Homework-02 (the submission time: the beginning of the class on Nov. 7)

*most problems are taken from the textbook (D.A. McQuarrie and J.D. Simon, "Physical chemistry – a molecular approach-"). For example, "#19-36" means the problem is given as #36 problem in Chapter 19 of the textbook.

***When required to derive/write something such as "describe in 150 words" including HW02-01, HW02-03, HW02-20 and HW02-21, you must write it by your hand, not typing using a computer.**

[HW02-01] Derive Maxwell relations for Helmholtz energy.

[HW02-02] Calculate $(\partial U/\partial V)_T$ for (1) a gas that obeys the equation of state for ideal gas and (2) a gas obeys the van der Waals equation. Then, discuss the difference between gas (1) and gas (2) in 150 words or less. Note that van der Waals equation gives more accurate description of a real gas: parameter a reflects the inter-molecular (attractive) interaction and parameter b reflects the molecular size. The van der Waals equation is:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

*Hint: you cannot directly calculate $(\partial U/\partial V)_T$. Instead, you should use some relation in the derivation of Maxwell relations for internal energy.

[HW02-03] Starting from the 2nd of thermodynamics, namely "*There is a thermodynamic state function of a system called as entropy, S, such that for any change in the thermodynamic state of the system, $dS \geq \frac{\delta q}{T}$, where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.*", please derive a condition to judge using Gibbs energy whether a given chemical reaction can spontaneously take place or not at constant-T constant-P conditions.

[HW02-04] Please judge whether the following statement is correct or not. If not, please modify it.
(1) The initial state of spontaneous reaction must be a thermodynamical equilibrium state.

(2) The condition for thermodynamical equilibrium state and reversible process is identical, because thermodynamical equilibrium states are assumed in reversible processes.

(3) For a closed system, if there is a reaction which holds "$dS > 0$", the reaction should proceed spontaneously.

[HW02-05] Derive the Gibbs –Helmholtz equation: $\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}$

[HW02-06:#19-36]

(1) Given the following data at 298.15 K and 1 bar:

$$\frac{1}{2}\mathrm{H_2(g)} + \frac{1}{2}\mathrm{F_2(g)} \rightarrow \mathrm{HF(g)}, \quad \Delta_{r1}\mathrm{H}^\circ = -273\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{H_2(s)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{H_2O(l)}, \quad \Delta_{r2}\mathrm{H}^\circ = -286\ \mathrm{kJ\ mol^{-1}}$$

Use these data to calculate the value of $\Delta_r\mathrm{H}$ at 298.15 K and 1 bar for the reaction described by

$$2\mathrm{F_2(g)} + 2\mathrm{H_2O(l)} \rightarrow 4\mathrm{HF(g)} + \mathrm{O_2(g)}$$

(2) Please determine whether this reaction proceeds spontaneously or not at const.-T and const.-P condition (298.15 K and 1 bar). You need to clearly explain the reason of the judgment in 150 words or less. (*Hint: you need not to exactly know Gibbs energy for this problem. Instead, you can use the tendency of entropy of gas, liquid and solid phases together with the result of (1).)

(3) At much higher temperature like 1000 K, do you think the direction of the spontaneous reaction can be changed from that at 298.15 K? Please give you answer with explanation in 100 words or less. Please assume at both temperatures, the system is maintained at const.-T const.-P (1 bar) conditions.

[HW02-07]

(1) Calculate the value of $\Delta_r\mathrm{H}$ (at 298.15 K and 1 bar) for the reaction described by

$$\mathrm{C_6H_{12}O_6}(s, \alpha - D - \mathrm{Glucose}) + 3\mathrm{O_2(g)} \rightarrow 6\mathrm{H_2O(l)} + 6\mathrm{CO(g)}$$

Regarding the data for standard molar enthalpies of formation at 298.15 K, please refer to the database on: http://courses.chem.indiana.edu/c360/documents/thermodynamicdata.pdf

(2) At constant temperature and constant pressure condition (298.15 K and 1 bar), please determine whether this reaction proceeds spontaneously or not.

(3) How much is the maximum energy to take out from this reaction at const.-T and const.-P condition (298.15 K and 1 bar).

[HW02-08] As a step to manufacture nuclear fuel (UO_2), we need to go through so-called "conversion" process from U_3O_8 (s) to UF_6 (g). If needed, you can use the database given in http://courses.chem.indiana.edu/c360/documents/thermodynamicdata.pdf

(1) Complete the following chemical equation by giving appropriate numerals to $\alpha, \beta, \gamma, \delta$.

$$\mathrm{U_3O_8(s)} + \alpha\ \mathrm{H_2(g)} + \beta\ \mathrm{F_2(g)} + \gamma\ \mathrm{HF(g)} \rightarrow 3\mathrm{UF_6(g)} + \delta\ \mathrm{H_2O(l)}$$

(2) Calculate the $\Delta_r\mathrm{H}$ (at 298.15 K and 1 bar) for this reaction.

