Chemistry 231   **Assignment #3**   (due Tuesday, 06 October, in class)

1.   Explain in terms of molecular energy levels why the heat capacities of air, to a reasonable first
[3]   approximation, are $C_{Vm} = (5/2)R$ and $C_{pm} = (7/2)R$.

2.   The valve on a tank of compressed air is opened, allowing air in the tank initially at 150 bar and
      300 K to expand rapidly and adiabatically against a constant external pressure of 1.00 bar to a
      final pressure of 1.00 bar.
[6]
      a) Calculate the final temperature of the expanded air. Assume ideal-gas behavior and use the
      heat capacities from Question 1.

      b) Calculate q, w, ΔU and ΔH per mole of air.

3.   **a)** Use the expression for the differential of the function $f(x,y)$ of two independent variables

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

[4]   to prove

$$dV_m = \frac{R}{p}dT - \frac{RT}{p^2}dp$$

      for the molar volume of an ideal gas.

      b) Prove that dV_m is an exact differential for an ideal gas.

4.   **a)** Calculate the heat required to raise the temperature of one mole of graphite (a form of solid
      carbon) from 298 K to 3000 K at a constant pressure of 1 bar. Data for graphite at 1 bar:
[7]

T/K	C_{pm}/J K^{-1} mol^{-1}
298	8.53
500	14.63
1000	21.54
1500	23.84
2000	24.54
2500	25.00
3000	25.34

      b) Heating graphite (density 2.26 g cm^{-3} at 298 K) causes it to expand by about 0.005 % per
      Kelvin. Use this information to show $w = 0$ and $\Delta U = \Delta H$ are excellent approximations for the
      process described in part **a.**

Chemistry 231 | Assignment #3 |

(1.) Air is mostly nitrogen and oxygen, diatomic N_2 and O_2 molecules.

The center of mass of each molecule can move ("translate") in the x, y, and z dimension, providing 3 modes of translational kinetic energy.

In addition, the nuclei of each N_2 and O_2 molecule can rotate around two axes of rotation (sketched below), providing 2 "modes" of rotational kinetic energy.

At room temperature and moderate temperatures (≤ 500 K) vibration in N_2 and O_2 are not active (almost all molecules in the ground (lowest) vibrational energy level)

These considerations suggest 5 modes of kinetic energy for each N_2 and O_2 molecule.

3 trans. + 2 rot.

no work (const. volume), only heating

Each of these 5 modes contributes $RT/2$ to the internal energy per mole, which gives

$$U_m \approx 5\frac{RT}{2} \quad \text{and} \quad C_{vm} \equiv \left(\frac{\partial U_m}{\partial T}\right)_V = \frac{5}{2}R$$
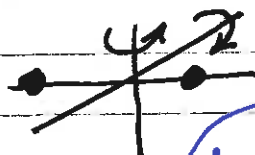
Assuming air is an ideal gas (a good approximation for a gas of nonpolar N_2 and O_2 molecules up to moderate pressure

same 3 trans. + 3 rot. modes

$$C_{pm} = C_{vm} + R \quad \text{(proved in class)}$$

which gives

$$C_{pm} = \frac{7}{2}R$$

the extra R for C_{pm} is due to the work of expansion for heating at constant p

(2.) Irreversible adiabatic expansion of an ideal gas

start: finish:

$P_i = 150$ bar $P_f = 1.00$ bar

$T_i = 300$ K $\frac{T_f}{} = ?$ (calculate T_f)

a) $P_{external} = 1.00$ bar (constant)

$C_{vm} = 5R/2$

$C_{pm} = 7R/2$

$dU = \cancel{dq}^0 + dW$ adiabatic ⎤

                                              ⎥ combine

$dU = C_v dT$ ideal gas ⎦

$C_v dT = dU = dW = -P_{external}\, dV$ $\div n$ $\dfrac{C_v}{n} = C_{vm}$

                                                          $\dfrac{V}{n} = V_m$

per mole: $C_{vm}\, dT = -P_{external}\, dV_m$

integrate: $\displaystyle\int_{T_i}^{T_f} C_{vm}\, dT = -\int P_{external}\, dV_m$

          T_i const.   const.

