Special Topics in Physical Chemistry. Homework 5 (Fall 08) **Due Dec. 2nd**

There are many interesting aspects to think about in the following cyclic reaction.

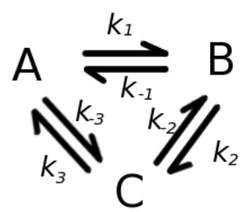

FIG. 1:

A. Calculate concentration of each chemical species (A, B, C) at steady state by using rate constants (k_1, k_{-1}, k_2, k_{-2}, $\ldots$).

B. The flux (J) can be defined as $J = k_1[A] - k_{-1}[B]$ or $(= k_2[B] - k_{-2}[C] = k_3[C] - k_{-3}[A])$. Calculate J and show that J can be again decomposed as $J = J_+ - J_-$ (J_+ is for the forward, and J_- is for the backward flux).

C. In fact, $J = 0$ condition corresponds to an equilibrium condition, where the *microscopic reversibility* is satisfied. Express the condition for $J = 0$, i.e., the microscopic reversibility, using the rate constants. Note that you have answered all the questions above by imposing the steady state condition, and that the equilibrium requires an additional constraint on the system.

D. For the above cyclic reaction, one can write the driving force, the free energy as

$$\Delta\mu = -k_BT\log K = -k_BT\log\frac{J_+}{J_-}. \tag{1}$$

Express the $\Delta\mu$ using the rate constants. What is the condition for $\Delta\mu = 0$.

E. Suppose that the rate constants $k_1 = k_1^o[T]$, $k_{-2} = k_{-2}^o[P]$, and $k_{-3} = k_{-3}^o[D]$ where T, D and P represent ATP, ADP and P. The net driving force in biological systems comes from ATP hydrolysis. Show that

$$\Delta\mu = \Delta\mu^o + k_BT\log\frac{[D][P]}{[T]}. \tag{2}$$

Note that as long as $\Delta\mu \neq 0$ the above reaction cycle is maintained at a nonequilibrium steady state. Look up the literature or the Internet and find (i) the Gibbs free energy for the ATP hydrolysis at standard condition (25^oC, 1 atm), and (ii) the concentrations of ATP, ADP, P in physiological condition. Estimate $\Delta\mu$ value in k_BT or $kcal/mol$ unit (a net driving force for biological systems) at physiological condition ($T = 37^oC$).