1. For an ideal gas, we proved $(\partial U/\partial V)_T = 0$. Use this result to prove $(\partial U/\partial p)_T$ is also zero for an ideal gas, which shows the internal energy of an isothermal ideal gas is constant.

[1]   *Hint:* $\left(\dfrac{\partial U}{\partial p}\right)_T = \left(\dfrac{\partial U}{\partial V}\dfrac{\partial V}{\partial p}\right)_T = \left(\dfrac{\partial U}{\partial V}\right)_T\left(\dfrac{\partial V}{\partial p}\right)_T$

2. The First Law states that the internal energy (U) is a function of the state variables of a system.
[1]   If U is a state function, then why is the enthalpy $(U + pV)$ also a state function?

3. 2.00 L of helium (assumed to be an ideal gas) initially at 300 K and 5.00 bar expands isothermally to a final volume of 8.00 L.

     a) Calculate ΔU, ΔH, w and q if the expansion is reversible ($p_{external} = p$).

     b) Calculate ΔU, ΔH, w and q if the expansion is irreversible with $p_{external} = p_{final}$.

[6]   **c)** Use parts **a** and **b** to illustrate U and H are **state functions**.

     d) Use parts **a** and **b** to illustrate w and q are **path-dependent** (*not* state functions).

4. The graph on the next page shows the molar heat capacities of He, H_2 and H_2O plotted against T.

     a) C_{pm} for He is independent of the temperature and equal to $5R/2$. Why?

     b) C_{pm} for H_2 is larger than C_{pm} for He. Why?

[4]   **c)** C_{pm} for H_2O is larger than C_{pm} for H_2. Why?

     d) The heat capacities of H_2 and H_2O increase as the temperature is raised. Why?

5. Calculate q, w, ΔU and ΔH for the combustion on one mole of propane at 25 °C and 1 bar.

[4] $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
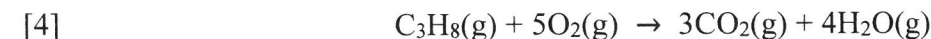
       Data: $\Delta H_{fm}°(C_3H_8, g) = -103.9$ kJ mol^{-1} $\Delta H_{fm}°(CO_2, g) = -393.5$ kJ mol^{-1}
                   $\Delta H_{fm}°(O_2, g) = 0$ $\Delta H_{fm}°(H_2O, g) = -241.8$ kJ mol^{-1}

       Hint: Recall that the enthalpy change of a chemical reaction if the enthalpy of formation of the products minus the enthalpy of formation of the reactants.

6. 5.00 moles of liquid water are heated from 20 °C to 85 °C at 1.00 bar.

     a) Why is it an excellent approximation to assume ΔV, and therefore w, are zero?

[4]   **b)** Calculate q, ΔU and ΔH.   *Data:* $C_{pm}°(H_2O, l) = 75.3$ J K^{-1} mol^{-1}