$C_{vm} \displaystyle\int_{T_i}^{T_f} dT = -P_{external} \int_{V_{mi}}^{V_{mf}} dV_m$

                                                    (ideal gas: $V_m = \dfrac{RT}{P}$)

$C_{vm}\left(\overset{?}{T_f} - T_i\right) = -P_{external}\left(\overset{?}{V_{mf}} - V_{mi}\right)$

$C_{vm}\left(T_f - T_i\right) = -P_{external}\left(\dfrac{RT_f}{P_f} - \dfrac{RT_i}{P_i}\right)$

2 a cont.) collect T_f terms:

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

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

(units of pressure (bar) cancel in pressure ratios)

$$T_f = \frac{\frac{5}{2} R + \frac{1.00}{150} R}{\frac{5}{2} R + \frac{1.00}{1.00} R} T_i = \frac{2.507}{3.500} \, 300 \text{ K}$$

$$\boxed{T_f = 214.8 \text{ K}} \qquad (-58 \,°C)$$

b) $\boxed{q = 0}$ (adiabatic)

$$\Delta U = U_f - U_i = \int_{U_i}^{U_f} dU = \int_{T_i}^{T_f} C_v \, dT$$

per mole: $$\Delta U_m = \int_{T_i}^{T_f} \overset{const.}{C_{vm}} \, dT = C_{vm} \int_{T_i}^{T_f} dT$$

$$\Delta U_m = C_{vm}(T_f - T_i)$$

$$= \frac{5}{2} R (T_f - T_i) = \frac{5}{2} \left(8.314 \, \frac{J}{K \, mol} \right)(214.8 - 300) K$$

$$\boxed{\Delta U_m = -1770 \text{ J}}$$

$$\Delta U_m = \overset{0}{\cancel{q}} + w \qquad \boxed{w = -1770 \text{ J}}$$

$$\Delta H_m = \int_{T_i}^{T_f} C_{pm} \, dT = C_{pm}(T_f - T_i) = \frac{7}{2} R (T_f - T_i) = \boxed{\overset{\Delta H_m}{-2480 \text{ J}}}$$

(3.) a) ideal gas: $V_m = \dfrac{V}{n} = \dfrac{RT}{P}$ $V_m(T,P)$

$$dV_m = \left(\dfrac{\partial V_m}{\partial T}\right)_P dT + \left(\dfrac{\partial V_m}{\partial P}\right)_T dP$$

$$\left(\dfrac{\partial V_m}{\partial T}\right)_P = \left[\dfrac{\partial}{\partial T}\left(\dfrac{RT}{P}\right)\right]_P = \dfrac{R}{P}\left(\dfrac{\partial T}{\partial T}\right)_P = \dfrac{R}{P}$$

$$\left(\dfrac{\partial V_m}{\partial P}\right)_T = \left[\dfrac{\partial}{\partial P}\left(\dfrac{RT}{P}\right)\right]_T = RT\left(\dfrac{\partial \frac{1}{P}}{\partial P}\right)_T = RT\left(\dfrac{-1}{P^2}\right) = \dfrac{-RT}{P^2}$$

$$dV_m = \dfrac{R}{P}dT - \dfrac{RT}{P^2}dP$$

b) If $dV_m = \dfrac{R}{P}dT - \dfrac{RT}{P^2}dP$ is an exact differential

$$\left(\dfrac{\partial \frac{R}{P}}{\partial P}\right)_T = \left[\dfrac{\partial}{\partial T}\left(\dfrac{-RT}{P^2}\right)\right]_P$$

test: $\left(\dfrac{\partial \frac{R}{P}}{\partial P}\right)_T = R\left(\dfrac{\partial \frac{1}{P}}{\partial P}\right)_T = R\left(\dfrac{-1}{P^2}\right) = -\dfrac{R}{P^2}$

$$\left[\dfrac{\partial}{\partial T}\left(\dfrac{-RT}{P^2}\right)\right]_P = -\dfrac{R}{P^2}\left(\dfrac{\partial T}{\partial T}\right) = -\dfrac{R}{P^2}$$

$\therefore$ dV_m is exact

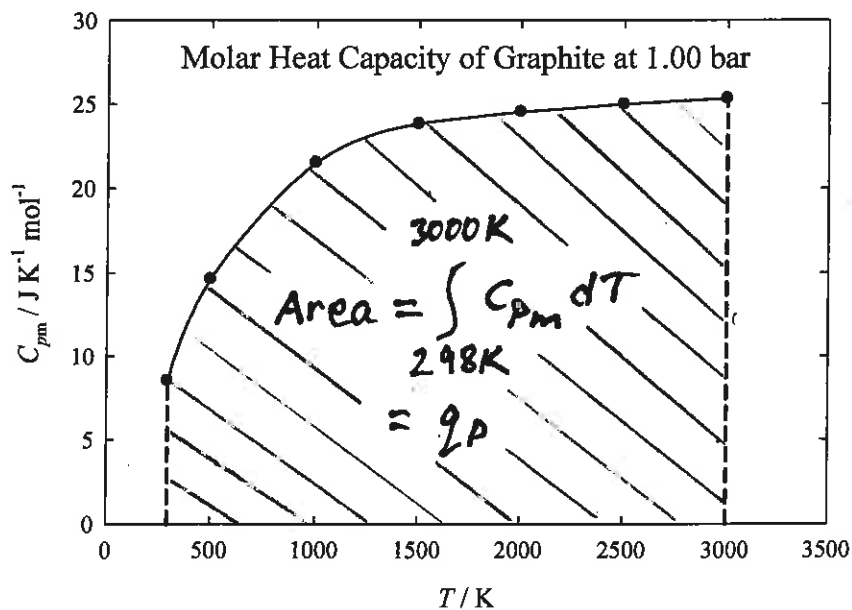④ a) At constant pressure, $dq_p = dH$

heat capacity at constant pressure

$$C_p = \frac{dq_p}{dT} = \frac{dH_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p$$

