Chapter 5: Diffusion in Solids

ISSUES TO ADDRESS...

- How does diffusion occur?
- Why is it an important part of processing?
- How can the rate of diffusion be predicted for some simple cases?
- How does diffusion depend on structure and temperature?

Diffusion

Diffusion - **The phenomena that occur during a heat treatment almost always involve atomic diffusion.**

Diffusion - Mass(material) transport by atomic motion, or
Matter is transported through matter.

Mechanisms

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

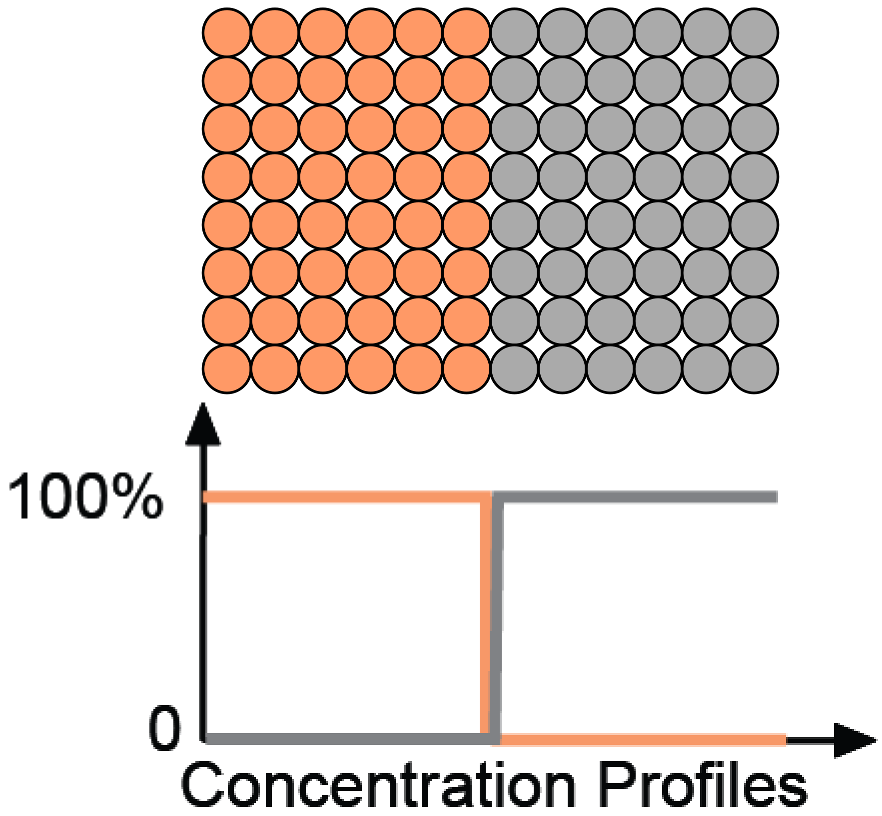
Inter-diffusion – atoms of one metal diffuse into another

self-diffusion - Diffusion also occurs for pure metals, but all atoms exchanging positions are of the same type

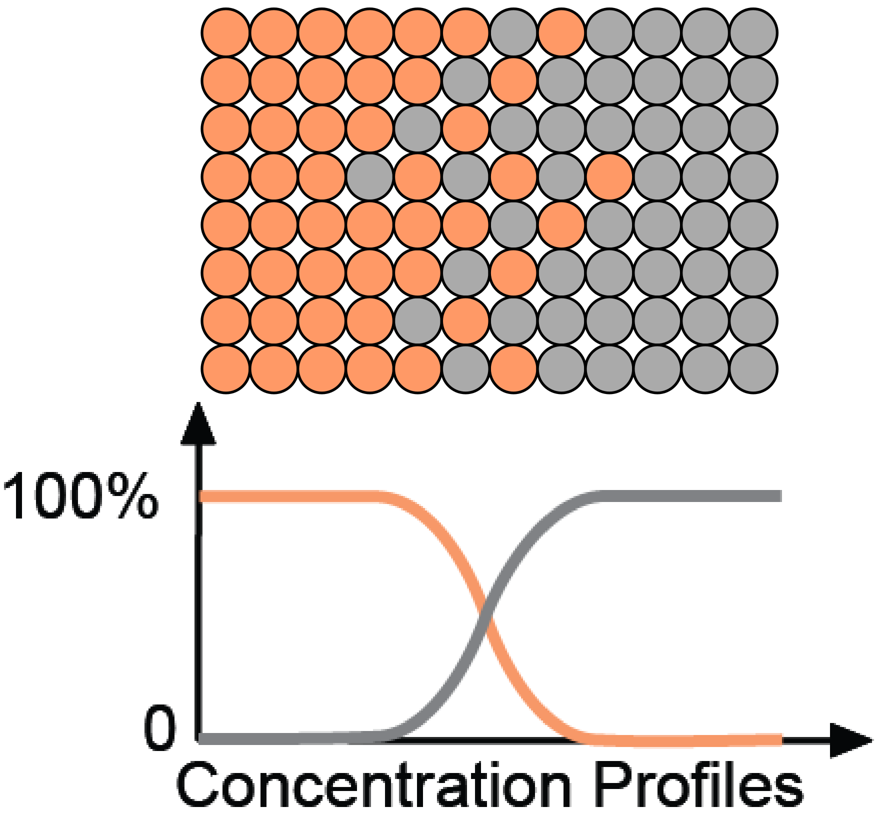
Diffusion

- Interdiffusion: In an alloy, atoms tend to migrate from regions of high concentration to regions of low conc. after high temp.(below melting temp.) heat treatment

Initially



After some time

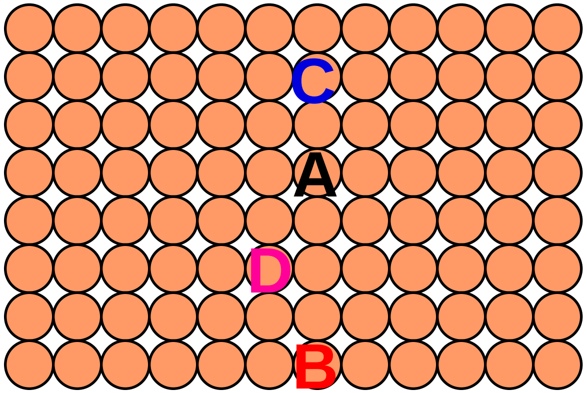


Diffusion

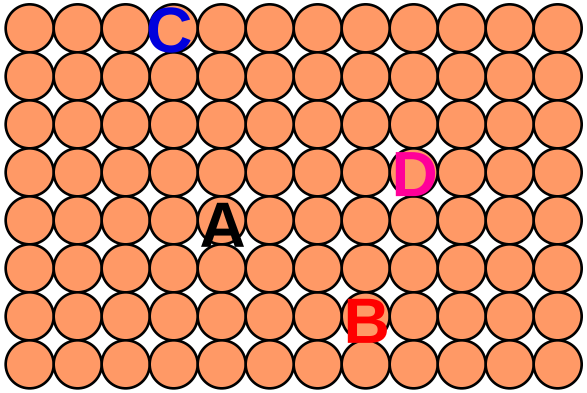
- Self-diffusion: (for pure material)

In an elemental solid, atoms also migrate.(no compositional change)

Label some atoms



After some time



Diffusion Mechanisms

- 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.

