Material Science
ME 221

Fall 2020

Dr. Raed Alharbi

Chapter 5: Diffusion

- Why Study Diffusion?
- Diffusion
- Diffusion Mechanisms
- Nonsteady-State Diffusion

Materials Contents in this Slides adapted from : Materials science and engineering: an introduction / William D. Callister, Jr., David G. Rethwisch.–8th ed.

Why Study Diffusion?

"Materials of all types are often heat-treated to improve their properties"

Example:

Hardness and resistance to failure of The steelgear shown have been enhanced by diffusing excess carbon or nitrogen into the outer surface layer.

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Why Study Diffusion?

- Processing/structure/properties/performance
- Diffusional processes
  - Utilized to introduce impurity atoms into silicon semiconductors
  - Heat treatment of steels
  - Conducted at elevated temperatures
  - Time dependent (diffusion rate)

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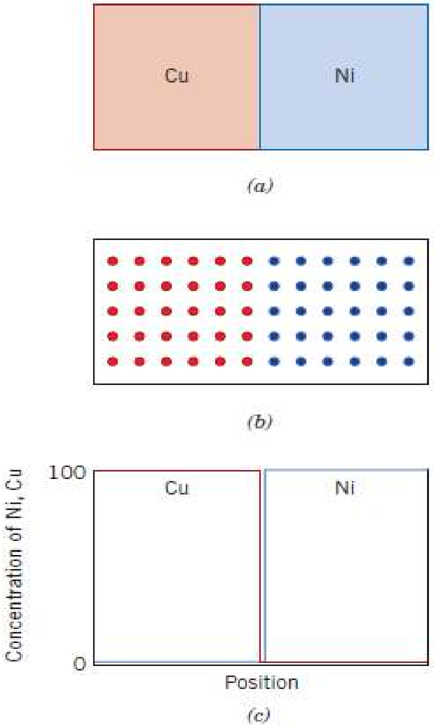
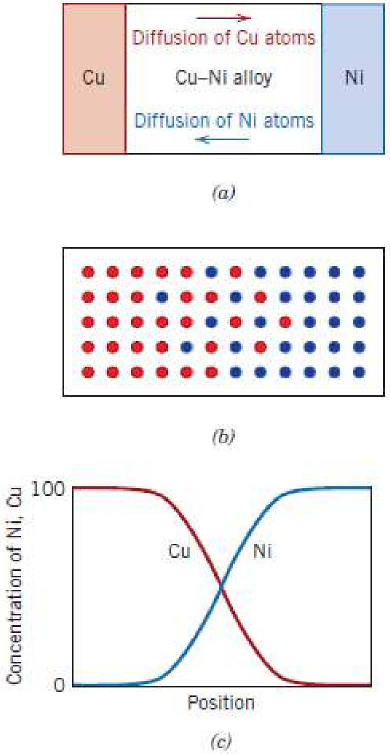
Introduction

Diffusion: is the phenomenon of material transport by atomic motion.

Heat treatment: Heating the two material in contact as shown to at elevated temperature (below melting point of both materials) and then cool down to room temperature.



Heat treatment



Interdiffusion, or **impurity diffusion:** atoms of one metal diffuse into another

Self-diffusion: Diffusion of pure metals, where all atoms exchanging positions are of the same type

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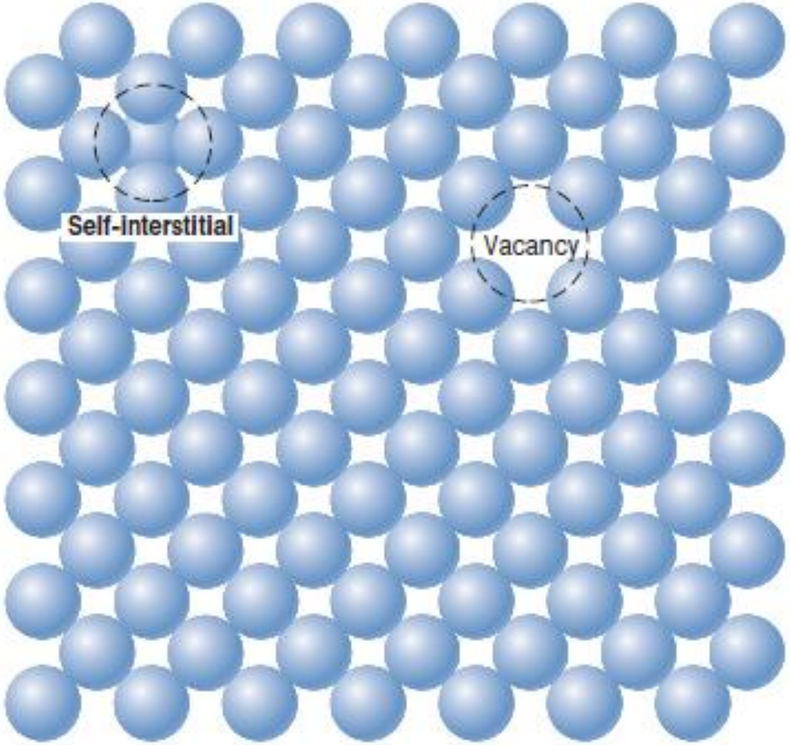
Point Defects

- **VACANCIES AND SELF-INTERSTITIALS**



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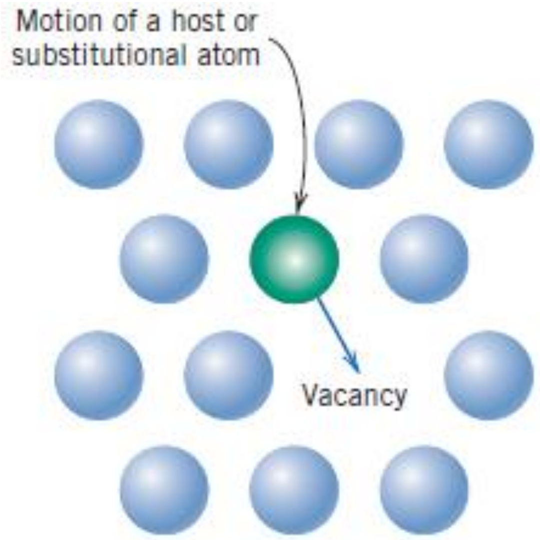
Diffusion Mechanisms

- Diffusion: migration of atoms from lattice site to lattice site.
  - Conditions:
    - Empty adjacent site
    - Sufficient energy to break bonds



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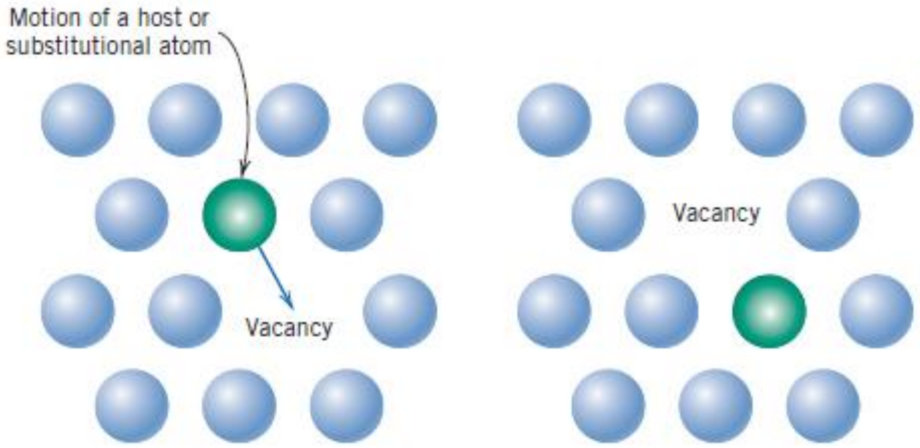
Diffusion Mechanisms

