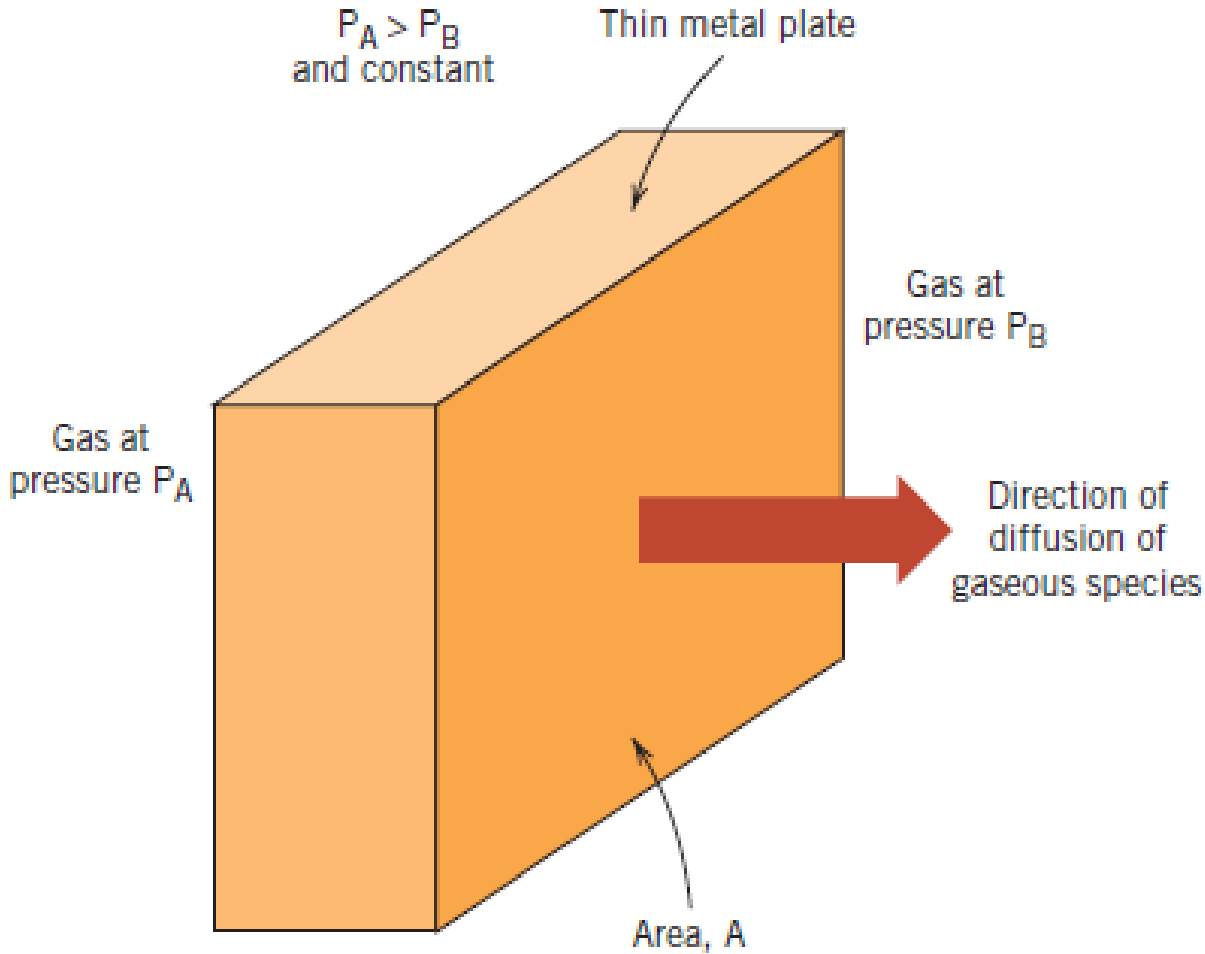
(a)

(b)

Steady-State Diffusion

- **Steady state diffusion: the diffusion flux does not** change with time.

- **Concentration profile: concentration of** atoms/molecules of interest as function of position in the sample.

- **Concentration gradient: dC/dx (Kg m^{-4}): the slope** at a particular point on concentration profile.

$$\text{concentration gradient} = \frac{dC}{dx}$$

$$\text{concentration gradient} = \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$

Steady-State Diffusion: Fick's first law

- **Fick's first law: the diffusion flux along direction x is** proportional to the concentration gradient.