- this energy is vibrational in nature, increases with rising temperature.
- two models for metallic diffusion.
  - Vacancy diffusion
  - Interstitial diffusion

ATOMIC VIBRATIONS

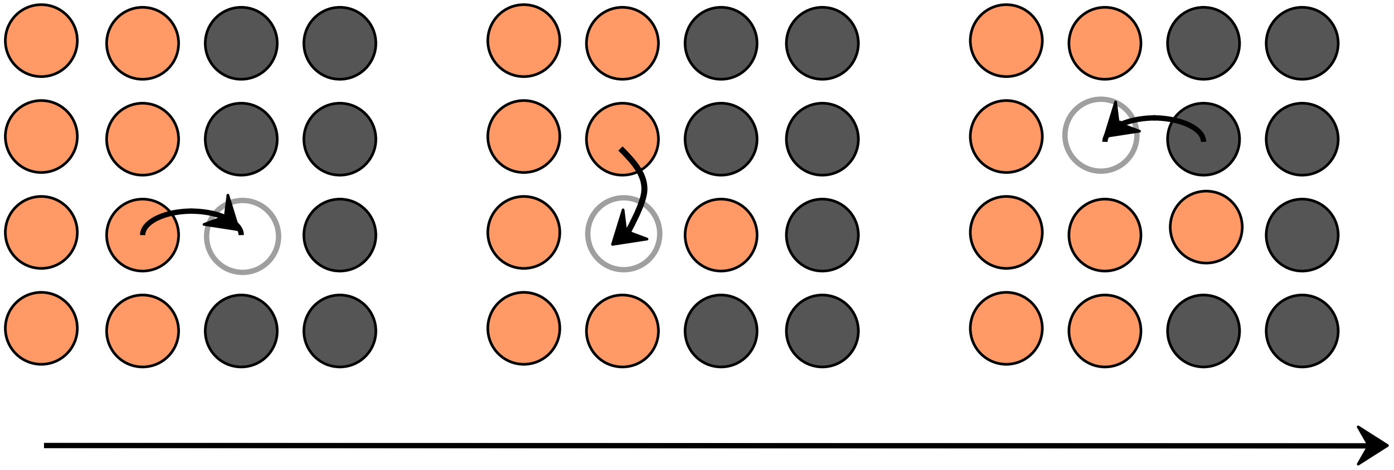
- **Every atom in a solid material is vibrating very rapidly about its lattice position within the crystal.**
- **At any instant of time not all atoms vibrate at the same frequency and amplitude, nor with the same energy.**
- **With rising temperature, this average energy increases, and, in fact, the temperature of a solid is really just a measure of the average vibrational activity of atoms and molecules.**
- **Many properties and processes in solids are manifestations of this vibrational**
- **atomic motion. For example, melting occurs when the vibrations are vigorous enough to rupture large numbers of atomic bonds.**

Diffusion Mechanisms

Vacancy Diffusion:

- atoms exchange with vacancies
- Both self-diffusion and inter-diffusion occur by this mechanism; for the latter, the impurity atoms must substitute for host atoms.

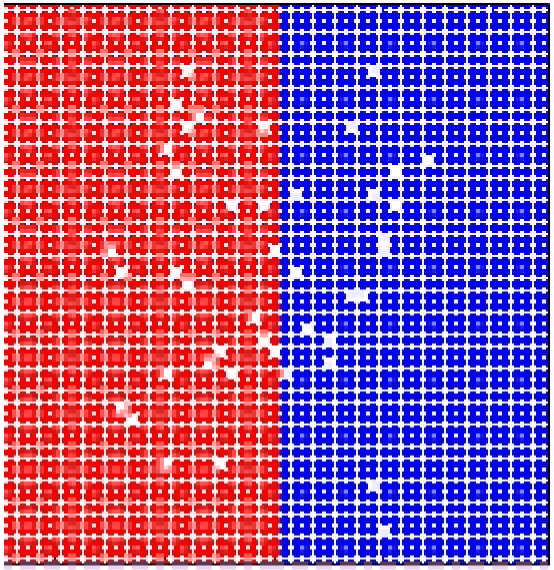
- rate depends on:
  --number of vacancies(increases with rising temp.)
  --activation energy to exchange(increases with rising temp.)



