1. (5%) What is the dimensionality of the three-phase coexistence region in a mixture of Al, Ni, and Cu? What type of geometrical region does this define?

**Strategy:**
Use the Gibbs phase rule (Equation 5.3). How many components are present?

**Solution:** The Gibbs phase rule (Equation 5.3) is

\[ f = c - r + 2 \]

There are three components present (Al, Ni and Cu), so \( c = 3 \). We are interested in three-phase coexistence, so \( r = 3 \). The number of degrees of freedom \( (f) \) is then

\[ f = 3 - 3 + 2 = 2 \]

The number of degrees of freedom is equal to the dimensionality of the phase-coexistence region, so the region of three-phase coexistence forms a two-dimensional surface of the overall phase diagram.

2. (5%) Without referring to a table, select from the following list the gas that has the largest value of \( b \) in the van der Waals equation: CH\(_4\), O\(_2\), H\(_2\)O, CCl\(_4\), or Ne.

**Solution**
CCl\(_4\) will have the largest effective molecular size of the list because of the four Cl atoms, which have a larger atomic radius than any of the elements making up the other compounds.

3. (5%) The boiling point and freezing point of sulfur dioxide at 1 bar are -10°C and -72.7°C, respectively. The triple point is at -75.5°C and 1.67 x 10\(^{-3}\) bar, and its critical point is at 157°C and 79 bar. On the basis of this information, draw a rough sketch of the phase diagram of SO\(_2\).
4. (5%) To what temperature must He atoms be cooled so that they have the same rms speed as O₂ at 25°C? (Hint: You do not have to calculate the value of the rms speeds to solve this problem.)

Solution

From Equation 5.35 we have

\[ \langle u \rangle_{\text{rms}} = \sqrt{\frac{3RT}{M}} \]

Equating \( \langle u \rangle_{\text{rms}} \) for He and O₂, we have

\[ \langle u \rangle_{\text{rms}}^{\text{He}} = \langle u \rangle_{\text{rms}}^{\text{O₂}} \]

\[ \sqrt{\frac{3RT_{\text{He}}}{M_{\text{He}}}} = \sqrt{\frac{3RT_{\text{O₂}}}{M_{\text{O₂}}}} \]

Squaring, canceling like terms and rearranging gives

\[ T_{\text{He}} = T_{\text{O₂}} \frac{M_{\text{He}}}{M_{\text{O₂}}} \]

So

\[ T_{\text{He}} = (298.15 \text{ K}) \frac{4.003 \text{ g mol}^{-1}}{32.00 \text{ g mol}^{-1}} = 37.3 \text{ K} \]
5. (5%) Which of the following molecules has the largest \( a \) value: CH\(_4\), F\(_2\), C\(_6\)H\(_6\), or Ne? Explain your answer in terms of intermolecular forces.

The value of \( a \) indicates how strongly molecules of a given type of gas attract one another. C\(_6\)H\(_6\) has the greatest intermolecular attractions due to its larger size compared to the other choices. Therefore, it has the largest \( a \) value.

6. (5%) Calculate the average translational kinetic energy for an N\(_2\) molecule and for 1 mole of N\(_2\) molecules at 20°C.

From Equation 5.34, the average kinetic energy per molecule is

\[
\text{kinetic energy per molecule} = \frac{3k_B T}{2}
\]

For an N\(_2\) molecule at 20°C, we have

\[
\text{kinetic energy/molecule} = \frac{3(1.38065 \times 10^{-23} \text{ J K}^{-1})(273.15 + 20)\text{K}}{2} = 6.07 \times 10^{-20} \text{ J}
\]

For a mole of N\(_2\) molecules:

\[
\text{kinetic energy/mol} = (6.07 \times 10^{-21} \text{ J/molecule})(6.022 \times 10^{23} \text{ molecules mol}^{-1})
\]

\[
= 3.65 \times 10^{3} \text{ J mol}^{-1} = 3.65 \text{ kJ mol}^{-1}
\]

7. (5%) Using the Lennard-Jones model (Equation 4.12), plot on the same graph the potential energy of interaction between (a) two Ar atoms and (b) two Xe atoms. If you knew nothing about these two gases, what could you conclude about relative physical properties of Ar and Xe based on this plot?

(Equation 4.12: \( V = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \))
The potential for the xenon has a more negative potential well indicating that xenon-xenon intermolecular interactions are stronger than argon-argon interactions and that xenon should have a higher boiling point. The xenon potential become positive at a large r, indicating that xenon atoms are larger than argon atoms.

