

Chapter 5, Problem 1

Write an equation for the number of vacancies present in a metal at equilibrium at a particular temperature, and define each of the terms. Give the units for each term, and use electron volts for the activation energy.

Chapter 5, Solution 1

$$n_v = NCe^{-E_v/kT}$$

where n_v = number of vacancies per cubic meter of metal
 N = total number of atom sites per cubic meter of metal
 E_v = activation energy to form a vacancy (eV)
 T = absolute temperature (K)
 k = Boltzmann's constant = 8.62×10^{-6} eV/K
 C = constant

Chapter 5, Problem 2

What is a thermally activated process? What is the activation energy for such a process?

Chapter 5, Solution 2

A thermally active process is one which requires a definite amount of thermal energy to overcome an *activation energy* barrier and enter the reactive state.

Chapter 5, Problem 3

What is the steady-state condition for diffusion?

Chapter 5, Solution 3

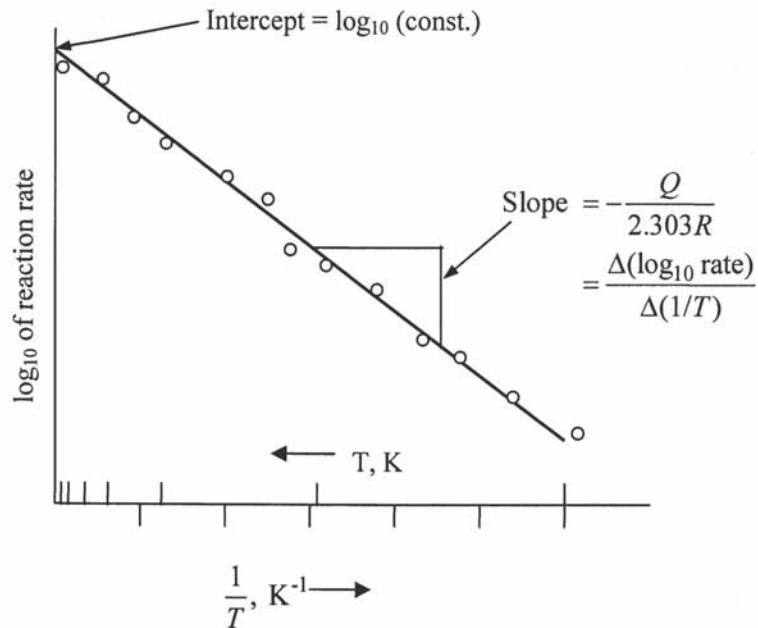
For a diffusing system, there is no change in the concentration of the diffusing species with time at different places in the system.

Chapter 5, Problem 4

Draw a typical Arrhenius plot of \log_{10} of the reaction rate versus reciprocal absolute temperature, and indicate the slope of the plot.

Chapter 5, Solution 4

A typical Arrhenius plot of the logarithmic reaction rate is shown below for the SI absolute Kelvin temperature scale. The relationship between the \log_{10} of the reaction rate and the inverse absolute temperature is linear with a slope of $-Q/(2.303R)$.



Chapter 5, Problem 5

What is the Kirkendall effect in solid state diffusion?

Chapter 5, Solution 5

Kirkendall effect showed that the markers at the diffusion interface moved slightly in the opposite direction to the most rapidly moving (faster diffusion) species of a binary diffusion couple.

Chapter 5, Problem 6

Write the equation for Fick's first law of diffusion, and define each of the terms in SI units.

Chapter 5, Solution 6

Fick's first law of diffusion is given by:

$$J = -D \frac{dC}{dx} \quad \text{or in SI unit form, } \left\{ \frac{\text{atoms}}{\text{m}^2 \cdot \text{s}} \right\} = \left\{ \left(\frac{\text{m}^2}{\text{s}} \right) \left(\frac{\text{atoms}}{\text{m}^3} \times \frac{1}{\text{m}} \right) \right\}$$

where J = flux or net flow of atoms;

D = proportionality constant called the *diffusivity* (atomic conductivity) or *diffusion coefficient*;

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

Chapter 5, Problem 7

Which type of diffusion will be easier?

- (a) C in FCC iron (b) Ni in FCC iron (c) Mn in FCC iron

Chapter 5, Solution 7

The diffusion of C in FCC iron will be easier. The activation energy of the diffusion of C in FCC iron is lower than the others.

Chapter 5, Problem 8

Write the equation for Fick's second law of diffusion in solids, and define each of the terms.

Chapter 5, Solution 8

Fick's second law of diffusion in solids, written for the x -direction, is:

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

where $\frac{dC_x}{dt}$ = rate of change of the concentration of the diffusing species in the x -direction;

$\frac{dC_x}{dx}$ = concentration gradient of the diffusing species in the x -direction;

D = diffusion coefficient of the diffusing species.

Chapter 5, Problem 9

Describe the gas-carburizing process for steel parts. Why is the carburization of steel parts carried out?

Chapter 5, Solution 9

In the gas carburizing process for steel parts, the parts are placed in a furnace in contact with a gas rich in CO at about 927°C. The carbon from the gas diffuses into the surface of the steel part and increases the carbon content of the outer surface region of the part. The higher carbon concentration at the surface makes the steel harder in this region. A steel part can thus be produced with a hard outer layer and a tough low carbon steel inner core. This duplex structure is important, for example, for many types of gears.

Chapter 5, Problem 10

Write the equation for the solution to Fick's second law for the diffusion of a gas into the surface of a solid metal crystal lattice.

Chapter 5, Solution 10

Fick's second law of diffusion, for the diffusion of a gas into the surface of a solid metal crystal lattice is:

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

where C_s = surface concentration of element in gas diffusing into the surface;

C_o = initial uniform concentration of element in solid;

C_x = concentration of element at distance x from surface at time t ;

x = distance from surface;

D = diffusivity of diffusing solute element;

t = time.

Chapter 5, Problem 11

(a) Calculate the equilibrium concentration of vacancies per cubic meter in pure copper at 850°C. Assume that the energy of formation of a vacancy in pure copper is 1.0 eV. (b) What is the vacancy fraction at 800°C?

Chapter 5, Solution 11

a) In general, the equilibrium number of vacancies is $n_v = NCe^{-E_v/kT}$. For copper,

$$N = \frac{N_o \rho_{Cu}}{\text{at. mass Cu}} = \frac{(6.02 \times 10^{23} \text{ atoms/at. mass})(8.96 \times 10^6 \text{ g/m}^3)}{(63.54 \text{ g/at. mass})} = 8.49 \times 10^{28} \text{ atoms/m}^3$$

Substituting and assuming $E_v = 1.00 \text{ eV}$ at 1123 K,

$$n_v = (8.49 \times 10^{28} \text{ atoms/m}^3) \left\{ \exp \left[-\frac{1.00 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(1123 \text{ K})} \right] \right\}$$

$$= 2.77 \times 10^{24} \text{ vacancies/m}^3$$

b) The vacancy fraction at 1073 K is,

$$\frac{n_v}{N} = \exp \left[\frac{-1.00 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(1073 \text{ K})} \right] = e^{-10.81} = 2.02 \times 10^{-5} \text{ vacancies/atom}$$

Chapter 5, Problem 12

(a) Calculate the equilibrium concentration of vacancies per cubic meter in pure aluminum at 550°C. Assume that the energy of formation of a vacancy in pure aluminum is 0.74 eV. (b) What is the vacancy fraction at 500°C?