per mole : $C_{pm} = \frac{C_p}{n} = \left(\frac{\partial H_m}{\partial T}\right)_p$

heat one mole of graphite from 298 K to 300 K
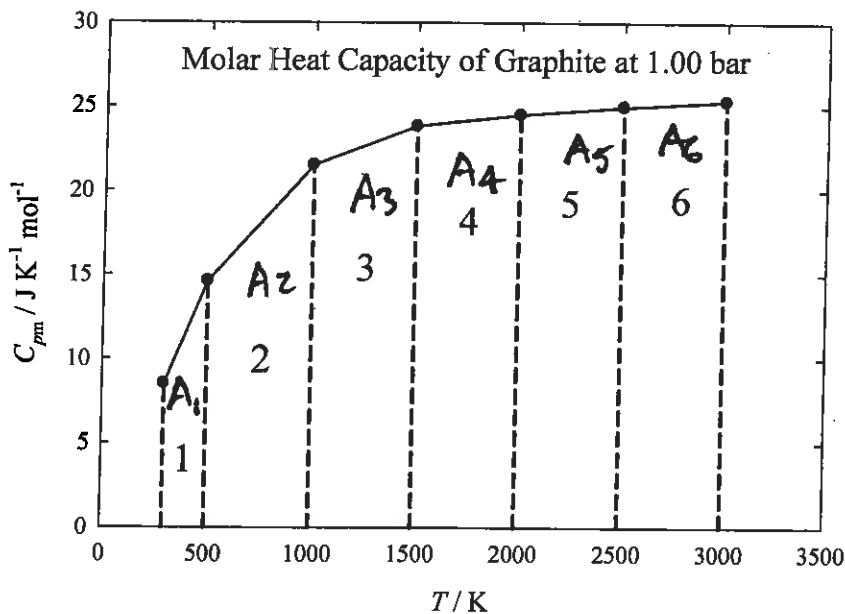
$$q_p = \Delta H_m = \int_{298K}^{3000\,K} C_{pm}\,dT$$

the area under the curve of C_{pm} plotted against T from 298 K to 3000 K

Molar Heat Capacity of Graphite at 1.00 bar

$$\text{Area} = \int_{298K}^{3000\,K} C_{pm}\,dT = q_p$$

4 a cont.)

<u>Problem!</u> C_{pm} for graphite is provided as tabulated values, not as an analytic equation that can be integrated

<u>Solution:</u>   Plot the measured C_{pm} values against the temperature and approximate the area under the C_{pm} as the area of the 6 "trapezoids" obtained by connecting each C_{pm} value with a straight line

