P2.4) A system consisting of 57.5 g of liquid water at 298 K is heated using an immersion heater at a constant pressure of 1.00 bar. If a current of 1.50 A passes through the 10.0-ohm resistor for 150 s, what is the final temperature of the water? The heat capacity for water can be found in Appendix B.

The heat produced by the resistor is:

\[
q = I^2 \cdot R \cdot t = n \cdot C_{p,m} \cdot (T_f - T_i)
\]

Solving for \(T_f\) yields:

\[
T_f = \frac{(I^2 \cdot R \cdot t + n \cdot C_{p,m} \cdot T_i)}{n \cdot C_{p,m}}
\]

\[
= \left( (1.5 \text{ A})^2 \times (10 \text{ Ohm}) \times (150 \text{ s}) + \left( \frac{57.5 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times (75.291 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K}) \right)
\]

\[
= \left( \frac{57.5 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times (75.291 \text{ J mol}^{-1} \text{ K}^{-1}) = 312 \text{ K}
\]

P2.32) Compare the energy of DNA bending calculated in Problem 2.31 to the thermal energy \(k_B T\), where \(k_B\) is Boltzmann’s constant. Assume \(T = 310. \text{ K}\). Propose a source for the excess energy required to bend the DNA in Problem 2.31.

The thermal energy at 310 K is:

\[
E_{\text{thermal}} = k_B \cdot T = (1.38 \times 10^{-23} \text{ J K}^{-1}) \times (310 \text{ K}) = 4.278 \times 10^{-21} \text{ J}
\]

The ratio between the energy from P2.31 and the thermal energy is:

\[
\frac{E_{\text{bend}}}{E_{\text{thermal}}} = \frac{2.25 \times 10^{-19} \text{ J}}{4.278 \times 10^{-21} \text{ J}} = 52.6
\]
The energy source could be the formation of intermolecular interactions.

Q3.3) Refer to Figure 1.7 and explain why \( (\partial U/\partial V)_T \) is generally small for a real gas.

The depth of the potential minimum is generally very small. Therefore, it only takes a small amount of energy to separate the atoms or molecules that make up the gas.

Q3.6) Why is the equation valid for an ideal gas even if \( P \) is not constant in the process? Is this equation also valid for a real gas? Why or why not?

It is valid because for an ideal gas, \( H \) is a function of \( T \) only, and not a function of \( V \) or \( p \). The formula is not accurate for a real gas, since \( H \) is a weak function of \( V \) and \( p \).

P3.2) The function \( f(x,y) \) is given by \( f(x,y) = xy \sin 5x + x^2\sqrt{y} \ln y + 3e^{-2x^2} \cos y \). Determine

\[
\left(\frac{\partial f}{\partial x}\right)_y, \left(\frac{\partial f}{\partial y}\right)_x, \left(\frac{\partial^2 f}{\partial x^2}\right)_y, \left(\frac{\partial^2 f}{\partial y^2}\right)_x, \left(\frac{\partial f}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x
\]

and \( \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y \)

a. Is \( \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y \) ?

b. Obtain an expression for the total differential \( df \).

\[
\left(\frac{\partial f}{\partial x}\right)_y = 5x y \cos[5x] + y \sin[5x] + 2x \sqrt{y} \ln y - 12x e^{-2x^2} \cos[y]
\]

\[
\left(\frac{\partial f}{\partial y}\right)_x = x \sin[5x] + \frac{x^2}{\sqrt{y}} + \frac{x^2 \ln y}{2\sqrt{y}} - 3e^{-2x^2} \sin[y]
\]
\[
\left( \frac{\partial^2 f}{\partial x^2} \right)_y = 5 y \cos[5x] - 25 x y \sin[5x] + 5 y \cos[5x] + 2 \sqrt{y} \ln y - 12 e^{-2x} \cos[y] + 48 x^2 e^{-2x} \cos[y]
\]

\[
\left( \frac{\partial^2 f}{\partial y^2} \right)_x = -\frac{x^2 \ln y}{4 y^3} - 3 e^{-2x} \cos[y]
\]

\[
\left( \frac{\partial f}{\partial x} \left( \frac{\partial f}{\partial y} \right)_x \right)_y = \sin[5x] + 5 x \cos[5x] + \frac{2 x}{\sqrt{y}} + \frac{x \ln y}{\sqrt{y}} + 12 x e^{-2x} \sin[y]
\]