Heat capacities of He(g), H₂(g) and H₂O(g) for Question 4
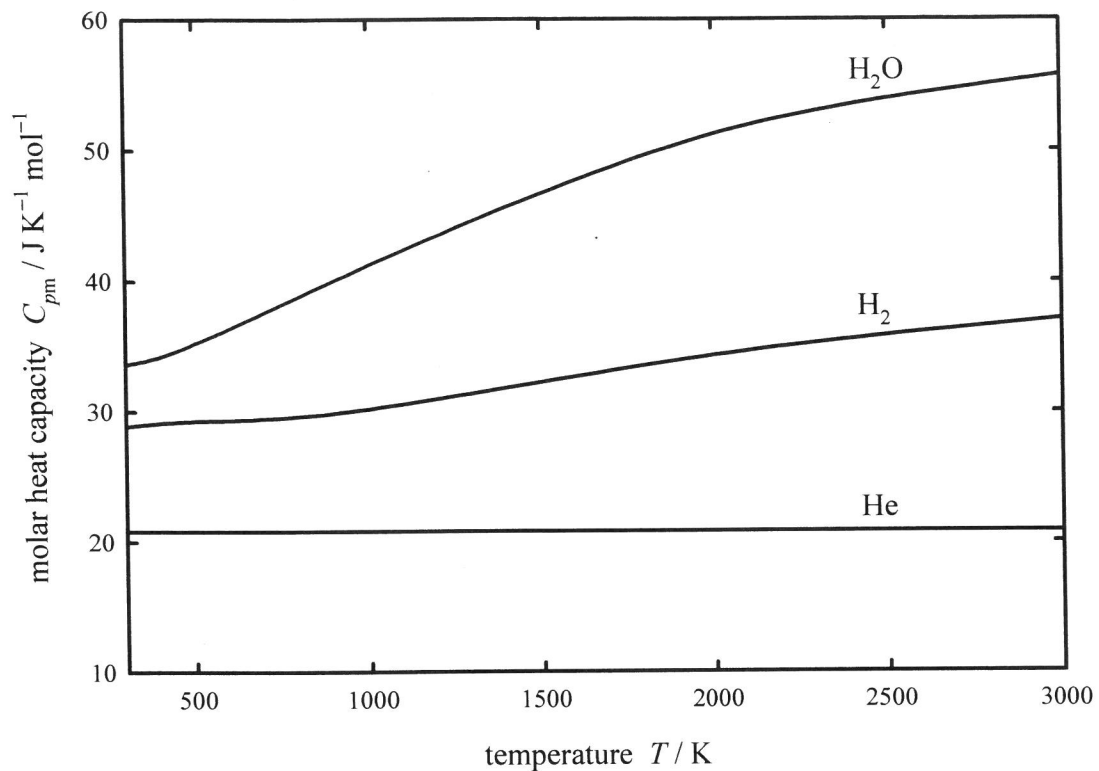
Usually in PSC 3072 or PSC 3020:

Mondays	9:30 to 11:00 am
	12:30 to 2:30 pm
Tuesdays	9:00 to 10:00 am
	11:30 am to 1:00 pm
Thursdays	10:30 am to noon
Wednesdays	12:30 to 2:00 pm
Fridays	12:30 to 2:00 pm

Chem 231   Assignment #2 $V = \dfrac{nRT}{P}$

Q1 Given $(\partial U / \partial V)_T = 0$ for an ideal gas,

show $(\partial U / \partial P)_T$ is also zero.

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V} \frac{\partial V}{\partial P}\right)_T$$

$$= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

$$= \left(\frac{\partial U}{\partial V}\right)_T \left[\frac{\partial}{\partial P}\left(\frac{nRT}{P}\right)\right]_T$$

$$= \left(\frac{\partial U}{\partial V}\right)_T nRT \left(\frac{\partial \frac{1}{P}}{\partial P}\right)_T$$

$$= \left(\frac{\partial U}{\partial V}\right)_T nRT \left(-\frac{1}{P^2}\right)$$

$$= \left(\frac{\partial U}{\partial V}\right)_T \left(-\frac{nRT}{P^2}\right) \quad \boxed{\neq \infty}$$

$$= (0)\left(-\frac{V}{P}\right)$$

$$= 0$$

(Q2)   the enthalpy (H) is defined as

$$H = U + pV$$

U is a function of state variables (First Law) and pV is a function of state variables p, V. So the sum $U + pV = H$ is a state function. (So is any other combination of U, p, V)

(Q3)   2.00 L of helium at 300 K and 5.00 bar expands to 8.00 L isothermally (constant T).

