MATERIALS SCIENCE

DIFFUSION

Many reactions and processes that are important in the treatment of materials rely on the transfer of mass either within a specific solid or from a liquid, a gas or another solid phase. This is **diffusion**, the phenomenon of material *transport* by atomic motion.

Demonstration of Diffusion

The mechanism of diffusion can be demonstrated by considering a **diffusion couple**. A diffusion couple is formed by joining bars of two different materials, in this case, copper (Cu) and nickel (Ni) is considered.

1. The couple is heated to high temperatures for a period of time (below melting point) and cooled at room temperature.
2. Chemical analysis will show pure copper and pure nickel on the left and right respectively, separated by a copper-nickel alloy.
3. This shows that copper atoms have diffused into the nickel and the nickel atoms have diffused into the copper.
4. This process whereby atoms of one metal diffuse into another is termed interdiffusion or impurity diffusion.
5. Diffusion also occurs in pure metals, this is termed self diffusion.

Diffusion Mechanism

For atoms to move, two conditions must be met.

1) There must be an empty adjacent site
2) The atoms must have enough energy to break the bonds with its neighbor atoms- vibrational energy through temperature increase.

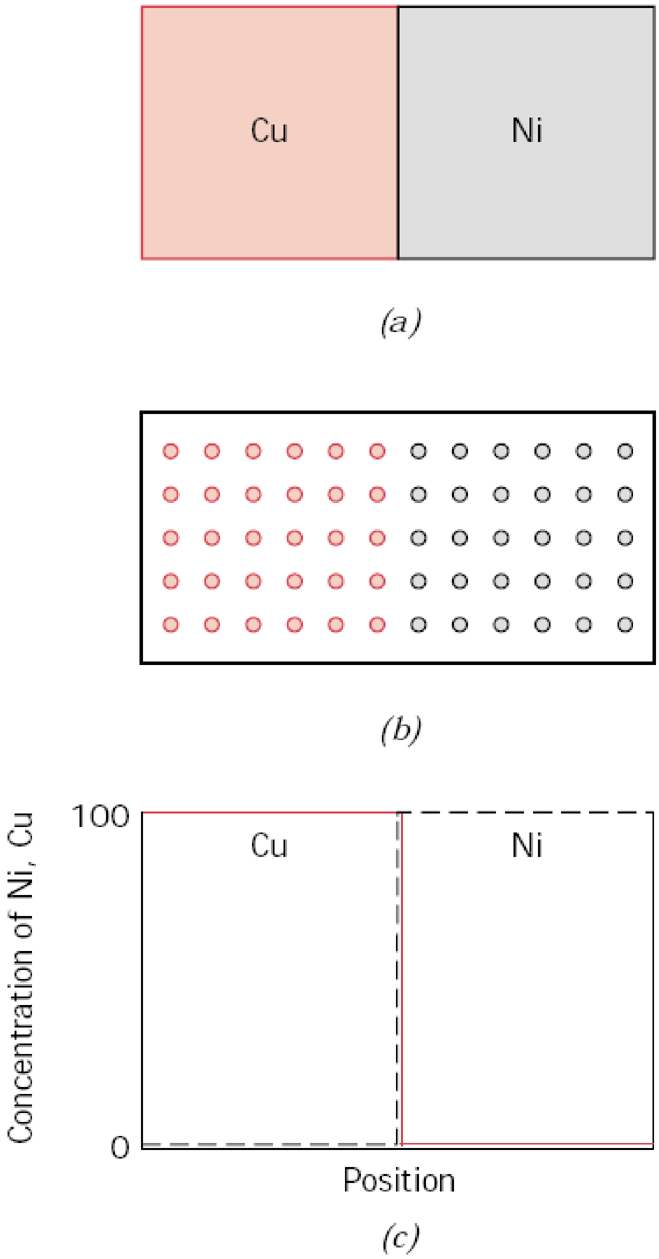


Figure 6.1 (*a*) A copper–nickel diffusion couple before a high-temperature heat treatment. (*b*) Schematic representations of Cu (colored circles) and Ni (gray circles) atom locations within the diffusion couple. (*c*) Concentrations of copper and nickel as a function of position across the couple.