8. (5%) Name the kinds of intermolecular interactions that must be overcome in order to (a) boil liquid ammonia, (b) melt solid phosphorus (P₄), and (c) dissolve CsI in liquid HF.

(a) Boiling liquid ammonia requires breaking hydrogen bonds between molecules. Dipole−dipole and dispersion forces must also be overcome.

(b) P₄ is a nonpolar molecule, so the only intermolecular forces are of the dispersion type.

(c) CsI is an ionic solid. To dissolve in any solvent ion−ion interparticle forces must be overcome. To dissolve something in HF, some of the hydrogen bonds, dipole-dipole and dispersion forces between HF molecules must also be overcome.

9. (5%) Calculate the number of spheres that would be found within sample cubic, body-centered cubic, and face-centered cubic cells. Assume that the spheres are the same.

A corner sphere is shared equally among eight unit cells, so only one-eighth of each corner sphere "belongs" to any one unit cell. A face-centered sphere is divided equally between the two unit cells sharing the face. A body-centered sphere belongs entirely to its own unit cell.

In a simple cubic cell there are eight corner spheres. One-eighth of each belongs to the individual cell giving a total of one whole sphere per cell. In a body-centered cubic cell, there are eight corner spheres and one body-center sphere giving a total of two spheres per unit cell (one from the corners and one from the body-center). In a face-center sphere, there are eight corner spheres and six face-centered spheres (six faces). The total number of spheres would be four: one from the corners and three from the faces.
10. (10%) and the curvature $\left(\frac{\partial^2 P}{\partial V^2}\right)_T$ along the critical isotherm are zero. Use these conditions to derive Equation 6.1, 6.2 and 6.3 for the critical volume, pressure and temperature of a system obeying the van der Waals equation of state (Equation 5.42).

Equation 6.1: $V_c = 3b$

Equation 6.2: $P_c = \frac{a}{27b^2}$

Equation 6.3: $T_c = \frac{8a}{27Rb}$

Equation 5.42: $P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$

Strategy

We have three unknowns ($P_c$, $T_c$ and $V_c$) that we need to determine. To do this we need to have three simultaneous equations to solve. One of these is the van der Waals equation itself (Equation 5.43), the other two are given in the problem; namely,

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

where $\left(\frac{\partial P}{\partial V}\right)_T$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_T$ are the first and second partial derivatives of the pressure with respect to the volume at constant temperature (See Appendix 1 for the definition of the partial derivative.)

Solution: At the critical point, the van der Waals equation (Equation 5.43) is

$$P_c = \frac{RT_c}{V_c-b} - \frac{a}{V_c^2}$$

Setting the first derivative to zero gives

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0$$

Setting the second derivative to zero gives
\[ \left( \frac{\partial^2 P}{\partial V^2} \right)_T = \frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4} = 0 \] (3)

This gives us three equations in three unknowns, which we can solve by the standard process of elimination. If we multiply Equation (2) by \((\bar{V}_c - b)^3\bar{V}_c^3\) to clear the denominators, we get

\[-\bar{V}_c^3 RT_c + 2a(\bar{V}_c - b)^2 = 0\] (2')

Similarly, multiplying Equation (3) by \((\bar{V}_c - b)^3\bar{V}_c^4\) gives

\[2\bar{V}_c^4 RT_c - 6a(\bar{V}_c - b)^3 = 0\] (3')

Solving Equation (2') for \(a\) gives

\[a = \frac{\bar{V}_c^3 RT}{2(\bar{V}_c - b)^2}\] (4)

Substituting Equation (4) into Equation (3') gives

\[2\bar{V}_c^3 RT_c - 6 \left( \frac{\bar{V}_c^3 RT}{2(\bar{V}_c - b)^2} \right) (\bar{V}_c - b)^3 = 0\]

Dividing both sides by \(2RT_c\bar{V}_c^3\) and simplifying gives the following expression for the critical molar volume, which agrees with Equation 6.1:

\[\bar{V}_c = 3b\] (5)

Now, we can go back and substitute this value of \(\bar{V}_c\) into Equation 2' to solve for the critical temperature:

\[-(3b)^3 RT_c + 2a(3b - b)^2 = 0\]
\[-27b^3 RT_c + 2a(4b^7) = 0\]
Rearranging gives an expression for \( T_c \), which agrees with Equation 6.3:

\[
T_c = \frac{8a}{27Rb}
\]  

(6)

Finally, we substitute \( T_c \) and \( V_c \) into the van der Waals Equation [Equation (1) above] to get an expression for the critical pressure:

\[
P_c = \frac{8a}{27Rb} \left( \frac{1}{3b - b} \right) - \frac{a}{(3b)^2}
\]

which gives, after simplification, the expression for the critical pressure in terms of the van der Waals parameters \( a \) and \( b \):

\[
P_c = \frac{a}{27b^2}
\]  

(7)

This expression agrees with Equation 6.2 in the text.