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

- where **D is the diffusion coefficient**

J = flux of atoms across plane with area, A

$$= -D\left(\frac{\partial c}{\partial x}\right)$$
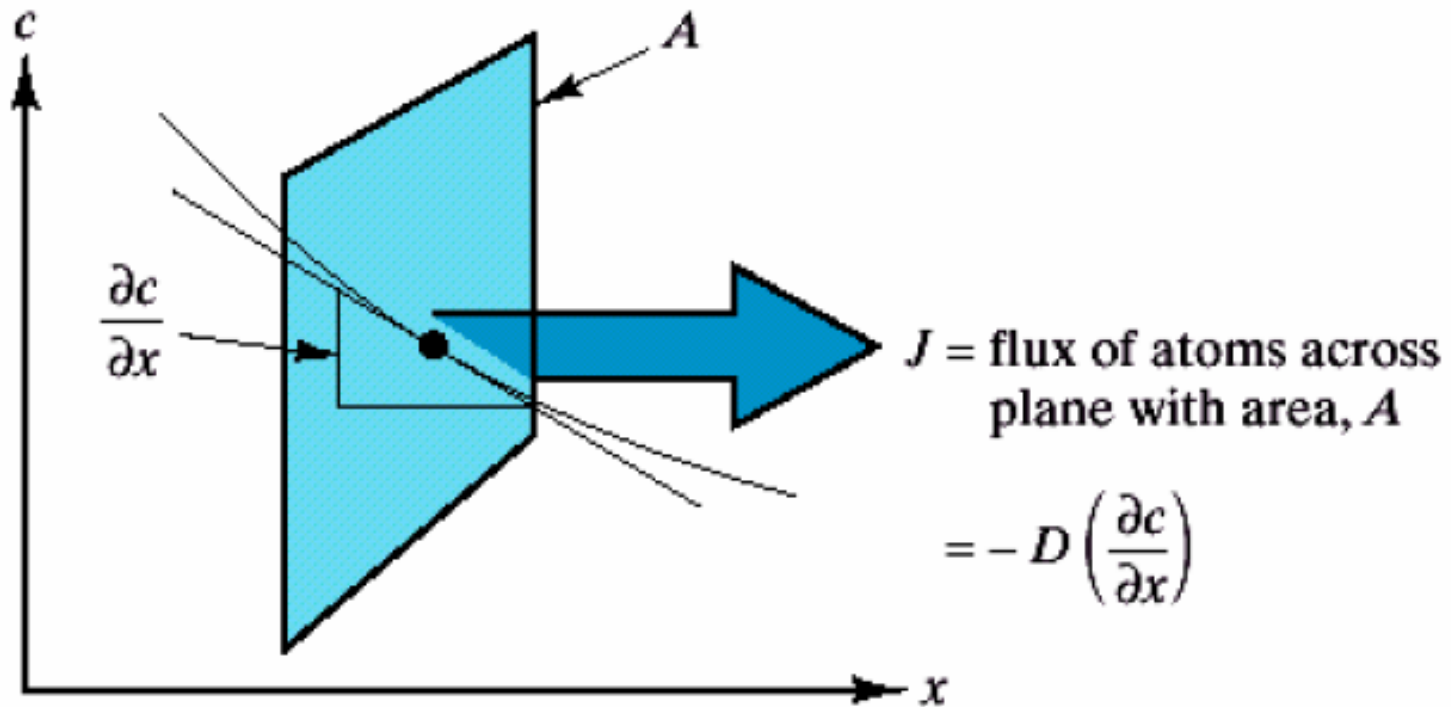
- The concentration gradient is often called the *driving force* in diffusion (but it is not a force in the mechanistic sense).
- The minus sign in the equation means that diffusion is down the concentration gradient.

Diffusion down the concentration gradient

- Why do the random jumps of atoms result in a flux of atoms from regions of high concentration towards the regions of low concentration?

Diffusion in this direction

Atoms here jump randomly both right and left

But there are not many atoms here to jump to the left
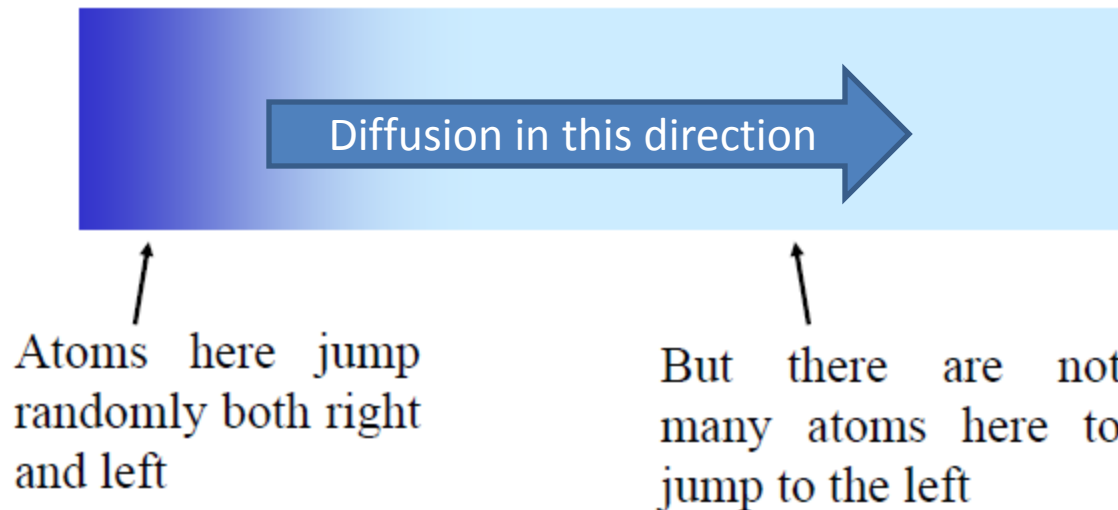
- As a result there is a net flux of atoms from left to right.