increasing elapsed time

Diffusion Simulation

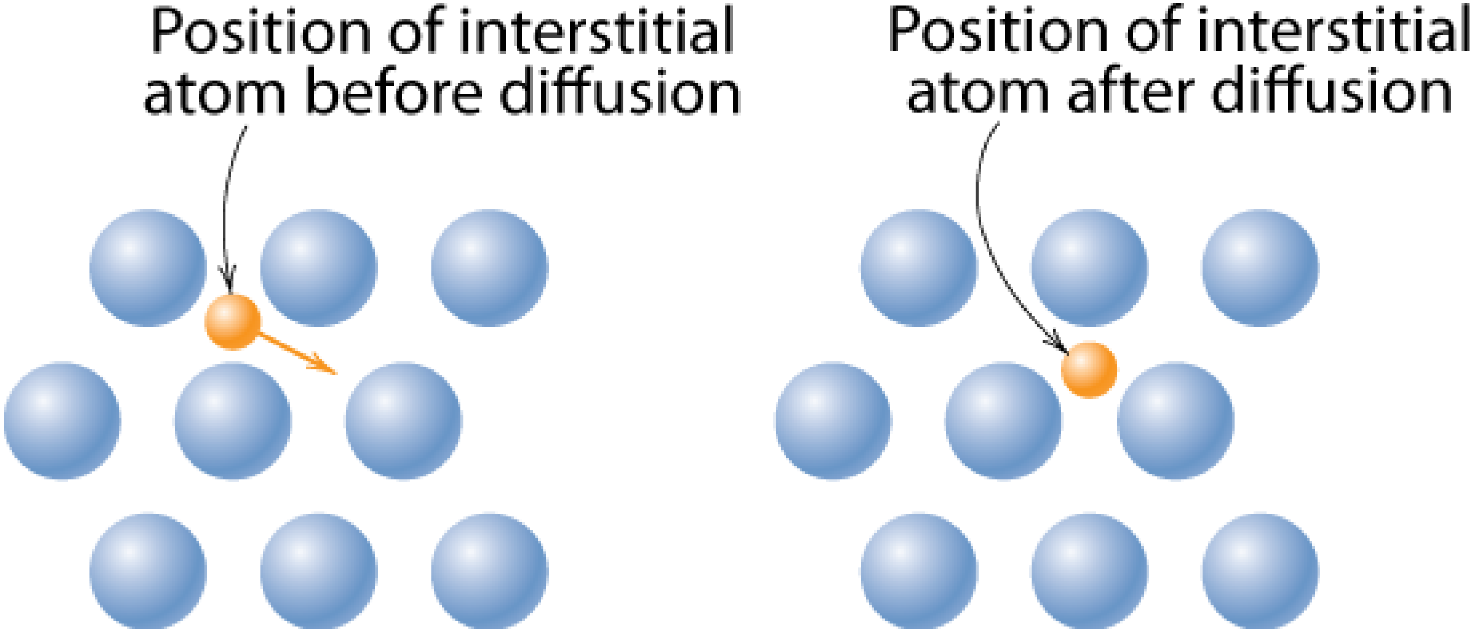
- Simulation of inter-diffusion across an interface:



- Rate of substitutional diffusion depends on:
  - --vacancy concentration
  - --frequency of jumping.

Diffusion Mechanisms

- Interstitial diffusion – smaller atoms can diffuse between atoms.(for inter-diffusion)



More rapid than vacancy diffusion

Processing Using Diffusion

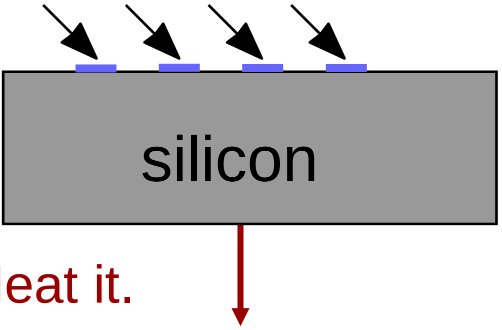
- Case Hardening:
  - --Diffuse carbon atoms into the host iron atoms at the surface.
  - --Example of interstitial diffusion is a case hardened gear.

- Result: The presence of C atoms makes iron (steel) harder and more resistance to failure by fatigue.

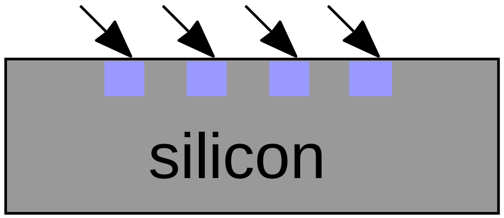
Processing Using Diffusion

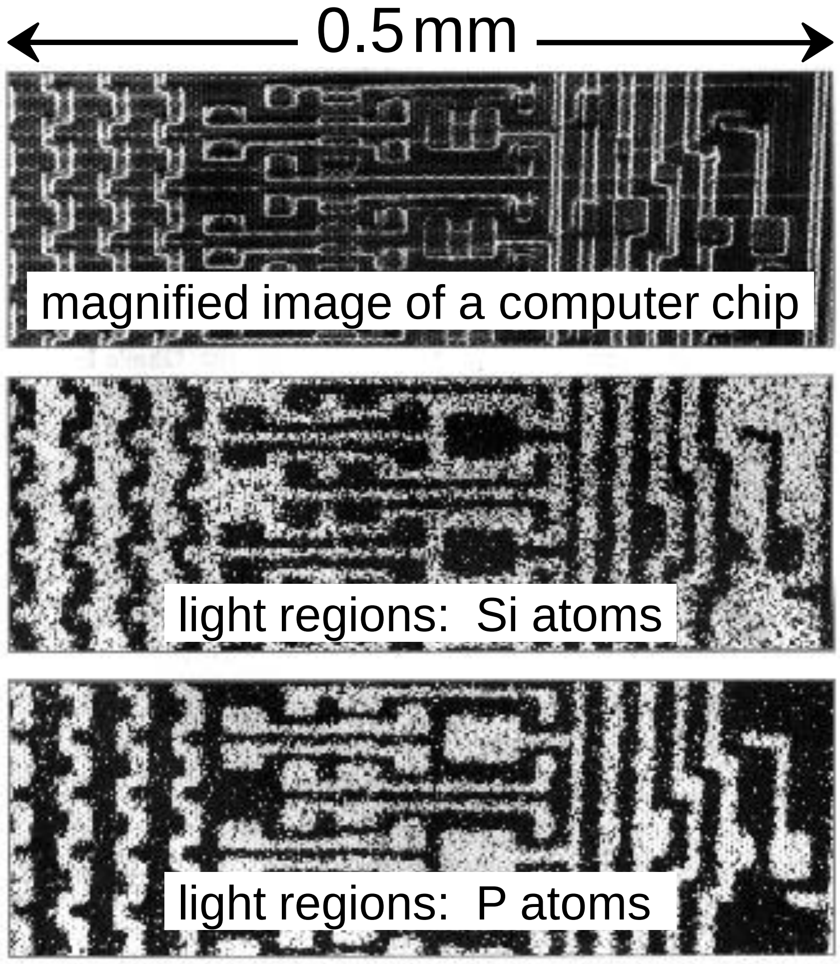
- Doping silicon with phosphorus for *n*-type semiconductors:
- Process:

1. Deposit P rich layers on surface.



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





Diffusion

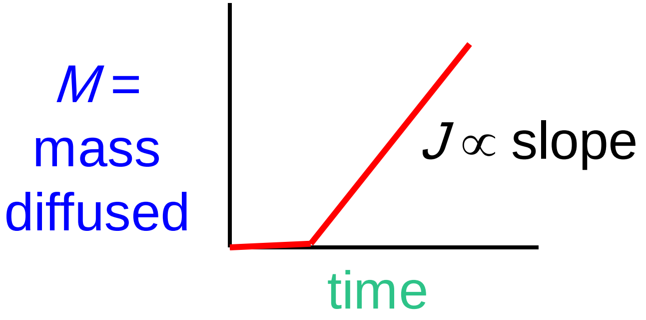
***Diffusion flux (J),* defined as the mass (or, equivalently, the number of atoms) M diffusing through and perpendicular to a unit cross-sectional area of solid per unit of time.**