11. (5%) The compound dichlorodifluoromethane (CCl2F2) has a normal boiling point of -30°C, a critical temperature of 112°C, and a corresponding critical pressure of 40.5 bar. If the gas is compressed to 18 bar at 20°C, Will the gas condense? Your answer should be based on a graphical interpretation.

**Solution**

From the data given, the liquid-vapor phase diagram on the right can be constructed. From this, we see that when a gas at 1 atm (~1.01 bar) and 20°C is compressed isothermally to 18 bar, it crosses the liquid-vapor coexistence line, indicating condensation into a liquid.
12. (5%) A quantitative measure of how efficiently spheres pack into unit cells is called packing efficiency, which is the percentage of the cell space occupied by the spheres. Calculate the packing efficiencies of a simple cubic cell, a body-centered cubic cell, and a face-centered cubic cell. (Hint: Refer to the following figure and use the relationship that the volume of a sphere is \(4\pi r^3/3\), where \(r\) is the radius of the sphere.)

The packing efficiency is:

\[
\text{packing efficiency} = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}} \times 100\%
\]

**Solution**

An atom is assumed to be spherical, so the volume of an atom is \((4/3)\pi r^3\). The volume of a cubic unit cell is \(a^3\) (\(a\) is the length of the cube edge). The packing efficiencies are calculated below:

(a) Simple cubic cell: cell edge \((a) = 2r\)
Packing efficiency $= \frac{\left(\frac{4\pi r^3}{3}\right) \times 100\%}{(2r)^3} = \frac{4\pi r^3 \times 100\%}{24r^3} = \frac{\pi}{6} \times 100\% = 52.4\%$

(b) Body-centered cubic cell: cell edge $= \frac{4r}{\sqrt{3}}$

Packing efficiency $= \frac{2 \times \left(\frac{4\pi r^3}{3}\right) \times 100\%}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{2 \times \left(\frac{4\pi r^3}{3}\right) \times 100\%}{\frac{64r^3}{3\sqrt{3}}} = \frac{2\pi \sqrt{3}}{16} \times 100\% = 68.0\%$

Remember, there are two atoms per body-centered cubic unit cell.

(c) Face-centered cubic cell: cell edge $= \sqrt{8}r$

Packing efficiency $= \frac{4 \times \left(\frac{4\pi r^3}{3}\right) \times 100\%}{\left(\sqrt{8}r\right)^3} = \frac{\left(\frac{16\pi r^3}{3}\right) \times 100\%}{8r^3 \sqrt{8}} = \frac{2\pi}{3\sqrt{8}} \times 100\% = 74.0\%$

Remember, there are four atoms per face-centered cubic unit cell.

13. (5%) Calculate the values of $\langle u \rangle_{rms}$ and $\langle u \rangle_{mp}$ for N$_2$ at 298.15K.

Strategy
The equations for the two measures of average speed are Equations 5.35 and 5.38. In general, the 5.35 and 5.38 employing R and M are most often used for this type of calculation.

Solution
The constants and parameters needed are $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $T = 298.15 \text{ K}$ and $M = 28.02 \text{ g mol}^{-1} = 0.02802 \text{ kg mol}^{-1}$.

The most probable speed is given by (Equation 5.38)

$$\langle u \rangle_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15K}{0.02802 \text{ kg mol}^{-1}}} = 420.6 \text{ m s}^{-1}$$

For the rms speed, we have (Equation 5.35)

$$\langle u \rangle_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15K}{0.02802 \text{ kg mol}^{-1}}} = 515 \text{ m s}^{-1}$$
14. (5%) Calculate the molar volume of carbon dioxide (CO$_2$) at 300K and 20 bar, and compare your result with that obtained using the ideal gas equation. The second virial coefficient for CO$_2$ at this temperature (B) is -0.123 L mol$^{-1}$.

\[
Z = \frac{PV}{nRT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots
\]

Strategy
Because we are only given the second virial coefficient, we must truncate the virial equation (Equation 5.44) after the second term and assume that the affect of C, D, …, are negligible.