Chapter 5, Solution 12

a) The equilibrium number of vacancies is calculated as $n_v = NCe^{-E_v/kT}$. Thus for aluminum,

$$N = \frac{N_o \rho_{Al}}{\text{at. mass Al}} = \frac{(6.02 \times 10^{23} \text{ atoms/at. mass})(2.70 \times 10^6 \text{ g/m}^3)}{(26.982 \text{ g/at.mass})} = 6.02 \times 10^{28} \text{ atoms/m}^3$$

Substituting and assuming $E_v = 0.74 \text{ eV}$ for vacancies formed at 823 K,

$$n_v = (6.02 \times 10^{28} \text{ atoms/m}^3) \left\{ \exp \left[-\frac{0.74 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(823 \text{ K})} \right] \right\}$$

$$= 1.78 \times 10^{24} \text{ vacancies/m}^3$$

b) The vacancy fraction at 773 K is,

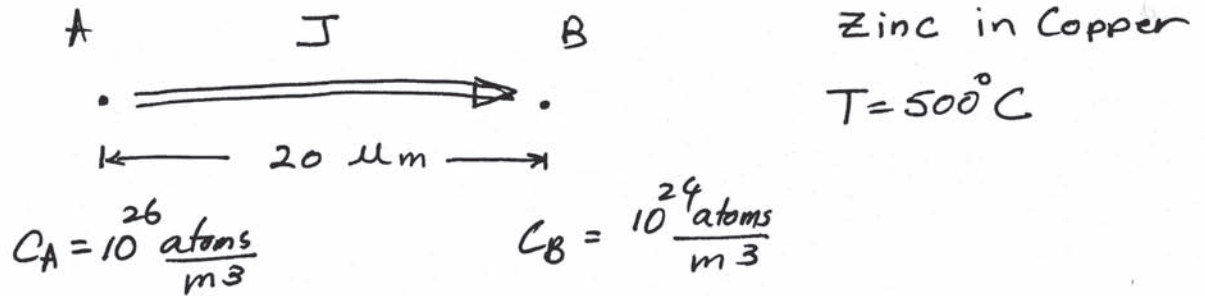
$$\frac{n_v}{N} = \exp \left[\frac{-0.74 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(773 \text{ K})} \right] = e^{-11.11} = 1.50 \times 10^{-5} \text{ vacancies/atom}$$

Chapter 5, Problem 13

Determine the diffusion flux of zinc atoms in a solid solution of zinc in copper between two points A and B, $20\mu\text{m}$ apart, at 500°C . $C_A = 10^{26}$ atoms/ m^3 and $C_B = 10^{24}$ atoms/ m^3 .

Chapter 5, Solution 13

5.13



$$J = -D \frac{\Delta c}{\Delta x} ; \text{ From Table 5-2 } D \Big|_{500^\circ\text{C}} = 4 \times 10^{-18} \frac{\text{m}^2}{\text{s}}$$

$$J = -4 \times 10^{-18} \frac{\text{m}^2}{\text{s}} \left(\frac{10^{24} - 10^{26} \left(\frac{\text{atoms}}{\text{m}^3} \right)}{20 \times 10^{-6} \text{ m}} \right) = 2 \times 10^{14} \frac{\text{atoms}}{\text{m}^2 \cdot \text{s}}$$

from A to B

Chapter 5, Problem 14

Consider the gas carburizing of a gear of 1018 steel (0.18 wt %) at 927°C (1700°F). 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 %. D (C in γ iron) at 927°C = $1.28 \times 10^{-11} \text{ m}^2/\text{s}$.

Chapter 5, Solution 14

The time required for this diffusion process is calculated using Fick's second law,

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

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

$0.8247 = \text{erf} \left[\frac{55.90}{\sqrt{t}} \right] = \text{erf } z$

Interpolating from Table 5.3,

erf z	z
0.8209	0.95
0.8247	x
0.8427	1.0

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

Thus,

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

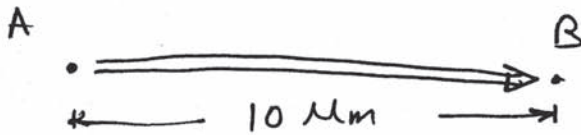
$$t = 3397.7 \text{ s} = \mathbf{56.6 \text{ min.}}$$

Chapter 5, Problem 15

The diffusion flux of copper solute atoms in aluminum solvent from point A to point B, 10 μm apart, is 4×10^{17} atoms/($\text{m}^2 \cdot \text{s}$) at 500°C . Determine (a) the concentration gradient and (b) difference in the concentration levels of copper between the two points.

Chapter 5, Solution 15

5.15



Copper in Aluminum
 $T = 500^\circ\text{C}$

$$J = 4 \times 10^{17} \frac{\text{atoms}}{\text{m}^2 \cdot \text{s}}$$

$$a) \quad J = -D \frac{\Delta c}{\Delta x} \Rightarrow \frac{\Delta c}{\Delta x} = -\frac{J}{D}$$

$$D \Big|_{500^\circ\text{C}} = 4 \times 10^{-14} \frac{\text{m}^2}{\text{s}}$$

$$\Rightarrow \frac{-J}{D} = -\frac{4 \times 10^{17} \frac{\text{atoms}}{\text{m}^2 \cdot \text{s}}}{4 \times 10^{-14} \frac{\text{m}^2}{\text{s}}} = -1 \times 10^{31} \frac{\text{atoms}}{\text{m}^4}$$

$$b) \quad \frac{\Delta c}{\Delta x} = -1 \times 10^{31} \Rightarrow \Delta c = (-1 \times 10^{31} \frac{\text{atoms}}{\text{m}^4}) (10 \times 10^{-6} \text{m})$$

$$\Rightarrow \Delta c = c_B - c_A = -1 \times 10^{26} \frac{\text{atoms}}{\text{m}^3}$$

Chapter 5, Problem 16

The surface of a steel gear made of 1022 steel (0.22 wt % C) is to be gas-carburized at 927°C. Calculate the time necessary to increase the carbon content to 0.30 wt % at 0.7 mm below the surface of the gear. Assume the carbon content of the surface to be 1.20 wt %. D (C in λ iron) at 927°C = 1.28×10^{-11} m²/s.

Chapter 5, Solution 16

Given: $C_s = 1.20\%$ $C_o = 0.22\%$ $C_x = 0.30\%$

$x = 0.7 \text{ mm} = 7 \times 10^{-4} \text{ m}$ $D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.20 - 0.30}{1.20 - 0.22} = \text{erf} \left[\frac{7 \times 10^{-4} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})t}} \right]$$

$$0.9184 = \text{erf} \left[\frac{97.83}{\sqrt{t}} \right] = \text{erf } z$$

Interpolating from Table 5.3,

erf z	$\frac{0.9184 - 0.9103}{0.9340 - 0.9103} = \frac{x - 1.2}{1.3 - 1.2} \quad x = 1.234$
	<p>Thus,</p> $t = \left[\frac{97.83}{z} \right]^2 = \left[\frac{97.83}{1.234} \right]^2 = 6,285.1 \text{ s} = \mathbf{105 \text{ min.}}$
	z
0.9103	1.2
0.9184	x
0.9340	1.3

Chapter 5, Problem 17

A gear made of 1020 steel (0.20 wt % C) is to be gas-carburized at 927°C. Calculate the carbon content at 1 mm below the surface of the gear after a 7.0-hour carburizing time. Assume the carbon content at the surface of the gear is 1.15 wt %. D (C in γ iron) at 927°C = $1.28 \times 10^{-11} \text{ m}^2/\text{s}$.

