1.   **a)** Air at 25 °C and 1.00 bar is compressed reversibly and adiabatically to 1/9 of its initial volume. In class, we showed the compressed air is *hot* (445 °C). But the compression is
[2]   adiabatic: no heat flows into the air as it is compressed. So why does the air get so hot? Explain.

   b) If helium is compressed in this process, instead of air, helium gets *hotter* (1020 °C)! Why?

2.   If the valve on the tank of compressed carbon dioxide in the Chem 231 lab is opened, the
[1]   expanding gas produces a jet of solid white particles resembling snow! Explain.

3.   For an ideal gas ($V = nRT/p$), evaluate the following partial derivatives of the volume:

[4]   **a)** $\left(\dfrac{\partial V}{\partial T}\right)_{p,n}$ **b)** $\left(\dfrac{\partial V}{\partial p}\right)_{T,n}$ **c)** $\left[\dfrac{\partial}{\partial p}\left(\dfrac{\partial V}{\partial T}\right)_{p,n}\right]_{T,n}$ **d)** $\left[\dfrac{\partial}{\partial T}\left(\dfrac{\partial V}{\partial p}\right)_{T,n}\right]_{p,n}$

   This Question illustrates the useful rule $\partial^2 f(x,y)/\partial x \partial y = \partial^2 f(x,y)/\partial y \partial x$.

4.   5.00 moles of liquid water at its normal boiling point (100 °C, 1.00 atm) evaporates to form
[4]   water vapor at the same temperature and pressure. Calculate q, w, ΔU and ΔH.

   Data: Use 40.7 kJ mol^{-1} for the enthalpy of vaporization, 0.958 g cm^{-3} for the density of liquid water.

5.   The First Law applies to chemical processes too! Calculate q, w, ΔU and ΔH for the combustion of methane at 25 °C and 1.00 bar.

[4] $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$
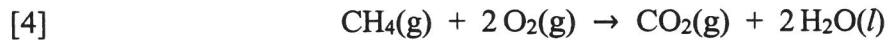
   Data at 25 °C, 1.00 bar: $\Delta H_{mf}°(CH_4, g) = -74.8$ kJ mol^{-1}
                     $\Delta H_{mf}°(CO_2, g) = -393.5$ kJ mol^{-1}
                     $\Delta H_{mf}°(H_2O, l) = -285.8$ kJ mol^{-1}
                     density $H_2O(l) = 0.997$ g cm^{-3}

6.   5.00 L of helium initially at 16.0 bar and 300 K expands adiabatically to 40.00 L and 0.500 bar.

[3]   **a)** Is the expansion reversible? Briefly justify your answer.

   b) Calculate q, w, ΔU and ΔH

7.   **a)** The isothermal compressibility is defined as $\kappa = -V^{-1}(\partial V/\partial p)_T$. Why is there a minus sign?

[2]   **b)** In terms of the density (ρ = mass per unit volume), show $\kappa = \rho^{-1}(\partial \rho/\partial p)_T$.

Chem 231   Assignment #3

(Q1)   a) Air (or any other gas) compressed adiabatically (q=0)
             gets hot! Why? No heat is flowing into the gas.

From the First Law: $\Delta U = q + w$.

For an adiabatic process $(q = 0)$: $\Delta U_{adi} = w_{ad}$.

During an adiabatic compression of an ideal gas,
work is done on the gas $(w > 0)$, so the energy of
the gas increases: $\Delta U_{ad} = w_{ad} > 0$.

