1.9 Kinetic Molecular Theory  Calculate the effective (rms) speeds of the He and Ne atoms in the He-Ne gas laser tube at room temperature (300 K).

Solution
To find the root mean square velocity \((v_{\text{rms}})\) of He atoms at \(T = 300 \text{ K}\):

The atomic mass of He is (from Periodic Table) \(M_{\text{at}} = 4.0 \text{ g/mol}\). Remember that 1 mole has a mass of \(M_{\text{at}}\) grams. Then one He atom has a mass \((m)\) in kg given by:

\[
m = \frac{M_{\text{at}}}{N_A} = \frac{4.0 \text{ g/mol}}{6.022 \times 10^{23} \text{ mol}^{-1}} \times (0.001 \text{ kg/g}) = 6.642 \times 10^{-27} \text{ kg}
\]

From kinetic theory (visualized in Figure 1Q9-1),

\[
\frac{1}{2} m (v_{\text{rms}})^2 = \frac{3}{2} kT
\]

\[
\therefore \quad v_{\text{rms}} = \sqrt{\frac{3 kT}{m}} = \sqrt{\frac{3 (1.381 \times 10^{-23} \text{ J K}^{-1}) (300 \text{ K})}{(6.642 \times 10^{-27} \text{ kg})}} = 1368 \text{ m/s}
\]

The root mean square velocity \((v_{\text{rms}})\) of Ne atoms at \(T = 300 \text{ K}\) can be found using the same method as above, changing the atomic mass to that of Ne, \(M_{\text{at}} = 20.18 \text{ g/mol}\). After calculations, the mass of one Ne atom is found to be \(3.351 \times 10^{-26} \text{ kg}\), and the root mean square velocity \((v_{\text{rms}})\) of Ne is found to be \(v_{\text{rms}} = 609 \text{ m/s}\).

![Figure 1Q9-1: The gas molecule in the container are in random motion.](image1)

![Figure 1Q9-2: The He-Ne gas laser.](image2)

Author’s Note: Radiation emerging from the He-Ne laser tube (Figure 1Q9-2) is due to the Ne atoms emitting light, all in phase with each other, as explained in Ch. 3. When a Ne atom happens to be moving towards the observer, due to the Doppler Effect, the frequency of the laser light is higher. If a Ne atom happens to moving away from the observer, the light frequency is lower. Thus, the random motions of the gas atoms cause the emitted radiation not to be at a single frequency but over a range of frequencies due to the Doppler Effect.

1.31 Pb-Sn solder  Consider the soldering of two copper components. When the solder melts, it wets both metal surfaces. If the surfaces are not clean or have an oxide layer, the molten solder cannot wet the surfaces and the soldering fails. Assume that soldering takes place at 250 \(^{\circ}\)C, and consider the diffusion of Sn atoms into the copper (the Sn atom is smaller than the Pb atom and hence diffuses more easily).
a. The diffusion coefficient of Sn in Cu at two temperatures is $D = 1.69 \times 10^{-9}$ cm$^2$ hr$^{-1}$ at 400 °C and $D = 2.48 \times 10^{-7}$ cm$^2$ hr$^{-1}$ at 650 °C. Calculate the rms distance diffused by an Sn atom into the copper, assuming the cooling process takes 10 seconds.

b. What should be the composition of the solder if it is to begin freezing at 250 °C?

c. What are the components (phases) in this alloy at 200 °C? What are the compositions of the phases and their relative weights in the alloy?

d. What is the microstructure of this alloy at 25 °C? What are weight fractions of the $\alpha$ and $\beta$ phases assuming near equilibrium cooling?

Solution

a. Given information:

Temperatures: $T_1 = 400 \, ^\circ \text{C} + 273 = 673 \, \text{K}$
$T_2 = 650 \, ^\circ \text{C} + 273 = 923 \, \text{K}$

Diffusion coefficients: $D_1 = 1.69 \times 10^{-9}$ cm$^2$/hr = $(1.69 \times 10^{-9}$ cm$^2$/hr)(0.01 m/cm)$^2$ / (1 hr) × (3600 sec/hr)
$D_1 = 4.694 \times 10^{-17}$ m$^2$/s