Chapter 5, Solution 17

$$D \text{ (C in } \lambda \text{ iron) at } 927^\circ\text{C} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}.$$

$$\text{Given: } C_s = 1.00\% \quad C_o = 0.20\% \quad C_x = ? \quad t = 4 \text{ h} = 14,400 \text{ s}$$

$$x = 0.09 \text{ mm} = 9.0 \times 10^{-4} \text{ m} \quad D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.15 - C_x}{1.15 - 0.20} = \text{erf} \left[\frac{1.00 \times 10^{-3} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})(25,200 \text{ s})}} \right]$$

$$\frac{1.15 - C_x}{0.95} = \text{erf}(0.88037)$$

Interpolating from Table 5.3,

erf z	z
0.7707	0.85
x	0.88037
0.7970	0.90

$$\frac{0.88037 - 0.85}{0.90 - 0.85} = \frac{x - 0.7707}{0.7970 - 0.7707} \quad x = 0.7867$$

$$\text{Thus, } 0.7867 = \text{erf}(0.88037)$$

Substituting,

$$\frac{1.15 - C_x}{0.95} = 0.7867 \quad C_x = \mathbf{0.403 \text{ wt \%}}$$

Chapter 5, Problem 18

A gear made of 1020 steel (0.20 wt % C) is to be gas-carburized at 927°C. Calculate the carbon content at 0.90 mm below the surface of the gear after a 4.0-hour carburizing time. Assume the carbon content at the surface of the gear is 1.00 wt %. D (C in γ iron) at 927°C = $1.28 \times 10^{-11} \text{ m}^2/\text{s}$.

Chapter 5, Solution 18

$$D \text{ (C in } \lambda \text{ iron) at } 927^\circ\text{C} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}.$$

$$\text{Given: } C_s = 1.00\% \quad C_o = 0.20\% \quad C_x = ? \quad t = 4 \text{ h} = 14,400 \text{ s}$$

$$x = 0.90 \text{ mm} = 9.0 \times 10^{-4} \text{ m} \quad D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.00 - C_x}{1.00 - 0.20} = \text{erf} \left[\frac{9.0 \times 10^{-4} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})(14,400 \text{ s})}} \right]$$

$$1.25(1 - C_x) = \text{erf}(1.0482)$$

Interpolating from Table 5.3,

erf z	z
0.8427	1.00
x	1.0482
0.8802	1.10

$$\frac{1.0482 - 1.00}{1.10 - 1.00} = \frac{x - 0.8427}{0.8802 - 0.8427} \quad x = 0.8608$$

$$\text{Thus, } 0.8608 = \text{erf}(1.0482)$$

Substituting,

$$1.25(1 - C_x) = 0.8608 \quad C_x = \mathbf{0.311 \text{ wt } \%}$$

Chapter 5, Problem 19

The surface of a steel gear made of 1018 steel (0.18 wt % C) is to be gas-carburized at 927°C. Calculate the time necessary to increase the carbon content to 0.35 wt % at 1.00 mm below the surface of the gear after an 8.0 hour carburizing time. Assume the carbon content at the surface of the gear is 1.20 wt %. D (C in γ iron) at 927°C = 1.28×10^{-11} m²/s.

Chapter 5, Solution 19

Given: $C_s = 1.20\%$ $C_o = 0.18\%$ $C_x = 0.35\%$

$x = 1.0 \text{ mm} = 1.0 \times 10^{-3} \text{ m}$ $D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.20 - 0.35}{1.20 - 0.18} = \text{erf} \left[\frac{1.00 \times 10^{-3} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})t}} \right]$$

$$0.8333 = \text{erf} \left[\frac{139.75}{\sqrt{t}} \right] = \text{erf } z$$

Interpolating from Table 5.3,

erf z	z
0.8209	0.95
0.8333	x
0.8427	1.0

$$\frac{0.8333 - 0.8209}{0.8427 - 0.8209} = \frac{x - 0.95}{1.0 - 0.95} \quad x = 0.978$$

Thus,

$$t = \left[\frac{139.75}{z} \right]^2 = \left[\frac{139.75}{0.978} \right]^2$$

$t = 20,400 \text{ s} = 340 \text{ min.} = 5.67 \text{ h}$

Chapter 5, Problem 20

The surface of a steel gear made of 1020 steel (0.20 wt % C) is to be gas-carburized at 927°C. Calculate the carbon content at 0.85 mm below the surface of the gear after a 9.0-hour carburizing time. Assume the carbon content at the surface of the gear is 1.20 wt %. D (C in γ iron) at 927°C = $1.28 \times 10^{-11} \text{ m}^2/\text{s}$,

Chapter 5, Solution 20

Given: $C_s = 1.20\%$ $C_o = 0.20\%$

$$x = 0.85 \text{ mm} = 0.85 \times 10^{-3} \text{ m} \quad D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.20 - C_x}{1.20 - 0.20} = \text{erf} \left[\frac{0.85 \times 10^{-3} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})(32400\text{s})}} \right] = \text{erf}(0.66)$$

$$\frac{1.20 - C_x}{1.0} = \text{erf}(0.66)$$

Interpolating from Table 5.3,

z	$\text{erf}z$
0.65	0.6420
0.66	x
0.70	0.6778

$$\frac{0.66 - 0.65}{0.70 - 0.65} = \frac{x - 0.6420}{0.6778 - 0.6420} \quad x = 0.6492$$

Thus, $0.6492 = \text{erf}(0.66)$

Substituting,

$$\frac{1.20 - C_x}{1.0} = 0.6492 \quad C_x = \mathbf{0.55 \text{ wt \%}}$$

Chapter 5, Problem 21

A steel gear made of 1018 steel (0.18 wt % C) is to be gas-carburized at 927°C. If the carburizing time is 7.5 h, at what depth in millimeters will the carbon content be 0.040 wt %? Assume the carbon content at the surface of the gear is 1.20 wt %. D (C in γ iron) at 927°C = $1.28 \times 10^{-11} \text{ m}^2/\text{s}$.

Chapter 5, Solution 21

Given: $C_s = 1.20\%$ $C_o = 0.18\%$ $C_x = 0.40\%$

$t = 7.5 \text{ h} = 27,000 \text{ s}$ $D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2 / \text{s}$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{1.20 - 0.40}{1.20 - 0.18} = \text{erf} \left[\frac{x}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2 / \text{s})(27,000 \text{ s})}} \right]$$

$0.7843 = \text{erf}(850.52x) = \text{erf } z$

Interpolating from Table 5.3,

erf z	z
0.7112	0.75
x	0.7823
0.7421	0.80

$$\frac{0.7843 - 0.7707}{0.7970 - 0.7707} = \frac{x_1 - 0.85}{0.90 - 0.85} \quad x_1 = 0.8759$$

Substituting,

$z = 0.8759 = 850.52x$

$x = 0.00103 \text{ m} = 1.03 \text{ mm}$

Chapter 5, Problem 22

If boron is diffused into a thick slice of silicon with no previous boron in it at a temperature of 1100°C for 5 h, what is the depth below the surface at which the concentration is 10^{17} atoms/cm³ if the surface concentration is 10^{18} atoms/cm³? $D = 4 \times 10^{-13}$ cm²/s for boron diffusing in silicon at 1100°C.

