1.   Use $V_m = RT/p$ for the molar volume of an ideal gas to prove:

     a) $dV_m = (R/p)dT - (RT/p^2)dp$

[4]

     b) $\dfrac{\partial}{\partial T}\left(\dfrac{\partial V_m}{\partial p}\right) = \dfrac{\partial}{\partial p}\left(\dfrac{\partial V_m}{\partial T}\right)$

2.   Given $df = (2x/y)dx - (x^2/y^2)d\,y$, does function $f(x,y)$ exist? Justify your answer. [2]

3.   5.00 moles of water evaporates at 1.00 bar and 25.0 °C.

[5]
$$H_2O(\text{liquid}) \rightarrow H_2O(\text{gas})$$

    a) Calculate q, w, ΔH and ΔU. Use 44.01 kJ mol^{-1} for the molar enthalpy of vaporization.

    b) This process is isothermal, prompting one of your classmates to believe ΔH and ΔU are zero. Why is this incorrect?

4.   One mole of CO_2 at 30.0 bar and 25.0 °C expands <u>adiabatically</u> to a final pressure of 1.00 bar.

[7]   **a)** Calculate q, w, ΔU and ΔH if the expansion is **reversible**. Useful equation (see next page):

$$\ln(T_{final}/T_{initial}) = (R/C_{pm})\ln(p_{final}/p_{initial})$$

    b) Calculate q, w, ΔU and ΔH if the expansion is **irreversible** with $p_{ext} = p_{final} = 1.00$ bar. Useful equation (see next page):

$$T_{final} = \left(\dfrac{C_{Vm} + R\dfrac{p_{final}}{p_{initial}}}{C_{pm}}\right) T_{initial}$$

In parts **a** and **b**, assume CO_2 behaves as an ideal gas with $C_{pm} = 37.1$ J K^{-1} mol^{-1}.

5.   The powerful cooling effect that can be obtained by adiabatic expansion is vividly illustrated by opening the valve on a tank of compressed CO_2 to produce a jet of cold CO_2 gas and CO_2 "snow" (solid carbon dioxide, also called dry ice)! For example, see:

[2]
https://www.youtube.com/watch?v=1BtdZKrMucM

Are the expansions described in the Question 4 likely to produce solid carbon dioxide? Explain.

Data: CO_2 gas and solid CO_2 are in equilibrium at −78 °C at 1.00 bar.

Tips for Question 4 for Adiabatic Expansion of an Ideal Gas

Starting with the First Law $dU = dq + dw$ and using $dU = C_V dT$ (ideal gas, U depends only on T), $dq = 0$ (adiabatic) and $dw = -p_{ext}dV$ gives

$$dU = dw$$

$$C_V dT = -p_{ext}dV$$

For an ideal gas $V = nRT/p$. Therefore $dV = d(nRT/p) = (nR/p)dT - (nRT/p^2)dp$ and

$$C_V dT = -p_{ext}dV = -p_{ext}\left(\frac{nR}{p}dT - \frac{nRT}{p^2}dp\right)$$

$$\left(C_V + nR\frac{p_{ext}}{p}\right)\frac{1}{T}dT = nR\frac{p_{ext}}{p^2}dp$$

Reversible Adiabatic Expansion of an Ideal Gas ($p_{ext} = p$)

$$\left(C_V + nR\right)\frac{1}{T}dT = nR\frac{1}{p}dp \qquad \text{(ideal gas: } C_V + nR = C_p\text{)}$$

$$C_p\frac{1}{T}dT = nR\frac{1}{p}dp$$

$$C_p\, d\ln T = nR\, d\ln p$$

Integrating at constant C_p gives

$$\ln\left(\frac{T_{final}}{T_{initial}}\right) = \frac{nR}{C_p}\ln\left(\frac{p_{final}}{p_{initial}}\right) = \frac{R}{C_{pm}}\ln\left(\frac{p_{final}}{p_{initial}}\right)$$

Irreversible Adiabatic Expansion of an Ideal Gas with $p_{ext} = p_{final}$

$$C_V dT = -p_{ext}dV = -p_{final}dV$$

Integrates at constant C_V and constant $p_{ext} = p_{final}$

$$C_V(T_{final} - T_{initial}) = -p_{final}(V_{final} - V_{initial}) = -p_{final}(nRT_{final}/p_{final} - nRT_{initial}/p_{initial})$$

to give

$$T_{final} = \left(\frac{C_V + nR\dfrac{p_{final}}{p_{initial}}}{C_p}\right)T_{initial} = \left(\frac{C_{Vm} + R\dfrac{p_{final}}{p_{initial}}}{C_{pm}}\right)T_{initial}$$