- **Vacancy Diffusion**

“significant concentrations of vacancies may exist in metals at elevated temperatures”

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right)$$



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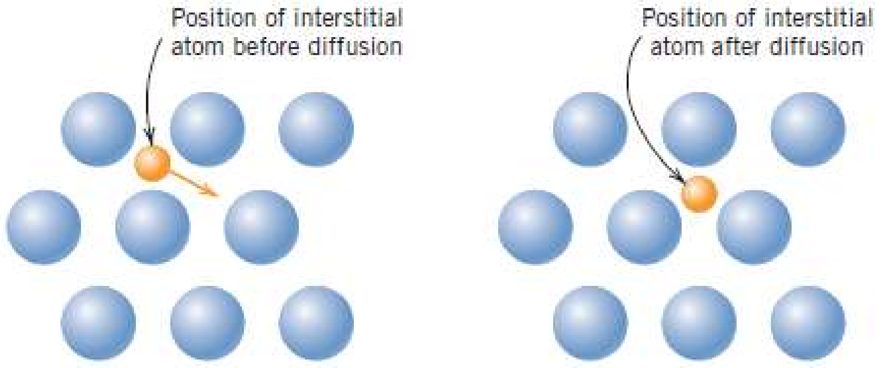
Diffusion Mechanisms

- **Interstitial Diffusion**



In most metal alloys, interstitial diffusion occurs much more rapidly than diffusion by the vacancy mode?

- Interstitial atoms are smaller and thus more mobile
- There are more empty interstitial positions than vacancies

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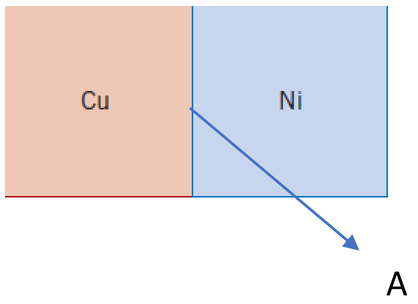
Steady-State Diffusion

- Diffusion is a time-dependent process.

“**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”

$$J = \frac{M}{At} \xrightarrow{\text{Differential form}} J = \frac{1}{A}\frac{dM}{dt} \qquad \begin{array}{c} \mathrm{kg/m^2 \cdot s} \\ \mathrm{atoms/m^2 \cdot s} \end{array}$$

A is constant and t is variant



- *A :*Area across which diffusion is occurring.
- *t :* Diffusion time

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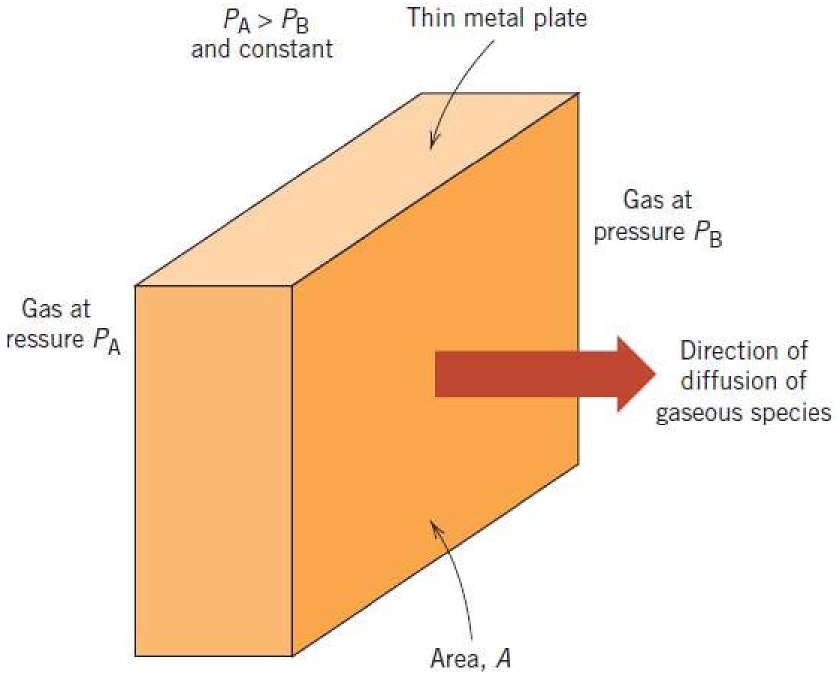
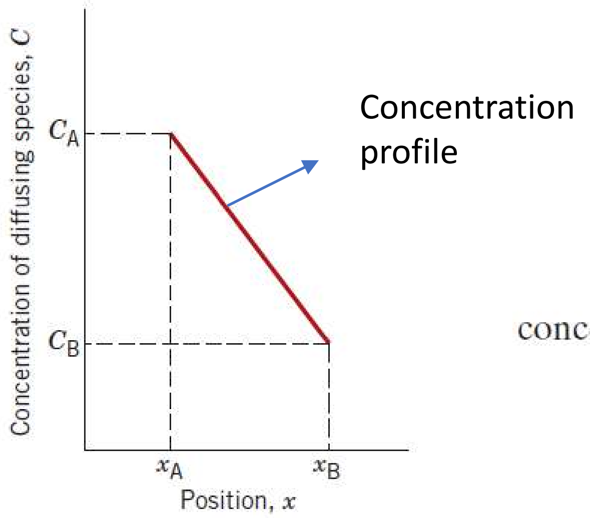
Steady-State Diffusion

Steady-state diffusion condition → Diffusion flux does not change with time



(a)



(b)

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

slope at a particular point on this curve (when the profile is linear)

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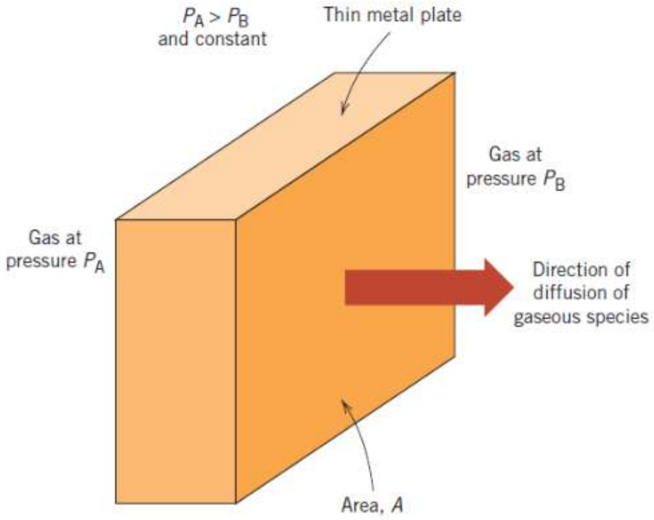
Steady-State Diffusion

- **Fick's first law**—diffusion flux for steady-state diffusion (in one direction)

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



- *D :* Constant, called ***"*diffusion coefficient"** (m^2/s)

