1. The volume of some liquid varies with temperature according to \( V = (a + bT + cT^2)V' \) where \( V' \) is the volume at 298 K and \( a, b, \) and \( c \) are empirically determined constants with the following values:
\[
a = 0.77 \\
b = 3.7 \times 10^{-4} \text{ K}^{-1} \\
c = 1.52 \times 10^{-6} \text{ K}^{-2}
\]
Calculate its thermal expansion coefficient at 310 K.

**Solution**

The expression for the thermal expansion coefficient is:
\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p
\]
Start by evaluating the derivative \( \left( \frac{\partial V}{\partial T} \right)_p \) of the given expression for the volume:
\[
\left( \frac{\partial V}{\partial T} \right)_p = \frac{\partial}{\partial T} (a + bT + cT^2)V'
\]
\[= (b + 2cT)V'
\]
Now we just evaluate the thermal expansion coefficient:
\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p
\]
\[
= \frac{1}{(a + bT + cT^2)} \times (b + 2cT)V'
\]
\[
= \frac{b + 2cT}{a + bT + cT^2}
\]
\[
= \frac{(3.72 \times 10^{-4} \text{ K}^{-1}) + 2(1.52 \times 10^{-6} \text{ K}^{-2})(310 \text{ K})}{0.77 + (3.72 \times 10^{-4} \text{ K}^{-1})(310 \text{ K}) + (1.52 \times 10^{-6} \text{ K}^{-2})(310 \text{ K})^2}
\]
make sure the units cancel leaving you with \( \text{K}^{-1} \)
\[= 1.26 \times 10^{-3} \text{ K}^{-1}
\]

2. Starting from the following expression:
\[
C_p - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_p
\]
use the appropriate relationships between partial derivatives to show that,
\[
C_p - C_V = -T \left( \frac{\partial V}{\partial T} \right)_p^2
\]
Then evaluate \( C_p - C_V \) for an ideal gas using this expression.

**Solution**

Both expressions have the derivative \( \left( \frac{\partial V}{\partial T} \right)_p \) in common, so the best way to proceed is to try to express \( \left( \frac{\partial P}{\partial T} \right)_V \) in other terms using the cyclic relationship:
\[
\left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial V}{\partial T} \right)_p = -1
\]
solve for the desired derivative (in red)
\[
\left( \frac{\partial P}{\partial T} \right)_V = -\left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p
\]
Substitute the result into the original expression for \( C_p - C_V \):
\[
C_p - C_V = -T \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial V}{\partial T} \right)_p
\]
\[= -T \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \]
write the derivative in red in terms of its reciprocal to get the desired expression
continued on next page
3. Argon is allowed to expand isothermally and reversibly at 298 K from an initial molar volume of 5 L mol\(^{-1}\) to a final molar volume of 10 L mol\(^{-1}\). Calculate the work done by treating it as a van der Waals gas. Use

\[
3.20 \times 10^{2} \text{Lmol}^{-1}
\]

Calculate the work for the same process by treating it as an ideal gas. Give your final answers in Joules.

**Solution**

First, we need to evaluate \( \frac{\partial V}{\partial T} \) for a van der Waals gas. Since its isothermal, we can simply substitute the van der Waals equation in for \( P \) and integrate:

\[
\frac{\partial V}{\partial T} = \left( \frac{\partial V}{\partial T} \right)_p = \frac{NRT}{P^2}
\]

Substitute these into the expression for \( C_p - C_V \):

\[
C_p - C_V = -T \left( \frac{\partial V}{\partial T} \right)_p = -\frac{NRT}{P^2}
\]

Now evaluate this expression using the given van der Waals constants and the given conditions:

\[
w = -(8.314 \times 10^{-3} \text{kJK}^{-1} \text{mol}^{-1})(298\text{K})\ln\left(\frac{10\text{Lmol}^{-1} - 3.2 \times 10^{-2} \text{Lmol}^{-1}}{5\text{Lmol}^{-1} - 3.2 \times 10^{-2} \text{Lmol}^{-1}}\right) - \left(1.34 \text{atml}^2 \text{mol}^{-2}\right)\left(\frac{1}{10\text{Lmol}^{-1}} - \frac{1}{5\text{Lmol}^{-1}}\right)
\]

\[
= -1.725 \text{kJ mol}^{-1} - (0.014 \text{kJmol}^{-1})
\]