Nonsteady – State Diffusion: Fick's second law

- In many real situations the concentration profile and the concentration gradient are changing with time. The changes of the concentration profile can be described in this case by a differential equation, **Fick's second law.**

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

- Solution of this equation is concentration profile as function C(x,t):
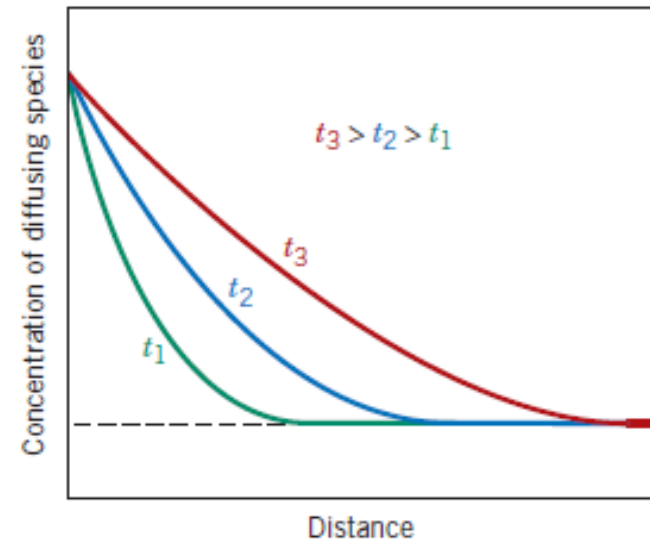
FACTORS THAT INFLUENCE DIFFUSION

1- Diffusing Species

The diffusing species as well as the host material influence the diffusion coefficient (Table 5.2). For example, there is a significant difference in magnitude between self-diffusion ($D = 3 \times 10^{-21}$) and carbon interdiffusion in iron at $500^{\circ}C$ ($D = 2.4 \times 10^{-12}$). This comparison also provides a contrast between rates of diffusion via vacancy and interstitial modes. Self-diffusion occurs by a vacancy mechanism, whereas carbon diffusion in iron is interstitial.

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	$T(°C)$	$D(m^2/s)$
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^{-5}	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^{-5}	148	1.53	900	5.9×10^{-12}
					1100	5.3×10^{-11}
Cu	Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-5}	189	1.96	500	4.0×10^{-18}
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^{-13}
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.