"The negative sign in this expression indicates that the direction of diffusion is down the concentration gradient, from a high to a low concentration"

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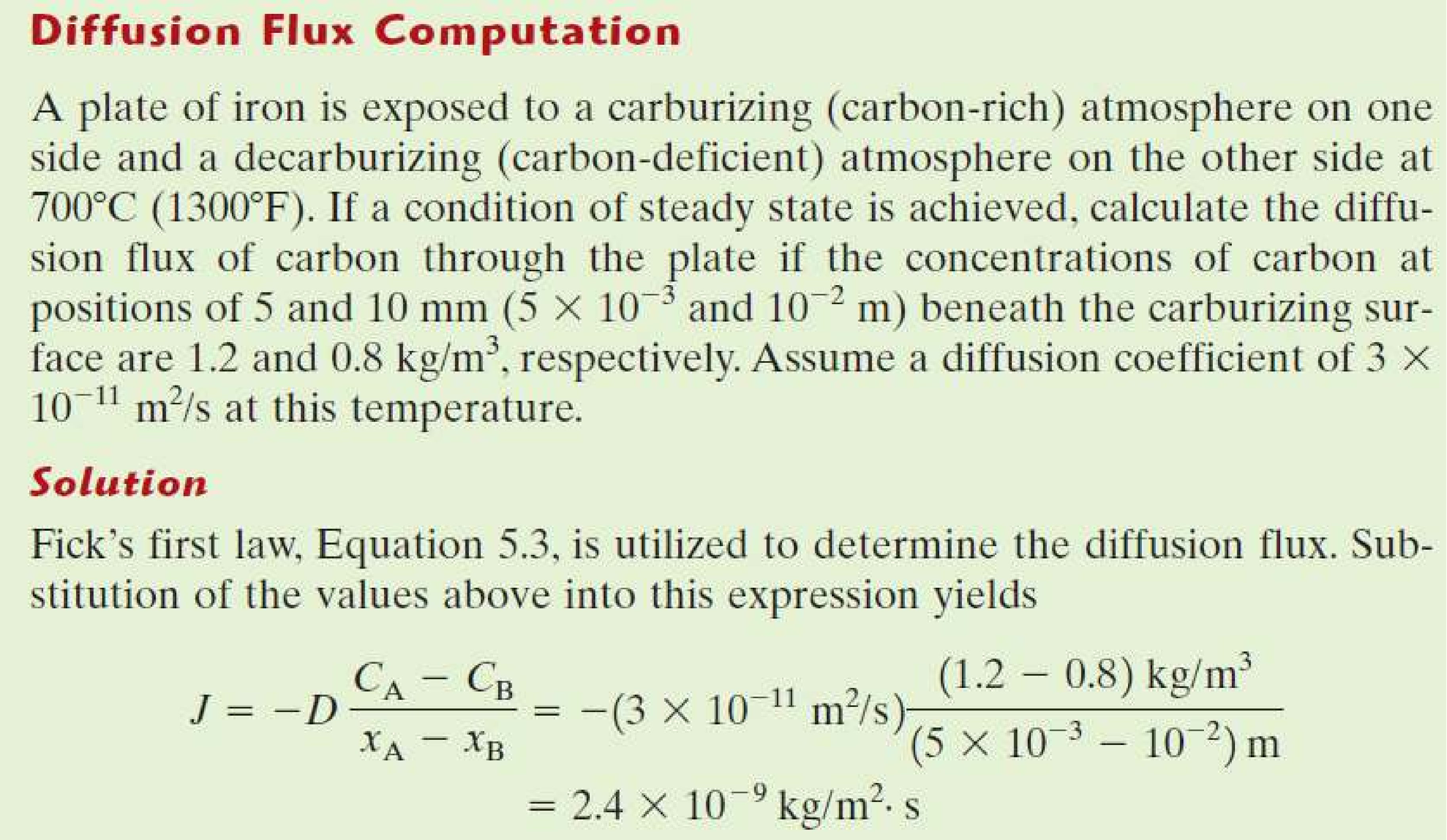


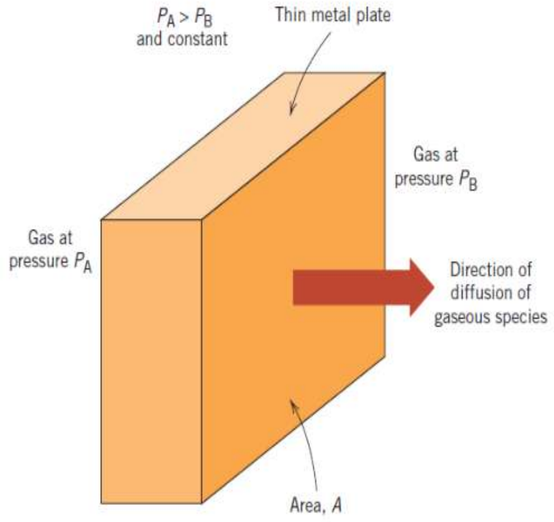
Diffusion Flux Computation

A plate of iron is exposed to a carburizing (carbon-rich) atmosphere on one side and a decarburizing (carbon-deficient) atmosphere on the other side at 700°C (1300°F). If a condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of 5 and 10 mm (5×10^{-3} and 10^{-2} m) beneath the carburizing surface are 1.2 and 0.8 $\mathrm{kg/m^3}$, respectively. Assume a diffusion coefficient of $3 \times 10^{-11}\ \mathrm{m^2/s}$ at this temperature.

Solution

Fick's first law, Equation 5.3, is utilized to determine the diffusion flux. Substitution of the values above into this expression yields

$$J = -D\frac{C_A - C_B}{x_A - x_B} = -(3 \times 10^{-11}\ \mathrm{m^2/s})\frac{(1.2 - 0.8)\ \mathrm{kg/m^3}}{(5 \times 10^{-3} - 10^{-2})\ \mathrm{m}}$$
$$= 2.4 \times 10^{-9}\ \mathrm{kg/m^2 \cdot s}$$



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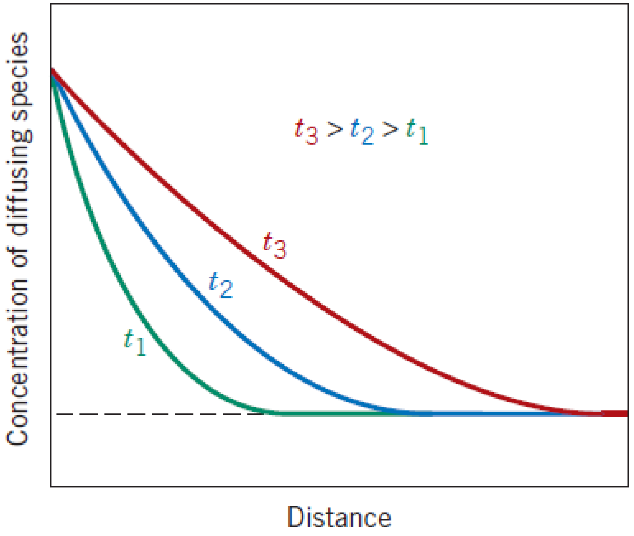
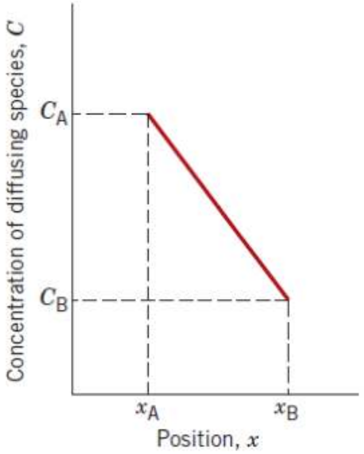
Nonsteady-State Diffusion

"Most practical diffusion situations are nonsteady-state ones"

-Diffusion flux and the concentration gradient vary with time at some point in a solid.





