CHEM352: Physical Chemistry I

Homework Set II - due 12^{th} of Oct, 5.00 pm

Instructor: Dr. Mateusz Marianski

Room#: HN-1321B

email: *mmarians@hunter.cuny.edu*

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

Office hours: Thu, 4-6 pm, **Library - Science Center, 7^{th} floor**

Problem 1 — CH3/5pts

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

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

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

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

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 $\Delta_f H^o$ of $CaC_{2(s)}$ at 298 K.

$$CaC_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + C_2H_{2(g)} \qquad \Delta H^o_R = -127.9[kJ/mol] \tag{2a}$$

$$Ca_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CaO_{(s)} \qquad \Delta H^o_R = -635.1[kJ/mol] \tag{2b}$$

$$CaO_{(s)} + H_2O(l) \rightarrow Ca(OH)_{2(s)} \qquad \Delta H^o_R = -65.2[kJ/mol] \tag{2c}$$

   The combustion enthalpies of $C_{(s)}$ and $C_2H_{2(g)}$ are -393.5 and -1299.8 kJ/mol respectively. Draw the respective thermodynamic cycle.

2. From the following data, compute $\Delta H^o_{R,391.4K}$ for the $CH_3COOH_{(g)} + 2O_{2(g)} \rightarrow 2H_2O_{(g)} + 2CO_{2(g)}$:

$$CH_3COOH_{(l)} + 2O_{2(g)} \rightarrow 2H_2O_{(l)} + 2CO_{2(g)} \qquad \Delta H^o_{R,298.1K} = -871.5[kJ/mol] \tag{3a}$$

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H^o_{R,298.1K} = 40.6[kJ/mol] \tag{3b}$$

$$CH_3COOH_{(l)} \rightarrow CH_3COOH_{(g)} \qquad \Delta H^o_{R,391.4K} = 24.4[kJ/mol] \tag{3c}$$

   The molar $\frac{C_P}{R}$ are equal 14.9, 3.53, 4.46, 9.055 and 4.048 for $CH_3COOH_{(l)}$, $O_{2(g)}$, $CO_{2(g)}$, $H_2O_{(l)}$ and $H_2O_{(g)}$ 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 expantion 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 efficency θ 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 ΔS if 1.00 mol of liquid water is heated from 0.00^oC to 10.00^oC 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^oC and the enthalpy of fusion is 6.010 [kJ/mol]. The boling point is 100^oC and the enthalpy of vaporization is 40.65 [kJ/mol]. Calculate ΔS for the transformation from ice to vapor: $H_2O(s, 0^oC) \rightarrow H_2O(g, 100^oC)$

Problem 5 (P6.24) CH6/5pts

Consider the reaction:

$$FeO_{(s)} + CO_{(g)} \rightleftarrows Fe_{(s)} + CO_{2(g)} \tag{4}$$

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

1. ΔG_R^o, ΔH_R^o and ΔS_R^o for this reaction at 700K. Assume that ΔH_R^o is independent of the temperature.
2. Calculate the mole fraction of $CO_{2(g)}$ present in the gas phase at 700^oC.