1. One mole of Ar, initially at 298 K, undergoes an adiabatic expansion against a pressure of $P_{\text{external}} = 0$ from an initial volume at 20.0 L to a final volume at 65.0 L.

Calculate the final temperature using the ideal gas and van der Waals equations of state.

The $P_{\text{external}} = 0$ and $w = 0$. It is an adiabatic expansion, and $q = 0$.

$$\Delta U = q + w = 0$$

$$\Delta U = 0 = \int_T \left( \frac{\partial U}{\partial T} \right)_V dT + \int_V \left( \frac{\partial U}{\partial V} \right)_T dV$$

and

$$\int_T \left( \frac{\partial U}{\partial T} \right)_V dT = - \int_V \left( \frac{\partial U}{\partial V} \right)_T dV$$

**Ideal Gas**

$$\int_T C_V dT = - \int_V \left( \frac{\partial U}{\partial V} \right)_T dV = 0$$

$(\frac{\partial U}{\partial V})_T = 0$ for an ideal gas, and $(\frac{\partial U}{\partial V})_V = C_V$.

$$C_V(T_2 - T_1) = 0 \quad \text{and} \quad T_2 = T_1$$

$\Delta T = 0$, because $\Delta U$ is a function of $T$ only.
van der Waals Gas

\[
\int_T C_V dT = - \int_V \left( \frac{\partial U}{\partial V} \right)_T dV
\]

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

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P = \frac{a}{V_m^2}
\]

\[
C_{V,m} \Delta T = a \left( \frac{1}{V_{m,f}} - \frac{1}{V_{m,i}} \right) - \frac{\Delta U_{T,m}}{\Delta U_{T,m}}
\]

\[
\Delta U_{T,m} = 1.355 \text{ dm}^5 \text{ bar mol}^{-2} \times \frac{10^5 \text{ Pa}}{1 \text{ bar}} \times \frac{1 \times 10^{-6} \text{ m}^3}{\text{dm}^6} \times \left( \frac{1}{65.0 \times 10^{-3} \times \text{m}^2 \times \text{mol}^{-1}} - \frac{1}{20.0 \times 10^{-3} \times \text{m}^2 \times \text{mol}^{-1}} \right)
\]

\[
\Delta U_{T,m} = -4.69 \text{ J mol}^{-1}
\]

\[
\Delta T = T_f - 298 \text{ K} = \frac{U_{T,m}}{C_{V,m}} = \frac{-4.69 \text{ J mol}^{-1}}{12.5 \text{ J K}^{-1} \text{ mol}^{-1}} = -0.376 \text{ K} \quad T_f = 297.6 \text{ K}
\]
2. One mole of Ar undergoes an isothermal reversible expansion from an initial volume of 1.00 L to a final volume of 65.0 L at 298 K.

Calculate the work done in this process using the ideal gas and van der Waals equations of state.

**Ideal Gas**

\[ w = -nRT \ln \frac{V_f}{V_i} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln \frac{65.0 \text{ L}}{1.00 \text{ L}} = -10.34 \text{ kJ} \]

**van der Waals Gas**

\[
\begin{align*}
    w &= \int_{V_i}^{V_f} \left( \frac{nRT}{V - nb} - \frac{n^2a}{V^2} \right) dV = -\left[ nRT \ln(V - nb) + \frac{n^2a}{V} \right]_{V_i}^{V_f} \\
    w &= \left[ -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln(V - 3.20 \times 10^{-5} \text{ m}^3) + \frac{0.1355 \text{ Pa m}^6}{V} \right]_{0.065 \text{ m}^3}^{0.001 \text{ m}^3} \\
    w &= -10.41 \text{ kJ}
\end{align*}
\]

What percentage of the work done by the van der Waals gas arises from the attractive potential?

\[
100 \times \frac{133 \text{ J}}{10.41 \times 10^4 \text{ J}} = 1.3\%
\]
3. Another equation of state used for the description of gases is the Berthelot equation:

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

Derive expressions for

\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \]

for the Berthelot equation in terms of \( V, T \) and \( P \).

\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left( \frac{nR}{P} + \frac{2na}{RT^3} \right) = \frac{1}{V_m} \left( \frac{R}{P} + \frac{2a}{RT^3} \right) \]

\[ \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( -\frac{nRT}{P^2} \right) = \frac{nRT}{P^2V} = \frac{RT}{P^2V_m} \]

Find an expression of the Boyle temperature in terms of \( a, b \) and \( R \).

For many purposes, it is convenient to use \( P \) as the independent variable, and write the virial equation as

\[ z = \frac{PV_m}{RT} = 1 + B'P + C'P^2 + \cdots \]

\[ z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT} + \frac{Pa}{R^2T^3} \]

At the Boyle temperature \( (T = T_B) \), \( \left( \frac{\partial z}{\partial P} \right)_T = 0 \), and therefore,

\[ \left( \frac{\partial z}{\partial P} \right)_T = \frac{b}{RT} - \frac{a}{R^2T^3} = 0 \]

which yields

\[ T_B = \sqrt[3]{\frac{a}{Rb}} \]
4. Show that the second virial coefficient for a van der Waals equation is given by

\[ B(T) = b - \frac{a}{RT} \]

The van der Waals equation is given by

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

Multiplying the above equation by \( \frac{V_m}{RT} \),

\[ \frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} \]

and

\[ \frac{PV_m}{RT} = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m} \]

Since \( \frac{b}{V_m} \ll V \), the term \( \frac{1}{1 - \frac{b}{V_m}} \) can be expanded in a series of \( \frac{1}{V_m} \), and the above equation becomes

\[ \frac{PV_m}{RT} = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \cdots - \frac{a}{RT} \left( \frac{1}{V_m} \right) \]

\[ \frac{PV_m}{RT} = 1 + \left( b - \frac{a}{RT} \right) \times \frac{1}{V_m} + \frac{b^2}{V_m^2} + \cdots \]

Comparing the \( \frac{1}{V_m} \) term with the virial expansion, we see that

\[ B(T) = b - \frac{a}{RT} \]