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Nonsteady-State Diffusion

- **Fick’s second law**

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

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

- c_0: Concentration at t = 0.
- c_s: Constant surface concentration at *x* = 0 & t > 0.
- c_x: Concentration at depth *x* after time *t*
- erf($x/2\sqrt{Dt}$) : Gaussian error function

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Nonsteady-State Diffusion

- Gaussian error function

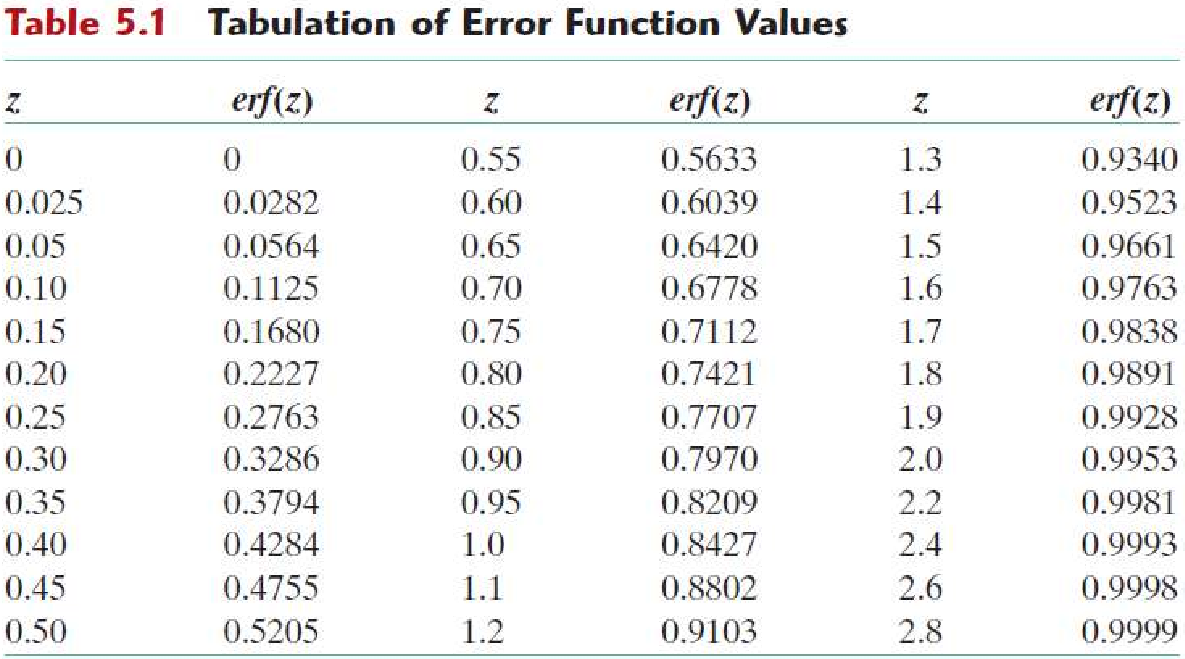

Table 5.1 **Tabulation of Error Function Values**

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

Where

Z = $x/2\sqrt{Dt}$

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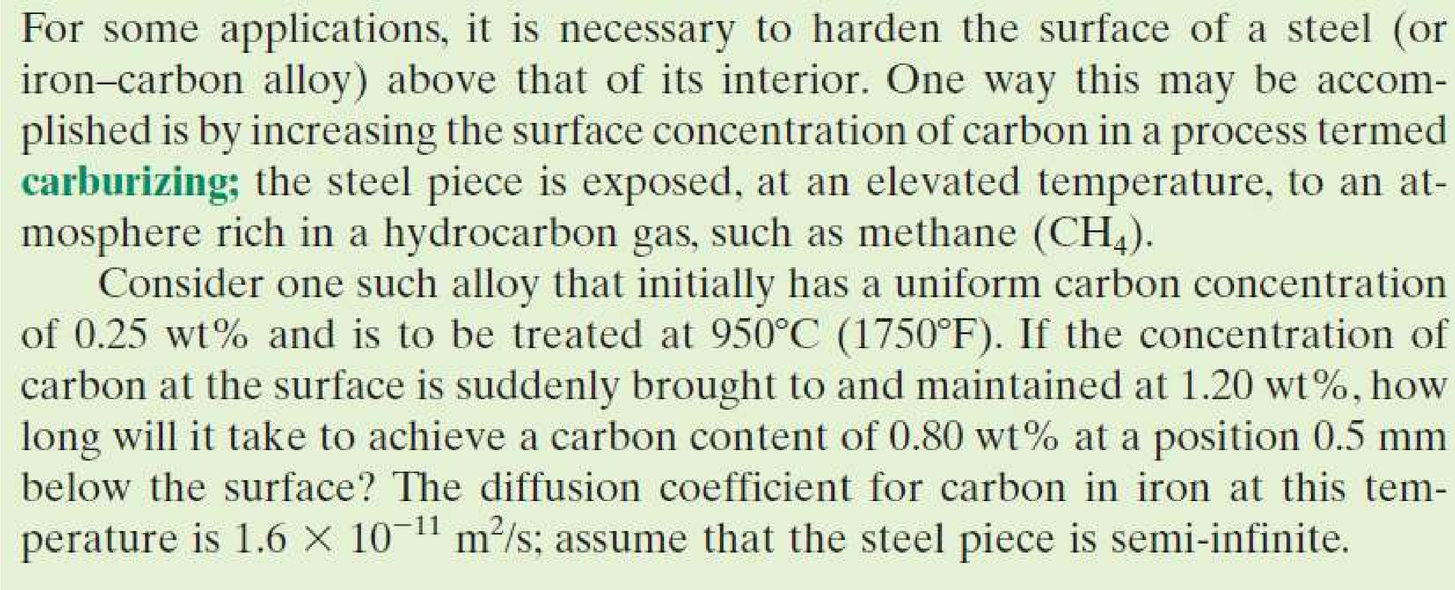
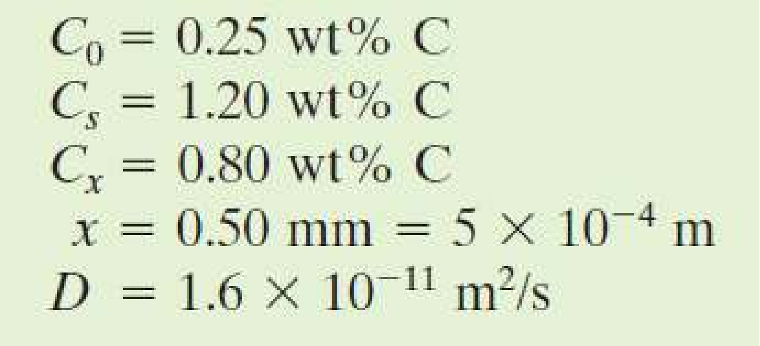
Example 1



For some applications, it is necessary to harden the surface of a steel (or iron–carbon alloy) above that of its interior. One way this may be accomplished is by increasing the surface concentration of carbon in a process termed **carburizing;** the steel piece is exposed, at an elevated temperature, to an atmosphere rich in a hydrocarbon gas, such as methane (CH_4).