Chapter 5, Solution 22

$$\text{Given: } C_s = 10^{18} \text{ atoms/cm}^3 \quad C_x = 10^{17} \text{ atoms/cm}^3 \quad C_o = 0.0$$

$$t = 5.0 \text{ h} = 1.8 \times 10^4 \text{ s} \quad D_{1100^\circ\text{C}} = 4.0 \times 10^{-13} \text{ cm}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{10^{18} - 10^{17}}{10^{18} - 0} = \text{erf} \left[\frac{x}{2\sqrt{(4.0 \times 10^{-13} \text{ cm}^2/\text{s})(1.80 \times 10^4 \text{ s})}} \right]$$

$$0.90 = \text{erf} \left(\frac{x}{1.697 \times 10^{-4}} \right) = \text{erf } z$$

Interpolating from Table 5.3,

erf z	z
0.8802	1.1
0.9000	x
0.9103	1.2

$$\frac{0.9000 - 0.8802}{0.9103 - 0.8802} = \frac{x_1 - 1.1}{1.2 - 1.1} \quad x_1 = 1.166$$

Substituting,

$$z = 1.166 = \frac{x}{1.697 \times 10^{-4}}$$

$$x = 1.98 \times 10^{-4} \text{ cm}$$

Chapter 5, Problem 23

Phosphorus is diffused into a thick slice of silicon with no previous phosphorus in it at a temperature of 1100°C. If the surface concentration of the phosphorus is 1×10^{18} atoms/cm³ and its concentration at $1 \mu\text{m}$ is 1×10^{15} atoms/cm³, how long must be the diffusion time? $D = 3.0 \times 10^{-13}$ cm²/s for P diffusing in Si at 1100°C.

Chapter 5, Solution 23

Given: $C_s = 10^{18}$ atoms/cm³ $C_x = 10^{15}$ atoms/cm³ $C_o = 0.0$
 $x = 1.0 \mu\text{m} = 1.0 \times 10^{-4}$ cm $D_{1100^\circ\text{C}} = 3.0 \times 10^{-13}$ cm²/s

$$\frac{C_s - C_x}{C_s - C_o} = \frac{10^{18} - 10^{15}}{10^{18} - 0} = \text{erf} \left[\frac{10^{-4} \text{ cm}}{2\sqrt{(3.0 \times 10^{-13} \text{ cm}^2/\text{s})t}} \right]$$

$$0.999 = \text{erf} \left(\frac{91.287}{\sqrt{t}} \right) = \text{erf } z$$

Interpolating from Table 5.3,

erf z	z
0.9981	2.2
0.9990	x
0.9993	2.4

$$\frac{0.9990 - 0.9981}{0.9993 - 0.9981} = \frac{x - 2.2}{2.4 - 2.2} \quad x = 2.35$$

Thus,

$$t = \left[\frac{91.287}{z} \right]^2 = \left[\frac{91.287}{2.35} \right]^2$$

$$t = 1508 \text{ s} = \mathbf{25.1 \text{ min.}}$$

Chapter 5, Problem 24

If aluminum is diffused into a thick slice of silicon with no previous aluminum in it at a temperature of 1100°C for 6 h, what is the depth below the surface at which the concentration is 10^{16} atoms/cm³ if the surface concentration is 10^{18} atoms/cm³?

$D = 2 \times 10^{-12}$ cm²/s for aluminum diffusing in silicon at 1100°C.

Chapter 5, Solution 24

Given: $C_s = 10^{18}$ atoms/cm³ $C_x = 10^{16}$ atoms/cm³ $C_o = 0.0$

$t = 6.0 \text{ h} = 2.16 \times 10^4 \text{ s}$ $D_{1100^\circ\text{C}} = 2.0 \times 10^{-12} \text{ cm}^2 / \text{s}$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{10^{18} - 10^{16}}{10^{18} - 0} = \text{erf} \left[\frac{x}{2\sqrt{(2.0 \times 10^{-12} \text{ cm}^2 / \text{s})(2.16 \times 10^4 \text{ s})}} \right]$$

$$0.99 = \text{erf} \left(\frac{x}{4.157 \times 10^{-4}} \right) = \text{erf } z$$

Interpolating from Table 5.3,

erf z	z
0.9891	1.8
0.9900	x
0.9928	1.9

$$\frac{0.9900 - 0.9891}{0.9928 - 0.9891} = \frac{x_1 - 1.8}{1.9 - 1.8} \quad x_1 = 1.824$$

Substituting,

$$z = 1.824 = \frac{x}{4.157 \times 10^{-4}}$$

$$x = 7.58 \times 10^{-4} \text{ cm}$$

Chapter 5, Problem 25

If the diffusivity in Prob. 5.23 had been $1.5 \times 10^{-13} \text{ cm}^2/\text{s}$, at what depth in micrometers would the phosphorus concentration be $1 \times 10^{15} \text{ atoms/cm}^3$?

Chapter 5, Solution 25

Since $\frac{C_s - C_x}{C_s - C_o} = 0.999$, erf z is still 2.35. Thus, for the same diffusion period,

$$z = \left[\frac{x}{2\sqrt{(1.5 \times 10^{-13} \text{ cm}^2/\text{s})(1509 \text{ s})}} \right] = 2.35, \quad x = 7.07 \times 10^{-5} \text{ cm} = \mathbf{0.707 \mu\text{m}}$$

Chapter 5, Problem 26

Arsenic is diffused into a thick slice of silicon with no previous arsenic in it at 1100°C . If the surface concentration of the arsenic is $5.0 \times 10^{18} \text{ atoms/cm}^3$ and its concentration at $1.2 \mu\text{m}$ below the silicon surface is $1.5 \times 10^{16} \text{ atoms/cm}^3$, how long must be the diffusion time? ($D = 3.0 \times 10^{-14} \text{ cm}^2/\text{s}$ for As diffusing in Si at 1100°C .)