Molar Heat Capacity of Graphite at 1.00 bar

$$\int_{298\,K}^{3000\,K} C_{pm}\, dT$$

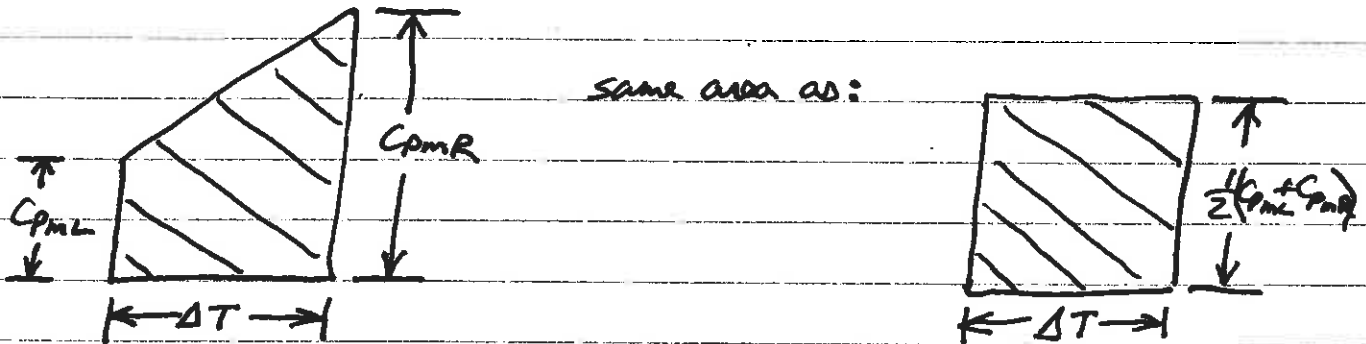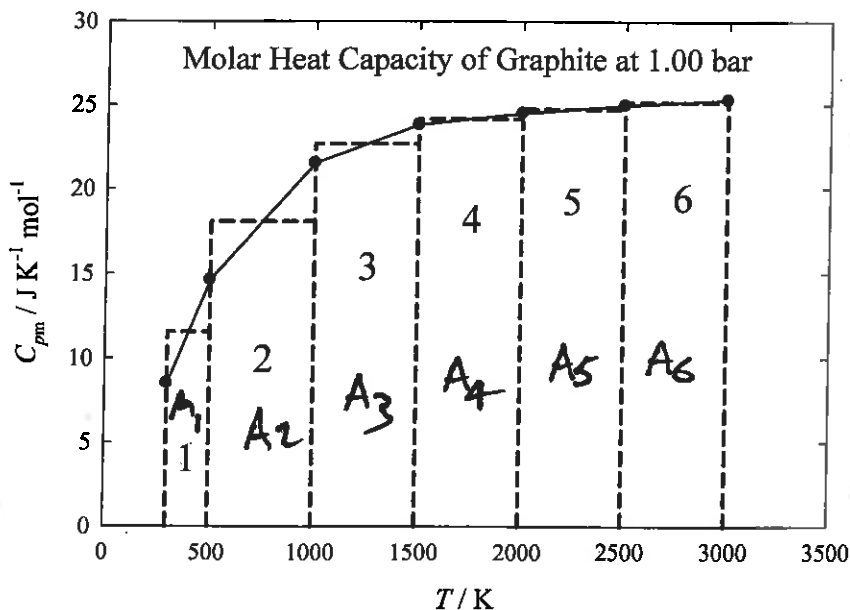$\approx$ area of the 6 trapezoids

$= A_1 + A_2 + A_3 + A_4 + A_5 + A_6$

4 a cont.)

Notice that the area of a trapezoid with "left height" C_{PmL} and "right height" C_{PmR} and base width ΔT is the same as the area of a rectangle of height $\frac{1}{2}(C_{PmL} + C_{PmR})$ and base width ΔT

same area as:

The area under the C_{Pm} curve is approximately equal to the area of the 6 rectangles: $A_1 + A_2 + A_3 + A_4 + A_5 + A_6$

Molar Heat Capacity of Graphite at 1.00 bar

$\int_{298 K}^{3000 K} C_{Pm} \, dT$

$\approx$ area of the 6 rectangles

$= A_1 + A_2 + A_3 + A_4 + A_5 + A_6$

4 a cont.)

$$q_p = \Delta H_m = \int_{298K}^{3000K} C_{pm}\, dT \approx A_1 + A_2 + A_3 + A_4 + A_5 + A_6$$

$$= \frac{8.53 + 14.63}{2}(500-298) + \frac{14.63 + 21.54}{2}(1000-500)$$

$$+ \frac{21.54 + 23.84}{2}(1500-1000) + \frac{23.84 + 24.54}{2}(2000-1500)$$

$$+ \frac{24.54 + 25.00}{2}(2500-2000) + \frac{25.00 + 25.34}{2}(3000-2500)$$

$$\boxed{q_p = \Delta H_m \approx 59,800 \ \frac{J}{mol}}$$ using the "trapezoid rule" of numerical integration

b) molar volume of graphite at 298 K

$$V_m(298K) = \frac{M}{\rho} = \frac{12.01 \ g\, mol^{-1}}{2.26 \ g\, cm^{-3}}$$

$$V_m(298K) = 5.31 \ \frac{cm^3}{mol} = 5.31 \times 10^{-6} \ \frac{m^3}{mol} \quad (SI)$$

$$V_m(3000K) \approx \left[1 + \frac{0.00005}{K}(3000-298)K \right] V_m(298K)$$

$$= 1.135 \ V_m(298K) = 6.03 \times 10^{-6} \ \frac{m^3}{mol}$$

$$\overset{const.}{w = -\int P_{ext}\, dV_m} = -P_{ext}(V_{mf} - V_{mi}) = -(10^5 Pa)(6.03 - 5.31)\times 10^{-6} \frac{m^3}{mol}$$

$$\boxed{w = -0.072 \ J}$$ completely negligible compared to q $59.8 \frac{kJ}{mol}$

$$\Delta H = \Delta(U + pV) = \Delta U + \overset{const.}{\Delta(pV)} = \Delta U + \boxed{p\Delta V} = 59800 \frac{J}{mol}$$

so $\Delta H = \Delta U$ only 0.072 $J\, mol^{-1}$