Consider one such alloy that initially has a uniform carbon concentration of 0.25 wt% and is to be treated at 950°C (1750°F). If the concentration of carbon at the surface is suddenly brought to and maintained at 1.20 wt%, how long will it take to achieve a carbon content of 0.80 wt% at a position 0.5 mm below the surface? The diffusion coefficient for carbon in iron at this temperature is 1.6×10^{-11} m²/s; assume that the steel piece is semi-infinite.



$C_0 = 0.25$ wt% C
$C_s = 1.20$ wt% C
$C_x = 0.80$ wt% C
$x = 0.50 \text{ mm} = 5 \times 10^{-4} \text{ m}$
$D = 1.6 \times 10^{-11} \text{ m}^2/\text{s}$

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Example 1

$$C_0 = 0.25 \text{ wt\% C}$$
$$C_s = 1.20 \text{ wt\% C}$$
$$C_x = 0.80 \text{ wt\% C}$$
$$x = 0.50 \text{ mm} = 5 \times 10^{-4} \text{ m}$$
$$D = 1.6 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.80 - 0.25}{1.20 - 0.25} = 1 - \text{erf}\left[\frac{(5 \times 10^{-4} \text{ m})}{2\sqrt{(1.6 \times 10^{-11} \text{ m}^2/\text{s})(t)}}\right]$$

$$0.4210 = \text{erf}\left(\frac{62.5 \text{ s}^{1/2}}{\sqrt{t}}\right)$$

z	**erf(z)**
0.35	0.3794
z	0.4210
0.40	0.4284

$$\frac{z - 0.35}{0.40 - 0.35} = \frac{0.4210 - 0.3794}{0.4284 - 0.3794}$$

$$z = 0.392$$

$$\frac{62.5 \text{ s}^{1/2}}{\sqrt{t}} = 0.392$$

$$t = \left(\frac{62.5 \text{ s}^{1/2}}{0.392}\right)^2 = 25{,}400 \text{ s} = 7.1 \text{ h}$$

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Example 2

The diffusion coefficients for copper in aluminum at 500 and 600°C are 4.8×10^{-14} and 5.3×10^{-13} m^2/s, respectively. Determine the approximate time at 500°C that will produce the same diffusion result (in terms of concentration of Cu at some specific point in Al) as a 10-h heat treatment at 600°C.

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

$$Dt = \text{constant}$$

$$D_{500}\, t_{500} = D_{600}\, t_{600}$$

$$t_{500} = \frac{D_{600} t_{600}}{D_{500}} = \frac{(5.3 \times 10^{-13}\ \mathrm{m^2/s})(10\ \mathrm{h})}{4.8 \times 10^{-14}\ \mathrm{m^2/s}} = 110.4\ \mathrm{h}$$

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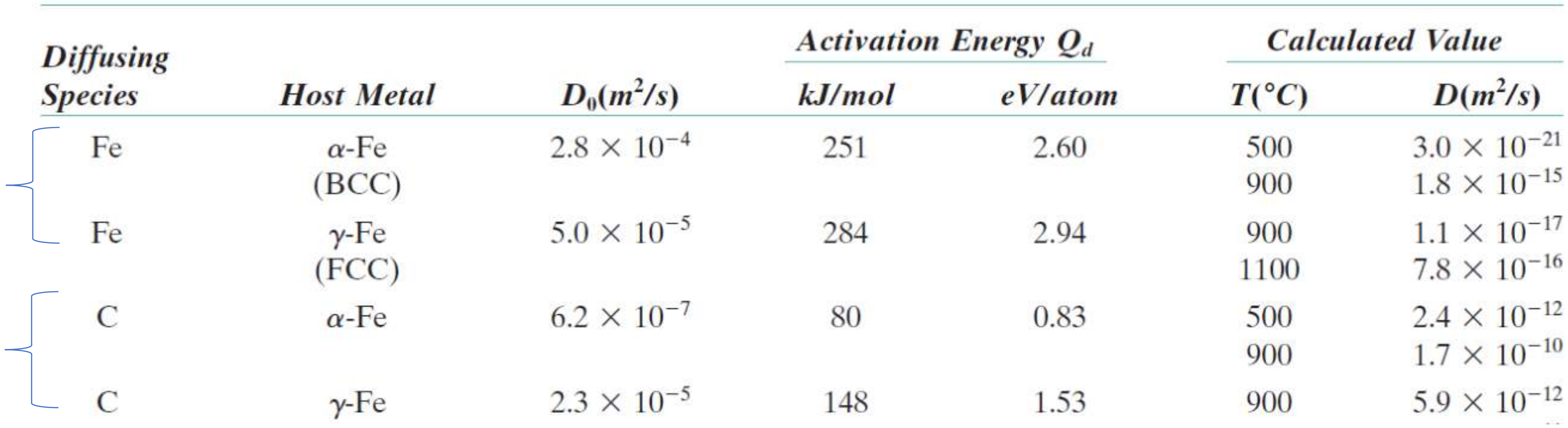
FACTORS THAT INFLUENCE DIFFUSION

- **Diffusing Species**

“The magnitude of the diffusion coefficient *D* is indicative of the rate at which atoms diffuse”



Diffusing Species	*Host Metal*	*D_0(m^2/s)*	*Activation Energy Q_d* kJ/mol	*Activation Energy Q_d* eV/atom	*Calculated Value* T(°C)	*Calculated Value* D(m^2/s)
Fe	α-Fe (BCC)	2.8×10^{-4}	251	2.60	500 900	3.0×10^{-21} 1.8×10^{-15}
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94	900 1100	1.1×10^{-17} 7.8×10^{-16}
C	α-Fe	6.2×10^{-7}	80	0.83	500 900	2.4×10^{-12} 1.7×10^{-10}
C	γ-Fe	2.3×10^{-5}	148	1.53	900	5.9×10^{-12}