$D_2 = 2.48 \times 10^{-7}$ cm$^2$/hr = $(2.48 \times 10^{-7}$ cm$^2$/hr)(0.01 m/cm)$^2$ / (1 hr) × (3600 sec/hr)
$D_2 = 6.889 \times 10^{-15}$ m$^2$/s

The diffusion coefficients $D_1$ and $D_2$ at $T_1$ and $T_2$ respectively are given by:

$$D_1 = D_o \exp\left(-\frac{E_A}{kT_1}\right)$$

$$D_2 = D_o \exp\left(-\frac{E_A}{kT_2}\right)$$

where $E_A$ is the activation energy in eV/atom and $q = 1.6 \times 10^{-19}$ J/eV (conversion factor from eV to J). Since

$$\exp(-x) = \exp(y - x)$$

we can take the ratio of the diffusion coefficients to express them in terms of $E_A$ (eV):

$$\frac{D_1}{D_2} = \frac{D_o \exp\left(-\frac{E_A}{kT_1}\right)}{D_o \exp\left(-\frac{E_A}{kT_2}\right)} = \exp\left(\frac{qE_A}{kT_2} - \frac{qE_A}{kT_1}\right) = \exp\left(\frac{q[T_1 - T_2]}{kT_1T_2}E_A\right)$$

$$\therefore \quad E_A = \frac{kT_1T_2 \ln \left(\frac{D_1}{D_2}\right)}{q(T_1 - T_2)}$$

(in eV)

$$\therefore \quad E_A = \frac{\left(1.381 \times 10^{-23} \, \text{J K}^{-1}\right)(673 \, \text{K})(923 \, \text{K})\ln \left(\frac{4.694 \times 10^{-17} \, \text{m}^2/\text{s}}{6.889 \times 10^{-15} \, \text{m}^2/\text{s}}\right)}{(1.602 \times 10^{-19} \, \text{J/eV})(673 \, \text{K} - 923 \, \text{K})}$$

(in eV)

$$\therefore \quad E_A = 1.068 \, \text{eV/atom}$$

Now the diffusion coefficient $D_o$ can be found as follows:
\[
D_1 = D_o \exp \left( - \frac{qE_A}{kT_1} \right)
\]
\[
\therefore \quad D_o = \frac{D_1}{\exp \left( - \frac{qE_A}{kT_1} \right)} = \frac{4.694 \times 10^{-17} \text{ m}^2/\text{s}}{\exp \left( - \frac{\left( 1.602 \times 10^{-19} \text{ J/eV} \right) \left( 1.068 \text{ eV} \right)}{\left( 1.381 \times 10^{-23} \text{ J K}^{-1} \right) \left( 673 \text{ K} \right)} \right)} = 4.638 \times 10^{-9} \text{ m}^2/\text{s}
\]

To check our value for \(D_o\), we can substitute it back into the equation for \(D_2\) and compare values:
\[
D_2 = D_o \exp \left( - \frac{qE_A}{kT_2} \right) = \left( 4.638 \times 10^{-9} \text{ m}^2/\text{s} \right) \exp \left( - \frac{\left( 1.602 \times 10^{-19} \text{ J/eV} \right) \left( 1.068 \text{ eV} \right)}{\left( 1.381 \times 10^{-23} \text{ J K}^{-1} \right) \left( 923 \text{ K} \right)} \right)
\]
\[
\therefore \quad D_2 = 6.870 \times 10^{-15} \text{ m}^2/\text{s}
\]
This agrees with the given value of \(6.889 \times 10^{-15} \text{ m}^2/\text{s}\) for \(D_2\).

Now we must calculate the diffusion coefficient \(D_3\) at \(T_3 = 250 \degree \text{C} + 273 = 523 \text{ K}\) (temperature at which soldering is taking place).
\[
D_3 = D_o \exp \left( - \frac{qE_A}{kT_3} \right) = \left( 4.638 \times 10^{-9} \text{ m}^2/\text{s} \right) \exp \left( - \frac{\left( 1.602 \times 10^{-19} \text{ J/eV} \right) \left( 1.068 \text{ eV} \right)}{\left( 1.381 \times 10^{-23} \text{ J K}^{-1} \right) \left( 523 \text{ K} \right)} \right)
\]
\[
\therefore \quad D_3 = 2.391 \times 10^{-19} \text{ m}^2/\text{s}
\]