Chapter 5, Solution 26

$$\text{Given: } C_s = 5.0 \times 10^{18} \text{ atoms/cm}^3 \quad C_x = 1.5 \times 10^{16} \text{ atoms/cm}^3 \quad C_o = 0.0 \\ x = 1.20 \times 10^{-6} \text{ m} = 1.20 \times 10^{-4} \text{ cm} \quad D_{1100^\circ\text{C}} = 3.0 \times 10^{-14} \text{ cm}^2/\text{s}$$

$$\frac{C_s - C_x}{C_s - C_o} = \frac{5.0 \times 10^{18} - 1.5 \times 10^{16}}{5.0 \times 10^{18} - 0} = \text{erf} \left[\frac{1.20 \times 10^{-4} \text{ cm}}{2\sqrt{(3.0 \times 10^{-14} \text{ cm}^2/\text{s})t}} \right]$$

$$0.9970 = \text{erf} \left(\frac{346.4}{\sqrt{t}} \right) = \text{erf } z$$

Interpolating from Table 5.3,

$$\frac{0.9970 - 0.9953}{0.9981 - 0.9953} = \frac{x - 2.0}{2.2 - 2.0} \quad x = 2.12 \text{ and,}$$

$$t = \left[\frac{346.4}{z} \right]^2 = \left[\frac{346.4}{2.12} \right]^2 = 26,700 \text{ s} = \mathbf{7.42 \text{ h}}$$

Chapter 5, Problem 27

Calculate the diffusivity D in square meters per second for the diffusion of nickel in FCC iron at 1200°C. Use values of $D_0 = 7.7 \times 10^{-5} \text{ cm}^2/\text{s}$; $Q = 280 \text{ kJ/mol}$; $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$.

Chapter 5, Solution 27

The diffusivity of the nickel into FCC iron at 1373 K is:

$$\begin{aligned} D &= D_0 e^{-Q/RT} = (7.7 \times 10^{-5} \text{ m}^2/\text{s}) \left\{ \exp \left[\frac{-280,000 \text{ J/mol}}{[8.314 \text{ J}/(\text{mol} \cdot \text{K})](1473 \text{ K})} \right] \right\} \\ &= (7.7 \times 10^{-5} \text{ m}^2/\text{s})(e^{-22.86}) \\ &= \mathbf{6.12 \times 10^{-12} \text{ m}^2/\text{s}} \end{aligned}$$

Chapter 5, Problem 28

Calculate the diffusivity in square meters per second for the diffusion of zinc in copper at 350°C. Use $D_0 = 3.4 \times 10^{-5} \text{ m}^2/\text{s}$; $Q = 191 \text{ kJ}/(\text{mol} \cdot \text{K})$, $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$.

Chapter 5, Solution 28

The diffusivity of zinc into copper at 623 K is:

$$\begin{aligned} D &= D_0 e^{-Q/RT} = (3.40 \times 10^{-4} \text{ m}^2/\text{s}) \left\{ \exp \left[\frac{-191,000 \text{ J/mol}}{[8.314 \text{ J}/(\text{mol} \cdot \text{K})](623 \text{ K})} \right] \right\} \\ &= (3.40 \times 10^{-5} \text{ m}^2/\text{s})(e^{-36.88}) \\ &= \mathbf{3.29 \times 10^{-21} \text{ m}^2/\text{s}} \end{aligned}$$

Chapter 5, Problem 29

Calculate the diffusivity in square meters per second of carbon in HCP titanium at 700°C. Use $D_0 = 5.10 \times 10^{-4} \text{ m}^2/\text{s}$; $Q = 182 \text{ kJ/mol}$; $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$.

Chapter 5, Solution 29

The diffusivity of carbon into HCP titanium is:

$$\begin{aligned} D &= D_0 e^{-Q/RT} = (5.10 \times 10^{-4} \text{ m}^2/\text{s}) \left\{ \exp \left[\frac{-182,000 \text{ J/mol}}{[8.314 \text{ J}/(\text{mol} \cdot \text{K})](973 \text{ K})} \right] \right\} \\ &= (5.10 \times 10^{-4} \text{ m}^2/\text{s})(e^{-22.49}) \\ &= \mathbf{8.64 \times 10^{-14} \text{ m}^2/\text{s}} \end{aligned}$$

Chapter 5, Problem 30

The diffusivity of copper atoms in the aluminum lattice is $7.50 \times 10^{-13} \text{ m}^2/\text{s}$ at 600°C and $2.50 \times 10^{-15} \text{ m}^2/\text{s}$ at 400°C. Calculate the activation energy for this case in this temperature range. $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$.

Chapter 5, Solution 30

The activation energy associated with copper diffusing into aluminum for this temperature range is,

$$\frac{D_{600^\circ\text{C}}}{D_{400^\circ\text{C}}} = \exp \left[\frac{-Q}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

where $T_1 = 400^\circ\text{C} = 673 \text{ K}$ and $T_2 = 600^\circ\text{C} = 873 \text{ K}$. Substituting,

$$\begin{aligned} \frac{7.5 \times 10^{-13} \text{ m}^2/\text{s}}{2.5 \times 10^{-15} \text{ m}^2/\text{s}} &= \exp \left[\frac{-Q}{8.314 \text{ J}/(\text{mol} \cdot \text{K})} \left(\frac{1}{873 \text{ K}} - \frac{1}{673 \text{ K}} \right) \right] \\ 300 &= \exp \left[(4.094 \times 10^{-5})Q \right] \\ \ln(300) &= (4.094 \times 10^{-5})Q \\ Q &= 139,320 \text{ J/mol} = \mathbf{139.3 \text{ kJ/mol}} \end{aligned}$$

Chapter 5, Problem 31

The diffusivity of iron atoms in the BCC iron lattice is $4.5 \times 10^{-23} \text{ m}^2/\text{s}$ at 400°C and $5.9 \times 10^{-16} \text{ m}^2/\text{s}$ at 800°C . Calculate the activation energy in kJ/mol for this case in this temperature range. $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$.

Chapter 5, Solution 31

The activation energy associated with iron diffusing into BCC iron for this temperature range is,

$$\frac{D_{800^\circ\text{C}}}{D_{400^\circ\text{C}}} = \exp\left[\frac{-Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

where $T_1 = 400^\circ\text{C} = 673 \text{ K}$ and $T_2 = 800^\circ\text{C} = 1073 \text{ K}$. Substituting,

$$\begin{aligned}\frac{5.9 \times 10^{-16} \text{ m}^2/\text{s}}{4.5 \times 10^{-23} \text{ m}^2/\text{s}} &= \exp\left[\frac{-Q}{8.314 \text{ J}/(\text{mol} \cdot \text{K})}\left(\frac{1}{1073 \text{ K}} - \frac{1}{673 \text{ K}}\right)\right] \\ 13,111,111.1 &= \exp\left[(6.662 \times 10^{-5})Q\right] \\ \ln(13,111,111.1) &= (6.662 \times 10^{-5})Q \\ Q &= 246,007 \text{ J/mol} = \mathbf{246 \text{ kJ/mol}}\end{aligned}$$

Chapter 5, Problem 32

The diffusivity of manganese atoms in the FCC iron lattice is $1.50 \times 10^{-14} \text{ m}^2/\text{s}$ at 1300°C and $1.50 \times 10^{-15} \text{ m}^2/\text{s}$ at 400°C . Calculate the activation energy in kJ/mol for this case in this temperature range. $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$.