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

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

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

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

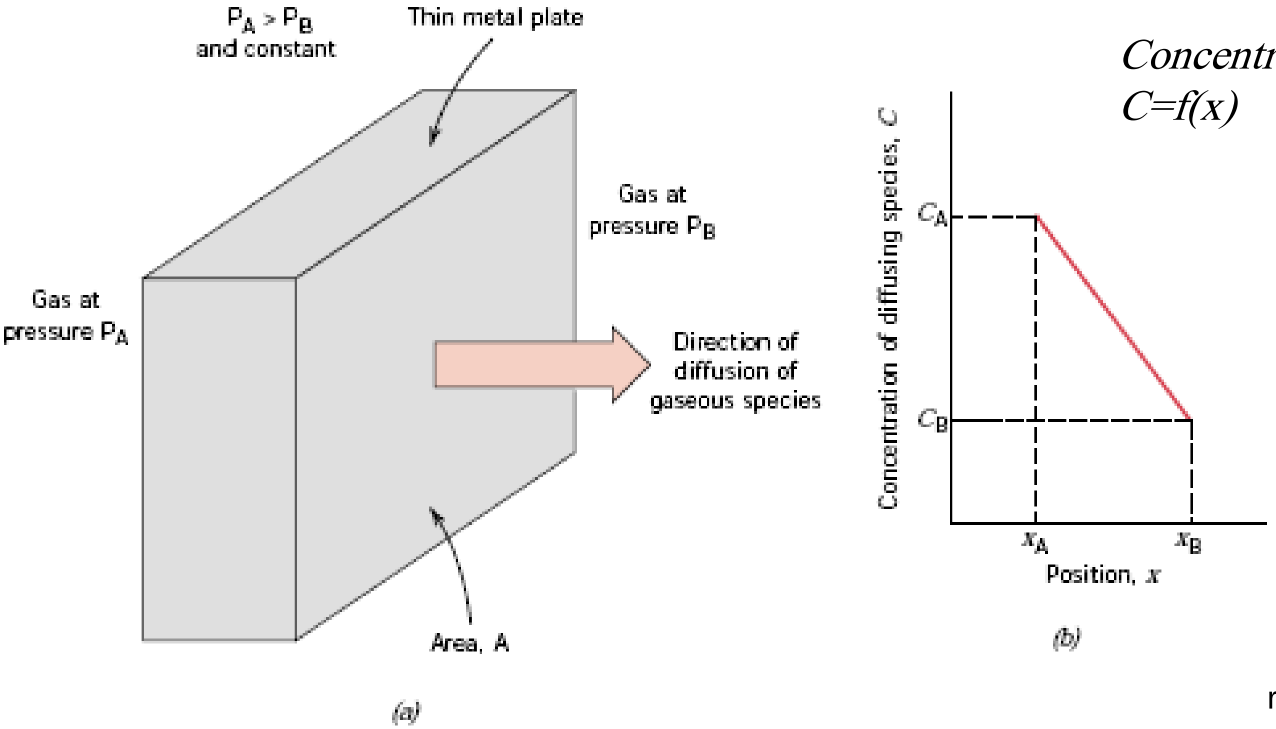


Steady-State Diffusion

- **The diffusion flux does not change with time**

  or, there is no change in concentration with time

- **example of steady-state diffusion is the diffusion of atoms of a gas through a plate of metal for which the concentrations (or pressures) of the diffusing species on both surfaces of the plate are held constant**

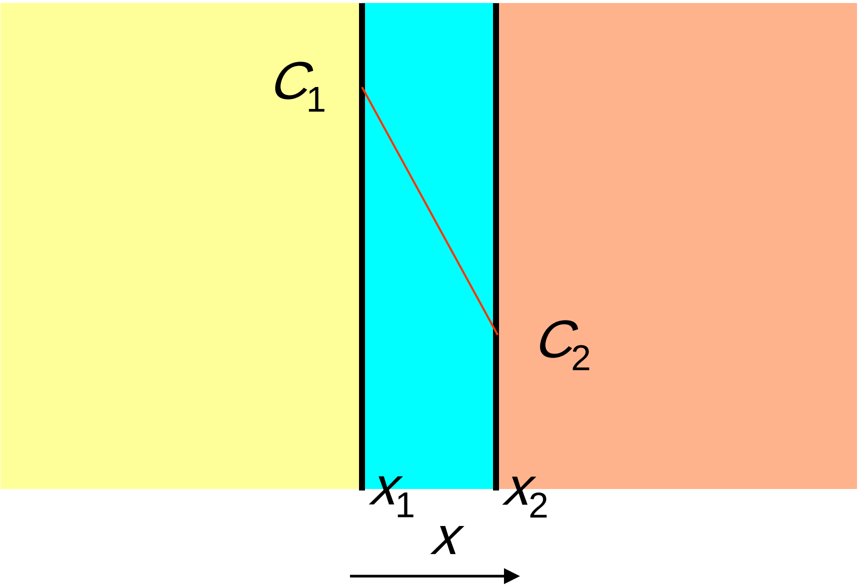


Concentration profile
$C=f(x)$

Steady-State Diffusion

Rate of diffusion independent of time

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



Fick’s first law of diffusion

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

$D \equiv$ diffusion coefficient (diffusivity)atomic conductivity

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

Fick`s first law of diffusion

A negative sign because from higher to lower concentration

One practical example of steady-state diffusion is found in the purification of hydrogen gas. One side of a thin sheet of palladium metal is exposed to the impure gas composed of hydrogen and other gaseous species such as nitrogen, oxygen, and water vapor. The hydrogen selectively diffuses through the sheet to the opposite side, which is maintained at a constant and lower hydrogen pressure.

The diffusivity values depend on many variables

1. **The type of diffusion mechanism**

(ex. Carbon diffuse interstitial in the BCC or FCC iron lattice. Copper atoms diffuse substatutionally in an aluminum solvent lattice since both the copper and aluminum atoms are about the same size.