FACTORS THAT INFLUENCE DIFFUSION

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

2- Temperature

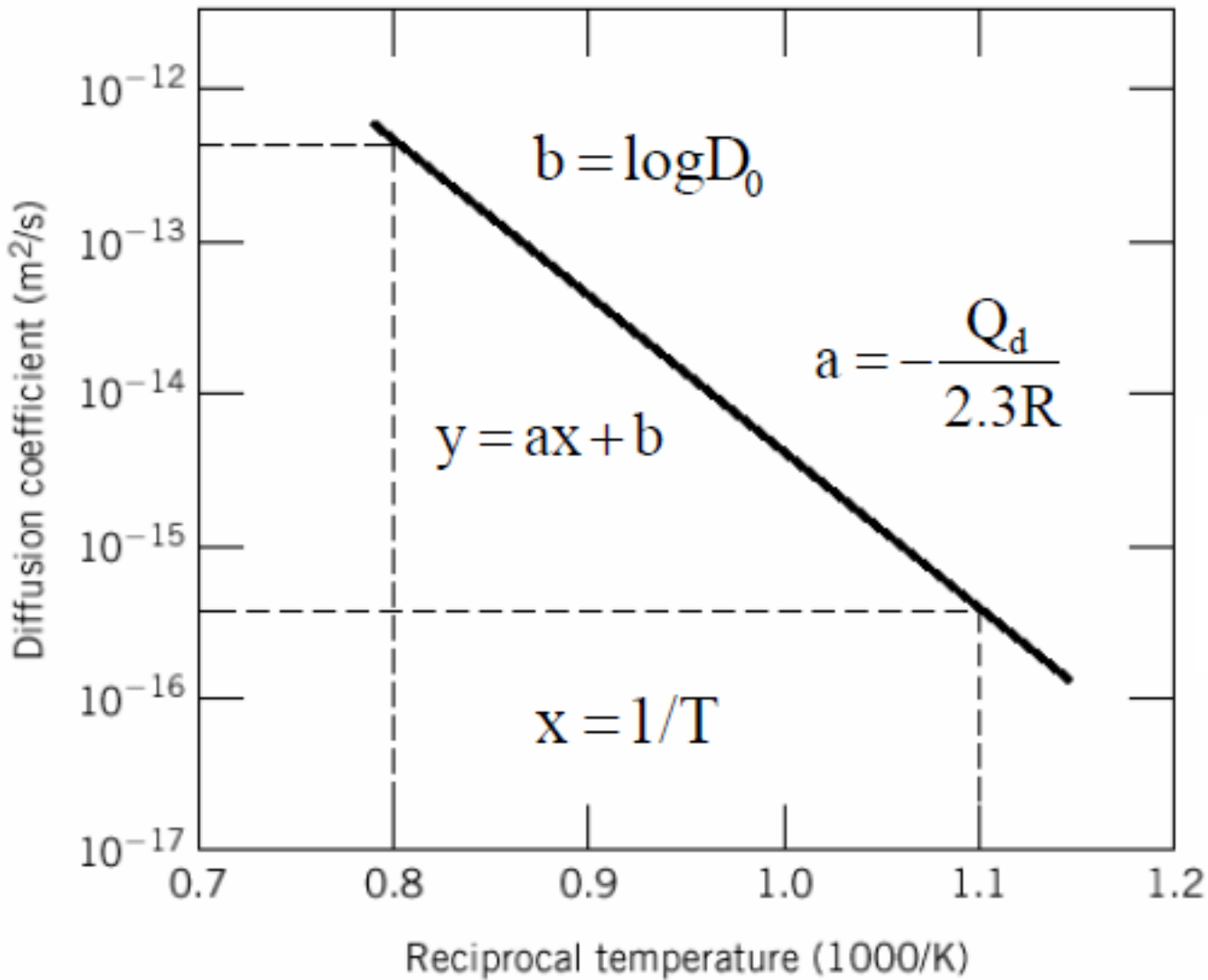- Diffusion coefficient is the measure of mobility of diffusing species.

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

- D_0 – temperature-independent preexponential (m^2/s)
- Q_d – the activation energy for diffusion (J/mol or eV/atom)
- R – the gas constant (8.31 J/mol-K or 8.62×10^{-5} eV/atom-K)
- T – absolute temperature (K)
- We can find D_0 And Q_d By drawing Arrhenius plots (lnD versus 1/T or logD versus 1/T)