The rms distance diffused by the Sn atom in time \(t = 10 \text{ s}\) (\(L_{rms}\)) is given by:
\[
L_{rms} = \sqrt{2D_3t} = \sqrt{2 \left( 2.391 \times 10^{-19} \text{ m}^2/\text{s} \right) \left( 10 \text{ s} \right)} = 2.19 \times 10^{-9} \text{ m} \text{ or } 2 \text{ nm}
\]

\[b.\] From Figure 1Q31-1, 250 \degree \text{C} cuts the liquidus line approximately at 33 wt.% Sn composition \((C_o)\).
\[
\therefore \quad C_o = 0.33 \quad (\text{Sn})
\]

\[c.\] For \(\alpha\)-phase and liquid phase \((L)\), the compositions as wt.% of Sn from Figure 1.69 or 1Q31-1 are:
\[
C_\alpha = 0.18 \quad \text{and} \quad C_L = 0.56
\]

The weight fraction of \(\alpha\) and \(L\) phases are:
\[
W_\alpha = \frac{C_L - C_o}{C_L - C_\alpha} = \frac{0.56 - 0.33}{0.56 - 0.18} = 0.605 \text{ or } 60 \text{ wt.% } \alpha\text{-phase}
\]
\[
W_L = \frac{C_o - C_\alpha}{C_L - C_\alpha} = \frac{0.33 - 0.18}{0.56 - 0.18} = 0.395 \text{ or } 39.5 \text{ wt.% liquid phase}
\]
The microstructure is a primary $\alpha$-phase and a eutectic solid ($\alpha + \beta$) phase. There are two phases present, $\alpha + \beta$. (See Figure 1Q31-2)

Assuming equilibrium concentrations have been reached:

$$C'_\alpha = 0.02 \quad \text{and} \quad C'_\beta = 1$$

The weight fraction of $\alpha$ in the whole alloy is then:

$$W'_\alpha = \frac{C'_\beta - C_\alpha}{C'_\beta - C'_\alpha} = \frac{1 - 0.33}{1 - 0.02} = 0.684 \text{ or } 68.4 \text{ wt.\% } \alpha\text{-phase}$$

The weight fraction of $\beta$ in the whole alloy is:

$$W'_\beta = \frac{C'_\alpha - C_\alpha}{C'_\beta - C'_\alpha} = \frac{0.33 - 0.02}{1 - 0.02} = 0.316 \text{ or } 31.6 \text{ wt.\% } \beta\text{-phase}$$

**2.5 TCR and Matthiessen’s rule** Determine the temperature coefficient of resistivity of pure iron and of electrotechnical steel (Fe with 4% C), which are used in various electrical machinery, at two temperatures: 0 °C and 500 °C. Comment on the similarities and differences in the resistivity versus temperature behavior shown in Figure 2.39 for the two materials.
The **temperature coefficient of resistivity** $\alpha_o$ (TCR) is defined as follows:

$$\alpha_o = \frac{1}{\rho_o} \frac{d\rho}{dT} \bigg|_{T_o} = \frac{\text{Slope at } T_o}{\rho_o}$$

where the slope is $d\rho/dT$ at $T = T_o$ and $\rho_o$ is the resistivity at $T = T_o$.

To find the slope, we draw a tangent to the curve at $T = T_o$ ($T_o = 0$ °C and then $T_o = 500$ °C) and obtain $\Delta\rho/\Delta T \approx d\rho/dT$. One convenient way is to define $\Delta T = 400$ °C and find $\Delta\rho$ on the tangent line and then calculate $\Delta\rho/\Delta T$.

**Iron at 0 °C:**

$\text{Slope}_o \approx (0.23 \times 10^{-6} \ \Omega \ \text{m} - 0 \ \Omega \ \text{m}) / (400 \ \text{°C}) = 5.75 \times 10^{-10} \ \Omega \ \text{m} \ \text{°C}^{-1}$

Since $\rho_o \approx 0.11 \times 10^{-6} \ \Omega \ \text{m}$, $\alpha_o = \text{Slope}_o/\rho_o \approx 0.00523 \ \text{°C}^{-1}$

**Fe + 4% C at 0 °C:**

$\text{Slope}_o \approx (0.57 \times 10^{-6} \ \Omega \ \text{m} - 0.4 \times 10^{-6} \ \Omega \ \text{m}) / (400 \ \text{°C}) = 4.25 \times 10^{-10} \ \Omega \ \text{m} \ \text{°C}^{-1}$
Since $\rho_o \approx 0.53 \times 10^{-6} \Omega \text{ m}$, $\alpha_o = \frac{\text{Slope}_o}{\rho_o} \approx 0.00802 \degree^{-1}$