Chapter 5, Solution 32

The activation energy may be calculated using the Arrhenius type equation,

$$\frac{D_{1300^\circ\text{C}}}{D_{400^\circ\text{C}}} = \frac{\exp(-Q/RT_2)}{\exp(-Q/RT_1)} = \exp\left[\frac{-Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

where $T_1 = 400^\circ\text{C} = 673 \text{ K}$ and $T_2 = 1300^\circ\text{C} = 1573 \text{ K}$. Substituting,

$$\begin{aligned}\frac{1.5 \times 10^{-14} \text{ m}^2/\text{s}}{1.5 \times 10^{-15} \text{ m}^2/\text{s}} &= \exp\left[\frac{-Q}{8.314 \text{ J}/(\text{mol} \cdot \text{K})}\left(\frac{1}{1573 \text{ K}} - \frac{1}{673 \text{ K}}\right)\right] \\ 10 &= \exp\left[(1.0226 \times 10^{-4})Q\right] \\ \ln(10) &= (1.0226 \times 10^{-4})Q \\ Q &= 22,518 \text{ J/mol} = \mathbf{22.5 \text{ kJ/mol}}\end{aligned}$$

*5.33 The concentration of Manganese (Mn) at 500°C on the surface of a sample of FCC iron (metastable) sample is 0.6 a%. At a distance of 2 mm below the surface, the concentration is 0.1 a%. Determine the flux of Mn atoms between the surface and plane 2 mm deep. Hint: convert a% to atoms/m³ using information in Table 3.2.

5.33

Convert atom% (a%) to $\frac{\text{atoms}}{\text{m}^3}$.

For FCC iron, lattice constant $a = 0.351 \text{ nm}$

$$\left(a = \frac{4R}{\sqrt{2}} = \frac{4(0.124 \text{ nm})}{\sqrt{2}} \right) = 0.351 \text{ nm}$$

There are 4 atoms per unit cell.

$$\begin{aligned} \text{Thus, } \frac{\text{atoms}}{\text{unit volume}} &= \frac{4 \text{ atoms}}{(0.351 \times 10^{-9} \text{ m})^3} \\ &= 9.24 \times 10^{28} \frac{\text{atoms}}{\text{m}^3} \end{aligned}$$

$$J = -D \frac{\Delta c}{\Delta x} ; \quad D \Big|_{500^\circ\text{C}} = 3 \times 10^{-24} \frac{\text{m}^2}{\text{s}} \quad (\text{metastable FCC iron})$$

$$\Delta x = 0.002 \text{ m}$$

$$\text{Surface } C_s = 0.006 \times (9.24 \times 10^{28} \frac{\text{atoms}}{\text{m}^3}) = 5.55 \times 10^{26} \frac{\text{atoms}}{\text{m}^3}$$

$$\text{Subsurface } C_{2\text{mm}} = 0.001 \times (9.24 \times 10^{28} \frac{\text{atoms}}{\text{m}^3}) = 9.24 \times 10^{25} \frac{\text{atoms}}{\text{m}^3}$$

$$\Rightarrow J = \left(-3 \times 10^{-24} \frac{\text{m}^2}{\text{s}} \right) \frac{C_{2\text{mm}} - C_s}{0.002 \text{ m}} = 6 \times 10^5 \frac{\text{atoms}}{\text{m}^2 \cdot \text{s}}$$

5.34 The concentration of carbon on the surface of a 1018 steel gear is 0.8 wt% at 1000°C. Determine the flux of carbon atoms from the surface to a plane 25 μm below the surface where carbon concentration is unaffected by the surface concentration. Hint: convert wt% to atoms/m³ using information in Table 3.2.

5.34

At 1000°C, the structure of iron will be FCC.

Convert wt% to $\frac{\text{atoms}}{\text{m}^3}$. (assume 100 grams)

$$\textcircled{1} \Rightarrow 0.8 \times \frac{6.02 \times 10^{23}}{12.01 \text{ g}} = 4.01 \times 10^{22} \text{ atoms of carbon in } 0.8 \text{ g}$$

$$99.2 \times \frac{6.02 \times 10^{23}}{55.85 \text{ g}} = 1.07 \times 10^{24} \text{ atoms of iron in } 99.2 \text{ g}$$

$$\textcircled{2} \Rightarrow \text{for FCC iron, } \frac{4 \text{ atoms}}{(0.351 \times 10^{-9} \text{ nm})^3} = 9.25 \times 10^{28} \frac{\text{atoms}}{\text{m}^3}$$

$$\text{note } a = \frac{4R}{\sqrt{2}} = \frac{4(0.124 \text{ nm})}{\sqrt{2}} = 0.351 \text{ nm}$$

$$\text{From } \textcircled{1} \text{ atom \% carbon} = \frac{4.01 \times 10^{22}}{(4.01 \times 10^{22} + 1.07 \times 10^{24})} \times 100 = 3.6\%$$

⇒ Carbon Concentration on the surface, $C_s \approx 0.036 \left(9.25 \times 10^{28} \frac{\text{atoms}}{\text{m}^3} \right)$

$$C_s \approx 3.33 \times 10^{27} \frac{\text{atoms}}{\text{m}^3}$$

⇒ $J = -D \frac{\Delta C}{\Delta x}$; $D \Big|_{1000^\circ\text{C}} = 3 \times 10^{-11}$ (carbon in FCC iron)

Carbon concentration $25 \mu\text{m}$ below the surface is unaffected. Thus $C_{25\mu\text{m}} = 0.18 \text{ wt}\% = 0.0018 \left(9.25 \times 10^{28} \right)$

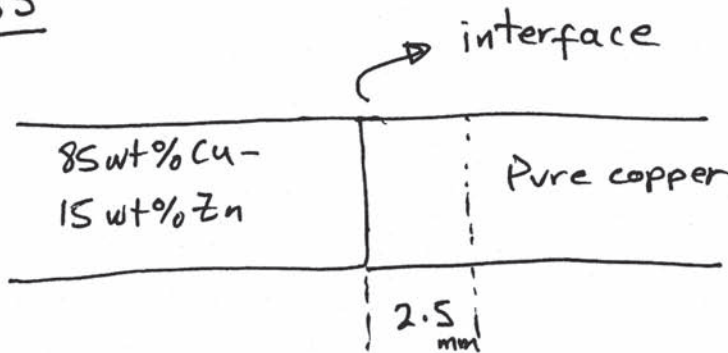
$$C_{25\mu\text{m}} = 1.66 \times 10^{26} \frac{\text{atoms}}{\text{m}^3}$$

$$J = -3 \times 10^{-11} \left(\frac{C_{25\mu} - C_s}{\Delta x} \right) = -3 \times 10^{-11} \left(\frac{1.66 \times 10^{26} - 3.33 \times 10^{27}}{25 \times 10^{-6} \text{ m}} \right)$$

$$J = 3.79 \times 10^{21} \frac{\text{atoms}}{\text{m}^2 \cdot \text{s}}$$

5.35 A copper-zinc alloy (85wt% Cu-10wt% zinc) is coupled with pure copper (interfaced). The diffusion couple is then heated to a temperature of 1000°C. (a) How long will it take for the concentration of zinc to reach 0.2%, 2.5 mm below the interface? (b) How much will the zinc concentration at the same point be in twice the time calculated in part a?