2. **The temperature of diffusion(increasing tem. Increasing D)**
3. **The type of crystal structure of the solvent lattice**
4. **The type of crystal imperfections present in the region of solid state diffusion**
5. **The concentration of the diffusing species(the higher concentration the more D)**

Example: Chemical Protective Clothing (CPC)

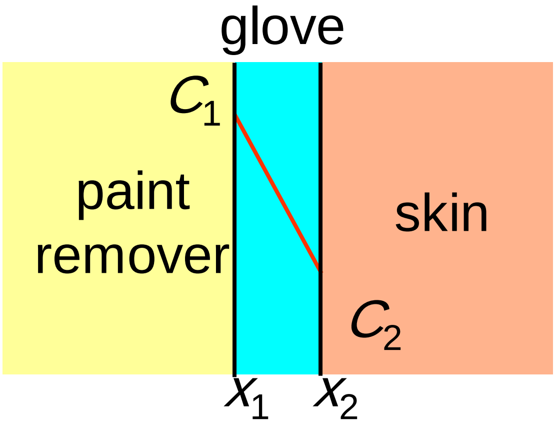
- Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using this paint remover, protective gloves should be worn.
- If rubber gloves (0.04 cm thick) are used, what is the diffusive flux of methylene chloride through the glove?
- Data:
  - diffusion coefficient in rubber:

    $D = 110 \times 10^{-8}\ \text{cm}^2/\text{s}$
  - surface concentrations: $C_1 = 0.44\ \text{g/cm}^3$

    $C_2 = 0.02\ \text{g/cm}^3$

Example (cont).

- Solution – assuming linear conc. gradient



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

Data:

$D = 110 \times 10^{-8}\ \mathrm{cm^2/s}$

$C_1 = 0.44\ \mathrm{g/cm^3}$

$C_2 = 0.02\ \mathrm{g/cm^3}$

$x_2 - x_1 = 0.04\ \mathrm{cm}$

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

Non-steady State Diffusion

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

Fick's Second Law

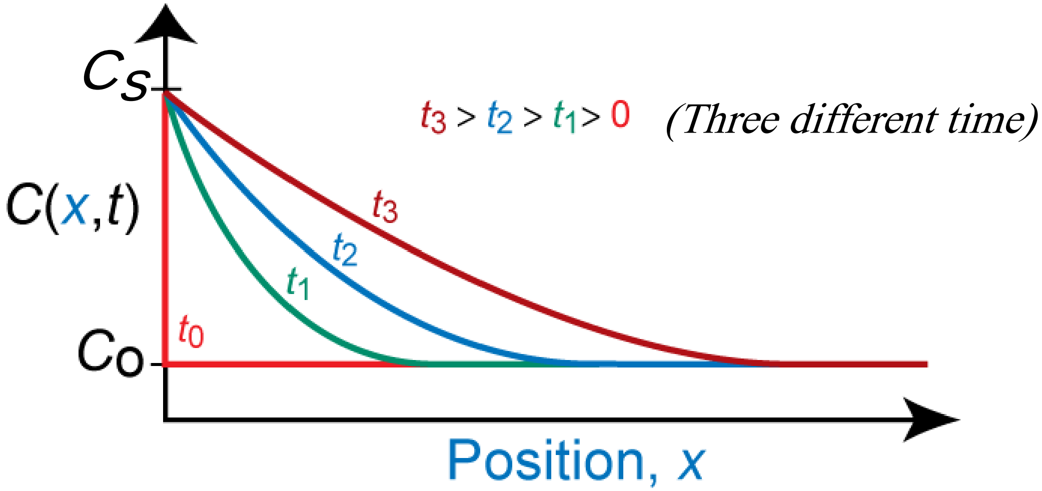
$$\boxed{\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}}$$

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

Surface conc., C_S of Cu atoms

pre-existing conc., C_o of copper atoms



Boundary conditions(for solving Fick`s second law)

at $t = 0$, $C = C_o$ for $0 \le x \le \infty$(before diff.process begin)

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

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

Solution:

Application these B.C to equation yield the solution

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

$C(x)$ = Conc. at depth x after time t

erf (z) = error function

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

erf(z) values are given in Table 6.1

X – distance from surface

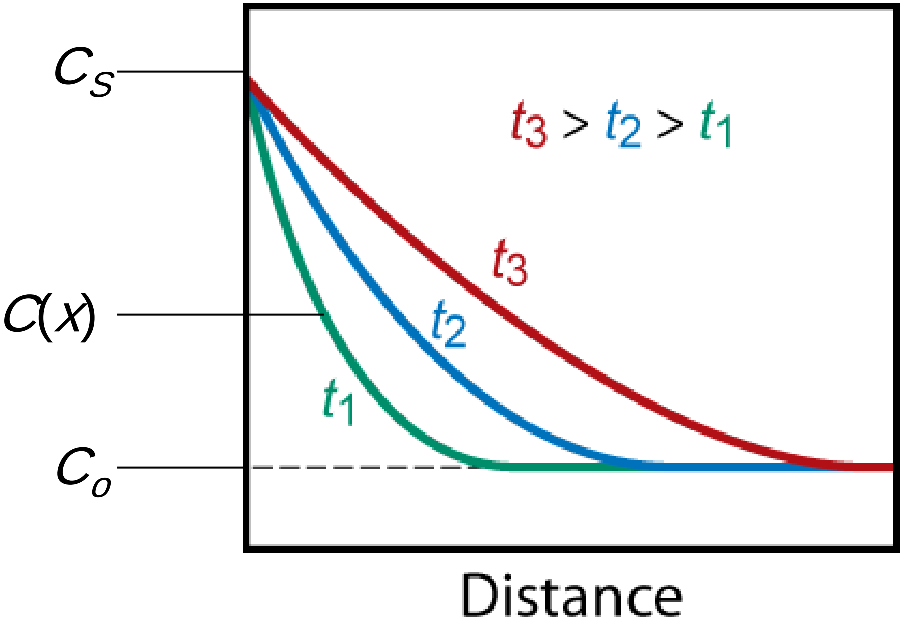


Table 6.1 Tabulation of Error Function Values

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

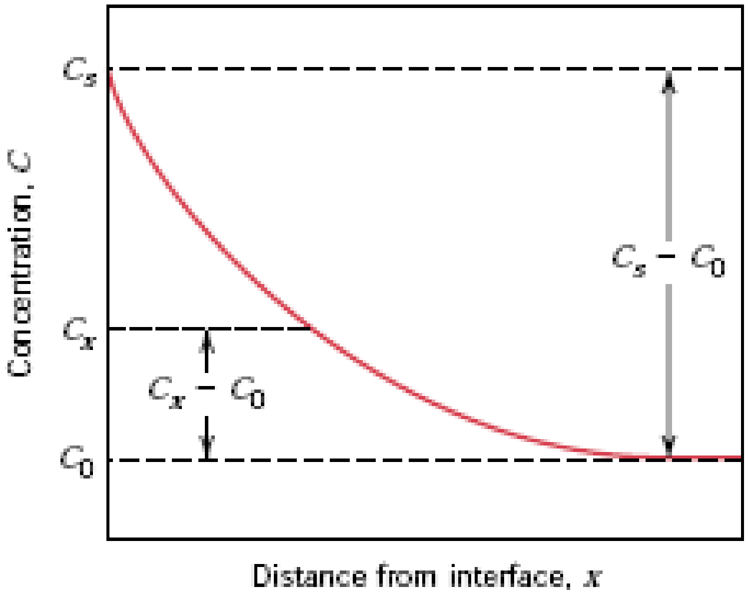


Figure 6.6 Concentration profile for nonsteady-state diffusion; concentration parameters relate to Equation 6.5.

Suppose that it is desired to achieve some specific concentration of solute, C1 ,in an alloy; the left-hand side of Equation now becomes

$$\frac{C_1 - C_0}{C_s - C_0} = \text{constant}$$

This being the case, the right-hand side of this same expression is also a constant, and subsequently

$$\frac{x}{2\sqrt{Dt}} = \text{constant}$$

or

$$\frac{x^2}{Dt} = \text{constant}$$

Some diffusion computations are thus facilitated on the basis of this relationship,

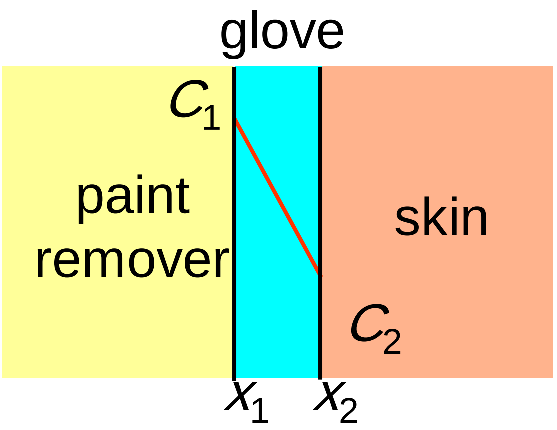
Example: Chemical Protective Clothing (CPC)

- 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 rubber gloves (0.04 cm thick) are used, what is the breakthrough time (t_b), i.e., how long could the gloves be used before methylene chloride reaches the hand?
- Data
  - diffusion coefficient in rubber:

$$D = 110 \times 10^{-8} \text{ cm}^2/\text{s}$$

Example (cont).

- Solution – assuming linear conc. gradient



$$t_b = \frac{\ell^2}{6D}$$

$$\ell = x_2 - x_1 = 0.04\,\text{cm}$$

$D = 110 \times 10^{-8}\ \text{cm}^2/\text{s}$

$$t_b = \frac{(0.04\ \text{cm})^2}{(6)(110 \times 10^{-8}\ \text{cm}^2/\text{s})} = 240\ \text{s} = \boxed{4\ \text{min}}$$

Time required for breakthrough ca. 4 min

FACTORS THAT INFLUENCE DIFFUSION

1. **DIFFUSING SPECIES**
2. **TEMPERATURE**

DIFFUSING SPECIES:

- The diffusing species as well as the host material influence the diffusion coefficient.
-
- Ex. there is a significant difference in magnitude between self- and carbon inter-diffusion in α iron at 500C, the D value being greater for the carbon inter-diffusion ($3.0\text{x}10^{-21}$ vs. $2.4\text{x}10^{-12}$ m ^{2}/s). (See table)

- Self-diffusion occurs by a vacancy mechanism, whereas carbon diffusion in iron is interstitial.