Self-diffusion

Interstitial diffusion

significant difference

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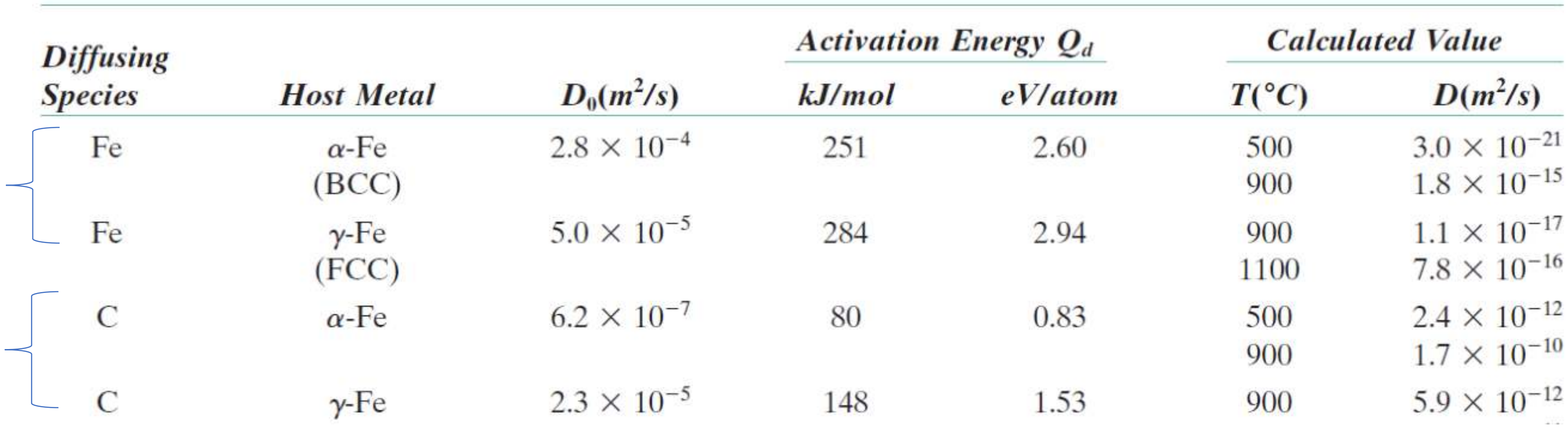
FACTORS THAT INFLUENCE DIFFUSION

- **Temperature**

“most profound influence on the coefficients and diffusion rates”



Diffusing Species	*Host Metal*	*$D_0(m^2/s)$*	*Activation Energy Q_d*		*Calculated Value*	
			kJ/mol	*eV/atom*	*T(°C)*	*$D(m^2/s)$*
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Self-diffusion

Interstitial diffusion

~ 6 order of magnitude increased

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FACTORS THAT INFLUENCE DIFFUSION

Energy required to produce the diffusive motion of one mole of atoms is called “activation energy”

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

large activation energy → small diffusion coefficient

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FACTORS THAT INFLUENCE DIFFUSION

- Taking logarithms to the base 10

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

- As D_0, Q_d, and R are all constants, the above equation takes the form of a straight-line equation

$$y = b + mx$$

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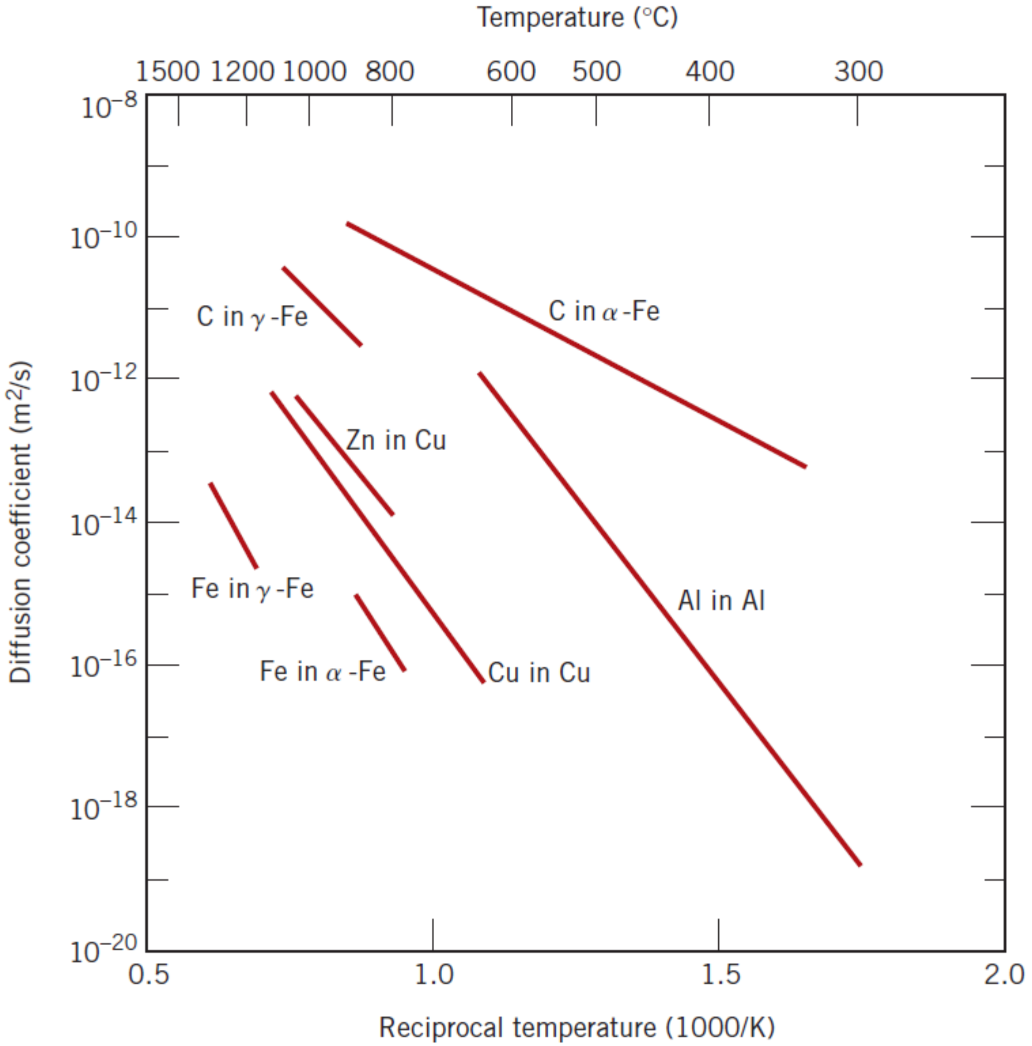
FACTORS THAT INFLUENCE DIFFUSION

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

$$y = b + mx$$



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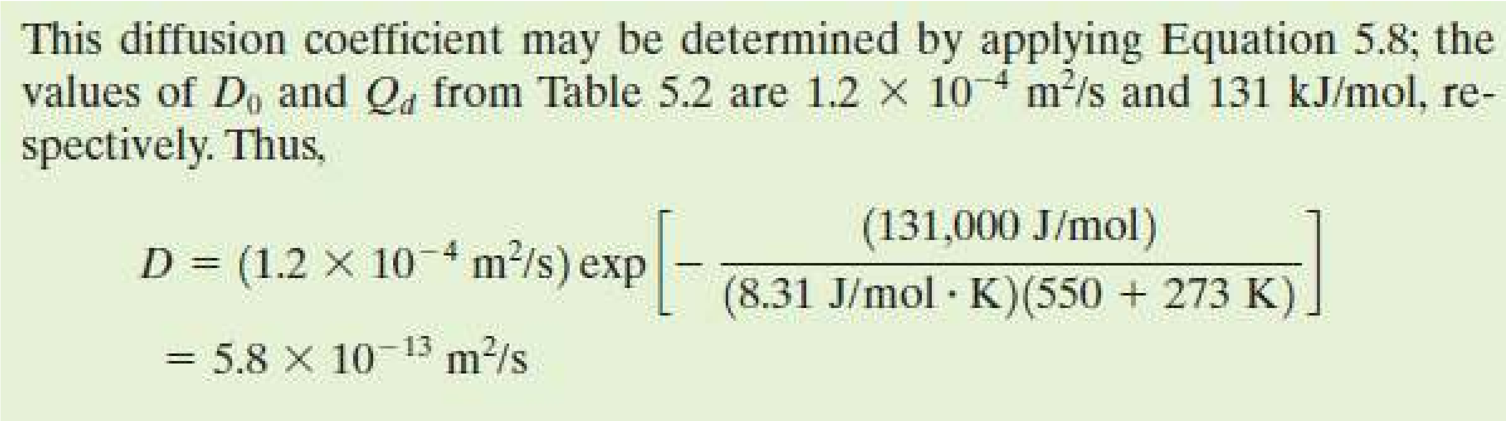
Example

- Using the data in Table 5.2, compute the diffusion coefficient for magnesium in aluminum at 550C.