a) \[
\left( \frac{\partial f}{\partial x} \left( \frac{\partial f}{\partial y} \right)_x \right)_y = 5 x \cos[5x] + \sin[5x] + \frac{2 x}{\sqrt{y}} + \frac{x \ln y}{\sqrt{y}} + 12 x e^{-2x} \sin[y] = \left( \frac{\partial f}{\partial x} \left( \frac{\partial f}{\partial y} \right)_x \right)_y
\]

b) \[
\begin{align*}
\text{df} &= \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy \\
&= \left( 5 x y \cos[5x] + y \sin[5x] + 2 x \sqrt{y} \ln y - 12 x e^{-2x} \cos[y] \right) dx \\
&\quad + \left( x \sin[5x] + \frac{x^2}{\sqrt{y}} + \frac{x^2 \ln y}{2 \sqrt{y}} - 3 e^{-2x} \sin[y] \right) dy
\end{align*}
\]

**P3.3)** This problem will give you practice in using the cyclic rule. Use the ideal gas law to obtain the three functions \( P = f(V, T), V = g(P, T), \text{ and } T = h(P, V) \). Show that the cyclic rule \( \left( \frac{\partial P}{\partial V} \right)_T \) \( \left( \frac{\partial V}{\partial T} \right)_P \) \( \left( \frac{\partial T}{\partial P} \right)_V = -1 \) is obeyed.

The functions: \( p = f(V, T) = \frac{nRT}{V} \), \( V = g(p, T) = \frac{nRT}{p} \), \( T = h(p, V) = \frac{pV}{nR} \)

The cyclic rule: \( \left( \frac{\partial p}{\partial V} \right)_T \times \left( \frac{\partial V}{\partial T} \right)_p \times \left( \frac{\partial T}{\partial p} \right)_V = -\frac{nRT}{V^2} \times \frac{nR}{p} \times \frac{V}{nR} = -p \times V \frac{V}{p} = -1 \)

**P3.4)** Using the chain rule for differentiation, show that the isobaric expansion coefficient expressed in terms of density is given by \( \beta = -1/\rho \left( \frac{\partial \rho}{\partial T} \right)_p \).
\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \rho \frac{m}{\partial \rho} \left( \frac{\partial m}{\partial T} \right)_p = \rho \frac{m}{\partial \rho} \left( \frac{\partial p}{\partial T} \right)_p = \rho \left( -\frac{m}{\rho^2} \right) \left( \frac{\partial p}{\partial T} \right)_p = -\frac{1}{\rho} \left( \frac{\partial p}{\partial T} \right)_p \]  

equation 3.9

P3.7) Because \( V \) is a state function, \( (\partial / \partial P(\partial V / \partial T)_P) = (\partial / \partial T(\partial V / \partial P)_T) \). Using this relationship, show that the isothermal compressibility and isobaric expansion coefficient are related by \( (\partial \beta / \partial P) = - (\partial \kappa / \partial T)_P \).

\[ \left( \frac{\partial (V \beta)}{\partial p} \right)_T = \left( \frac{\partial (V \kappa)}{\partial T} \right)_P \]

Because \( \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \) and \( \kappa = - \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \)  

equation 3.9

\[ \left( \frac{\partial (V \beta)}{\partial p} \right)_T = - \left( \frac{\partial (V \kappa)}{\partial T} \right)_P \]  

[1]

Left = \( \left( \frac{\partial (V \beta)}{\partial p} \right)_T = V \left( \frac{\partial (\beta)}{\partial p} \right)_T + \beta \left( \frac{\partial V}{\partial p} \right)_T = V \left( \frac{\partial (\beta)}{\partial p} \right)_T - V \beta \kappa \)  

[2]

Right = - \( \left( \frac{\partial (V \kappa)}{\partial T} \right)_P = -V \left( \frac{\partial (\kappa)}{\partial T} \right)_P - \kappa \left( \frac{\partial V}{\partial T} \right)_P = -V \left( \frac{\partial (\kappa)}{\partial T} \right)_P - V \kappa \beta \)  

[3]

Left = Right \( \Rightarrow V \left( \frac{\partial (\beta)}{\partial p} \right)_T - V \beta \kappa = -V \left( \frac{\partial (\kappa)}{\partial T} \right)_P - V \kappa \beta \Rightarrow \left( \frac{\partial (\beta)}{\partial p} \right)_T = - \left( \frac{\partial (\kappa)}{\partial T} \right)_P \)