If the gas is treated as ideal then we can use the expression for the work that we've already derived in class:

\[
w = -RT \ln \frac{V_{m,2}}{V_{m,1}}
\]

\[
= -(8.314 \times 10^{-3} \text{kJK}^{-1} \text{mol}^{-1})(298\text{K})\ln\left(\frac{10\text{Lmol}^{-1}}{5\text{Lmol}^{-1}}\right)
\]

\[
= -1.717 \text{kJ mol}^{-1} \quad \text{Comment: The results are nearly identical. This means that Argon behaves ideally under these conditions.}
\]

4. Express each of the following units as a combination of meters, kilograms, and seconds: (a) Joule, (b) Pascal, (c) liter, (d) Newton, and (e) Watt.

continued on next page
5. Specific heat capacities can be measured in a drop calorimeter; here, a heated sample is dropped into the calorimeter and the final temperature is measured. When 45.0 g of a certain metal at 343 K is added to 24.0 g of water (with \( C_p = 4.19 \text{ J g}^{-1} \text{ K}^{-1} \)) at 283 K in an insulated container, the final temperature is 293 K. (a) Find the heat capacity of the metal. (b) How much heat flowed from the metal to the water? Note: In (a), we are finding the average \( C_p \) over the temperature range of the experiment. To determine \( C_p \) as a function of \( T \), one repeats the experiment many times, using different initial temperatures for the metal.

**Solution**

a. The expression for the constant pressure heat capacity is:

\[
C_p = \left( \frac{\partial H}{\partial T} \right)_p
\]

\( \downarrow \) separating variables and integrating gives an expression for \( \Delta H \) (assuming \( C_p \) is independent of \( T \))

\[
\Delta H = C_p \Delta T
\]

When \( P \) is constant, \( \Delta H \) is the amount of heat exchanged:

\[
\Delta H = q_p
\]

From the First Law we know that:

\[
\Delta U_{\text{H}_2\text{O}} = -\Delta U_{\text{metal}}
\]

\( \downarrow \) \( \Delta U = q + w \), \( w = -P \Delta V \)

\[
q_{\text{H}_2\text{O}} - P \Delta V_{\text{H}_2\text{O}} = -q_{\text{metal}} + \Delta V_{\text{metal}}
\]

\( \downarrow \)

\[
q_{\text{H}_2\text{O}} = -q_{\text{metal}} + P \left( \Delta V_{\text{metal}} + \Delta V_{\text{H}_2\text{O}} \right)
\]

The quantity in parentheses is zero because \( \Delta V_{\text{metal}} = -\Delta V_{\text{H}_2\text{O}} \):

\[
q_{\text{H}_2\text{O}} = -q_{\text{metal}}
\]

We can relate this to the temperature changes:

\[
C_{p,\text{H}_2\text{O}} (T_f - T_{i,\text{H}_2\text{O}}) m_{\text{H}_2\text{O}} = -C_{p,\text{metal}} (T_f - T_{i,\text{metal}}) m_{\text{metal}}
\]

don't forget to include the masses in this expression!

Now we just solve for \( C_{p,\text{metal}} \):

\[
C_{p,\text{metal}} = -\frac{C_{p,\text{H}_2\text{O}} (T_f - T_{i,\text{H}_2\text{O}}) m_{\text{H}_2\text{O}}}{(T_f - T_{i,\text{metal}}) m_{\text{metal}}}
\]

\[
= -\frac{(4.19 \text{ J g}^{-1} \text{ K}^{-1}) (293 \text{ K} - 283 \text{ K}) (24.0 \text{ g})}{(293 \text{ K} - 343 \text{ K}) (45.0 \text{ g})}
\]

\[
= 0.447 \text{ J g}^{-1} \text{ K}^{-1}
\]

b. Use the initial expression that relates \( q \) to \( C_p \) and \( \Delta T \):

\[
q_{\text{metal}} = C_{p,\text{metal}} \Delta T
\]

\[
= (0.447 \text{ J g}^{-1} \text{ K}^{-1}) (293 \text{ K} - 343 \text{ K}) (45.0 \text{ g}) = -1.01 \text{ kJ}
\]

it's negative because the metal lost this amount of energy in the form of heat (and the water gained it)
6. A sample consisting of 1 mole of an ideal gas (for which \( C_{V,m} = \frac{3}{2}R \)) is taken through the cycle shown below. (a) Determine the temperature at the points 1, 2, and 3. (b) Calculate \( q \), \( w \), \( \Delta U \), and \( \Delta H \) for each step and for the overall cycle.