a) the expansion is reversible (gas pressure $p = P_{external}$)

$$W = - \int_{V_i}^{V_f} P_{external} \, dV = - \int_{V_i}^{V_f} p \, dV$$

$$= - \int_{V_i}^{V_f} \frac{nRT}{V} \, dV = - nRT \int_{V_i}^{V_f} \frac{1}{V} \, dV$$

$$= - p_i V_i \ln\left(\frac{V_f}{V_i}\right)$$

$$= - (5.00 \, bar)(2.00 \, L) \ln\left(\frac{8.00 L}{2.00 L}\right) = -13.86 \, L \, bar$$

$$= - (13.86 \, L \, bar)(10^{-3} \, m^3 L^{-1})(10^5 \, Pa \, bar^{-1})$$

$$\boxed{W = -1386 \, J}$$

(Q3 a cont,)

a/ use $n = \dfrac{P_i V_i}{RT} = \dfrac{(5.00 \text{ bar})(2.00 \text{ L})}{(0.08314 \text{ L bar } K^{-1} mol^{-1})(300K)}$

$n = 0.401 \text{ mol}$

then $w = -nRT \ln\left(\dfrac{V_f}{V_i}\right)$

$$= -(0.401 \text{ mol})\left(8.314 \dfrac{J}{K mol}\right)(300K) \ln\left(\dfrac{8.00 \text{ L}}{2.00 \text{ L}}\right)$$

$w = -1386 \text{ J}$

isothermal ideal gas $\Rightarrow$ U constant
$(T = 300 K)$

$\therefore$ $\boxed{\Delta U = 0}$ $\qquad \Delta U = q + w = 0$

$\boxed{q = -w = 1386 \text{ J}}$

constants

$\Delta H = \Delta(U + PV) = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT)$

$\boxed{\underline{\Delta H = 0}}$

$\left(\begin{array}{l} \text{notice:} \quad P_i V_i = P_f V_f = nRT \quad \left(\begin{array}{l}\text{isothermal}\\ \text{ideal gas}\end{array}\right) \\[2em] P_f = \left(\dfrac{V_i}{V_f}\right) P_i = \dfrac{2.00 \text{ L}}{8.00 \text{ L}} \, 5.00 \text{ bar} = 1.25 \text{ bar} \end{array}\right)$

(Q3 cont.)

b) the gas expands from $V_i = 2.00$ L, $P_i = 5.00$ bar

to $V_f = 8.00$ L, $P_f = 1.25$ bar against

constant external pressure $P_{external} = P_f = 1.25$ bar.

$$w = -\int P_{external} \, dV = -P_{external} \int_{V_i}^{V_f} dV$$

$$= -P_{external}(V_f - V_i)$$

$$= -(1.25 \text{ bar})(8.00 - 2.00) \text{ L}$$

$$= -7.5 \text{ L bar}$$

$\boxed{w = -750 \text{ J}}$

$\Delta U = 0$	isothermal
$\Delta H = 0$	ideal gas

$$\left[\begin{array}{l} \text{notice: } q \neq \Delta H \\ \left(\begin{array}{c} \text{pressure not} \\ \text{constant} \end{array} \right) \end{array} \right]$$

$(1 \text{ L bar} = 100 \text{ J})$

$\Delta U = 0 = q + w$

$\boxed{q = -w = 750 \text{ J}}$

path a) $\Delta U = \Delta H = 0$
$w = -q = -1386$ J

path b)
$\Delta U = \Delta H = 0$
$w = -q = -750$ J
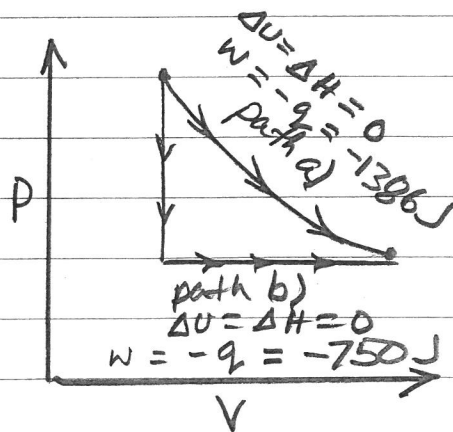
c) identical values of ΔU for different paths, so $\Delta U = U_f - U_i$ independent of the path taken, and ditto for ΔH