The energy of a gas increases with temperature.
If $\Delta U_{ad} > 0$, then $\Delta T_{ad} > 0$.

b) For a reversible adiabatic compression:
       $(P_{ext} = P)$ $(q=0)$

$dU = \cancel{dq} + dw$ (First Law)

He has a smaller
heat capacity,
than air, "easier"
to warm up

$dU_{ad} = dw_{ad} = -P_{ext}\,dV = -p\,dV$

for an ideal gas, the internal energy U depends only on T:

so $dU = C_V\,dT = -p\,dV$

$$dT = -\frac{P}{C_V}\,dV \quad \left(\text{proportional to } \frac{1}{C_V}\right)$$

C_V for He $\left(\frac{3}{2}R \text{ per mole}\right)$ is smaller than C_V for air $\left(\frac{5}{2}R \text{ per mole}\right)$
so the change in temperature for He is larger than ΔT for air

(Q2) High-pressure CO_2 in the tank expands rapidly and therefore adiabatically ($q=0$, no time for heat flow) into the Chem 231 lab at 1.00 bar external pressure.

$$dU = \cancelto{0 \text{ (adiabatic)}}{dq} + dw$$

$$C_V dT = -P_{ext} dV \qquad\qquad dT = -\frac{P_{ext}}{C_V} dV$$

for the expansion of the CO_2 gas, $dV > 0$

$P_{ext} > 0$ and $C_V > 0$, so $dT < 0$

The adiabatically expanding CO_2 gas cools ($dT < 0$), reaching temperatures below the sublimation temperature of CO_2 (195 K at 1 bar)

$$CO_2 (g) \rightleftharpoons CO_2 (solid) \qquad \boxed{\text{some } CO_2 \text{ freezes}}$$

The "snow" consists of $\boxed{\text{solid } CO_2 \text{ particles}}$ (aka dry ice).

$\boxed{CO_2 \text{ gas cooled by the adiabatic expansion freezes}}$

(Q3) a) $\left(\dfrac{\partial V}{\partial T}\right)_{P,n} = \left(\dfrac{\partial}{\partial T} \dfrac{nRT}{P}\right)_{P,n} = \dfrac{nR}{P}\left(\dfrac{\partial T}{\partial T}\right)_{P,n}$

$$= \frac{nR}{P}$$

$$= \frac{V}{T}$$

(Q3 cont.)

b) $\left(\dfrac{\partial V}{\partial P}\right)_{T,n} = \left(\dfrac{\partial}{\partial P}\dfrac{nRT}{P}\right)_{T,n} = nRT\left(\dfrac{\partial \frac{1}{P}}{\partial P}\right)_{T,n}$

$$= nRT\left(\dfrac{-1}{P^2}\right) = -\dfrac{nRT}{P^2} = -\dfrac{V}{P}$$

c) $\left[\dfrac{\partial}{\partial P}\left(\dfrac{\partial V}{\partial T}\right)_{P,n}\right]_{T,n} = \left(\dfrac{\partial}{\partial P}\dfrac{nR}{P}\right)_{T,n} = nR\left(\dfrac{\partial \frac{1}{P}}{\partial P}\right)_{T,n}$

$$= nR\left(-\dfrac{1}{P^2}\right) = -\dfrac{nR}{P^2} = -\dfrac{V}{TP}$$

d) $\left[\dfrac{\partial}{\partial T}\left(\dfrac{\partial V}{\partial P}\right)_{T,n}\right]_{P,n} = \left(\dfrac{\partial}{\partial T}\dfrac{-nRT}{P^2}\right)_{P,n}$

$$= -\dfrac{nR}{P^2}\left(\dfrac{\partial T}{\partial T}\right)_{P,n} = -\dfrac{nR}{P^2} = -\dfrac{V}{TP}$$

notice $\quad \dfrac{\partial^2 V}{\partial P\,\partial T} = \dfrac{\partial^2 V}{\partial T\,\partial P}$

$\qquad\qquad\qquad \nearrow \qquad\qquad \nwarrow$

$\qquad\qquad c \qquad\qquad\qquad\quad d$

(Q4)　　　$5.00 \text{ mol } H_2O(l) \xrightarrow[1.00\text{ atm}]{100°C} 5.00 \text{ mol } H_2O(g)$
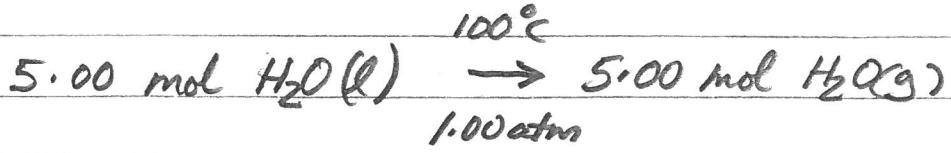
$$\Delta H = n \Delta H_{vap,m} = (5.00 \text{ mol})(40.7 \text{ kJ mol}^{-1})$$