5.35



Copper is solvent
 Zn is solute
 (non-steady diffusion)

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

$C_s = 10 \text{ wt} \%$ (amount of zinc present at the surface)

$C_x = 0.2 \text{ wt} \%$ (concentration at 2.5 mm)

$C_0 = 0\%$ (pure copper)

$x = 2.5 \times 10^{-3} \text{ m}$;

$$D \Big|_{1000^\circ\text{C}} = 5 \times 10^{-13} \frac{\text{m}^2}{\text{sec}} \quad (\text{Table 5.2})$$

$$a) \frac{10\% - 0.2\%}{10\% - 0\%} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \operatorname{erf}(z)$$

$$0.98 = \operatorname{erf}(z) \quad \text{from Table 5.3 using interpolation}$$

z	$\operatorname{erf}(z)$	
1.6	0.9763	$\Rightarrow \frac{1.6 - z}{1.6 - 1.7} = \frac{0.9763 - 0.9800}{0.9763 - 0.9838} \Rightarrow z = 1.65$
z	0.9800	
1.7	0.9838	

$$1.65 = \frac{2.5 \times 10^{-3} \text{ m}}{2\sqrt{5 \times 10^{-13} \text{ t}}} \Rightarrow t = 318 \text{ hrs}$$

$$b) z = \frac{2.5 \times 10^{-3}}{2\sqrt{5 \times 10^{-13} \times 2.29 \times 10^6}} = 1.25 \Rightarrow \operatorname{erf}(z) = 0.916$$

From Table 5.3

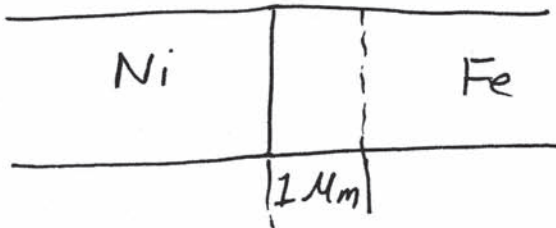
$$0.916 = \frac{10 \text{ wt}\% - C_x}{10 \text{ wt}\% - 0} \Rightarrow C_x = (0.1) - (0.916)(0.1)$$

$$\Rightarrow C_x = 0.84 \text{ wt}\%$$

(increases by more than 4 times)

*5.36 A bar of pure nickel is coupled with a bar of pure iron (interfaced). The diffusion couple is then heated to a temperature of 1000°C. (a) How long will it take for the concentration of nickel to reach 0.1 wt%, 1.0 μm below the interface? (b) How long will it take for the concentration of nickel to reach 0.1 wt%, 1.0 mm below the interface? (c) What does the comparison of the two answers show?

5.36



Iron is solvent
 Ni is solute
 (non-steady diffusion)
 $T = 1000^\circ\text{C}$

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

$$C_s = 100\% \quad (\text{Pure nickel})$$

$$C_x = 0.1 \text{ wt}\% \quad (\text{at } x = 1 \times 10^{-6} \text{ m})$$

$$C_0 = 0 \text{ wt}\% \quad (\text{Pure iron}) \quad ; \quad D \Big|_{1000^\circ\text{C}} = 2 \times 10^{-16} \frac{\text{m}^2}{\text{s}}$$

$$a) \quad \frac{100 - 0.1}{100 - 0} = \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right) = \text{erf}(z)$$

$$\text{erf}(z) = 0.999 \quad \Rightarrow \quad z = 2.8$$

$$\Rightarrow \frac{x}{2\sqrt{Dt}} = 2.8 \quad \Rightarrow \quad \frac{1 \times 10^{-6} \text{ m}}{2\sqrt{2 \times 10^{-16} \frac{\text{m}^2}{\text{s}} \cdot t}} = 2.8$$

5.36 cont.

$$\Rightarrow t = \frac{(1 \times 10^{-6})^2}{(2.8)^2 (4) (2 \times 10^{-16})} = 159 \text{ s}$$

b) for concentration of 0.1 wt% at 1.0 mm

$$t = \frac{(1 \times 10^{-3})^2}{(2.8)^2 (4) (2 \times 10^{-16})} = 1.59 \times 10^8 \text{ s}$$

The conclusion is that diffusion is a slow process. Also, a small change in Δx (by a factor of 1000) will increase the time by a factor of 10^8 .

5.37 The activation energy of nickel atoms in FCC iron is 280 kJ/mol and carbon atoms in FCC iron is 142 kJ/mol. (a) What does this tell you about the comparative diffusion of nickel and carbon in iron? (b) Can you explain why the activation energies are so drastically different? (c) Find a way to qualitatively explain how much energy is 142 kJ to a non-engineer or a non-scientist.

5.37

a) since $Q_{C-Fe} < Q_{Ni-Fe}$, it can be concluded that carbon has an easier time diffusing in Fe than Ni atoms do in Fe.

b) The difference in activation energies is due to differences in mechanisms (interstitial diffusion for C-Fe and substitutional for Ni-Fe).

c) You would need 4.2 J of heat to increase the temperature of one gram of water by one degree C. Thus, 142000 J would raise the temperature of 33,809 g ($\frac{142000}{4.2}$) of water by 1°C. Other ways to explain:

336 J to boil one gram of water
142000 J to boil 422 grams of water
(or 0.422 Kg).

Note that the activation energy is per mol. Therefore, the actual energy for practical applications will be significantly higher, and depends on the number of moles.

*5.38 The proportionality constant, D_0 , of iron in BCC iron is 9.1 times higher than in FCC iron. The activation energy of iron in BCC iron is 90.3% that of iron in FCC iron. Determine Q and D_0 for iron in FCC iron. Verify your answers with those in Table 5.4.

5.38

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

$$D_{\text{BCC}} = 9.11 D_{\text{FCC}} \quad ; \quad Q_{\text{BCC}} = 0.903 Q_{\text{FCC}}$$

From Table 5.2

$$D_{\text{BCC}} \Big|_{500^\circ\text{C}} = 10^{-20} \frac{\text{m}^2}{\text{s}} \quad ; \quad D_{\text{FCC}} \Big|_{500^\circ\text{C}} = 2 \times 10^{-23} \frac{\text{m}^2}{\text{s}}$$

Thus, at 500°C

$$\frac{D_{\text{BCC}}}{D_{\text{FCC}}} = \frac{D_{\text{BCC}}}{D_{\text{FCC}}} e^{-\frac{Q_{\text{BCC}} + Q_{\text{FCC}}}{RT}}$$

$$\Rightarrow \frac{10^{-20}}{2 \times 10^{-23}} = 9.11 e^{-\frac{0.903 Q_{\text{FCC}} + Q_{\text{FCC}}}{(8.314)(773)}}$$

$$\text{a) } \Rightarrow Q_{\text{FCC}} = \frac{\ln(54.9)}{1.50 \times 10^{-5}} = 265384 \text{ J/mol} \quad \left(\begin{array}{l} \text{Table 5.4} \\ 268 \frac{\text{kJ}}{\text{mol}} \end{array} \right)$$

$$\text{b) } D_{\text{FCC}} = \frac{D_{\text{FCC}}}{e^{-\frac{Q_{\text{FCC}}}{RT}}} = \frac{2 \times 10^{-23}}{e^{-\frac{265384}{(8.314)(773)}}} = 1.72 \times 10^{-5} \quad \left(\begin{array}{l} \text{Table 5.4} \\ 2.20 \times 10^{-5} \end{array} \right)$$

To get accurate values of D_0 , one needs very accurate values of Q . (The $\frac{D_{\text{BCC}}}{D_{\text{FCC}}}$ and $\frac{Q_{\text{BCC}}}{Q_{\text{FCC}}}$ must be measured very accurately)