Chem 231   Assignment #3

(Q1) a) V_m is a function of T and p $\left(V_m = RT/p\right)$,

therefore V_m can be differentiated with respect to T and p

and $dV_m = \left(\dfrac{\partial V_m}{\partial T}\right)_p dT + \left(\dfrac{\partial V_m}{\partial p}\right)_T dp$

$\left(\dfrac{\partial V_m}{\partial T}\right)_p = \left(\dfrac{\partial}{\partial T}\dfrac{RT}{p}\right)_p = \dfrac{R}{p}\left(\dfrac{\partial T}{\partial T}\right)_p = \boxed{\dfrac{R}{p}}$

$\left(\dfrac{\partial V_m}{\partial p}\right)_T = \left(\dfrac{\partial}{\partial p}\dfrac{RT}{p}\right)_T = RT\left(\dfrac{\partial \frac{1}{p}}{\partial p}\right)_T = RT\left(\dfrac{-1}{p^2}\right) = \boxed{-\dfrac{RT}{p^2}}$

$$\boxed{dV_m = \dfrac{R}{p}\,dT - \dfrac{RT}{p^2}\,dp}$$

b) Prove $\dfrac{\partial}{\partial T}\dfrac{\partial V_m}{\partial p} = \dfrac{\partial}{\partial p}\dfrac{\partial V_m}{\partial T}$ $\left(\begin{array}{c}\text{the "order" of}\\ \text{differentiation}\\ \text{"doesn't matter"}\end{array}\right)$

$LS = \left[\dfrac{\partial}{\partial T}\left(\dfrac{\partial V_m}{\partial p}\right)_T\right]_p = \left[\dfrac{\partial}{\partial T}\left(-\dfrac{RT}{p^2}\right)\right]_p = -\dfrac{R}{p^2}\left(\dfrac{\partial T}{\partial T}\right)_p = -\dfrac{R}{p^2}$

$RS = \left[\dfrac{\partial}{\partial p}\left(\dfrac{\partial V_m}{\partial T}\right)_p\right]_T = \left[\dfrac{\partial}{\partial p}\left(\dfrac{R}{p}\right)\right]_T = R\left(\dfrac{\partial \frac{1}{p}}{\partial p}\right)_T = R\left(-\dfrac{1}{p^2}\right)$

$\boxed{LS = RS}$

(Q2) $df = (2x/y)\,dx - (x^2/y^2)\,dy = g(x,y)\,dx + h(x,y)\,dy$

Notice $\left(\dfrac{\partial g}{\partial y}\right)_x = \left[\dfrac{\partial}{\partial y}\left(\dfrac{2x}{y}\right)\right]_x = 2x\left(\dfrac{\partial \frac{1}{y}}{\partial y}\right)_x = 2x\left(\dfrac{-1}{y^2}\right) \Rightarrow \boxed{\left(\dfrac{\partial g}{\partial y}\right)_x = \left(\dfrac{\partial h}{\partial x}\right)_y}$

$\left(\dfrac{\partial h}{\partial x}\right)_y = \left[\dfrac{\partial}{\partial x}\left(-\dfrac{x^2}{y^2}\right)\right]_y = -\dfrac{1}{y^2}\left(\dfrac{\partial x^2}{\partial x}\right)_y = \left(-\dfrac{1}{y^2}\right)2x$ $\therefore f(x,y)$ exists

$\left(\text{e.g. } f(x,y) = x^2/y\right)$

(Q3) Evaporation of five moles of water at 25.0°C and 1.00 bar:

$$5 H_2O(l) \rightarrow 5 H_2O(g)$$

notes: $(V_l = 0.090 L)$ $(V_g = 5nRT/p = 124.0 L \ (\text{much larger}))$

$$\Delta H = q \quad (\text{pressure constant})$$

$$= (5.00 \ mol) \ \Delta H_{vap,m} = (5.00 \ mol) \ 44.01 \ kJ \ mol^{-1}$$

$$\boxed{\Delta H = q = 220.0 \ kJ}$$

volume of $H_2O(l)$ is very small compared to volume of $H_2O(g)$
$\Rightarrow$ can omit $V_m(l)$
(pressure constant)

$$w = -\int P_{ext} \, dV = -p \int dV$$

$$= -p \left(V_f - V_i \right) = -p \left(5 V_m(g) - 5 V_m(l) \right)$$

liquid water has a density of about $1.00 \ g \ cm^{-3}$.
molar volume of liquid water is about $18 \ cm^3 \ mol^{-1}$
$$V_m(l) \approx 0.018 \ L \ mol^{-1}$$

b) $\Delta U_T = 0$ and $\Delta H_T = 0$
for isothermal ideal gases
liquid water here!