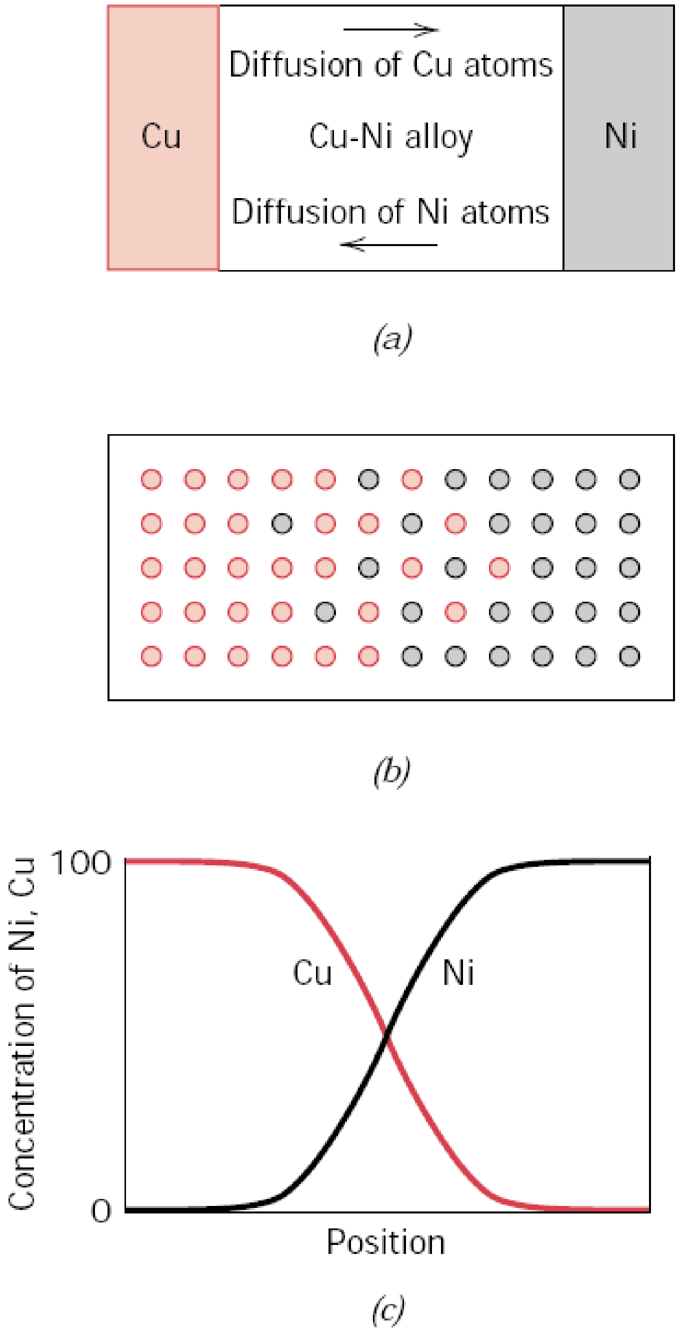


FIGURE 6.2 (*a*) A copper–nickel diffusion couple after a high-temperature heat treatment, showing the alloyed diffusion zone. (*b*) Schematic representations of Cu (colored circles) and Ni (gray circles) atom locations within the couple. (*c*) Concentrations of copper and nickel as a function of position across the couple.