Solution
Neglecting terms containing virial coefficients higher than B, the virial equation (Equation 5.44) become

\[
Z = \frac{PV}{RT} = 1 + \frac{B}{V}
\]

Multiplying \(V/RT\) and rearranging gives a quadratic equation for \(V\):

\[
V^2 - \frac{RT}{P}V - \frac{BRT}{P} = 0
\]

Substituting in the given values (T = 300K, P = 100 bar, R = 0.08314 L bar mol$^{-1}$ k$^{-1}$) gives

\[V^2 - 1.247V + 0.1534 = 0\]

Where \(V\) is in L mol$^{-1}$. Using the quadratic equation (see Appendix 1) gives

\[
V = \frac{1.247 \pm \sqrt{1.247^2 - 4(1)(0.1534)}}{2}
\]

\[V = 1.11 L \text{ mol}^{-1} \text{ or } 0.138 L \text{ mol}^{-1}\]

Because we have two solution, we must choose the more physical one. The ideal gas equation \(\bar{V} = \frac{RT}{P}\) gives a value of 1.247 L mol$^{-1}$, which is obtained from the coefficient of \(\bar{V}\) in the quadratic. For the truncated virial equation to be valid, the molar volume must no be too small, so we can reject the smaller value above and conclude that \(\bar{V} = 1.11 \text{ mol}^{-1}\).

15. (5%) Gold (Au) crystallizes in a cubic close-packed structure (the face-centered cubic unit cell) and has a density of 19.3 g cm$^{-3}$. Calculate the atomic radius of gold in picometers.
Strategy

We want to calculate the radius of a gold atom. For a face-centered cubic unit cell, the relationship between radius \( r \) and edge length \( a \), according to Figure 6.21, is \( a = \sqrt{8}r \). Therefore, to determine \( r \) of a gold atom, we need to find \( a \). The volume of a cube is \( V = a^3 \) or \( a = \sqrt[3]{V} \). Thus, if we can determine the volume of the unit cell, we can calculate \( a \). We are given the density in the problem.

\[
\text{density} = \frac{\text{mass}}{\text{volume}}
\]

The sequence of step is summarized as follows:

| Density of unit cell | volume of unit cell | Edge length of unit cell | radius of Au atom |

Solution

Step 1:

We know the density, so to determine the volume, we find the mass of the unit cell. Each unit cell has eight corners and six faces. The total number of atoms within such a cell, according to Figure 6.16 and 6.18, is

\[
(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4
\]

The mass of a unit cell in grams is

\[
m = \frac{1 \text{ atoms}}{1 \text{ unit cell}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{197.0 \text{ g Au}}{1 \text{ mol Au}} = 1.31 \times 10^{-21} \text{ g per unit cell}
\]

From the definition of density \( (d = m/V) \), we calculate the volume of the unit cell as follows:

\[
V = \frac{m}{d} = \frac{1.31 \times 10^{-21} \text{ g}}{19.3 \text{ g cm}^{-3}} = 6.79 \times 10^{-23} \text{ cm}^3
\]

Step 2

Because volume is length cubed, we take the cubic root of the volume of the unit cell to obtain the edge length \( a \) of the cell

\[
a = \sqrt[3]{V} = \sqrt[3]{6.79 \times 10^{-23} \text{ cm}^3} = 4.08 \times 10^{-8} \text{ cm}
\]

Step 3

From Figure 6.21 we see that the radius of an Au sphere \( r \) is related to the edge length by

\[
a = \sqrt{8}r
\]

Therefore

\[
r = \frac{a}{\sqrt{8}} = \frac{4.08 \times 10^{-8} \text{ cm}}{\sqrt{8}} = 1.44 \times 10^{-8} \text{ cm} = 144 \text{ pm}
\]
16. (5%) The edge length of the NaCl unit cell is 564 pm. What is the density of NaCl in g cm\(^{-3}\)?

Solution

From Example 6.3 we see that there are four NA\(^+\) ions and four Cl\(^-\) ions each unit cell. So the total mass (in u) of a unit cell is

\[
\text{mass} = 4(22.99 \text{ u} + 35.45 \text{ u}) = 233.8 \text{ u}
\]

Converting u to grams, we write

\[
233.8 \text{ u} \times \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ u}} = 3.882 \times 10^{-22} \text{ g}
\]

The volume of the unit cell is

\[
V = a^3 = (564 \text{ pm})^3 = (564 \times 10^{-10})^3 = 1.794 \times 10^{-22} \text{ cm}^3
\]

Finally, from the definition of density

\[
\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{3.882 \times 10^{-22} \text{ g}}{1.794 \times 10^{-22} \text{ cm}^3} = 2.16 \text{ g cm}^{-3}
\]

17. (5%) (a) Express the van der Waals equation in the form of Equation 5.44 (the virial equation). Derive relationships between the van der Waals constants (\(a\) and \(b\)) and the virial coefficients (\(B\), \(C\), and \(D\)), given that

\[
\frac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots \quad \text{for} \ |x| < 1
\]