Alternative solution:

\[ \left( \frac{\partial (\beta)}{\partial p} \right)_T = \frac{\partial}{\partial p} \left( \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \right) = \left[ \frac{\partial}{\partial p} \left( \frac{1}{V} \right) \right] \left( \frac{\partial V}{\partial T} \right)_P + \frac{1}{V} \left( \frac{\partial}{\partial \rho} \left( \frac{\partial V}{\partial T} \right)_P \right)_T \]

\[ = \left( - \frac{1}{V^2} \right) \left( \frac{\partial V}{\partial T} \right)_P + \frac{1}{V} \left( \frac{\partial}{\partial T} \left( \frac{\partial V}{\partial p} \right)_P \right)_T \]  

[4]

The first term =

\[ \frac{V}{V^2} \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial V}{\partial p} \right)_T + \frac{\partial V}{\partial p} \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \]

\[ = \frac{\partial V}{\partial p} \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \]
Using this \[4\] = \(\left(\frac{\partial l}{\partial V}\right)_p\left(\frac{\partial V}{\partial T}\right)_p + \frac{1}{V}\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial p}\right)_T\right)_p = \left[\frac{\partial}{\partial T}\left(\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\right)\right]_p = \left[\frac{\partial}{\partial T} \kappa\right]_p\]

**P3.10** Starting with the van der Waals equation of state, find an expression for the total differential \(dP\) in terms of \(dV\) and \(dT\). By calculating the mixed partial derivatives \(\frac{\partial}{\partial T}(\frac{\partial P}{\partial V})_T\) and \(\frac{\partial}{\partial V}(\frac{\partial P}{\partial T})_V\), determine if \(dP\) is an exact differential.

Van der Waals equation: 
\[
P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}\
\]

\[
\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left[\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right]\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3}\
\]

\[
\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\left[\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right]\right)_V = \frac{R}{(V_m - b)}\
\]

\[
dp = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT = \left(\frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2}\right) dV + \left(\frac{R}{(V_m - b)}\right) dT\
\]

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

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

Therefore, \(dp\) is an exact differential.

**P3.12** Regard the enthalpy as a function of \(T\) and \(P\). Use the cyclic rule to obtain the expression

The enthalpy as a function of \(T\) and \(p\):
\[
dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp\
\]
Using the cyclic rule: \( \left( \frac{\partial p}{\partial H} \right)_T \times \left( \frac{\partial T}{\partial p} \right)_H \times \left( \frac{\partial H}{\partial T} \right)_p = -1 \), \( C_p \) can be expressed as:

\[
C_p = \left( \frac{\partial H}{\partial T} \right)_p = -1 \frac{1}{\left( \frac{\partial p}{\partial H} \right)_T \left( \frac{\partial T}{\partial p} \right)_H} = - \frac{\left( \frac{\partial H}{\partial p} \right)_T}{\left( \frac{\partial p}{\partial T} \right)_H}
\]

**P3.15)** An 80.0-g piece of gold at 650. K is dropped into 100.0 g of \( \text{H}_2\text{O}(l) \) at 298 K in an insulated container at 1 bar pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that \( C_{P,m} \) for \( \text{Au} \) and \( \text{H}_2\text{O} \) is constant at their values for 298 K throughout the temperature range of interest.

\[
n_{\text{Au}} C_{P,m}^{\text{Au}} (T_f - T_i^{\text{Au}}) + n_{\text{H}_2\text{O}} C_{P,m}^{\text{H}_2\text{O}} (T_f - T_i^{\text{H}_2\text{O}}) = 0
\]

\[
T_f = \left( \frac{n_{\text{Au}} C_{P,m}^{\text{Au}} T_i^{\text{Au}} + n_{\text{H}_2\text{O}} C_{P,m}^{\text{H}_2\text{O}} T_i^{\text{H}_2\text{O}}}{n_{\text{Au}} C_{P,m}^{\text{Au}} + n_{\text{H}_2\text{O}} C_{P,m}^{\text{H}_2\text{O}}} \right)
\]

\[
T_f = \frac{\left( \frac{80.0 \text{ g mol}^{-1}}{196.97 \text{ g}} \right) \times (25.42 \text{ J mol}^{-1} \text{ K}^{-1}) \times (650 \text{ K}) + \left( \frac{100.0 \text{ g mol}^{-1}}{18.02 \text{ g}} \right) \times (75.291 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})}{\left( \frac{80.0 \text{ g}}{196.97 \text{ g mol}^{-1}} \right) \times (25.42 \text{ J mol}^{-1} \text{ K}^{-1}) + \left( \frac{100.0 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times (75.291 \text{ J mol}^{-1} \text{ K}^{-1})}
\]

\[
T_f = 306 \text{ K}
\]