water vapor molar volume (assumed to be an ideal gas) $V_m = \dfrac{RT}{p}$

$$V_m(g) = \frac{(0.08314 \ L \ bar \ K^{-1} mol^{-1})(298.15 \ K)}{1.00 \ bar} = 24.79 \ L \ mol^{-1}$$

$$w = -p(V_f - V_i) = -p \left[\underline{5 V_m(g)} - \underbrace{5 V_m(l)}_{\text{negligible}} \right]$$

$$= -1.00 \ bar \left[(5 \ mol) 24.79 \frac{L}{mol} - (5 \ mol) \ 0.018 \frac{L}{mol} \right]$$

$$= -1.00 \ bar \left(123.95 - 0.09 \right) L = -123.9 \ L \ bar$$

$$= -(123.9 \ L \ bar)\left(10^{-3} \frac{m^3}{L}\right)\left(10^5 \frac{Pa}{bar}\right) = \boxed{-12.4 \ kJ = w}$$

$$\boxed{\Delta U = q + w = 207.6 \ kJ}$$

Q4 a) One mole of CO_2 gas expands reversibly ($P = P_{ext}$) and adiabatically ($q = 0$) from 30.0 bar, 25.0 °C to a final pressure of 1.00 bar.

$$C_{pm} = 37.1 \ J \ K^{-1} mol^{-1} \qquad \left(\begin{array}{l} C_{vm} = C_{pm} - R \ \boxed{\text{ideal gas}} \\ \quad = C_{pm} - 8.314 \ J K^{-1} mol^{-1} \end{array} \right)$$

$$C_{vm} = 28.8 \ J K^{-1} mol^{-1}$$

reversible adiabatic expansion, constant C_{pm} and C_{vm}:

$$\ln\left(\frac{T_f}{T_i}\right) = \frac{R}{C_{pm}} \ln\left(\frac{P_f}{P_i}\right) = \ln\left(\frac{P_f}{P_i}\right)^{R/C_{pm}}$$

"exponentiate" to get $\qquad \dfrac{T_f}{T_i} = \left(\dfrac{P_f}{P_i}\right)^{R/C_{pm}}$

$$T_f = \left(\frac{P_f}{P_i}\right)^{R/C_{pm}} T_i = \left(\frac{1.00 \ bar}{30.0 \ bar}\right)^{\frac{8.314}{37.1}} 298.15 \ K = 0.4666 \ T_i$$

$$T_f = 139.1 \ K \quad (\text{final temperature})$$

$$dU = \cancel{dq}^{0} + dw \qquad \text{adiabatic}$$

$$C_v dT = -P_{ext} dV = -p dV \qquad \begin{array}{l} dU = C_v dT \qquad p = P_{ext} \\ (\text{ideal gas, reversible}) \end{array}$$

$$\Delta U = w = \int_{T_i}^{T_f} C_v dT = C_v \int_{T_i}^{T_f} dT = C_v(T_f - T_i) \qquad (C_v \ const.)$$

$$= (28.8 \ J \ K^{-1} mol^{-1})(1.00 \ mol)(139.1 - 298.15)K = \boxed{-4580 J}$$

$$\Delta H = \int_{T_i}^{T_f} C_p \ dT = C_p \int_{T_i}^{T_f} dT = \left(37.1 \frac{J}{K}\right)(139.1 - 298.15)K = \boxed{-5900 J}$$

(Q4 cont.)

b) One mole of CO_2 gas expands <u>irreversibly</u> ($P_{ext} = 1.00$ bar)
and adiabatically $\boxed{q = 0}$ from 30.0 bar
and 25.0 °C to 1.00 bar

$C_{pm} = 37.1$ J K^{-1} mol^{-1} $C_{vm} = 28.8$ J K^{-1} mol^{-1}

$$T_f = \frac{C_{vm} + R \frac{P_f}{P_i}}{C_{pm}} T_i$$

$$= \frac{\left(28.8 + 8.314 \frac{1.00 \text{ bar}}{30.0 \text{ bar}}\right) \text{J K}^{-1}\text{mol}^{-1}}{37.1 \text{ J K}^{-1}\text{mol}^{-1}} \quad 298.15 \text{ K}$$

$T_f = 233.7$ K

$w = \Delta U = \int C_v dT = C_v \int dT = 28.8 \frac{J}{K} (233.7 - 298.15) K$

$= \boxed{-1860 \text{ J}}$ (less work done on surroundings for the irreversible expansion)

$\Delta H = \int C_p dT = C_p(T_f - T_i) = 37.1 \frac{J}{K} (233.7 - 298.15) K$

$= \boxed{-2390 \text{ J}}$

(Q5) At the final pressure (1.00 bar), solid CO_2 can
form if the temperature is below -78 °C (195 K)

(part a)
Solid CO_2 forms in the reversible expansion ($T_{final} = 139$ K calculated)

(part b)
but not the irreversible expansion $T_{final} = 234$ K