d) different paths give different q and w values

(Q4) For ideal gases: $C_{pm} = C_{vm} + R$

a) He atoms have kinetic energy of motion in <u>three</u> dimensions (e.g., x, y and z), each contributing $\frac{1}{2} R$ to C_{vm}:
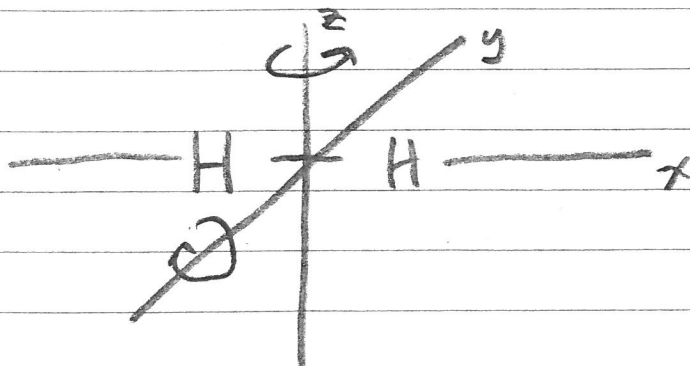
$$C_{vm} = \underline{\underline{\frac{3}{2} \frac{R}{2}}} \qquad \Rightarrow \quad C_{pm} = C_{vm} + R$$
$$= \frac{3}{2} R + R$$
$$C_{pm} = \frac{5}{2} R$$

He is monatomic, no vibrational or rotational kinetic energy. As a result, $C_{pm} = \frac{5}{2} R$ independent of the temperature.
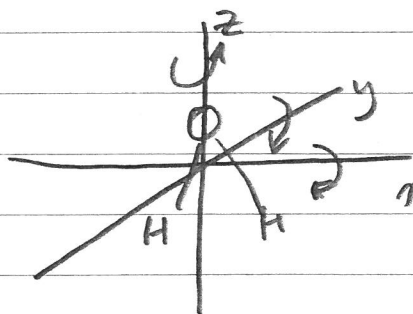
b) $C_{pm}(H_2) > C_{pm}(He)$ why?

H_2, in addition to 3 translational modes like He, has <u>two axes of rotation</u> which gives an additional rotational heat capacity $2 \frac{R}{2} = R$, and also some vibrational heat capacity
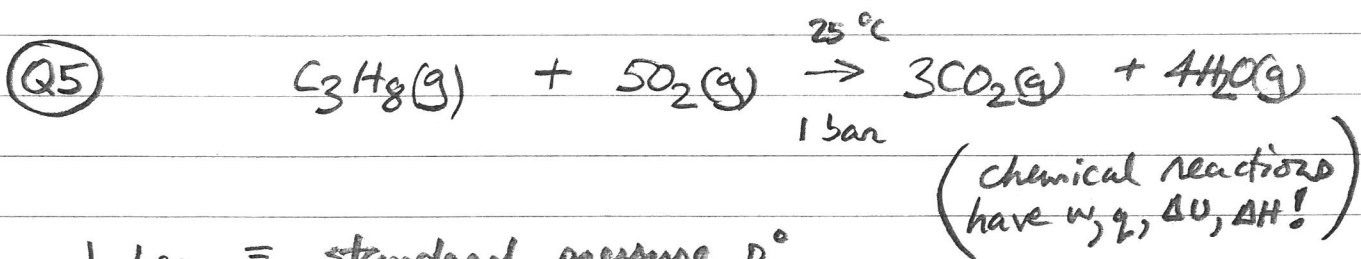
(Q 4 cont.)

c) $C_{pm}(H_2O) \geq C_{pm}(H_2)$ why?

H_2O is a nonlinear molecule with 3 rotation axes, compared to only 2 rotation axes for linear H_2 molecules.