$$\boxed{\Delta H = q = 203.5 \text{ kJ}}$$

$$W = -\int P_{ext} \, dV$$

$$= -\int p \, dV \quad (\text{p constant})$$

$$= -p \int dV$$

$$= -p \, \Delta V$$

at constant pressure

$$q = \Delta H$$

why?　$dH = d(U + pV)$

$$= dU + d(pV)$$

$$= dU + p\,dV$$

$$= dq - p\,dV + p\,dV$$

$$dH_p = dq$$

density $\varrho = \dfrac{mass}{volume}$

$volume = \dfrac{mass}{\varrho}$

$$\Delta V = n V_m (H_2O, g) - n V_m (H_2O, l)$$

$$= n \frac{RT}{P} - n \frac{molar \; mass}{density}$$

$$= 5.00 \text{ mol} \left[\frac{(0.08314 \text{ L bar K}^{-1}\text{mol}^{-1})(373.15K)}{1.01325 \text{ bar}} - \frac{18.01 \text{ g mol}^{-1}}{0.958 \text{ g cm}^{-3}} \right]$$

$$= 5.00 \text{ mol} \left[30.62 \text{ L mol}^{-1} - 18.80 \text{ cm}^3 \text{ mol}^{-1} \right]$$

$$= 5.00 \text{ mol} \left[30.62 \text{ L mol}^{-1} - \underset{(\text{negligibly small})}{0.01880 \text{ L mol}^{-1}} \right]$$

$$= (5.00 \text{ mol})(30.60 \text{ L mol}^{-1}) = 153.0 \text{ L} = 0.1530 \text{ m}^3$$

$$W = -p\Delta V = -(101325 \text{ Pa})0.1530 \text{ m}^3$$

$$\boxed{W = -15,500 \text{ J}}$$

$$\Delta U = q + W = 203.5 - 15.5$$

$$\boxed{\Delta U = 188.0 \text{ kJ}}$$

(Q5) $CH_4(g) + 2 O_2(g) \xrightarrow[\substack{1 \text{ bar}}]{\substack{25°C}} CO_2(g) + 2H_2O(\ell)$
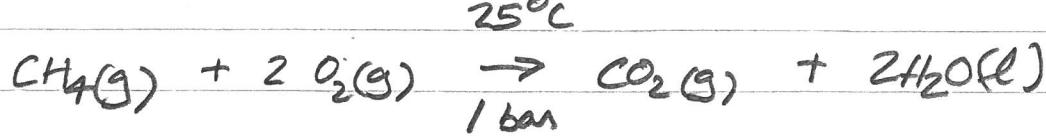
$q = \Delta H \quad \text{(constant pressure)} \qquad \left(\begin{array}{l} 1 \text{ bar} = p^{\circ} \\ \text{standard pressure} \end{array}\right)$

$\quad = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$

$\quad = \Delta H_{fm}^{\circ}(CO_2, g) + 2\Delta H_{fm}^{\circ}(2H_2O, \ell) - \Delta H_{fm}^{\circ}(CH_4, g) - 2\Delta H_{fm}^{\circ}(O_2, g)$

$\quad = \left[-393.5 + 2(-285.8) - (-74.8) - 2(0)\right] \text{ kJ}$

$$\boxed{\Delta H = -890.3 \text{ kJ} = q}$$

$W = -\int P_{ext}\, dV = -\int p\, dV = -p\int dV = -p\Delta V$

$\Delta V = V(\text{products}) - V(\text{reactants})$

$\quad = V_m(CO_2, g) + 2V_m(H_2O, \ell) - V_m(CH_4, g) - 2V_m(O_2, g)$

$\quad = \dfrac{RT}{P} + 2\dfrac{M_{H_2O(\ell)}}{\rho_{H_2O(\ell)}} - \dfrac{RT}{P} - 2\dfrac{RT}{P} \qquad \boxed{\begin{array}{c}\text{negligible}\\\text{volume for}\\H_2O(\ell)\end{array}}$