This diffusion coefficient may be determined by applying Equation 5.8; the values of D_0 and Q_d from Table 5.2 are 1.2×10^{-4} m^2/s and 131 kJ/mol, respectively. Thus,

$$D = (1.2 \times 10^{-4}\ \mathrm{m^2/s}) \exp\left[-\frac{(131{,}000\ \mathrm{J/mol})}{(8.31\ \mathrm{J/mol \cdot K})(550 + 273\ \mathrm{K})}\right]$$
$$= 5.8 \times 10^{-13}\ \mathrm{m^2/s}$$

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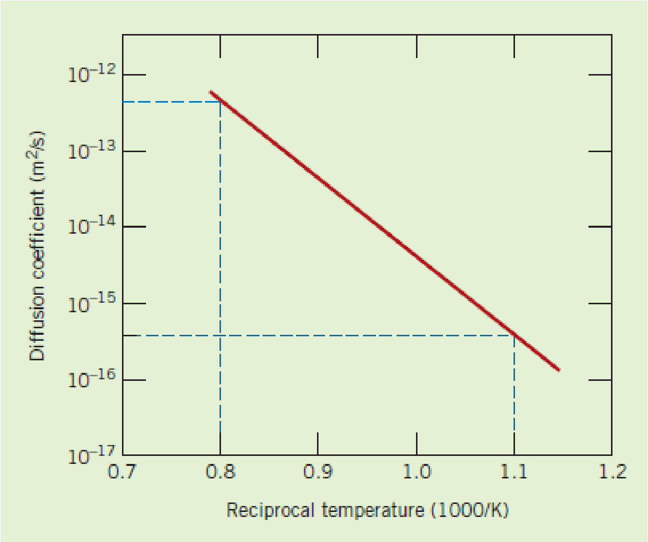
Example

Figure below is shown a plot of the logarithm (to the base 10) of the diffusion coefficient versus reciprocal of absolute temperature, for the diffusion of copper in gold. Determine values for the activation energy and the preexponential.



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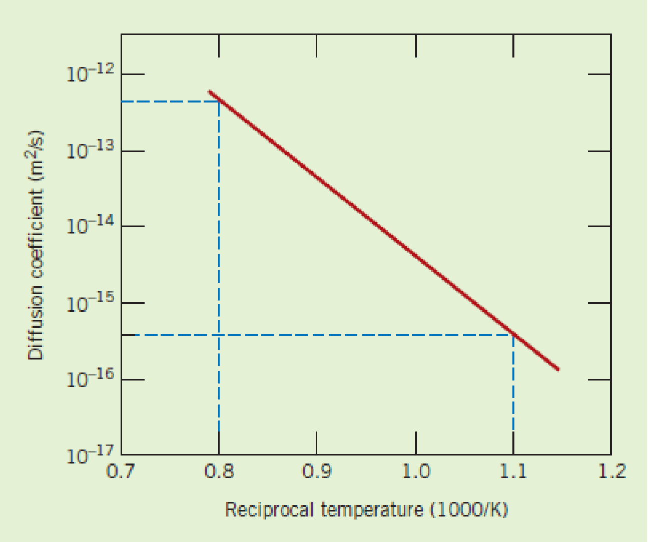
Example

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

$$y = b + mx$$

$$Q_d = -2.3R\,(\text{slope}) = -2.3R\left[\frac{\Delta(\log D)}{\Delta\left(\frac{1}{T}\right)}\right]$$

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



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

$$= -2.3(8.31\ \text{J/mol}\cdot\text{K})\left[\frac{-12.40 - (-15.45)}{0.8\times 10^{-3}(\text{K})^{-1} - 1.1\times 10^{-3}(\text{K})^{-1}}\right]$$

$$= 194{,}000\ \text{J/mol} = 194\ \text{kJ/mol}$$

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Example

- Preexponential is D_0

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

$$\begin{aligned}
\log D_0 &= \log D + \frac{Q_d}{2.3R}\left(\frac{1}{T}\right) \\
&= -15.45 + \frac{(194{,}000\ \text{J/mol})(1.1 \times 10^{-3}[\text{K}]^{-1})}{(2.3)(8.31\ \text{J/mol}\cdot\text{K})} \\
&= -4.28
\end{aligned}$$

Thus, $D_0 = 10^{-4.28}\ \text{m}^2/\text{s} = 5.2 \times 10^{-5}\ \text{m}^2/\text{s}$.

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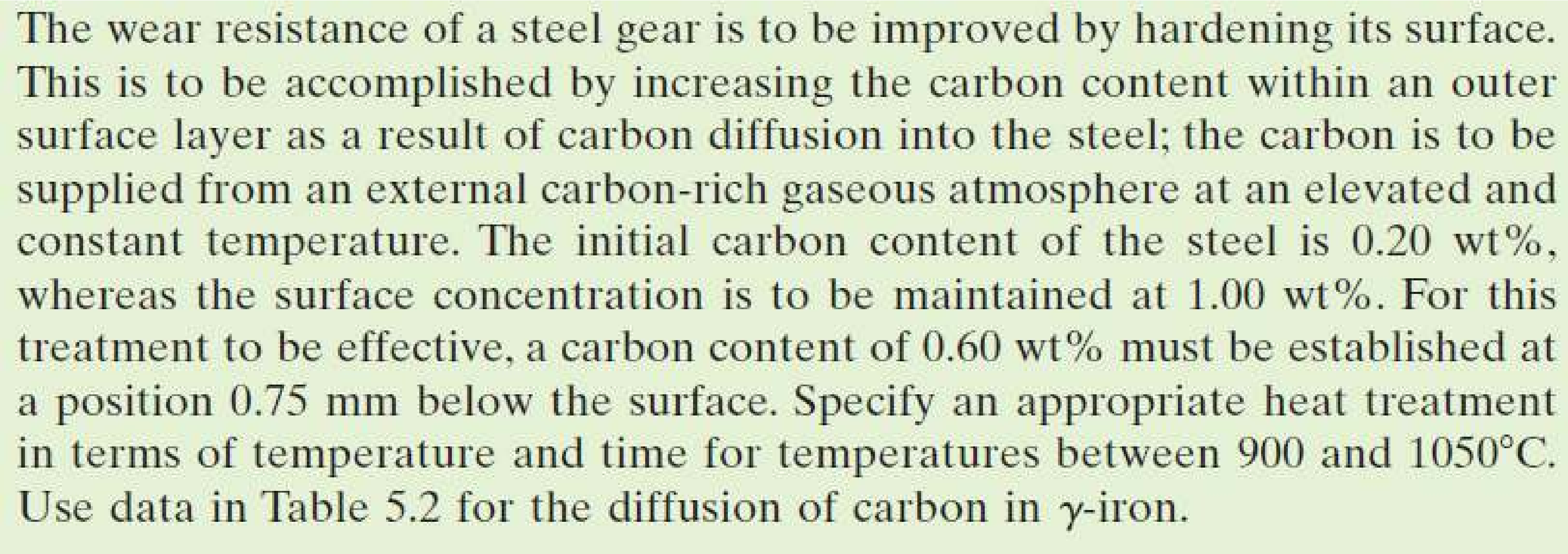
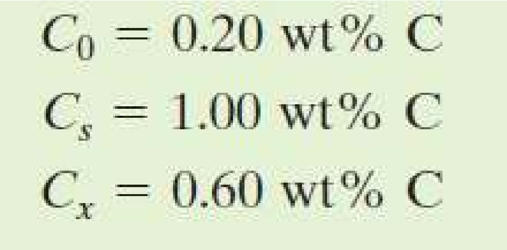
Design Example