5.39 The proportionality constant, D_0 , of carbon in HCP titanium is 25.5 times higher than carbon in FCC iron. The activation energy of carbon in HCP titanium is 1.28 times of carbon in FCC iron. Determine Q and D_0 for carbon in FCC iron. Verify your answers with those in Table 5.4.

$$\underline{5.39} \quad D = D_0 e^{-\frac{Q}{RT}}$$

$$D_{0\text{C-Ti}} = 25.5 D_{0\text{C-Fe}} \quad ; \quad Q_{\text{C-Ti}} = 1.28 Q_{\text{C-Fe}}$$

From Table 5.2 a) 500°C :

$$D_{\text{C-Ti}} \Big|_{500^\circ\text{C}} = 3 \times 10^{-16} \frac{\text{m}^2}{\text{s}} \quad ; \quad D_{\text{C-Fe}} \Big|_{500^\circ\text{C}} = 5 \times 10^{-15} \frac{\text{m}^2}{\text{s}}$$

$$\Rightarrow \frac{3 \times 10^{-16}}{5 \times 10^{-15}} = \frac{D_{0\text{C-Ti}} e^{-\frac{Q_{\text{C-Ti}}}{RT}}}{D_{0\text{C-Fe}} e^{-\frac{Q_{\text{C-Fe}}}{RT}}}$$

$$\Rightarrow \frac{3 \times 10^{-16}}{5 \times 10^{-15}} = 25.5 e^{\frac{-Q_{\text{C-Ti}} + Q_{\text{C-Fe}}}{RT}} = 25.5 e^{\frac{-1.28 Q_{\text{C-Fe}} + Q_{\text{C-Fe}}}{(8.314)(773)}}$$

$$\text{a) } \Rightarrow Q_{\text{C-Fe}} = \frac{\ln(0.00235)}{-4.35 \times 10^{-5}} \approx 139 \frac{\text{kJ}}{\text{mol}} \quad \left(\begin{array}{l} \text{Table 5.4} \\ 142 \frac{\text{kJ}}{\text{mol}} \end{array} \right)$$

$$\text{b) } D_{0\text{C-Fe}} = \frac{5 \times 10^{-15}}{e^{-\left(\frac{139,000}{(8.314)(773)}\right)}} = 1.2 \times 10^{-5} \quad \left(\begin{array}{l} \text{Table 5.4} \\ 2.0 \times 10^{-5} \end{array} \right)$$

The differences are due to inaccuracies in relative measurement of $D_{0\text{C-Ti}}$ to $D_{0\text{C-Fe}}$ and $Q_{\text{C-Ti}}$ to $Q_{\text{C-Fe}}$.

5.40 The self-diffusion of iron atoms in BCC iron is significantly higher than in FCC iron (See Table 5.2). Explain why.

5.40

The packing factor for BCC metals is lower than that of FCC metals. As a result, there is more space for diffusion in BCC iron (APF = 0.68) than in FCC iron (APF = 0.74).

5.41 The melt temperatures of copper and aluminum are 1083°C and 657°C respectively. Compare the diffusivities of copper in copper and copper in aluminum at 500°C (use Table 5.2). Can you explain why a drastic difference exists?

5.41

Copper has a higher melting temp than aluminum. This means that the bonds between copper atoms are stronger and therefore harder to break. Diffusion will likely be more difficult in copper than aluminum.

A second reason could be that although both metals are FCC, the void spaces in aluminum are larger (see example 4.3) since $r_{Al} > r_{Cu}$.

5.42 Would you expect the diffusion rate of copper (self diffusion) to be lower or higher in copper with ASTM grain size 4 than in copper with ASTM grain size 8? Explain your answer.

5.42

There are more grains and grain boundaries in fine grained copper (the one with $n=8$). Grain boundaries are less efficiently packed and allow for higher diffusion rates. Thus copper with ASTM grain size of 8 will have higher self diffusion.

5.43 Would you expect the diffusion rate of copper (self-diffusion) to be lower in a pure copper sample that is loaded with dislocations or in a pure copper sample that is free of dislocations (refer to Sec. 4.4.2 for characteristics of dislocations)? Explain your answer.

5.43

Metals loaded with dislocation possess higher stored energy. The atoms are forced out of their normal position and this causes lattice strain. The atoms have a higher state of energy than in a unstrained array. The extra energy could help with the diffusion process.

5.44 Is the non-steady diffusion process more sensitive to temperature or time? Explain using appropriate equations.

5.44

In the non-steady diffusion equation

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

note that time, t , appears in the denominator under the radical sign.

Temperature, T , also appears in the same place through " D ".

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

Small changes in temperature, T , will cause large changes in D .

Thus cutting the temperature by half will have a more significant impact on the diffusion process than cutting the time by half.

5.45 In NaCl, would you expect the activation energy of cation (Na^+) to be higher or the anion (Cl^-)? Why?

5.45

Cations are smaller in size than their bonding anions. This offers an advantage for higher rates of diffusion for cations. Na^+ will have a lower activation energy.

5.46 Show, using equations only, that as time increases in the gas carburization process, the concentration C_x increases.

5.46

In the non-steady diffusion equation

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

as time increases the denominator in the argument of erf also increases.

as denominator increases, the argument $\left(\frac{x}{2\sqrt{Dt}} \right)$ will decrease. As the argument becomes smaller, the erf $\left(\frac{x}{2\sqrt{Dt}} \right)$ will also become smaller (see Table 5.3). As erf $\left(\frac{x}{2\sqrt{Dt}} \right)$ becomes smaller, the difference between C_s and C_x also becomes smaller.

Thus C_x is approaching C_s (becoming larger).

5.47 If hydrogen diffuses in ferrous alloys, it will make the material significantly more brittle and susceptible to fracture. The activation energy of hydrogen in steel is 3.6 kcal/mol. Should we worry about hydrogen embrittlement of steels (is it very likely to occur)? Explain.

5.47

Compare the activation energy of hydrogen in iron ($3.6 \frac{\text{kcal}}{\text{mol}}$) to that of carbon in iron ($29 \text{ to } 34 \frac{\text{kcal}}{\text{mol}}$) in Table 5.4. It is clear that $Q_{\text{H-Fe}}$ is 10 times smaller than $Q_{\text{C-Fe}}$.

Now consider the equation for diffusivity:

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

as Q is decreased by a factor of 10, $-\frac{Q}{RT}$ also decreases resulting in a large increase in $e^{-\frac{Q}{RT}}$. We should be concerned with diffusion of hydrogen in ferrous alloys.

5.48 In powder metallurgy, solid parts are formed by first densifying powder through pressure/compaction at room temperature. The particles are pressed against each other and form necks at the point of contact with each other (see Fig. P5.48a). The next stage is then sintering in which the densified compact is heated to elevated temperatures. The sintering stages are between 1000°C (Fig. P5.48b) and 1050°C (Fig. P5.48d). What observation can you make regarding the physical features of the compact going from the room temperature compact to sintering at 1050°C? What is the reason for this change?

5.48 It is clear that high pressure alone can not densify the powder to acceptable levels (see Figure a). There is a great deal of porosity in figure a.

However, as temperature is increased, the degree of porosity decreases significantly (Compare figure a to figure d). The reduction in void space or densification of compact occurs because of diffusion across the contact areas between particles. Thus diffusion is the main mechanism of densification.