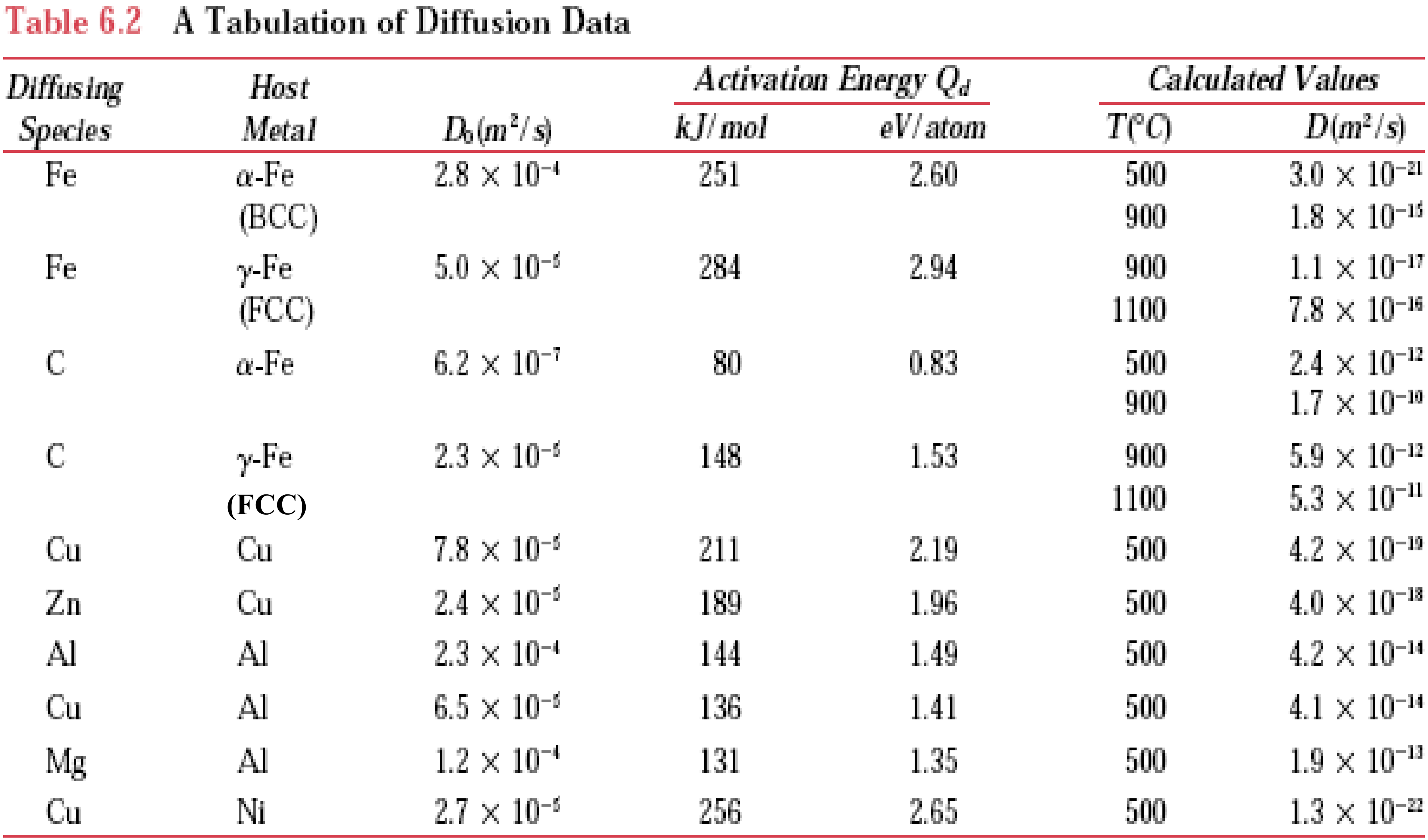


Table 6.2 A Tabulation of Diffusion Data

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	2.8×10^{-4}	251	2.60	500	3.0×10^{-21}
	(BCC)				900	1.8×10^{-15}
Fe	γ-Fe	5.0×10^{-5}	284	2.94	900	1.1×10^{-17}
	(FCC)				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}
	(FCC)				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}

Diffusion and Temperature

- Temperature has a most profound influence on the coefficients and diffusion rates.

- 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] (temp.indepen.)

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

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

T = absolute temperature [K]

The activation energy is the energy required to produce the diffusive motion of one mole of atoms. A large activation energy a small diffusion coefficient

Taking natural logarithms of Equation 6.8 yields

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

Or in terms of logarithms to the base 10

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

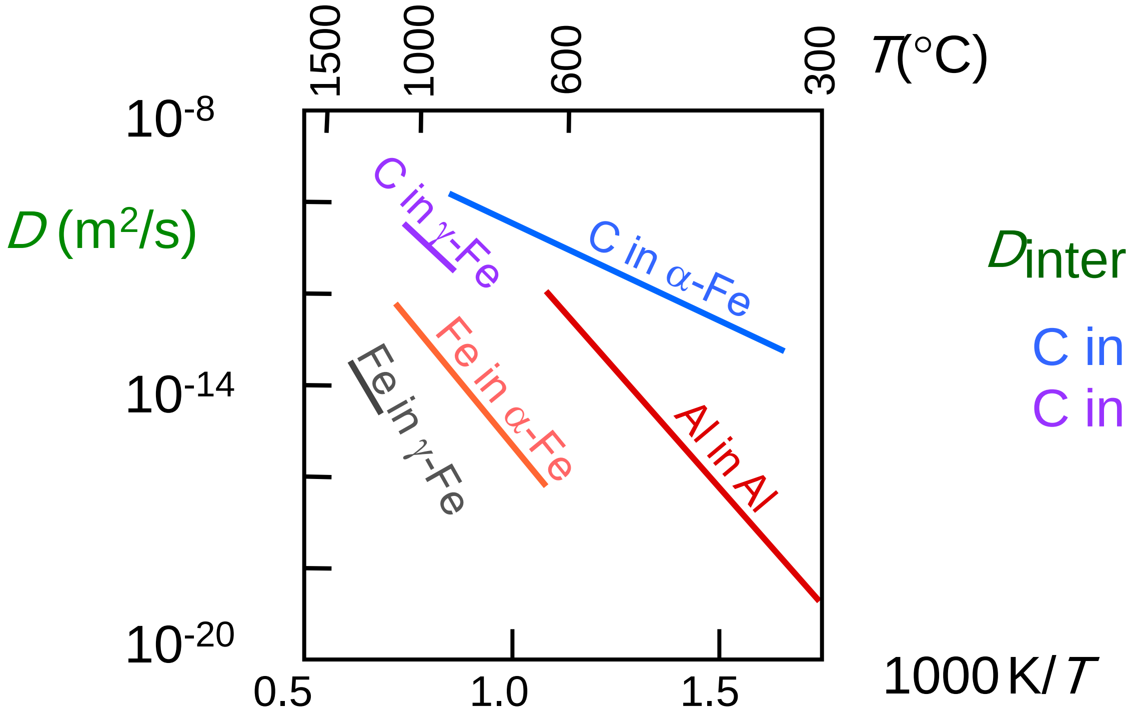
Since D_0, Q_d, and R are all constants, Equation 6.9b takes on the form of an equation of a straight line:

$$y = b + mx$$

where y and x are analogous, respectively, to the variables $\log D$ and $1/T$.

Diffusion and Temperature

D has exponential dependence on *T*



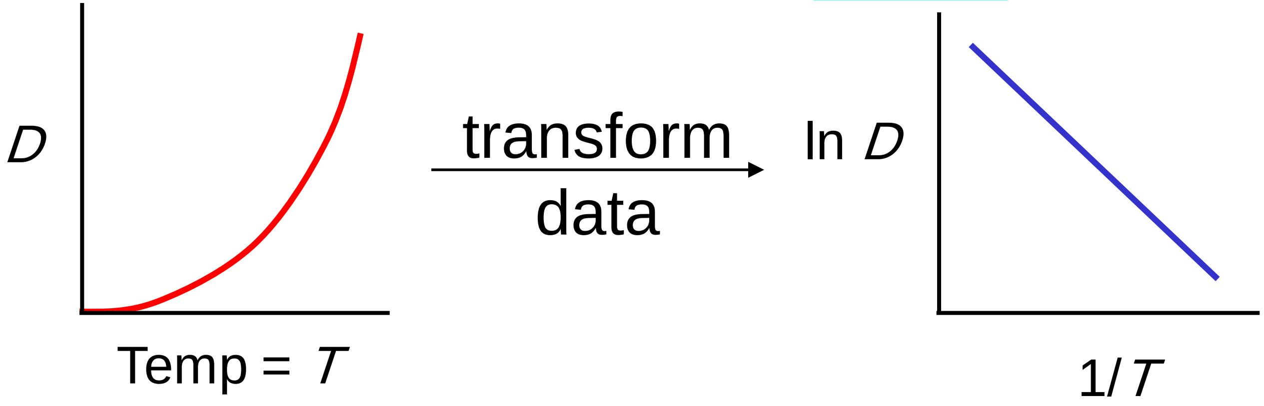
$D_{interstitial}$ >>	$D_{substitutional}$
C in α-Fe	Al in Al
C in γ-Fe	Fe in α-Fe
	Fe in γ-Fe

Ex. For the self-diffusion of Fe in α-Fe, the diffusion coefficient increases approximately six orders of magnitude (from $3.0\text{x}10^{-21}$ to $1.8\text{x}10^{-15}$ m ^{2}/s) in rising temperature from 500 to 900 C (see table)

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

$$D(300ºC) = 7.8 \times 10^{-11}\ \mathrm{m^2/s}$$
$$Q_d = 41.5\ \mathrm{kJ/mol}$$

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.)