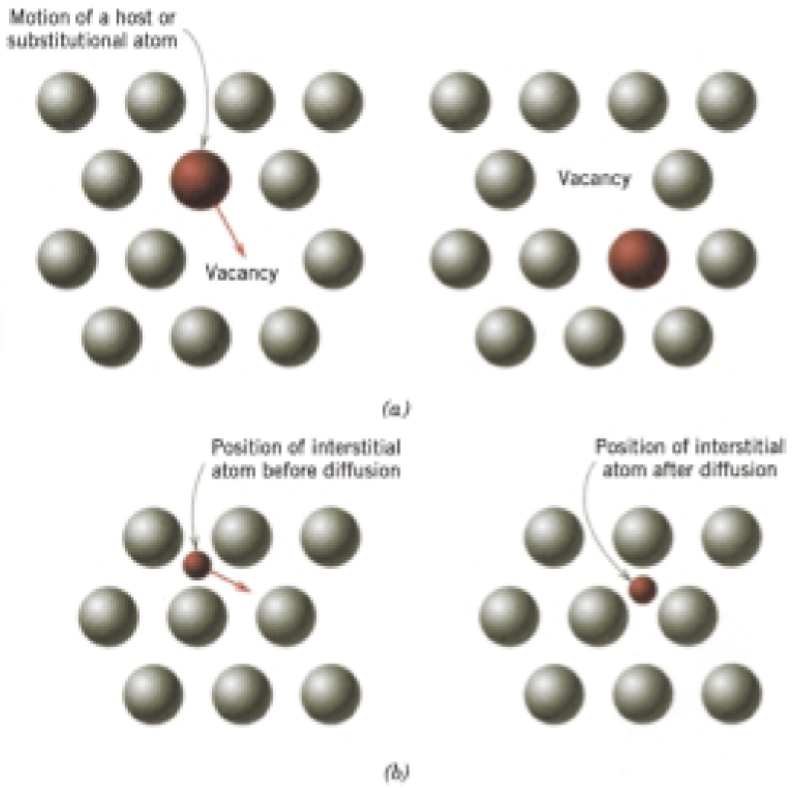
Vacancy Diffusion

1) This mechanism involves the interchange of an atom from a normal lattice position to an adjacent vacant site.
2) Atoms move in one direction corresponding to the vacancy moving in the opposite direction.
3) This process is not possible without vacancies and the more vacancies the higher the chances of vacancy diffusion.

Interstitial Diffusion

1) Small impurity atoms diffuse through the interstices of the parent metal.
2) This method of diffusion takes place faster because the impurities are smaller and are more mobile.

FIGURE 6.3 Schematic representations of (*a*) vacancy diffusion and (*b*) interstitial diffusion.



Steady State Diffusion

1) Diffusion is a time dependent process.
2) The rate of diffusion or the rate of mass transfer is express as **diffusion flux** and it is denoted by ***J***.
3) It is given by

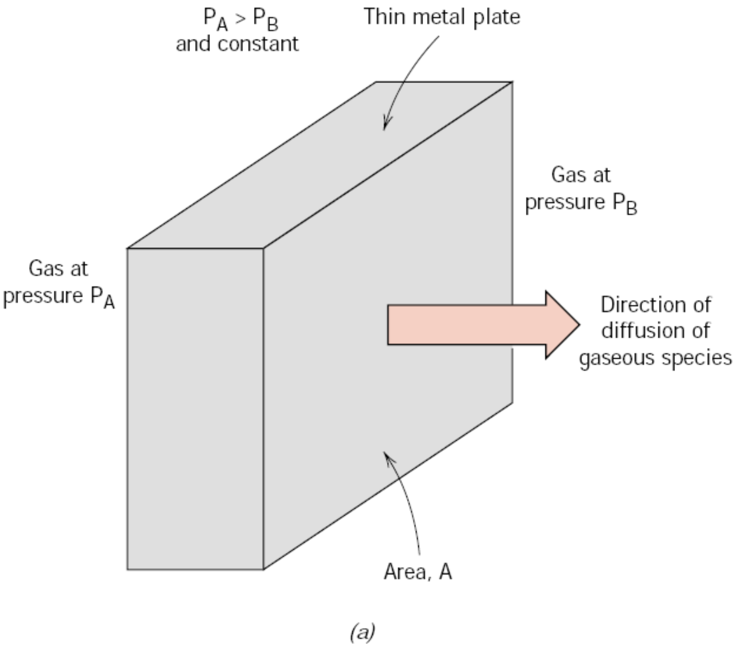
$$J = \frac{M}{At} \qquad \text{(atoms / m}^2\text{s) or (kg/m}^2\text{s)}$$

M is the mass or no of atoms diffusion through a specimen

A is the cross-sectional area perpendicular to the direction of flux.