The wear resistance of a steel gear is to be improved by hardening its surface. This is to be accomplished by increasing the carbon content within an outer surface layer as a result of carbon diffusion into the steel; the carbon is to be supplied from an external carbon-rich gaseous atmosphere at an elevated and constant temperature. The initial carbon content of the steel is 0.20 wt%, whereas the surface concentration is to be maintained at 1.00 wt%. For this treatment to be effective, a carbon content of 0.60 wt% must be established at a position 0.75 mm below the surface. Specify an appropriate heat treatment in terms of temperature and time for temperatures between 900 and 1050°C. Use data in Table 5.2 for the diffusion of carbon in γ-iron.



$C_0 = 0.20$ wt% C

$C_s = 1.00$ wt% C

$C_x = 0.60$ wt% C

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Design Example

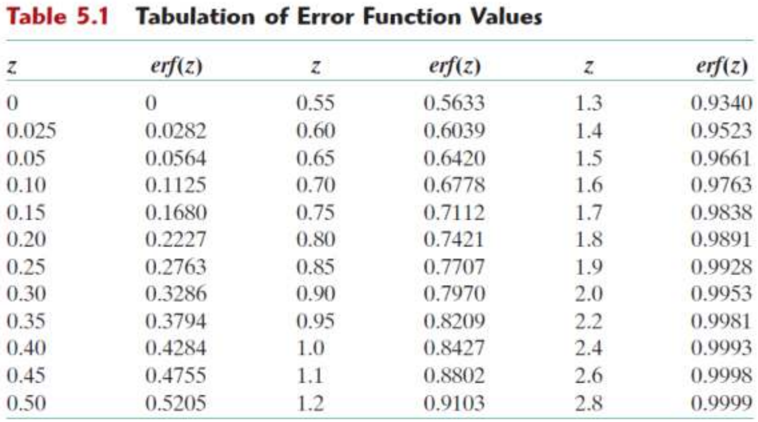


Table 5.1 **Tabulation of Error Function Values**

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

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.60 - 0.20}{1.00 - 0.20} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$0.5 = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{x}{2\sqrt{Dt}} = 0.4747$$

$$\frac{7.5 \times 10^{-4}\ \text{m}}{2\sqrt{Dt}} = 0.4747$$

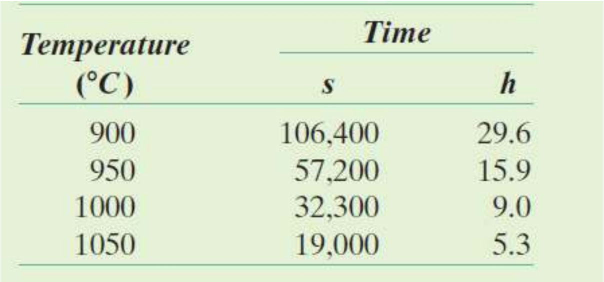
$$Dt = 6.24 \times 10^{-7}\ \text{m}^2$$

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

$$Dt = D_0 \exp\left(-\frac{Q_d}{RT}\right)(t) = 6.24 \times 10^{-7}\,\text{m}^2$$

$$(2.3 \times 10^{-5}\,\text{m}^2/\text{s}) \exp\left[-\frac{148{,}000\ \text{J/mol}}{(8.31\ \text{J/mol}\cdot\text{K})(T)}\right](t) = 6.24 \times 10^{-7}\ \text{m}^2$$

$$t(\text{in s}) = \frac{0.0271}{\exp\left(-\dfrac{17{,}810}{T}\right)}$$



Temperature (°C)	*Time* s	*Time* h
900	106,400	29.6
950	57,200	15.9
1000	32,300	9.0
1050	19,000	5.3

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Homework

Q1. An FCC iron-carbon alloy initially containing 0.35 wt% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1400 K (1127°C). Under these circumstances the carbon diffuses from the alloy and reacts at the surface with the oxygen in the atmosphere; that is, the carbon concentration at the surface position is maintained essentially at 0 wt% C. (This process of carbon depletion is termed decarburization.) At what position will the carbon concentration be 0.15 wt% after a 10-h treatment? The value of D at 1400 K is 6.9×10^{-11} m^2/s.

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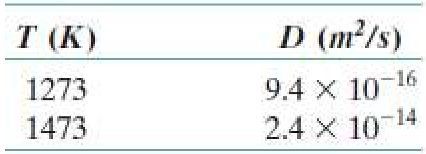
Homework

Q2. Using the data in Table 5.2, compute the value of D for the diffusion of zinc in copper at 650ºC.

- Q3. The diffusion coefficients for iron in nickel are given at two temperatures:



T (K)	D (m^2/s)
1273	9.4×10^{-16}
1473	2.4×10^{-14}

(a) Determine the values of D_0 and the activation energy Q_d.

(b) What is the magnitude of D at 1100ºC (1373 K)?

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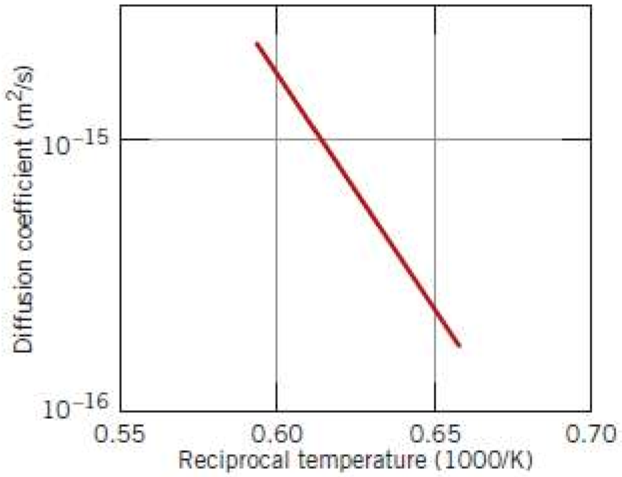
Homework

- Q4. Below is shown a plot of the logarithm (to the base 10) of the diffusion coefficient versus reciprocal of the absolute temperature, for the diffusion of iron in chromium. Determine values for the activation energy and preexponential.



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Homework

Q1. An FCC iron-carbon alloy initially containing 0.35 wt% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1400 K (1127°C). Under these circumstances the carbon diffuses from the alloy and reacts at the surface with the oxygen in the atmosphere; that is, the carbon concentration at the surface position is maintained essentially at 0 wt% C. (This process of carbon depletion is termed decarburization.) At what position will the carbon concentration be 0.15 wt% after a 10-h treatment? The value of D at 1400 K is 6.9×10^{-11} m^2/s.

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