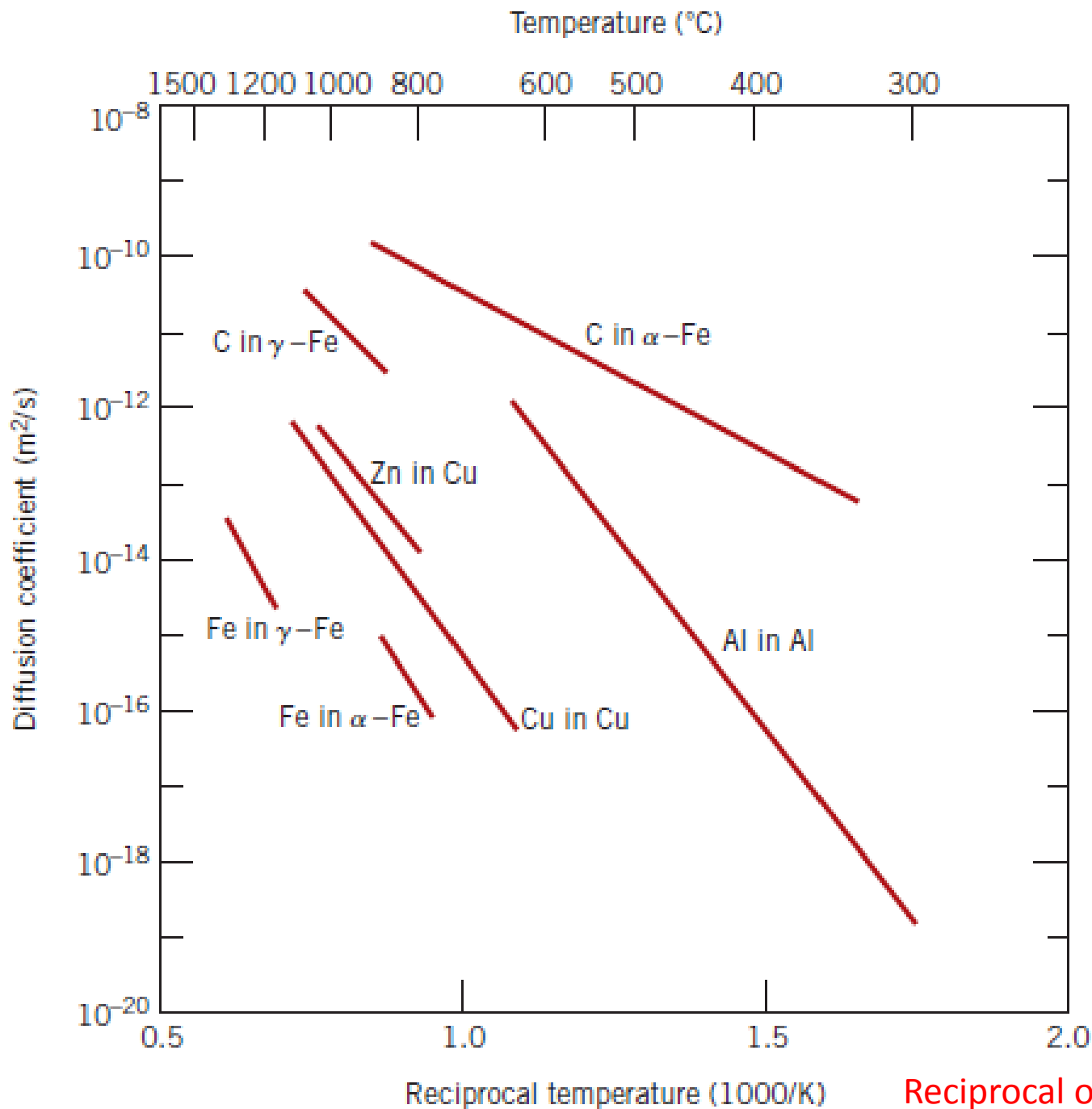$$\ln D = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T}\right)$$

$$Y = b + a \; X$$

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

The graph shows $\log D$ (Diffusion coefficient in m^2/s) on the y-axis versus Reciprocal temperature ($1000/K$) on the x-axis.

$$b = \log D_0$$

$$a = -\frac{Q_d}{2.3R}$$

$$y = ax + b$$

$$x = 1/T$$

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

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

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

Figure 5.7 Plot of the logarithm of the diffusion coefficient versus the reciprocal of absolute temperature for several metals. [Data taken from E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1992.]

Reciprocal of temperature = 1/T

FACTORS THAT INFLUENCE DIFFUSION

3- Interstitial and vacancy diffusion mechanisms

- Diffusion of interstitials is typically faster as compared to the vacancy diffusion mechanism (self-diffusion or diffusion of substitutional atoms).

- Smaller atoms cause less distortion of the lattice during migration and diffuse more readily than big ones (the atomic diameters decrease from C to N to H).

- Diffusion is faster in open lattices or in open directions

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

Interstitial diffusion mechanism

Impurity	D_0, mm^2/s^{-1}	Q_d, kJ/mol
C in FCC Fe	23	138
C in BCC Fe	1.1	87
N in FCC Fe	0.34	145
N in BCC Fe	0.47	77
H in FCC Fe	0.63	43
H in BCC Fe	0.12	15

Vacancy diffusion mechanism

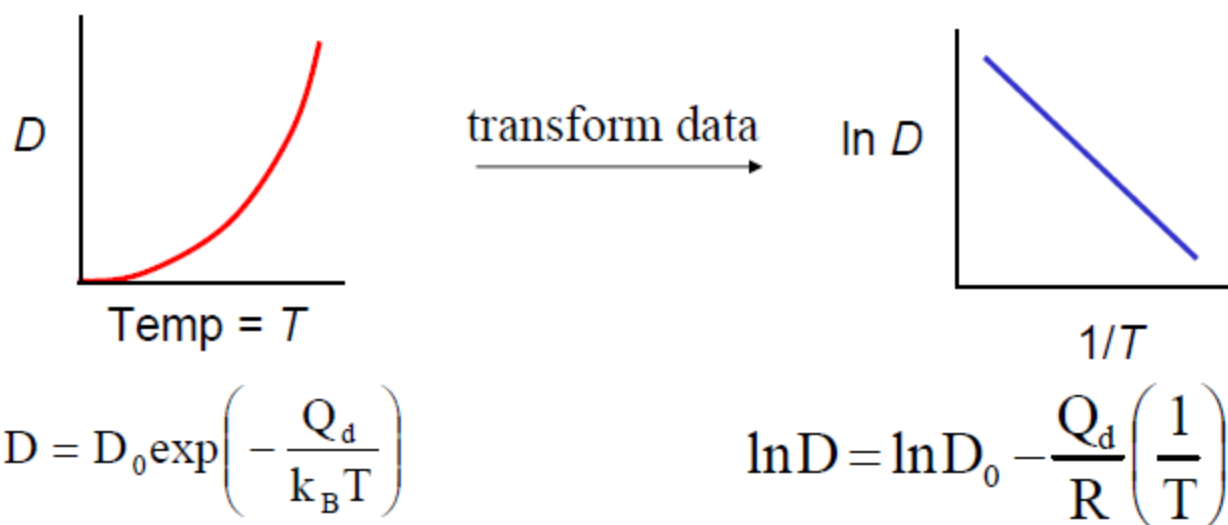|	D_0, mm^2/s^{-1}	Q_d, kJ/mol
Fe in FCC Fe	65	279
Fe in BCC Fe	410	246
Ni in Cu	230	242
Si in Si	180000	460