(3) This reaction is apparently endothermic. To forcibly make this reaction proceed at 298.15 K at 1 bar with 1 mol of U_3O_8 (s), please determine how much energy must be added to the system at least?

[HW02-09] Calculate the reaction enthalpy for

$$\mathrm{C}(s, graphite) + \mathrm{H_2O(g)} \rightarrow \mathrm{CO(g)} + \mathrm{H_2(g)}$$

at 1273 K and 1 bar. Assume that the following heat capacity equations are valid between 298 K and 1273 K at 1 bar.

$$C_P^\circ[\mathrm{CO(g)}]/R = 3.23 + (8.38 \times 10^{-4}\mathrm{K}^{-1})T - (9.86 \times 10^{-8}\mathrm{K}^{-2})T^2$$

$$C_P^\circ[H_2(\mathrm{g})]/R = 3.50 + (1.01 \times 10^{-4}\mathrm{K}^{-1})T + (2.42 \times 10^{-7}\mathrm{K}^{-2})T^2$$

$$C_P^\circ[H_2\mathrm{O(g)}]/R = 3.65 + (1.16 \times 10^{-3}\mathrm{K}^{-1})T + (1.42 \times 10^{-7}\mathrm{K}^{-2})T^2$$

$$C_P^\circ[\mathrm{C(s, graphite)}]/R = -0.637 + (7.05 \times 10^{-3}\mathrm{K}^{-1})T - (5.20 \times 10^{-6}\mathrm{K}^{-2})T^2 + (1.38 \times 10^{-9}\mathrm{K}^{-3})T^3$$

If you need some thermodynamic data, please refer to the database on:
http://courses.chem.indiana.edu/c360/documents/thermodynamicdata.pdf

[HW02-10]
(1) Vaporization at the normal boiling point (T_{vap}) of a substance (the boiling point at 1 atm) can be regarded as a reversible process because if the temperature is decreased infinitesimally below T_{vap}, all the vapor will condense to liquid, whereas if it is increased infinitesimally above T_{vap}, all the liquid will vaporize. Calculate the entropy change when two moles of water vaporize at 100.0 °C. The value of $\Delta_{vap}\overline{H}$ is 40.65 kJ mol^{-1}.

(2) Melting at the normal melting point (T_{fus}) of a substance (the melting point at 1 atm) can be regarded as a reversible process because if the temperature is changed infinitesimally from exactly T_{fus}, then the substance will either melt or freeze. Calculate the change in entropy when two moles of water melt at 0 °C. The value of $\Delta_{fus}\overline{H}$ is 6.01 kJ mol^{-1}.

(3) Please compare the result with the result of (1) and (2), and discuss the reason of large difference in results in 100 words or less.

[HW02-11]
(1) The molar heat capacity of H_2O(l) has an approximately constant value of $\overline{C_P}$=75.4 J K^{-1} mol^{-1} from 273 K to 373 K. Calculate ΔS if two moles of H_2O(l) are heated from 273 K to 363 K at a constant pressure.

(2) The molar heat capacity of CO_2 at 1 bar can be expressed by

$$\overline{C_P}/R = 3.23 + (8.38 \times 10^{-4}\mathrm{K}^{-1})T - (9.86 \times 10^{-8}\mathrm{K}^{-2})T^2$$

over the temperature range $800\ K \leq T \leq 1300\ K$. Calculate ΔS if three moles of CO_2 is heated from 900 K to 1200 K at a constant pressure (1 bar).

[HW02-12] The standard molar heat capacity of solid, liquid, and gaseous chlorine at 1 bar can be expressed as

$15.0\ K \leq T \leq 172.12\ K$

$$C_P^\circ[Cl_2(\mathrm{s})]/R = -1.55 + (0.150\ \mathrm{K}^{-1})T - (1.18 \times 10^{-3}\mathrm{K}^{-2})T^2 + (3.44 \times 10^{-6}\mathrm{K}^{-3})T^3$$

$172.12\ K \leq T \leq 239.0\ K$

$$C_P^\circ[Cl_2(\mathrm{l})]/R = 7.69 + (5.58 \times 10^{-3}\ \mathrm{K}^{-1})T - (1.95 \times 10^{-5}\mathrm{K}^{-2})T^2$$

$239.0\ K \leq T \leq 1000\ K$

$$C_P^\circ[Cl_2(g)]/R = 3.81 + (1.22 \times 10^{-3}\ \mathrm{K}^{-1})T - (4.86 \times 10^{-7}\mathrm{K}^{-2})T^2$$

At 15.0 K, the standard molar entropy of Cl_2(s) is given as 1.400 J K^{-1} mol^{-1}. Using these heat capacities data, and T_{fus}=172.12 K, $\Delta_{fus}\bar{H}$=6.41 kJ mol^{-1}, T_{vap}=239.0 K and $\Delta_{vap}\bar{H}$=20.4 kJ mol^{-1} at 1 bar, and the correction for non-ideality =0.502 J K^{-1} mol^{-1}, please calculate the standard molar entropy of chlorine at 400 K at 1 bar. (*Hint: regarding the correction for non-ideality, please just simply add it up.)