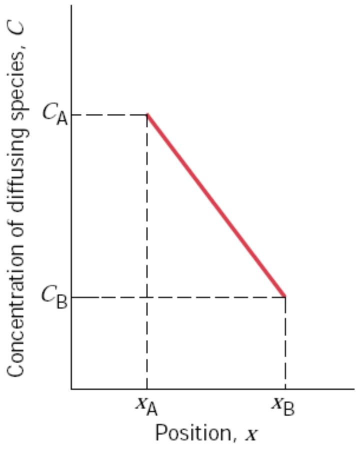
t is the diffusion time

FIGURE 6.4 (*a*) Steady-state diffusion across a thin plate. (*b*) A linear concentration profile for the diffusion situation in (*a*).



For steady state diffusion of atoms of a gas through a plate of metal to occur, the concentration (pressure) of the diffusion species on both surface must be held constant.

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



(b)

Fick’s First Law

Fick’s first law of diffusion state that for steady state diffusion condition, the net flow of atoms by atomic diffusion is equal to the **diffusivity** (***D***) times the diffusion gradient dC/dx.

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

D is the diffusivity (diffusion coefficient)

J is the diffusion flux

dC/dx is the concentration gradient

The **negative sign** indicated the direction of the diffusion in m^2/s from higher to lower concentration

Diffusivity/Diffusion Coefficient Depends Upon

- **Type of diffusion**: whether the diffusion is interstitial or substitutional.
- **Temperature**: as the temperature increases diffusivity increases.
- Type of **crystal structure**: BCC crystal has lower APF than FCC and hence has higher diffusivity.
- Type of **crystal imperfection**: more open structures (grain boundaries) increases diffusion.
- The **concentration** of diffusing species: higher concentrations of diffusing solute atoms will affect diffusivity.

Non Steady State Diffusion

1) In a non-steady state diffusion condition, the concentration of atoms at any point in the material changes with time.
2) Most diffusion situations are non steady state.
3) The diffusion flux and the concentration gradient at some particular point in a solid vary with time.

Fick's Second Law

Fick's Second Law is given by

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

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

C_s is the surface concentration of the diffusing element

C_x represents the concentration at depth x after time t

C_o is the initial concentration of the specimen

x is the distance from the surface

D is the diffusivity of the diffusing element

t is the time

The Effect of Temperature on Diffusion in Solids

1) Since atomic diffusion involves atomic movements, it is to be expected that increasing the temperature of a diffusion system will increase the diffusion rate.
2) Temperature has the most influence on the coefficients of diffusion rates.
3) Arhenius equation:

$$D = D_o \exp\left[\frac{-Q}{RT}\right]$$

D is diffusivity, m2/s

D_O is the proportionality constant, m2/s

Q is the activation energy of the diffusing species, J/mol

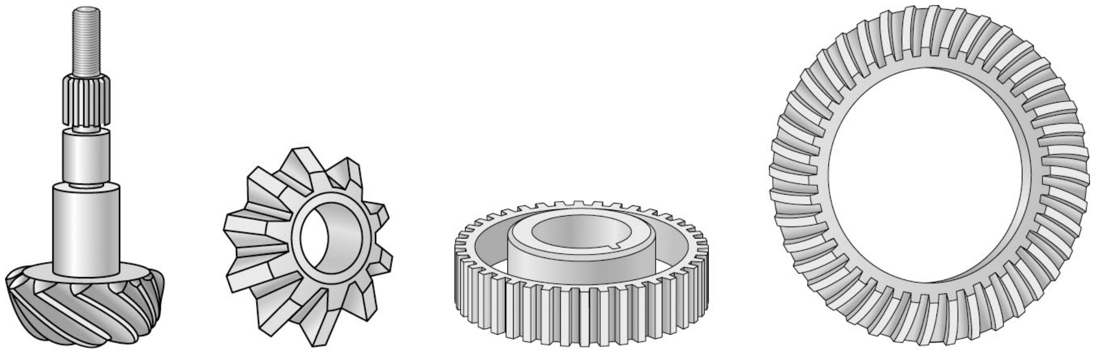
R is the molar gas constant (87.304 J/mol.K)