**Appendix B Table 2.2**

**P3.16)** A mass of 35.0 g of \( \text{H}_2\text{O}(s) \) at 273 K is dropped into 180.0 g of \( \text{H}_2\text{O}(l) \) at 325 K in an insulated container at 1 bar of pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that \( C_{P,m} \) for \( \text{H}_2\text{O} \) is constant at its values for 298 K throughout the temperature range of interest.
\[ n_{\text{ice}} H_{\text{fusion}}^{\text{ice}} + n_{\text{ice}} C_{p,m}^{H_2O} (T_f - T_{i}^{\text{ice}}) + n_{\text{H}_2\text{O}} C_{p,m}^{H_2O} (T_f - T_{i}^{\text{H}_2\text{O}}) = 0 \]

\[ T_f = \left( \frac{n_{\text{ice}} C_{p,m}^{H_2O} + n_{\text{H}_2\text{O}} C_{p,m}^{H_2O}}{n_{\text{ice}} C_{p,m}^{H_2O} + n_{\text{H}_2\text{O}} C_{p,m}^{H_2O}} \right) \left( \frac{n_{\text{ice}} C_{p,m}^{H_2O} + n_{\text{H}_2\text{O}} C_{p,m}^{H_2O}}{n_{\text{ice}} C_{p,m}^{H_2O} + n_{\text{H}_2\text{O}} C_{p,m}^{H_2O}} \right) \]

Molar enthalpy of fusion of ice \(6008 \text{Jmol}^{-1}\). Use \(C_{p,m}^{\text{H}_2\text{O}}\) for water for both ice and liquid since all the ice cubes melt into water at 273K.

\[
\begin{align*}
T_f &= \frac{\left( \frac{35.0 \text{ g mol}^{-1}}{18.02 \text{ g}} \right) \times \left( 75.291 \text{ J mol}^{-1} \text{ K}^{-1} \right) \times (273 \text{ K}) + \left( \frac{180.0 \text{ g mol}^{-1}}{18.02 \text{ g}} \right) \times \left( 75.291 \text{ J mol}^{-1} \text{ K}^{-1} \right) \times (325 \text{ K})}{\left( \frac{35.0 \text{ g mol}^{-1}}{18.02 \text{ g}} \right) \times (6008 \text{ J mol}^{-1})} \\
&= 304 \text{ K}
\end{align*}
\]

**P3.19**) Because \((\partial H/\partial P)_T = -C_P \mu_{J,T}\), the change in enthalpy of a gas expanded at constant temperature can be calculated. To do so, the functional dependence of \(\mu_{J,T}\) on \(P\) must be known. Treating Ar as a van der Waals gas, calculate \(\Delta H\) when 1 mol of Ar is expanded from 400. to 1.00 bar at 300. K.

Assume that \(\mu_{J,T}\) is independent of pressure and is given by \(\mu_{J,T} = [(2a/RT) - b]/C_{p,m}\) and \(C_{p,m} = 5/2R\) for Ar. What value would \(\Delta H\) have if the gas exhibited ideal gas behavior?

\[
\Delta H_m = -\int_{p_i}^{p_f} C_{p,m} \mu_{J,T} \, dp \approx -C_{p,m} \mu_{J,T} (p_f - p_i) \\
= -C_{p,m} \left( \frac{1}{C_{p,m}} \left( \frac{2 \times (1.355 \text{ dm}^{-2} \text{ bar mol}^{-2})}{0.083 \text{ dm}^{-3} \text{ bar mol}^{-1} \text{ K}^{-1}} \times (300 \text{ K}) \right) - 0.0320 \text{ dm}^{-3} \text{ mol}^{-1} \right) \times (1.00 \text{ bar} - 400 \text{ bar}) \\
= 30.66 \text{ dm}^{-3} \text{ bar} \text{ mol}^{-1} \times 30.66 \text{ dm}^{-3} \text{ bar} \text{ mol}^{-1} \times 10^5 \text{ Pa} \text{ bar}^{-1} \times 10^{-3} \text{ m}^{-3} \\
= 3.06 \times 10^3 \text{ J}
\]