Example: Temperature dependence of D

At 300°C the diffusion coefficient and activation energy for Cu in Si are

$$D(300°C) = 7.8 \text{ x } 10^{-11} \text{ m}^2/\text{s}$$
$$Q_d = 41.5 \text{ kJ/mol}$$

What is the diffusion coefficient at 350°C?

transform data

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

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

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

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

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

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

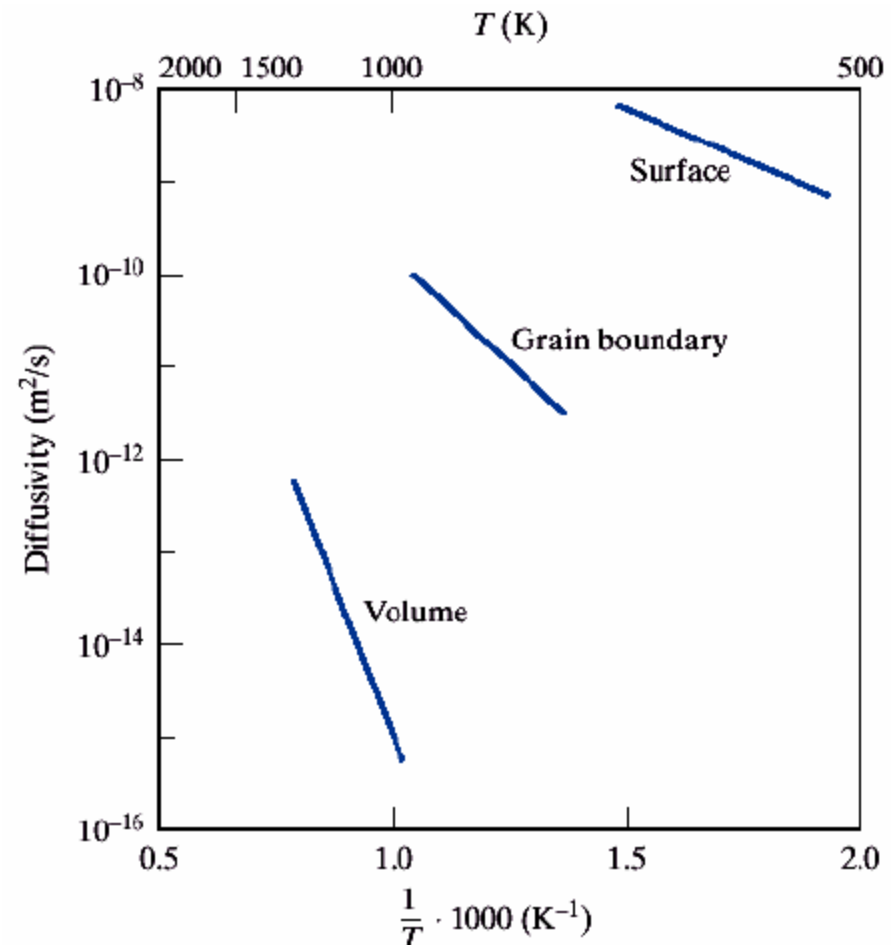$T_1 = 273 + 300 = 573\,\text{K}$

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

$$D_2 = (7.8\times10^{-11}\ \text{m}^2/\text{s})\exp\left[\frac{-41{,}500\ \text{J/mol}}{8.314\ \text{J/mol-K}}\left(\frac{1}{623\ \text{K}} - \frac{1}{573\ \text{K}}\right)\right]$$

$$\boxed{D_2 = 15.7\times10^{-11}\ \text{m}^2/\text{s}}$$

FACTORS THAT INFLUENCE DIFFUSION

4- Role of the microstructure

- Self-diffusion coefficients for Ag depend on the diffusion path. In general the diffusivity is greater through less restrictive structural regions – grain boundaries, dislocation cores, external surfaces.

