Due: Workshop+1d

# **Physical Chemistry II**

## Exercises Set 7

#### 1. <u>Conceptual Questions</u>

- a) Discuss the dynamic nature of thermodynamic equilibrium, e.g., stability against exchanges in thermal energy, the role of entropy production, entropy at its maximum.
- b) Explain the concept of a reversible process. What could go wrong?
- c) What property of materials does the enthalpy of formation represent? How is this function used in devising conditions for chemical reactions?
- d) Review the relations between free energy G,  $G^0$ ,  $\mu$ , the corresponding balances  $\Delta_{rxn}$  for a chemical reaction and the associated equilibrium constant.

### 2. Ideal-Gas Partition Functions

Consider a cylinder containing a gas of  $N \gg 1$  Ar atoms in contact with a heat bath at temperature T.

- a) Derive an expression for the entropy of the above gas in terms of the partition function Q<sub>N</sub>, Use Stirling's approximation formula for Ln *N*!.
- b) Derive an expression for the chemical potential of the above gas in terms of the partition function  $Q_N$ ,
- c) How does the chemical potential of an ideal gas depend on pressure?

### 3. <u>Chemical potential and Equilibrium Constants</u>

Equilibrium rate constants can vary over a large range, as illustrated by the examples below. Using the tables for the chemical potentials,  $\mu^0(p_0, T_0) = \Delta G_f^0$ , deduce the constants for the following reactions at T=298.15K:

- a)  $2NO_2(g) \rightleftharpoons N_2O_4(g)$
- b)  $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$
- c)  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

#### 4. Temperature Dependence of Reaction Rates

When atmospheric CO<sub>2</sub> dissolves in water, it produces carbonic acid, H<sub>2</sub>CO<sub>3</sub> in the concentration of [H<sub>2</sub>CO<sub>3</sub>]=1.2.10<sup>-5</sup>M. This causes natural rain to be slightly acidic. At 25<sup>0</sup>C, the equilibrium constant  $K_a$  for the reaction  $H_2CO_3 \rightarrow H^+ + HCO_3^-$  is given by pKa=6.63. The enthalpy of the reaction is equal to  $\Delta H_{rxn} = 7.66 \, kJ/mol$ .

- a) Express the reaction rate constant in terms of reaction enthalpy and entropy.
- b) Deduce the reaction entropy.
- c) Calculate the reaction rate constant for  $35^{\circ}$ C.
- d) Calculate the pH value of the rain at  $25^{\circ}$ C.
- e) Calculate the pH value of the rain at  $35^{\circ}$ C.