For an ideal gas, \(\Delta H_m = 0\), because \(\mu_{J,T} = 0\) for and ideal gas.
**P3.21** The Joule coefficient is defined by \((\partial T/\partial V)_U = 1/C_V[P - T(\partial P/\partial T)_V]\). Calculate the Joule coefficient for an ideal gas and for a van der Waals gas.

For an ideal gas:

\[
p = \frac{n R T}{V}
\]

\[
\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] = \frac{1}{C_V}\left[p - \frac{n R T}{V}\right] = 0
\]

For a van der Waals gas:

\[
p = \frac{n R T}{(V - n b)} - \frac{n^2 a}{V^2}
\]

\[
\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] = \frac{1}{C_V}\left[p - \frac{n R T}{(V - nb)}\right] = \frac{1}{C_V}\left[-\frac{n^2 a}{V^2}\right]
\]

**P3.22** Use the relation \((\partial U/\partial V)_T = T(\partial P/\partial T)_V - P\) and the cyclic rule to obtain an expression for the internal pressure, \((\partial U/\partial V)_T\), in terms of \(P\), \(\beta\), \(T\), and \(\kappa\):

\[
\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = T\left[-\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right] - p = -T\left(\frac{\partial V}{\partial p}\right)_T - p = -T\frac{V\beta}{-V\kappa} - p = T\frac{\beta}{\kappa} - p
\]

Equation 3.8  3.9

**P3.23** Derive the following relation,

\[
\left(\frac{\partial U}{\partial V_m}\right)_T = \frac{3a}{2\sqrt{T} V_m\left(V_m + b\right)}
\]

for the internal pressure of a gas that obeys the Redlich–Kwong equation of state,
\[ P = \frac{RT}{V_m - b} - \frac{a}{\sqrt[3]{V_m (V_m + b)}} \]

Using the Redlich–Kwong equation:

\[ \left( \frac{\partial p}{\partial T} \right)_V = \frac{R}{(V_m - b)} + \frac{1}{2} \frac{a}{T \sqrt[3]{V_m (V_m + b)}} \]

Then

\[ \left( \frac{\partial U}{\partial V_m} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p = \frac{RT}{(V_m - b)} + \frac{1}{2} \frac{a}{\sqrt[3]{V_m (V_m + b)}} - \left( \frac{RT}{(V_m - b)} - \frac{a}{\sqrt[3]{V_m (V_m + b)}} \right) \]

\text{equation 3.19}

\[ = \frac{1}{2} \frac{a}{\sqrt[3]{V_m (V_m + b)}} + \frac{a}{\sqrt[3]{V_m (V_m + b)}} = \frac{3a}{2 \sqrt[3]{V_m (V_m + b)}} \]

**P3.30** Use the relation

the cyclic rule, and the van der Waals equation of state to derive an equation for \( C_{P,m} - C_{V,m} \) in terms of \( V_m, T \), and the gas constants \( R, a, \) and \( b \).

Using the van der Waals equation:

\[ p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2} \]

We start by evaluating:

\[ T \left( \frac{\partial p}{\partial T} \right)_V = \frac{RT}{(V_m - b)} \]

Applying the cyclic rule:
\[
\left( \frac{\partial V_m}{\partial T} \right)_p = \left\{ \left( \frac{\partial p}{\partial T} \right)_{V_m} \left( \frac{\partial p}{\partial V_m} \right) \right\} = \left\{ \frac{R T}{(V_m - b)} \left( \frac{2 a}{V_m^3} - \frac{R T}{(V_m - b)^2} \right) \right\} = \frac{-1}{R T}
\]

Therefore:

\[
C_{p,m} - C_{V,m} = \frac{-1}{R T} \left( \frac{2 a}{V_m^3} - \frac{R T}{(V_m - b)^2} \right)
\]
1. Show \( Dq = dU - Dw \) is not an exact differential with respect to \( V \) and \( T \) for an ideal gas using (Hint: \( D_w = -P(V,T)dV \) and \( dU = Cv(T)dT \).)