T is the temperature in K

Industrial Applications of Diffusion Processes

Case Hardening of Steel by Gas Carburizing

Many rotating or sliding steel parts such as gears and shafts must have a hard outside case for wear resistance and a though inner core for fracture resistance. In the manufacture of carburized steel parts, the part is usually machined to shape in its soft condition, and then the outer layer is hardened by gas carburizing.



Part 1
3.0 in. long

Part 2
2.6 in. diam

Part 3
4.5 in. diam

Part 4
7.75 in. diam

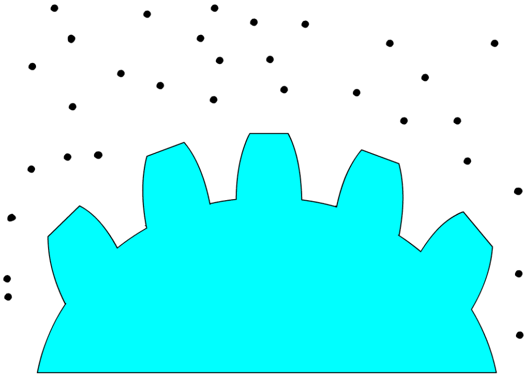
Typical Gas-Carburized Steel Parts

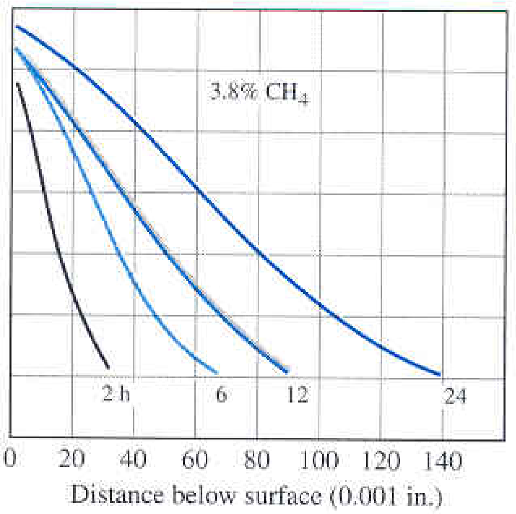
In the first part of the gas carburizing process, the steel parts are placed in a furnace in contact with gasses containing methane (CH_4) or other hydrocarbon gases at about 927°C (1700°F). The carbon from the atmosphere diffuses into the surface of the gears so that gears are left with high carbon cases i.e. carbon diffuses into iron surface and fills interstitial space to make it harder.

Example 1:

Consider the gas carburizing of a gear of 1020 steel at 927°C (1700°F). Calculate the time in minutes necessary to increase the carbon content to 0.40% at 0.50 mm below the surface. Assume that the carbon content at the surface is 0.90% and the steel has nominal carbon content of 0.20%.