Iron at 500 ºC:
$\text{Slope}_o \approx (0.96 \times 10^{-6} \Omega \text{ m} - 0.4 \times 10^{-6} \Omega \text{ m}) / (400 \degree \text{ C}) = 1.40 \times 10^{-9} \Omega \text{ m} \degree^{-1}$

Since $\rho_o \approx 0.57 \times 10^{-6} \Omega \text{ m}$, $\alpha_o = \frac{\text{Slope}_o}{\rho_o} \approx 0.00245 \degree^{-1}$

Fe + 4% C at 500 ºC:
$\text{Slope}_o \approx (1.05 \times 10^{-6} \Omega \text{ m} - 0.4 \times 10^{-6} \Omega \text{ m}) / (400 \degree \text{ C}) = 1.40 \times 10^{-9} \Omega \text{ m} \degree^{-1}$

Since $\rho_o \approx 0.85 \times 10^{-6} \Omega \text{ m}$, $\alpha_o = \frac{\text{Slope}_o}{\rho_o} \approx 0.00109 \degree^{-1}$

*2.6 TCR of isomorphous alloys

a. Show that for an isomorphous alloy $A\%$-$B\%$ ($B\%$ solute in $A\%$ solvent), the temperature coefficient of resistivity $\alpha_{AB}$ is given by

$$\alpha_{AB} \approx \frac{\alpha_A \rho_A}{\rho_{AB}}$$

where $\rho_{AB}$ is the resistivity of the alloy (AB) and $\rho_A$ and $\alpha_A$ are the resistivity and TCR of pure $A$. What are the assumptions behind this equation?

b. Determine the composition of the Cu-Ni alloy that will have a TCR of $4 \times 10^{-4} \text{ K}^{-1}$, that is, a TCR that is an order of magnitude less than that of Cu. Over the composition range of interest, the resistivity of the Cu-Ni alloy can be calculated from $\rho_{\text{CuNi}} \approx \rho_{\text{Cu}} + C_{\text{eff}} X (1-X)$, where $C_{\text{eff}}$, the effective Nordheim coefficient, is about $1310 \text{ n} \Omega \text{ m}$.

**Solution**

a. By the Nordheim rule, the resistivity of the alloy is $\rho_{\text{alloy}} = \rho_o + C X (1-X)$. We can find the TCR of the alloy from its definition

$$\alpha_{\text{alloy}} = \frac{1}{\rho_{\text{alloy}}} \frac{d\rho_{\text{alloy}}}{dT} = \frac{1}{\rho_{\text{alloy}}} \frac{d}{dT} \left[ \rho_o + C X (1-X) \right]$$

To obtain the desired equation, **we must assume that $C$ is temperature independent** (i.e. the increase in the resistivity depends on the lattice distortion induced by the impurity) so that $d[CX(1-X)]/dT = 0$, enabling us to substitute for $d\rho_{o}/dT$ using the definition of the TCR: $\alpha_o = (d\rho_{o}/dT)/\rho_{o}$. Substituting into the above equation:

$$\alpha_{\text{alloy}} = \frac{1}{\rho_{\text{alloy}}} \frac{d\rho_{o}}{dT} = \frac{1}{\rho_{\text{alloy}}} \alpha_o \rho_o$$

i.e. $\alpha_{\text{alloy}} \rho_{\text{alloy}} = \alpha_o \rho_o \quad \text{or} \quad \alpha_{AB} \rho_{AB} = \alpha_A \rho_A$

Remember that all values for the alloy and pure substance must all be taken at the same temperature, or the equation is invalid.