- The plots are from the computer simulation by T. Kwok, P. S. Ho, and S. Yip. Initial atomic positions are shown by the circles, trajectories of atoms are shown by lines. We can see the difference between atomic mobility in the bulk crystal and in the grain boundary region.
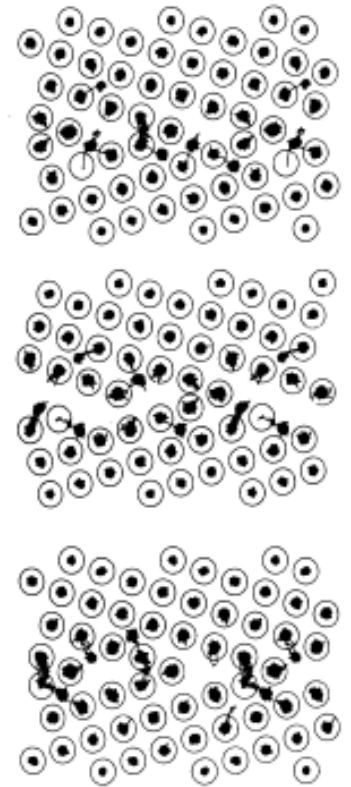
Example: Diffusion in nanocrystalline materials
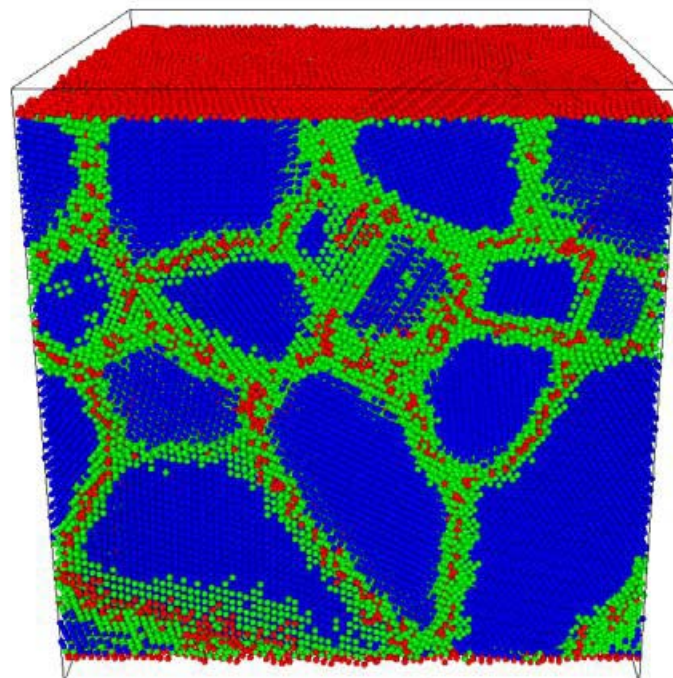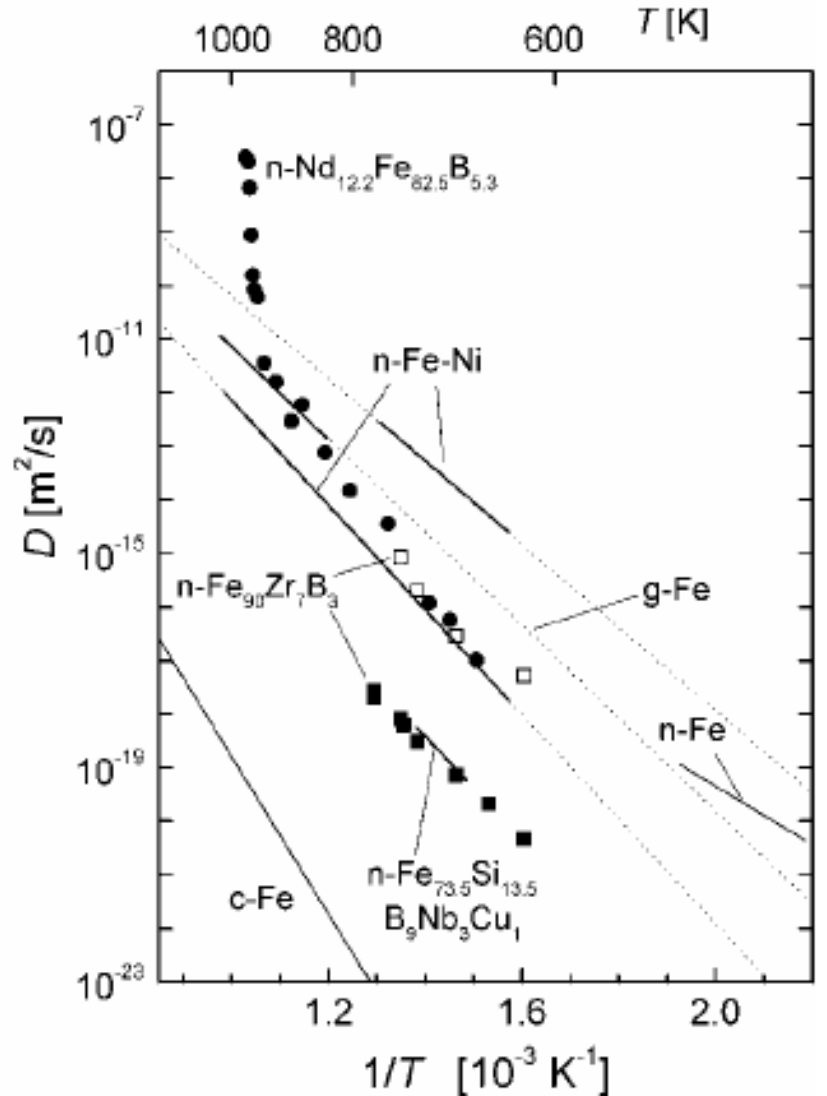
Lin *et al. J. Phys. Chem. C* **114, 5686, 2010**