Parts to be carburized in a nitrogen-methanol carburizing atmosphere

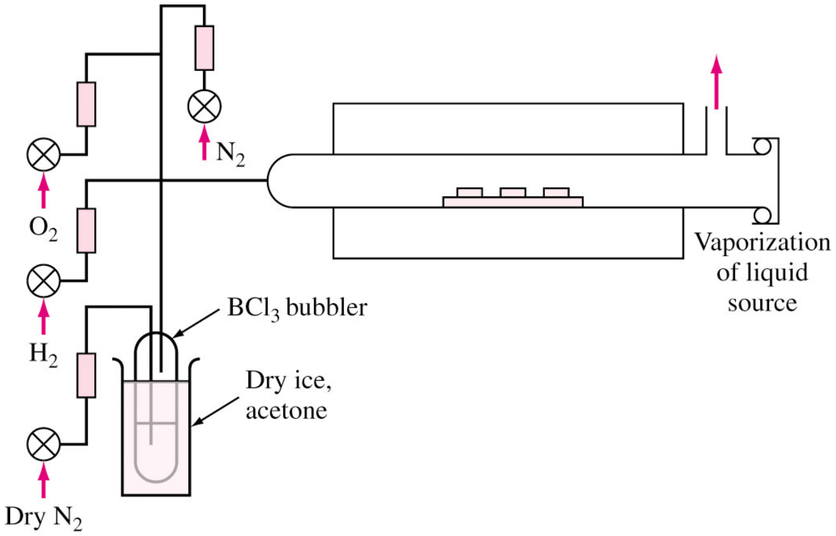




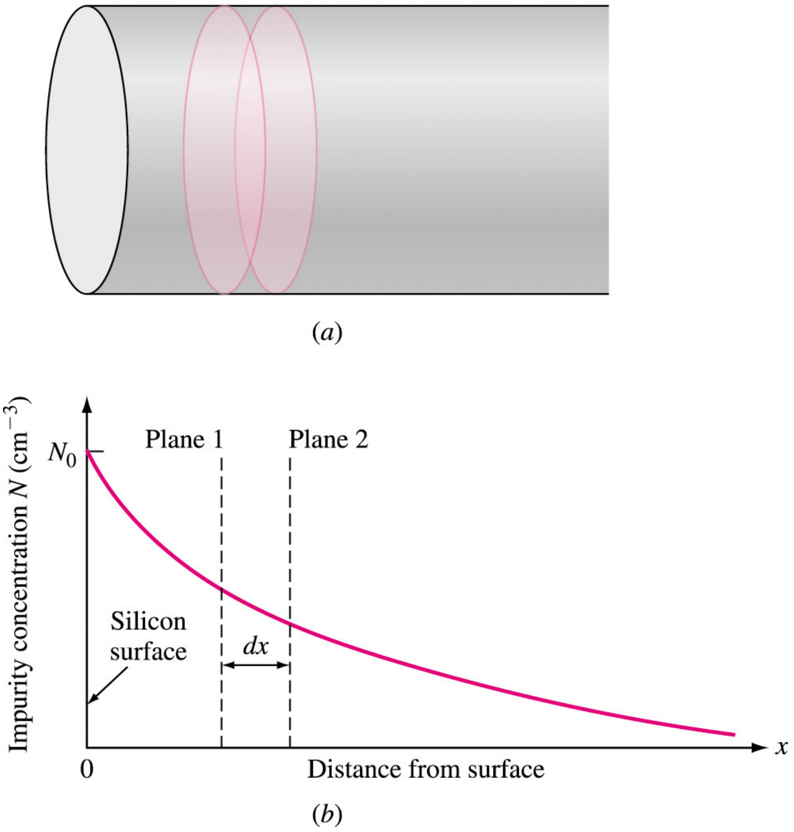
Carbon gradients in test bars of 1022 steel carburized at 918°C in a 20% CO–40% H2 gas with 1.6 and 3.8% methane (CH_4) added

Impurity Doping of Silicon Waters for Integrated Electronic Circuits

Impurity diffusion into silicon wafers is carried out to change their electrical conducting characteristics. In one method, the silicon surfaces is exposed to the vapour of an appropriate impurity at a temperature above 1100C in a quarts tube furnace. The parts not to be exposed to the impurity are masked off so that impurities diffuse only into the desired surfaces.



Diffusion method for diffusing boron into silicon wafers.



Impurity diffusion into a silicon wafer from one face. (a) A silicon wafer with thickness greatly exaggerated having an impurity concentration which diminishes form the left face toward the interior. (b) Graphical representation of the some impurity distribution.