\[
\delta q = dU - \delta w = C_v(T)dT + P(V,T)dV
\]

\[
\left( \frac{\partial P(V,T)}{\partial T} \right)_V = \left( \frac{\partial (nRT)}{\partial T} \right)_V = \frac{nR}{V}
\]

\[
\left( \frac{\partial C_v(T)}{\partial V} \right)_T = 0
\]

Because \( \left( \frac{\partial P(V,T)}{\partial T} \right)_V \neq \left( \frac{\partial C_v(T)}{\partial V} \right)_T \), \( \delta q \) is not an exact differential with respect to \( V \) and \( T \).

2. Assuming that \( dH \) is an exact differential, show \( dU \) is an exact differential for \( P \) and \( V \).

(Define \( dH = f(P,V)dP + g(P,V)dV \) & use \( \left( \frac{\partial f}{\partial V} \right)_P = \left( \frac{\partial g}{\partial P} \right)_V \)). You can also use \( dU = d(H-PV) = dH - pdV - VdP \).

\[
dU = d(H-PV) = dH - PdV - VdP
\]

\[
= f(P,V)dP + g(P,V)dV - PdV - VdP
\]

\[
= \left[ f(P,V) - V \right]dP + \left[ g(P,V) - P \right]dV
\]

Let \( F(P,V) = f(P,V) - V; G(P,V) = g(P,V) - P \) then \( dU = F(P,V)dP + G(P,V)dV \)

\[
\left( \frac{\partial F}{\partial V} \right)_P = \left( \frac{\partial [f(P,V) - V]}{\partial V} \right)_P = \left( \frac{\partial f}{\partial V} \right)_P - \left( \frac{\partial V}{\partial V} \right)_P = \left( \frac{\partial f}{\partial V} \right)_P - 1
\]

\[
\left( \frac{\partial G}{\partial P} \right)_V = \left( \frac{\partial [g(P,V) - P]}{\partial P} \right)_V = \left( \frac{\partial g}{\partial P} \right)_V - \left( \frac{\partial P}{\partial P} \right)_V = \left( \frac{\partial g}{\partial P} \right)_V - 1
\]

Because \( \left( \frac{\partial f}{\partial V} \right)_P = \left( \frac{\partial g}{\partial P} \right)_V \), so

\[
\left( \frac{\partial F}{\partial V} \right)_P = \left( \frac{\partial G}{\partial P} \right)_V
\]

\( dU \) is an exact differential for \( P \) and \( V \)

3. Consider the isothermal expansion of 1.00 mol of an ideal gas at 450. K from an initial pressure of 25.0 bar to a final pressure of 3.00 bar. Plot \( P_{ext} \) vs \( V \) graphs for (a) a reversible case that \( P = P_{ext} \) and (b) a case that \( P_{ext} = 3.00 \) bar. (c) Indicate the area that corresponds to the work \( |w| \) done by system in each graph. (d) Which graph gives you a greater work?

\[
P_{f_1}V = nRT
\]
25\text{bar} \times V_1 = 1\text{mol} \times 0.0831451\text{dm}^3\text{bar}^{-1}\text{mol}^{-1} \times 450\text{K} \\
V_1 = 1.49\text{dm}^3 \\
P_2V_2 = nRT \\
5\text{bar} \times V_2 = 1\text{mol} \times 0.0831451\text{dm}^3\text{bar}^{-1}\text{mol}^{-1} \times 450\text{K} \\
V_2 = 7.48\text{dm}^3 \\

a)

reversible isothermal expansion

\[ w_{\text{expansion}} = -nRT \ln \frac{V_2}{V_1} = -1\text{mol} \times 8.314\text{JK}^{-1}\text{mol}^{-1} \times 450\text{K} \times \ln 5 = -6021.4\text{J} \]

b)
irreversible isothermal expansion

\[ w_{\text{expansion}} = -P_{\text{external}} \Delta V = -P_{\text{external}} \times (V_2 - V_1) = -5 \text{bar} \times \frac{10^5 \text{Pa}}{\text{bar}} \times (7.48 \text{dm}^3 - 1.49 \text{dm}^3) \times \frac{10^{-3} \text{m}^3}{\text{dm}^3} = -2995 \text{J} \]

d) Graph (a) reversible process gives greater work, \( w_1 > w_2 \).