(Equation 5.44 : \(Z = \frac{PV}{nRT} = 1 + B\frac{V}{V_0} + C\frac{V^2}{V_0^2} + D\frac{V^3}{V_0^3} + \ldots\))

The van der Waals equation (Equation 5.44) is

\[
P = \frac{RT}{V - b} - \frac{a}{V^2}
\]

We are trying to put this into the form of a virial equation (Equation 5.44):

\[
\frac{P\sqrt[3]{V}}{RT} = 1 + B\frac{V}{V_0} + C\frac{V^2}{V_0^2} + D\frac{V^3}{V_0^3} + \ldots
\]

which is a power series in \(\frac{V}{V_0}\).

First, multiply the van der Waals equation by \(\frac{\sqrt[3]{V}}{RT}\) so that the left hand side is
the same as in the virial expansion:

\[
\left( \frac{V}{RT} \right) P = \left( \frac{V}{RT} \right) \frac{RT}{V-b} - \left( \frac{V}{RT} \right) \frac{a}{V^2}
\]

\[
\frac{P V}{RT} = \frac{1}{1-b/V} - \frac{a}{RT} \frac{1}{V}
\]

The second term on the right hand side is in the correct form for the virial equation, using the expansion for \(1/(1-x)\) we can write

\[
\frac{1}{1-b/V} = 1 + \frac{b}{V} + \left( \frac{b}{V} \right)^2 + \left( \frac{b}{V} \right)^3 + \left( \frac{b}{V} \right)^4 + ...
\]

Substituting into the above gives

\[
\frac{P V}{RT} = \left[ 1 + \frac{b}{V} + \left( \frac{b}{V} \right)^2 + \left( \frac{b}{V} \right)^3 + \left( \frac{b}{V} \right)^4 + ... \right] - \frac{a}{RT} \frac{1}{V}
\]

Collecting like terms in \(1/V\) gives

\[
\frac{P V}{RT} = 1 + \frac{b - \frac{a}{RT}}{V} + \left( \frac{b}{V} \right)^2 + \left( \frac{b}{V} \right)^3 + \left( \frac{b}{V} \right)^4 + ...
\]

so we can identify the virial coefficients of the van der Waals equation as

\[
B = b - \frac{a}{RT} \quad C = b^2 \quad D = b^3, \text{ etc.}
\]

(b) Using your results, determine the Boyle temperature for a van der Waals gas in term of \(a\) and \(b\).

Because ideal gas: \(Z = 1\), then \(B = 0\)

So

\[
b - \frac{a}{RT_B} = 0
\]

\[
T_B = \frac{a}{Rb}
\]
18. (5%) The following diagram shows the Maxwell-Boltzmann speed distributions for gas at two different temperature $T_1$ and $T_2$. Calculate the value of $T_2$.

Solution
The maximum of the Maxwell-Boltzmann distribution is located at the value of the most probable speed, given by Equation 5.37. The ratio of the most probable speeds for a given gas at different temperatures is given by

$$\frac{\langle u \rangle_{\text{mp}}(1)}{\langle u \rangle_{\text{mp}}(2)} = \frac{\sqrt{\frac{2RT_1}{M}}}{\sqrt{\frac{2RT_2}{M}}} = \sqrt{\frac{T_1}{T_2}}$$

Looking at the diagram, let's assume that the most probable speed at $T_1 = 300$ K is 500 m s$^{-1}$, and the most probable speed at $T_2$ is 1000 m s$^{-1}$. Substitute into the above equation to solve for $T_2$.

$$\frac{500 \text{ m s}^{-1}}{1000 \text{ m s}^{-1}} = \sqrt{\frac{300 \text{ K}}{T_2}}$$

$$(0.5)^2 = \frac{300}{T_2}$$

$$T_2 = 1200 \text{ K}$$

19. (10%) Given the phase diagram of carbon shown here, answer the following questions:
(a) How many triple points are there and what are the phases that can coexist at each triple point?
(b) Which has a higher density, graphite or diamond?
(c) Synthetic diamond can be made from graphite. Based on the phase diagram, how would you do this?

Solution
(a) Two triple points: Diamond/graphite/liquid and graphite/liquid/vapor.
(b) Diamond.
(c) Apply high pressure at high temperature.

20. (5%) What type(s) of intermolecular interactions exist between the following pairs:
(a) HBr and H₂S, (b) Cl₂ and CBr₄, (c) I₂ and NO₃⁻, (d) NH₃ and C₆H₆?

Solution
Example 4.10