

**Problem Set 6A Key (due Friday, 9PM 2/10/12)**

**Q1)** When measuring the energy of combustion of a hydrocarbon (as an example of a reaction), the most frequent method to use is the bomb calorimeter. However this measures energies, called  $\Delta U_{rxn}$  processes under constant V and T. The table in the back of your text contains energies determined for reactions under constant P and T, called  $\Delta H_{rxn}$ . So we need to develop a formula that relates these two quantities.

A) Begin with  $H = U + PV$  for each and every species and show that, for any

$$\text{species } k, \left( \frac{\partial H}{\partial n_k} \right)_{T,P} = \left( \frac{\partial U}{\partial n_k} \right)_{T,V} + T \left( \frac{\partial P}{\partial T} \right)_{V,n} \left( \frac{\partial V}{\partial n_k} \right)_{T,P}$$

B) Whether or not you could derive this term, Determine  $T \left( \frac{\partial P}{\partial T} \right)_{V,n} \left( \frac{\partial V}{\partial n_k} \right)_{T,P}$  for

an ideal gas at 1Atm and 298K.

C) Evaluate this term for liquid water at 1Atm and 298K. (Compare with the result in part B.)

D) Use the expression from part A to relate  $\Delta H_{rxn}$  to  $\Delta U_{rxn}$ .

E) Apply your formula from part D to determine the correction for the combustion of methane, assume the water is a gas. Assume all gasses behave as ideal gasses. (Why do we not need to know how much methane is burned?)

F) Repeat part E but assume the water is a liquid, and assume all other substances behave as ideal gasses (at one atm and 298K).

G) Comment on the relative magnitude of the correction term that relates  $\Delta H_{rxn}$  to  $\Delta U_{rxn}$ .

H) Determine  $\Delta H_{rxn}$  for the combustion of methane using the heats of formation in the back of the book.

I) How well does the result compare with the general rule: any hydrocarbon gives 9 Cal/gram for the combustion reaction?

**Q2)** In problem **Q1)** we studied the chemical reaction of burning methane at 298. Now we consider what the  $\Delta H_{rxn}$  and the  $\Delta U_{rxn}$  should be at 600K (and still at 1 atm).

- a) Derive the expression that relates  $\Delta H_{rxn}$  at an elevated temperature to  $\Delta H_{rxn}^{\circ}$  at  $T=298K$ , the “reference temperature”. One should start with the observation that for each and every species  $C_P = \left(\frac{\partial H}{\partial T}\right)_{P,n}$  and derive a  $C_{P,rxn}$  such that  $\Delta H_{rxn}(T) = \Delta H_{rxn}^{\circ}(T_o) + \int_{T_o}^T C_{P,rxn} dT$
- b) Apply the result from part a) and Q1 to determine the  $\Delta H_{rxn}(T = 600K)$  for the combustion of methane. Comment on the relative magnitudes of the two terms. You may assume the heat capacities are independent of temperature.

**Q3)**

- a) In class we derived the expression that  $\left(\frac{\partial S}{\partial T}\right)_{V,n} = \frac{C_V}{T}$ . Follow the logic in that derivation and use the parallel expressions for H to find  $\left(\frac{\partial S}{\partial T}\right)_{P,n} = \frac{C_P}{T}$ .
- b) In class we derived the expression that  $\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$ . Follow the logic in that derivation and use the parallel expressions for H to find  $\left(\frac{\partial S}{\partial P}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{P,n}$ . [See chapter 6 of text and notes if you are stuck.] These are the two useful Maxwell relations from Euler’s rule for an exact differential.]
- c) Use the expression  $\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$  to derive the Thermodynamic Equation of State, which was quoted in chapter 3 but not proved.
- d) Use the above expressions (as needed) to determine how much the Entropy changes, per mole, when the volume of an ideal monatomic gas doubles at constant temperature. Comment on the sign of the entropy change.
- e) We noted that the definition of entropy was heat transferred, reversibly, at constant temperature, but now we want to find the entropy, per mole, for an ideal monatomic gas when the temperature is doubled at constant volume. [After you obtain a number: Explain how this is possible? Note the sign change in the entropy and relate that to the sign change in part c). ]

- f) Find the entropy change for the case of an ideal, monatomic gas when both T and V change (which implies P changes as well). The volume doubles and the temperature decreases with  $T_2 = 0.630 \cdot T_1$ . Do you see anything odd or familiar about this result? What is the process that caused the result to come out this way?