[HW02-13:#21-46*] Calculate the value of $\bar{S}^\circ[H_2O(\mathrm{g})]$ at 298.15 K at 1 bar using the following data: $\bar{S}^\circ[H_2O(\mathrm{l})]$ =70.0 J K^{-1} mol^{-1} at 298.15 K, T_{vap}=373.15 K, $\Delta_{vap}\bar{H}$=40.7 kJ mol^{-1}, and $\overline{C_P}[H_2O(\mathrm{l})]$=75.3 J K^{-1} mol^{-1} and $\overline{C_P}[H_2O(\mathrm{g})]$=33.8 J K^{-1} mol^{-1} over 298.15-373.15 K at 1 bar.

[HW02-14] Arrange the following reactions to increasing values of $\Delta_r S^\circ$, according to typical differences of entropy among gas, liquid and solid states, with some explanation in 150 words or less. (*please do not check a database to evaluate the exact value of entropy)

a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
b) $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$
c) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$
d) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
e) $NH_4Cl(l) \rightarrow NH_3(g) + HCl(g)$
f) $4CO(g) + 2O_2(g) \rightarrow 4CO_2(g)$

[HW02-15]
(1) Please derive the following equation: $(\partial\bar{G}/\partial P)_T = \bar{V}$

(2) Then, please draw a general P-$\bar{G}$ diagram at a temperature (constant) around the boiling point. (Please show 2 lines corresponding to $\bar{G}$ for gas and $\bar{G}$ for liquid. And use x-axis for P and y-axis for $\bar{G}$)

[HW02-16]
(1) Please derive the following equation: $(\partial\bar{G}/\partial T)_P = -\bar{S}$

(2) Then, please draw a general T-$\bar{G}$ diagram at a usual pressure around the boiling point. (Please show 2 lines corresponding to $\bar{G}$ for gas and $\bar{G}$ for liquid. And use x-axis for T and y-axis for $\bar{G}$)

[HW02-17: #23-2] Sketch the phase diagram for I_2 using the following data: triple point at 113°C and 0.12 atm; critical point at 512°C and 116 atm; normal melting point at 114°C; and normal boiling point at 184°C. The x-axis should be temperature over 300-800 K, the y-axis should be pressure in atm unit (common logarithms).

[HW02-18: #23-22]
(1) Please drive the *Clapeyron equation, namely*

$$\frac{dP}{dT} = \frac{\Delta_{trs}\bar{H}}{T\Delta_{trs}\bar{V}}$$

(2) The vapor pressure of mercury from 400°C to 1300°C can be expressed by

$$\ln(P/torr) = -\frac{7060.7\ K}{T} + 17.85$$

The density of the vapor at its normal boiling point is 3.82 g L^{-1} and that of the liquid is 12.7 g cm^{-3}. Estimate the molar enthalpy of vaporization of mercury at its normal boiling point. The molar mass of mercury is 200.59 g mol^{-1}.

[HW02-19: #23-17*] Using the following data for methanol at 1 atm, plot $\bar{G}(T\ K)$, $\bar{H}(T\ K, 1\ atm) - \bar{H}(T_{melt}\ K, 1\ atm)$, and $\bar{S}(T\ K, 1\ atm)$, against T over 300-380 K at 1 atm. Then, determine the normal melting point (the melting point at 1 atm) of methanol. Please assume that $\bar{G}, \bar{H}$ and $\bar{S}$ are proportional to temperature on this temperature range (300-380 K) for both liquid and gas, unless a phase transition is involved.

Temperature (K)	$\bar{H}(T\ K, 1\ atm) - \bar{H}(T_{melt}\ K, 1\ atm)$ / kJ mol^{-1}	$\bar{S}(T\ K, 1\ atm)$ / J mol^{-1} K^{-1}
300 [liquid]	9.301	129.4
320 [liquid]	10.99	134.8
330 [liquid]	11.87	137.4
350 [gas]	48.51	245.9
360 [gas]	49.06	247.5
380 [gas]	50.15	250.4

Here, $\bar{H}(T\ K, 1\ atm)$ and $\bar{S}(T\ K, 1\ atm)$ are molar enthalpy and molar entropy for $T\ K$ and $1\ atm$, respectively. The molar entropy is given with an absolute value. $\bar{G}(T\ K)$ is defined as: $\bar{G}(T\ K) = \bar{H}(T\ K, 1\ atm) - \bar{H}(T_{melt}\ K, 1\ atm) - T\bar{S}(T\ K, 1\ atm)$

[HW02-20] Please draw a typical temperature dependence of the following thermodynamical quantities at around the boiling point at 1 bar for a general substance.
(1) molar Gibbs energy (2) molar enthalpy (3) molar entropy (4) molar volume
(5) molar Helmholtz energy