**University of Washington**
**Department of Chemistry**
**Chemistry 453**
**Winter Quarter 2015**

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Homework Assignment 8; Due at midnight on 3/13/15
Note: In this homework, you may encounter some very, very large numbers. Always express such numbers in scientific notation before using your calculator. Otherwise you will just overflow or underflow the registers in your calculator.

This table will be useful for working several problems:

| Molecule | $\theta_{vib}(K)$ | $\theta_{rot}(K)$ | $\nu(\text{x}10^{13}\ \text{s}^{-1})$ | $g_1$ | $D_e(\text{kJ mol}^{-1})$ | $D_0(\text{kJ mol}^{-1})$ |
|---|---|---|---|---|---|---|
| $H_2$ | 6215 | 85.3 | 12.960 | 1 | 457.6 | 432.1 |
| $Cl_2$ | 808 | 0.351 | 1.683 | 1 | 242.3 | 239.2 |
| $I_2$ | 308 | 0.0537 | 0.642 | 1 | 150.3 | 148.8 |
| CO | 3103 | 2.77 | 6.471 | 1 | 1085 | 1070 |
| NO | 2719 | 2.45 | 5.670 | 2 | 638.1 | 626.8 |

1) The rotational motion of CO carbon monoxide can be modeled as a rigid rotor. Calculate the probabilities of CO molecules being in the J=0, 4, 8, 12, and 16 states. Assume T=300K. Explain the trend.

2) Consider the diatomic molecule NO

a) Calculate the thermal wavelength for $^{14}N^{16}O$ at T=1000K.

b) Using the reasults from part a and the data in the table, calculate the translational, rotational, and vibrational partition functions for NO at T=1000K State any assumptions that you make. Assume $V=1m^3$.

c) Using the results in part b, and the data provided in the table, calculate the value for the overall partition function for NO at T=1000K, including the electronic contribution. Note $D_e$ is given in the table in units of kJ $\text{mol}^{-1}$.

d) Using the data provided, calculate the internal energy and heat capacity for one mole of NO molecules at T=1000K. How close is the value for Cv that you calculate to classically predicted value? Explain any difference.

3) A chemical equilibrium that is a classic example of a statistical derivation of thermodynamic reaction properties is the gas phase dissociation of iodine: $I_2(g) \rightleftharpoons 2I(g)$

a) Calculate the thermal wavelengths for $I_2$ and I at T=298K.

b) Using the data in the table above calculate the rotational and vibrational partition functions of $I_2$ at T=298K.

c) Calculate the translational partition functions for I and $I_2$. Assume V=0.0244 $m^3$ and T=298K

d) Using your results from parts a-c, calculate the overall partition functions for I and $I_2$ at T=298K. including the contributions from electronic motions. Express your answers in scientific notation and remember that $D_e$ is in kJ per mole units. The ground state degeneracy for I is $g_{1,I} = 4$.

e) Using your results from part d, calculate the equilibrium constant $K_P$ for the gas phase dissociation of $I_2$. Assume $N=N_A$.

f) Using your result from part e, calculate the standard free energy change for the gas phase dissociation of $I_2$ at T=298K.. Is the dissociation of $I_2$ energetically favorable at T=298K?

g) How good is this statistical calculation? Tables of thermodynamic data for inorganic compounds at T=298K give for I (g) $\Delta G_f^\circ(I) = 70.2 kJmol^{-1}$ and for $I_2$ (g) $\Delta G_f^\circ(I_2) = 19.3 kJmol^{-1}$. Using these data calculate $\Delta G^0$ for the gas phase dissociation of iodine at T=298K. How close is this to your theory?

4) Assume two hydrogen atoms collide to form $H_2$ via a transition state complex: $H + H \overset{K^\dagger}{\rightleftharpoons} [H \cdots H]^\dagger \xrightarrow{k^\dagger} H_2$. For the transition state complex assume the bond length is $R^\dagger = 110 pm$ and the dissociation energy is $D_0^\dagger = 400 kJmol^{-1}$. Calculate the molar rate constant $k_2$ at T=300K. Assume the collision constant κ=0.50. For the transition

complex assume also $g_1^\dagger = 1$. Assume N=$N_A$. Convert the rate constant to units of L $mol^{-1}$ $s^{-1}$.

5) Diffusion-controlled reactions are extremely fast and are in fact some of the fastest known simple reactions in solution. For two spherical macromolecular reactants with radii $R_A$ and $R_B$ and with diffusion coefficients $D_A$ and $D_B$, the reaction rate constant is given by

$$rate = 4\pi N_A(1000)(D_A + D_B)(R_A + R_B)\overline{C}_A\overline{C}_B = k_{diffusion}\overline{C}_A\overline{C}_B$$

where the concentrations are in molarity units and the factor of 1000 puts the rate in units of liters per mole per second.

   a) Write out the rate expression for the case in which the spherical reactants have the same radii, i.e. $R_A$=$R_B$.
   b) Calculate the rate constant $k_{diffusion}$ assuming T=300K and the viscosity $\eta = 1.00 \times 10^{-3} kgm^{-1}s^{-1}$.
   c) Assume $\overline{C}_A = \overline{C}_B = 0.001M$. Using your results from part b, calculate the rate of reaction.

6) Consider the following data for the proteins myoglobin and hemoglobin

| Protein | Molecular Weight (kg) | Diffusion Coefficient $Dx10^{11}m^2s^{-1}$ | Specific Volume $V_2$ $(mLg^{-1})$ | Frictional ratiof/$f_0$ |
|---|---|---|---|---|
| Myoglobin | 16.900 | 11.3 | 0.74 | 1.11 |
| Hemoglobin | 64.500 | 6.9 | 0.75 | 1.16 |

a) Calculate the radii of myoglobin and hemoglobin assuming they are unhydrated spheres.
b) Calculate the radii and volumes of myoglobin and hemoglobin that would account for the frictional ratios, assuming they are hydrated spheres.
c) For each protein, calculate $\delta_1$, the mass of water bound per mass of protein. Assume the density of water is 1g $mL^{-1}$.
d) Myoglobin is a oxygen storage protein found in the body tissues. Hemoglobin is an oxygen transport protein. Hemoglobin is composed of n sub-units each roughly the size of myoglobin. Based on your answers in part b, how many myoglobin-like sub-units does hemoglobin contain?