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

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

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

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

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

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 Eqn. 5.5

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

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

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	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*

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

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

Solution (cont.):

- To solve for the temperature at which D has above value, we use a rearranged form of Equation (5.9a);

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

from Table 5.2, for diffusion of C in FCC Fe

$D_o = 2.3 \times 10^{-5}\ \text{m}^2/\text{s}$ $Q_d = 148{,}000$ J/mol

D0 temp.independent preexponential

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

$$\boxed{T = 1300\ \text{K} = 1027°\text{C}}$$

Summary

Diffusion FASTER for...	Diffusion SLOWER for...
• open crystal structures	• close-packed structures
• materials w/secondary bonding	• materials w/covalent bonding
• smaller diffusing atoms	• larger diffusing atoms
• lower density materials	• higher density materials

problem

- Determine the carburizing time necessary to achieve a carbon concentration of 0.30 wt% at a position 4 mm into an iron–carbon alloy that initially contains 0.10 wt% C. The surface concentration is to be maintained at 0.9 wt% C, and the treatment is to be conducted at 1100C. Use the diffusion data for γ-Fe in Table 5.2.

We are asked to compute the carburizing (i.e., diffusion) time required for a specific non steady-state diffusion situation. It is first necessary to use Equation 5.5:

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

wherein, Cx = 0.30, C0 = 0.10, Cs = 0.90, and x = 4 mm = 4 x 10 -3 m. Thus,

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.30 - 0.10}{0.90 - 0.10} = 0.2500 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

or

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - 0.2500 = 0.7500$$

By linear interpolation using data from Table 5.1

z	$\operatorname{erf}(z)$
0.80	0.7421
z	0.7500
0.85	0.7707

$$\frac{z - 0.800}{0.850 - 0.800} = \frac{0.7500 - 0.7421}{0.7707 - 0.7421}$$

From which

$$z = 0.814 = \frac{x}{2\sqrt{Dt}}$$

Now, from Table 5.2, at 1100°C (1373 K)

$$D = (2.3 \times 10^{-5}\ \mathrm{m^2/s}) \exp\left[-\frac{148{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(1373\ \mathrm{K})}\right]$$

$$= 5.35 \times 10^{-11}\ \mathrm{m^2/s}$$

problem

- For a steel alloy it has been determined that a carburizing heat treatment of 15 h duration will raise the carbon concentration to 0.35 wt% at a point 2.0 mm from the surface. Estimate the time necessary to achieve the same concentration at a 6.0-mm position for an identical steel and at the same carburizing temperature.

This problem calls for an estimate of the time necessary to achieve a carbon concentration of 0.35 wt% at a point 6.0 mm from the surface. From Equation 5.6b,

$$\frac{x^2}{Dt} = \text{constant}$$

But since the temperature is constant, so also is D constant, and

$$\frac{x^2}{t} = \text{constant}$$

or

$$\frac{x_1^2}{t_1} = \frac{x_2^2}{t_2}$$

Thus,

$$\frac{(2.0\ \text{mm})^2}{15\ \text{h}} = \frac{(6.0\ \text{mm})^2}{t_2}$$

Fro which

$$t_2 = 135\ \text{h}$$

problem

The outer surface of a steel gear is to be hardened by increasing its carbon content. The carbon is to be supplied from an external carbon-rich atmosphere, which is maintained at an elevated temperature. A diffusion heat treatment at 600C (873 K) for 100 min increases the carbon concentration to 0.75 wt% at a position 0.5 mm below the surface. Estimate the diffusion time required at 900C(1173 K) to achieve this same concentration also at a 0.5-mm position. Assume that the surface carbon content is the same for both heat treatments, which is maintained constant. Use the diffusion data in Table 5.2 for C diffusion in α-Fe.

In order to compute the diffusion time at 900°C to produce a carbon concentration of 0.75 wt% at a position 0.5 mm below the surface we must employ Equation 5.6b with position constant; that is

$$Dt = \text{constant}$$

or

$$D_{600}t_{600} = D_{900}t_{900}$$

In addition, it is necessary to compute values for both D600 and D900 using Equation 5.8. From Table 5.2, for the diffusion of C in α-Fe, Qd = 80,000 J/mol and D0 = 6.2 x 10-7 m2/s. Therefore,

$$D_{600} = (6.2 \times 10^{-7}\ \text{m}^2/\text{s})\exp\left[-\frac{80{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(600 + 273\ \text{K})}\right]$$

$$= 1.01 \text{ x } 10^{-11}\ \text{m}^2/\text{s}$$

$$D_{900} = (6.2 \times 10^{-7}\ \mathrm{m^2/s})\exp\left[-\frac{80{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(900 + 273\ \mathrm{K})}\right]$$

$$= 1.69 \times 10^{-10}\ \mathrm{m^2/s}$$

Now, solving the original equation for t900 gives

$$t_{900} = \frac{D_{600}t_{600}}{D_{900}}$$

$$= \frac{(1.01 \times 10^{-11}\ \mathrm{m^2/s})(100\ \mathrm{min})}{1.69 \times 10^{-10}\ \mathrm{m^2/s}}$$

$$= 5.98\ \mathrm{min}$$

problem

- The diffusivity of silver atoms in solid silver metal is

$$1.0\,x10^{-17}m^2/s\,at\;500^oC\;\;and$$

$$7.0\,x10^{-13}m^2/s\,at\,1000^oC.$$

Calculate the activation energy (Jules per mole) for the diffusion of Ag in Ag in the temperature range 500 – 1000 C.

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

$$\frac{7x10^{-13}}{1x10^{-17}} = \exp\left\{-\frac{Q}{R}\left[\left(\frac{1}{1273}-\frac{1}{373}\right)\right]\right\}$$

$$\ln\left(7x10^{4}\right) = \frac{Q}{8.314}\left(5.08x10^{-4}\right)$$

$$Q = 183{,}000\ J/mol$$