**Solution**

a. The gas is ideal, so we can use the ideal gas equation:

\[
T_3 = T_1 \quad \text{1 \( \rightarrow \) 3 is isothermal}
\]

\[
= \frac{P_1 V_1}{N R}
\]

\[
= \frac{(1 \text{ atm})(22.44 \text{ L})}{(1 \text{ mol})(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1})}
\]

\[
= 273.5 \text{ K}
\]

\[
\rightarrow
\]

\[
T_2 = \frac{P_2 V_2}{N R}
\]

\[
= \frac{(1 \text{ atm})(44.88 \text{ L})}{(1 \text{ mol})(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1})}
\]

\[
= 546.9 \text{ K}
\]

b. For 1 \( \rightarrow \) 2:

\[
w = -P \Delta V
\]

\[
= -(1 \text{ atm})(44.88 \text{ L} - 22.44 \text{ L}) \times 101.32 \text{ J/L atm} \quad \text{don't forget to convert L atm to J!}
\]

\[
= -2.27 \times 10^3 \text{ J}
\]

\[
\Delta H = q_v
\]

\[
= NC_{P,m} \Delta T
\]

\[
= (1 \text{ mol}) \left( \frac{5}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (546.9 \text{ K} - 273.5 \text{ K})
\]

\[
= 5.68 \times 10^3 \text{ J}
\]

\[
\Delta U = q + w
\]

\[
= 3.41 \times 10^3 \text{ J}
\]

For 2 \( \rightarrow \) 3:

\[
w = -P \Delta V
\]

\[
= 0
\]

\[
\Delta U = q_v
\]

\[
= NC_{V,m} \Delta T
\]

\[
= (1 \text{ mol}) \left( \frac{3}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (273.5 \text{ K} - 546.9 \text{ K})
\]

\[
= -3.41 \times 10^3 \text{ J}
\]

continued on next page
7. One mole of He gas with \( C_{V,m} = 3R/2 \) essentially independent of temperature expands reversibly from 24.6 L and 300 K to 49.2 L. Calculate the final pressure and temperature if the expansion is (a) isothermal or (b) adiabatic. (c) Sketch these two processes on a \( P-V \) diagram. You may treat He gas as ideal.

**Solution**

a. It's isothermal so \( T_2 = T_1 = 300 \text{ K} \). The gas is ideal and we know \( T_2 \) and \( V_2 \), so

\[
P_2 = \frac{NRT_2}{V_2} = \frac{(1 \text{ mol})(8.21 \times 10^{-5} \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{49.2 \text{ L}}
\]

= 0.5 atm

b. \( T_2 \) is related to \( T_1, V_1 \), and \( V_2 \) according to

\[
T_2 = T_1 \left(\frac{V_2}{V_1}\right)^{1-\gamma} \quad \text{where} \quad \gamma = \frac{C_p}{C_v} \quad C_p \text{ is given and we know that } C_p - C_v = R \text{, therefore, } C_v = \frac{5}{2} R \quad \text{and} \quad \gamma = \frac{5}{3}
\]

\[
= (300 \text{ K})^{2/3} = 188.9 \text{ K}
\]

Now that we have \( T_2 \), we can use the ideal gas equation to determine \( P_2 \):

\[
P_2 = \frac{NRT_2}{V_2} = \frac{(1 \text{ mol})(8.21 \times 10^{-5} \text{ L atm K}^{-1} \text{ mol}^{-1})(188.9 \text{ K})}{49.2 \text{ L}}
\]

= 0.315 atm

c. On next page
8. For \( N_2(g) \), \( C_{p,m} \) is nearly constant at \( 3.5R \) for temperatures in the range of 100 to 400 K and low or moderate pressures. (a) Calculate \( q, w, \Delta H, \) and \( \Delta U \) for the reversible adiabatic compression of 1.12 g of \( N_2 \) from 400 torr and 1000 cm\(^3\) to a final volume of 250 cm\(^3\). Assume the gas is ideal. (b) Suppose we want to cool a sample of \( N_2 \) at room \( T \) and \( P(25^\circ C \text{ and } 101 \text{ kPa}) \) to 100 K using a reversible adiabatic expansion. What should the final pressure be?

