

CHEM352: PHYSICAL CHEMISTRY I  
HOMEWORK SET II - DUE 12<sup>th</sup> OF OCT, 5.00 PM

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Lecture: Tue, 2.10-3.25 pm & Fri 2.10-3.25 pm, **C111**

Office hours: Thu, 4-6 pm, **Library - Science Center, 7<sup>th</sup> floor**

### Problem 1

CH3/5pts

Using definitions of heat capacities at constant volume and pressure, cyclic rule (equations a/P3.32 and b/P3.37) and expression for  $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$  (equation c/P3.38), prove that:

$$C_P = - \frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial T}{\partial P}\right)_H} \quad (1a)$$

$$C_V = - \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U \quad (1b)$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad (1c)$$

Show that the equation 1c simplifies to 0 for ideal and van der Waals gas (P3.39).

### Problem 2 (P4.14 and P4.21)

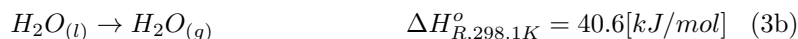
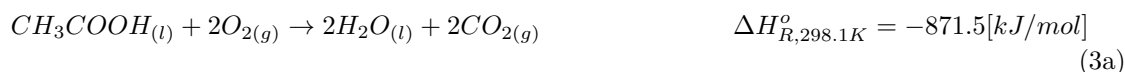
CH4/5pts

1. From the following data, compute the  $\Delta_f H^\circ$  of  $\text{CaC}_2(s)$  at 298 K.



The combustion enthalpies of  $\text{C}(s)$  and  $\text{C}_2\text{H}_2(g)$  are -393.5 and -1299.8 kJ/mol respectively. Draw the respective thermodynamic cycle.

2. From the following data, compute  $\Delta H_{R,391.4\text{K}}^\circ$  for the  $\text{CH}_3\text{COOH}(g) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + 2\text{CO}_2(g)$ :



The molar  $\frac{C_P}{R}$  are equal 14.9, 3.53, 4.46, 9.055 and 4.048 for  $\text{CH}_3\text{COOH}(l)$ ,  $\text{O}_2(g)$ ,  $\text{CO}_2(g)$ ,  $\text{H}_2\text{O}(l)$  and  $\text{H}_2\text{O}(g)$  respectively ( $C_P = \frac{C_P}{R} \cdot R$ ). Be careful about the temperature and the states. Draw the respective thermodynamic cycle.

### Problem 3 (variation of P5.7)

CH5/5pts

Consider a classical reversible Carnot cycle with 2.5 moles of an ideal gas with  $C_V = \frac{5}{2}R$  as a working substance that undergoes, as we discussed in the lecture (figure 5.2 in the book), following transitions:

1. ( $a \rightarrow b$ ) Isothermal expansion from  $V_a=5.5$  L to  $V_b=21$  L at  $T_{hot} = 780$  K
2. ( $b \rightarrow c$ ) Adiabatic expansion until system reaches  $T_{cold} = 280$  K
3. ( $c \rightarrow d$ ) Isothermal compression at  $T_{cold} = 280$  K.

4. ( $d \rightarrow a$ ) Adiabatic compression until gas reaches the  $T_{hot}$  and  $V_a=5.5$  L.

Please calculate:

1. Volume at points c and d ( $V_c$  and  $V_d$ ).
2. Work for the each step of the cycle and the total work.
3. The efficiency  $\theta$  of the cycle and the amount of heat that needs to be extracted from the reservoir  $T_{hot}$  to provide 1.5 kJ of work in the surroundings.

#### Problem 4 (P5.39)

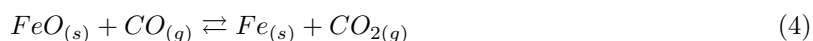
CH5/5pts

1. Calculate  $\Delta S$  if 1.00 mol of liquid water is heated from  $0.00^\circ C$  to  $10.00^\circ C$  under constant pressure and  $C_{P,m}=75.3$  [J/mol·K].
2. The melting point of water at the pressure of interest is  $0.00^\circ C$  and the enthalpy of fusion is 6.010 [kJ/mol]. The boiling point is  $100^\circ C$  and the enthalpy of vaporization is 40.65 [kJ/mol]. Calculate  $\Delta S$  for the transformation from ice to vapor:  $H_2O(s, 0^\circ C) \rightarrow H_2O(g, 100^\circ C)$

#### Problem 5 (P6.24)

CH6/5pts

Consider the reaction:



for which  $K_P$  is found to be equal 0.688 and 0.310 and  $700^\circ C$  and  $1200^\circ C$  respectively. Using this data, calculate:

1.  $\Delta G_R^\circ$ ,  $\Delta H_R^\circ$  and  $\Delta S_R^\circ$  for this reaction at 700K. Assume that  $\Delta H_R^\circ$  is independent of the temperature.
2. Calculate the mole fraction of  $CO_{2(g)}$  present in the gas phase at  $700^\circ C$ .