Also, H_2O has more vibrational modes (bending, stretching) than H_2 (one stretch vibration)

d) $C_{pm}(H_2)$ and $C_{pm}(H_2O)$ increase with temperature because vibrations become more active (more molecules in excited vibrational states) and absorb more heat

⸻

Q5 $C_3H_8(g) + 5O_2(g) \xrightarrow[1\,bar]{25\,°C} 3CO_2(g) + 4H_2O(g)$

(chemical reactions have $w, q, \Delta U, \Delta H$!)

1 bar = standard pressure $p°$

(pressure = 1 bar)

$\Delta H = \Delta H° = \Delta H_f°(products) - \Delta H_f°(reactants)$

$= 3\Delta H_{fm}°(CO_2, g) + 4\Delta H_{fm}°(H_2O, g) - \Delta H_{fm}°(C_3H_8, g) - 5\Delta H_{fm}°(O_2, g)$

$= (3\,mol)\left(-393.5\,\frac{kJ}{mol}\right) + 4(-241.8) - (1)(-103.9) - 5(0)$

$\Delta H = -2043.8\ kJ$

(Q5 cont.)

$$\left(\text{recall } \Delta H_{fm}^{\circ}(O_2, g) = \text{enthalpy of formation of } O_2 \text{ from elemental } O_2, \text{ but } O_2 \text{ is already elemental, so } \Delta H_{fm}^{\circ}(O_2, g) = 0 \right)$$

At constant pressure (1 bar here) : $q = \Delta H$

$$q = \Delta H = -2043.8 \text{ kJ}$$

work $w = -\int P_{external} \, dV$ $\quad\left(\begin{array}{c} \text{pressure is constant} \\ P_{external} = P = \text{constant} \\ = 1 \text{ bar} \end{array} \right)$

$$= -\int P \, dV$$

$$= -P \int dV \qquad \left(\begin{array}{c} \text{here, } \Delta n_{gas} = +1.00 \text{ mol} \\ w = -\Delta n_{gas} RT \\ = -RT \end{array} \right)$$

$$= -P \, \Delta V$$

$$= -P \left[V_{products} - V_{reactants} \right]$$

$$= -P \left[3 V_{m CO2} + 4 V_{m H2O} - V_{m C3H8} - 5 V_{m O2} \right]$$

$$= -P \left[(3 \text{mol}) \frac{RT}{P} + 4 \frac{RT}{P} - (1) \frac{RT}{P} - 5 \frac{RT}{P} \right]$$

$$= -(1 \text{ mol}) RT = -(1 \text{ mol})(8.314 \text{ J K}^{-1} \text{mol}^{-1})(298.15 \text{ K})$$

$$\boxed{w = -2479 \text{ J} = -2.479 \text{ kJ}}$$

(Q5 cont.)

know $q = \Delta H = -2043.8 \text{ kJ}$ and $w = -2.479 \text{ kJ}$

$\Delta U = q + w$

$\quad = -2043.8 - 2.5 \quad \text{kJ}$

$\boxed{\Delta U = -2046.3 \quad \text{kJ}}$

(Q6)   5.00 moles of liquid water are heated
from 20 ℃ to 85 ℃ at 1.00 bar

$\qquad\qquad\qquad (p = P_{external} = constant = 1 \text{ bar})$

a) The molar volume of liquid water is very small
(compared to V_m for water vapor) and almost
constant during heating $\Rightarrow \Delta V \approx 0$

$w = -\int P_{external} dV \quad = -p \int dV \quad = -p \Delta V$

$\quad \cong -p(0) = 0$

b) heat
   capacity $C_p = \dfrac{dq}{dT} \quad \Rightarrow \quad dq = C_p dT$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(constants)}$

$q = \int dq = \int C_p dT = \int n C_{pm} dT = n C_{pm} \int dT$

$\quad = (5.00 \text{ mol})\left(75.3 \dfrac{J}{K \text{ mol}}\right)(358.15 - 293.15) K$

$\boxed{q = 24{,}470 \text{ J} = \Delta H}$ (pressure is constant)

$\Delta U = q + w = 24{,}470 \text{ J} + 0 = \boxed{24{,}470 \text{ J} = \Delta U}$