$\quad = -\dfrac{2RT}{P} + 2\dfrac{18.01 \text{ gmol}^{-1}}{0.997 \text{ g cm}^{-3}} = -\dfrac{2(0.08314)(298.15)}{1.00} L + 36.0 \text{ cm}^3$ ↓

$\quad = -49.58\, L + 0.036\, L = -49.54\, L = -0.04954 \text{ m}^3$

$W = -p\Delta V = -(1.00 \text{ bar})(-49.54\, L) = 49.54 \text{ L bar}$

$w = (49.54 \text{ L bar})\left(100 \dfrac{J}{\text{L bar}}\right) = \boxed{4954\, J = w}$

$\Delta U = q + w = -890.3 \text{ kJ} + 4.954 \text{ kJ} = \boxed{-885.3 \text{ kJ} = \Delta U}$

(Q6) a) for helium: $C_{Vm} = \frac{3}{2}R$ $\left(\begin{array}{l}\frac{1}{2}R \text{ for kinetic} \\ \text{energy in the} \\ x, y, z \text{ directions}\end{array}\right)$

$C_{Pm} = C_{Vm} + R$ (ideal gas)
$= \frac{5}{2}R$

$\gamma = \frac{C_{Pm}}{C_{Vm}} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$

If the adiabatic expansion is <u>reversible</u>, then $P_i V_i^{\gamma} = P_f V_f^{\gamma}$

$P_i V_i^{\gamma} = (16.0 \text{ bar})(5.00 \text{ L})^{5/3} = 233.92 \text{ bar L}^{5/3}$

$P_f V_f^{\gamma} = (0.500 \text{ bar})(40.00 \text{ L})^{5/3} = 233.92 \text{ bar L}^{5/3}$

$\boxed{P_i V_i^{\gamma} = P_f V_f^{\gamma} \text{ so the expansion is reversible}}$

b) $n = \frac{P_i V_i}{RT_i} = \frac{P_f V_f}{RT_f}$ $T_f = \frac{P_f V_f}{P_i V_i} T_i$

$T_f = \frac{(0.500 \text{ bar})(40.0 \text{ L})}{(16.0 \text{ bar})(5.00 \text{ L})} 300 K = 75 K$

recall:
$C_{Pm} = C_{Vm} + R$ (ideal gas)

$\Delta U = W = nC_{Vm}(T_f - T_i)$

$\left(n = \frac{16.0 \cdot 5.00}{0.0814(300)}\right.$

$\left. n = 3.21 \text{ mol}\right)$

$= \frac{3}{2}(3.21 \text{ mol})\left(8.314 \frac{J}{K mol}\right)(75-300)K$

$\boxed{\Delta U = W = -9,010 \text{ J}}$

$\Delta H = nC_{Pm}\Delta T = n\frac{5}{2}R\Delta T$

$\boxed{\Delta H = -15,020 \text{ J}}$

(Q7) a) $\left(\dfrac{\partial V}{\partial P}\right)_T$ is always negative $\left(\begin{array}{l}\text{systems shrink in}\\ \text{volume if the}\\ \text{pressure is increased}\end{array}\right)$

defining κ as $-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$ is convenient

because κ is always positive (don't have to include a minus sign for κ values)

b) volume $V = \dfrac{mass}{density} = \dfrac{m}{\rho}$

$\kappa = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T = -\dfrac{1}{\frac{m}{\rho}}\left(\dfrac{\partial}{\partial P}\dfrac{m}{\rho}\right)_T = -\dfrac{m}{\frac{m}{\rho}}\left(\dfrac{\partial \frac{1}{\rho}}{\partial P}\right)_T$

$= -\rho\left(\dfrac{-1}{\rho^2}\right)\left(\dfrac{\partial \rho}{\partial P}\right)_T = \dfrac{1}{\rho}\left(\dfrac{\partial \rho}{\partial P}\right)_T$