**Solution**

a. The formulas we need are:

\[
\Delta U = N C_{v,m} (T_2 - T_1) \\
\Delta H = N C_{p,m} (T_2 - T_1) \\
q = 0 \\
w = \Delta U 
\]

We need \( N, T_1, T_2, \) and \( C_{p,m} \). Three of these, \( N, T_1, \) and \( C_{p,m} \), can be calculated directly using the given information:

\[
N = 1.12 \text{ g} \times \frac{\text{mol}}{28.02 \text{ g}} = 0.04 \text{ mol} \\
T_1 = \frac{PV}{NR} \\
\quad = \frac{(0.526 \text{ atm})(1 \text{ L})}{(0.04 \text{ mol})(8.21 \times 10^{-5} \text{ L atm K}^{-1} \text{ mol}^{-1})} \\
\quad = 160.2 \text{ K} \\
C_{p,m} - C_{v,m} = R \\
\quad \updownarrow \\
C_{v,m} = C_{p,m} - R \\
\quad = 2.5R \\
\]

To find \( T_2 \) we use:

\[
T_2 = T_1 \left( \frac{V_2}{V_1} \right)^{\frac{y}{1-y}} \\
\quad \updownarrow \\
\quad = (160.2 \text{ K}) \left( \frac{0.250 \text{ L}}{1 \text{ L}} \right)^{-0.4} \\
\quad = 278.9 \text{ K} 
\]

Now we can calculate the desired quantities (on next page):
\[ \Delta U = N C_v (T_2 - T_1) \]
\[ = (0.04 \text{ mol})(2.5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1})(278.9 \text{ K} - 160.2 \text{ K}) \]
\[ = 98.7 \text{ J} \]
\[ \Delta H = N C_p (T_2 - T_1) \]
\[ = (0.04 \text{ mol})(3.5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1})(278.9 \text{ K} - 160.2 \text{ K}) \]
\[ = 138.2 \text{ J} \]
\[ w = \Delta U \]
\[ = 98.7 \text{ J} \]

b. We want \( P_2 \) for an adiabatic expansion given \( P_1 = 101 \text{ kPa} \) (1 atm), \( T_1 = 25^\circ \text{C} \) (298 K), and \( T_2 = 100 \text{ K} \). We could find \( P_2 \) in a couple of ways. The most straightforward is to use:
\[ PV_1^\gamma = PV_2^\gamma \]
\[ \downarrow \text{ solve for } P_2 \]
\[ P_2 = \frac{P_1 V_1^\gamma}{V_2^\gamma} \]

To use this formula, we need \( V_1 \) and \( V_2 \). We can find \( V_1 \) using the ideal gas equation:
\[ V_1 = \frac{NRT_1}{P_1} \]
\[ = \frac{(0.04 \text{ mol})(8.21 \times 10^{-5} \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{1 \text{ atm}} \]
\[ = 0.978 \text{ L} \]

Next, we can find \( V_2 \) using:
\[ \frac{T_2}{T_1} = \left( \frac{V_2}{V_1} \right)^{1-\gamma} \]
\[ \downarrow \text{ solve for } V_2 \]
\[ V_2 = \left( \frac{V_1}{T_2} \right)^{\frac{1}{1-\gamma}} \]
\[ = V_1 \left( \frac{T_2}{T_1} \right)^{\frac{1}{1-\gamma}} \]
\[ = (0.978 \text{ L}) \left( \frac{100 \text{ K}}{298 \text{ K}} \right)^{2.5} \]
\[ = 14.99 \text{ L} \]

Now we can find \( P_2 \):
\[ P_2 = \frac{P_1 V_1^\gamma}{V_2^\gamma} \]
\[ = (1 \text{ atm}) \left( \frac{0.978 \text{ L}}{14.99 \text{ L}} \right)^{14} \]
\[ = 0.022 \text{ atm} \]

Note that we could have substituted the formula for \( V_2 \) into the expression for \( P_2 \) and that the \( V_1 \)'s would have cancelled:
\[ P_2 = \frac{P_1 V_1^\gamma}{V_2^\gamma} \left( \frac{T_2}{T_1} \right)^{1/\gamma} \]
\[ = \left( \frac{T_2}{T_1} \right)^{\gamma/\gamma - 1} P_1 \left( \frac{T_2}{T_1} \right)^{\gamma - 1} \]

So we could have found \( P_2 \) without first finding \( V_1 \).