b. Assume room temperature $T = 293 \text{ K}$. Using values for copper from Table 2.1 in Equation 2.19, $\rho_{\text{Cu}} = 17.1 \text{ n} \Omega \text{ m}$ and $\alpha_{\text{Cu}} = 4.0 \times 10^{-3} \text{ K}^{-1}$, and from Table 2.3 the effective Nordheim coefficient of Ni dissolved in Cu is $C = 1310 \text{ n} \Omega \text{ m}$. We want to find the composition of the alloy such that $\alpha_{\text{CuNi}} = 4 \times 10^{-4} \text{ K}^{-1}$. Then,
Using Nordheim’s rule:

$$\rho_{\text{alloy}} = \frac{\rho_{\text{Cu}} \rho_{\text{Cu}}}{\rho_{\text{alloy}}} = \frac{(0.0040 \text{ K}^{-1})(17.1 \text{ n}\Omega \text{ m})}{0.0004 \text{ K}^{-1}} = 171.0 \text{ n}\Omega \text{ m}$$


\[\rho_{\text{alloy}} = \rho_{\text{Cu}} + CX(1 - X)\]

\[i.e.\quad 171.0 \text{ n}\Omega \text{ m} = 17.1 \text{ n}\Omega \text{ m} + (1310 \text{ n}\Omega \text{ m})X(1 - X)\]

\[\therefore X^2 - X + 0.1175 = 0\]

solving the quadratic, we find \(X = 0.136\)

Thus the composition is \textbf{86.4\% Cu-13.6\% Ni}. However, this value is in \textit{atomic percent} as the Nordheim coefficient is in atomic percent. Note that as Cu and Ni are very close in the Periodic Table this would also be the weight percentage. Note: the quadratic will produce another value, namely \(X = 0.866\). However, using this number to obtain a composition of 13.6\% Cu-86.4\% Ni is incorrect because the values we used in calculations corresponded to a solution of Ni dissolved in Cu, not vice-versa (\textit{i.e.} Ni was taken to be the impurity).

**2.10 TCR and alloy resistivity** Table 2.10 shows the resistivity and TCR (\(\alpha\)) of Cu–Ni alloys. Plot TCR versus \(1/\rho\), and obtain the best-fit line. What is your conclusion? Consider the Matthiessen rule, and explain why the plot should be a straight line. What is the relationship between \(\rho_{\text{Cu}},\ \alpha_{\text{Cu}},\ \rho_{\text{CuNi}},\ \text{and}\ \alpha_{\text{CuNi}}\)? Can this be generalized?

### Table 2.10 Cu–Ni alloys, resistivity, and TCR

<table>
<thead>
<tr>
<th>Ni wt.% in Cu–Ni</th>
<th>0</th>
<th>2</th>
<th>6</th>
<th>11</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (nΩ m)</td>
<td>17</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>TCR (ppm °C⁻¹)</td>
<td>4270</td>
<td>1350</td>
<td>550</td>
<td>430</td>
<td>160</td>
</tr>
</tbody>
</table>

**Solution**

The plot of temperature coefficient of resistivity TCR (\(\alpha\)) versus \(1/\rho\), is as follows:

**Figure 2Q10-1: TCR (\(\alpha\)) versus reciprocal of resistivity \(1/\rho\)**
From Matthiessen’s rules, we have
\[ \rho_{\text{alloy}} = \rho_{\text{matrix}} + \rho_{I} = \rho_{o} + \rho_{I} \]
where \( \rho_{o} \) is the resistivity of the matrix, determined by scattering of electrons by thermal vibrations of crystal atoms and \( \rho_{I} \) is the resistivity due to scattering of electrons from the impurities. Obviously, \( \rho_{o} \) is a function of temperature, but \( \rho_{I} \) shows very little temperature dependence. From the definition of temperature coefficient of resistivity,
\[ \alpha_{o} = \frac{1}{\rho_{o}} \left( \frac{\delta \rho_{o}}{\delta T} \right) \quad \text{or} \quad \frac{\delta \rho_{o}}{\delta T} = \alpha_{o} \rho_{o} \]
and
\[ \alpha_{\text{alloy}} = \frac{1}{\rho_{\text{alloy}}} \left( \frac{\delta \rho_{\text{alloy}}}{\delta T} \right) = \frac{\delta (\rho_{o} + \rho_{I})}{\rho_{\text{alloy}} \delta T} \approx \frac{\delta \rho_{o}}{\rho_{\text{alloy}} \delta T} = \frac{\alpha_{o} \rho_{o}}{\rho_{\text{alloy}}} \propto \frac{1}{\rho_{\text{alloy}}} \]
Clearly the TCR of the alloy is inversely proportional to the resistivity of the alloy. The higher the resistivity, the smaller the TCR, which is evident from the plot.