Example 2:

Consider the impurity diffusion of gallium into a silicon wafer. If gallium is diffused into a silicon wafer with no previous gallium in it at a temperature of 1100°C for 3 hours, what is the depth below the surface at which the concentration of 10^{22} atoms/m^3 if the surface concentration is 10^{24} atoms/m^3?

Example 3:

Calculate the value of the diffusivity D in meters squared per second for the diffusion of carbon in γ iron (FCC) at 927°C (1700°F). Use values of $D_0 = 2.0 \times 10^{-5}$ m^2/s, Q = 142 kJ/mol, R = 8.314 J/(mol·K)

Questions

1) A gear made of 1020 steel (0.2 wt% C) is to be gas-carburized at 927°C (1700°F). Calculate the carbon content at 0.040 in. 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 %. Assume D for C in Fe at 927°C = 1.28×10^{-11} m^2/s. *(Ans: 0.394 wt %)*

2) A gear mad of 1018 steel (0.18 wt % C) is to be gas carburized at 927°C. If the carburizing time is 7.5 hours, at what depth in millimeters will the carbon content be 0.40 wt %? Assume the carbon content at the surface of the gear is 1.20 wt %. Assume D for C in Fe at 927°C = 1.28×10^{-11} m^2/s. *(Ans: 1.03 mm)*

3) The surface of a steel gear made of 1018 steel (0.18 wt % C) is to be carburized at 927°C. Calculate the time necessary to increase the carbon content to 0.40 wt % at 0.95 mm below the surface. Assume the carbon content of the surface of the gear is 1.10 wt %. Assume D for C in Fe at 927°C = 1.28×10^{-11} m^2/s.

4) If boron is diffused into a thick slice of silicon with no previous boron in it at a temperature of 1100°C for 5 hours, what is the depth below the surface at which the concentration is 10^{17} atoms/cm^3 if the surface concentration is 10^{18} atoms/cm^3? $D = 4 \times 10^{-13}$ cm^2/s for boron diffusing in silicon at 1100°C. *(Ans: 1.98×10^{-4} cm)*

5) Calculate the diffusivity in square meter per second of nickel in FCC iron at 1200°C. Use $D_0 = 7.7 \times 10^{-5}$ m^2/s, Q = 280 kJ/mol; R = 8.314 J/(mol·K) *(Ans: 9.06×10^{-15} m^2/s)*

6) Calculate the diffusivity in square meter per second of carbon in HCP titanium at 800°C. Use $D_0 = 5.10 \times 10^{-4}$ m^2/s, Q = 182 kJ/mol; R = 8.314 J/(mol·K) *(Ans: $9.06 \times 10^{-15} m^2/s$)*

7) Calculate the diffusivity in square meter per second for the diffusion of zinc in copper at 300°C. Use $D_0 = 3.4 \times 10^{-5}$ m^2/s, Q = 191 kJ/mol; R = 8.314 J/(mol·K) *(Ans: $9.06 \times 10^{-15} m^2/s$)*

8) The diffusivity of copper atoms in the aluminum lattice is 7.0×10^{-13} m^2/s at 600°C and 2.0×10^{-15} m^2/s at 400°C. Calculate the activation energy in kilojoules per mole for this case in this temperature range. [R = 8.314 J/(mol · K)] *(Ans: 143 kJ/mol)*

9) The diffusivity of manganese atoms in FCC iron lattice is 1.0×10^{-14} m^2/s at 1300°C and 1.0×10^{-15} m^2/s at 400°C. Calculate the activation energy in kilojoules per mole for this case in this temperature range. [R = 8.314 J/(mol · K)] *(Ans: 27.5 kJ/mol)*

10) The diffusivity of iron atoms in BCC Fe lattice is 4.2×10^{-23} m^2/s at 400°C and 5.6×10^{-16} m^2/s at 800°C. Calculate the activation energy in kilojoules per mole for this case in this temperature range. [R = 8.314 J/(mol · K)] *(Ans: 246 kJ/mol)*

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

12) What factors affect the diffusion rate in solid metal crystals?

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

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}
					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.