Arrhenius plots for ^{59}Fe diffusivities in nanocrystalline Fe and other alloys compared to the crystalline Fe (ferrite). [Wurschum *et al. Adv. Eng. Mat. 5, 365, 2003]*

Factors that influence diffusion: Summary

- **Temperature -** diffusion rate increases very rapidly with increasing temperature

- **Diffusion mechanism –** diffusion by interstitial mechanism is usually faster than by vacancy mechanism.

- **Diffusing and host species –** D_0, Q_d are different for every solute, solvent pair.

- **Microstructure -** diffusion is faster in polycrystalline materials compared to single crystals because of the accelerated diffusion along grain boundaries.

Diffusion in material processing 1

- **Case Hardening: Hardening the surface of a metal by** exposing it to impurities that diffuse into the surface region and increase surface hardness.

- Common example of case hardening is carburization of steel. Diffusion of carbon atoms (interstitial mechanism) increases concentration of C atoms and makes iron (steel) harder.

Diffusion in material processing 2

- **Doping silicon with phosphorus for *n-type semiconductors.***

- Process of doping:
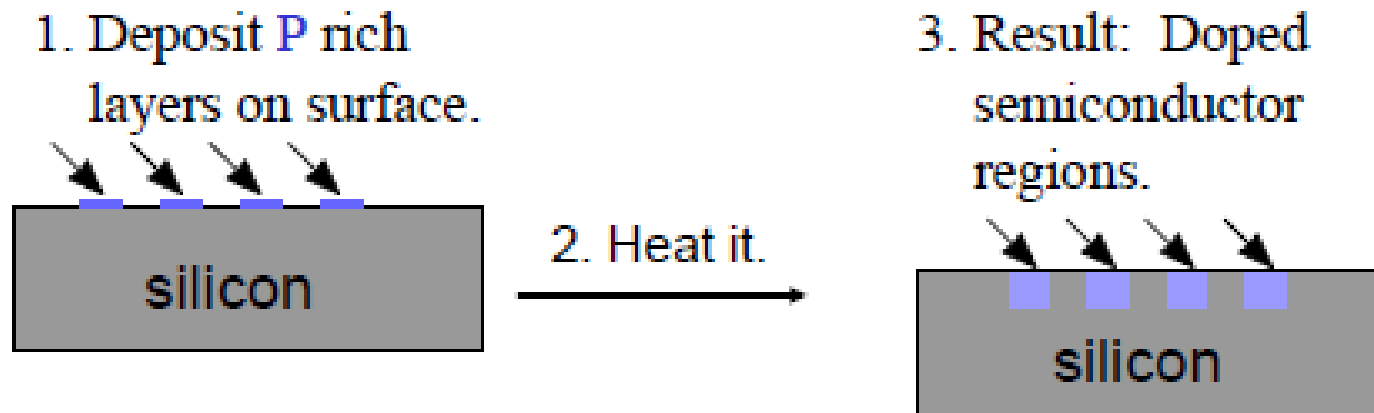
Summary

Make sure you understand language and concepts:

- ➤ Activation energy
- ➤ Concentration gradient
- ➤ Diffusion
- ➤ Diffusion coefficient
- ➤ Diffusion flux
- ➤ Driving force
- ➤ Fick's first and second laws
- ➤ Interdiffusion
- ➤ Interstitial diffusion
- ➤ Self-diffusion
- ➤ Steady-state diffusion
- ➤ Nonsteady-state diffusion
- ➤ Temperature dependence of D
- ➤ Vacancy diffusion