1.1 Homework # 1 (Due Friday, Oct. 14)

1. Consider the following nonlinear chemical reaction system:

$$A + X \underset{\beta}{\overset{\alpha}{\rightleftharpoons}} 2X, \quad X \xrightarrow{\lambda} B.$$

We keep the convention that X, Y, Z are *dynamic chemical species* and A, B, C are chemical species with *maintained*, constant concentrations. Use lower cases x, y, z and a, b, c for the concentrations of the corresponding chemical species.

(a) Following the *Law of Mass Action*, write the ordinary differential equation (ODE) for the chemical reaction system.

(b) Find all the steady states (also called fixed points) of the ODE.

(c) Carry out *linear stability analysis* for all the steady states.

(d) Let the initial concentration of X be x_0, try to solve the ODE for $x(t)$.

(e) Use λ as a parameter, is there a bifurcation? If so please draw a bifurcation diagram.

2. Consider the following chemical reaction system:

$$A \xrightarrow{\alpha} X, \quad X + Y \xrightarrow{\beta} 2Y, \quad Y \xrightarrow{\phi} X, \quad Y \xrightarrow{\psi} B.$$

We again follow the convention as in Problem 1.

(a) Following the Law of Mass Action, write the ordinary differential equations for the chemical reaction system.

(b) Find all the steady states of the ODE system.

(c) Carry out *linear stability analysis* for all the fixed points.

(d) Using internet resource to learn more about SIR model in epidemiology. In terms of the language of epidemiological dynamics, what is the system of ODEs in (a) called?

3. Consider a general reaction

$$\nu_1 X_1 + \nu_2 X_2 + \cdots + \nu_n X_n \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \kappa_1 X_1 + \kappa_2 X_2 + \cdots + \kappa_n X_n. \tag{1.1}$$

The *chemical potential* of the species X_k is defined as

$$\mu_{X_k} = \mu^o_{X_k} + k_B T \ln x_k,$$

in which $\mu^o_{X_k}$ is a constant specific to the chemical species X_k, independent of its concentration. k_B is the Boltzmann constant and T is temperature in Kelvin. One of the most important properties of the chemical potentials is that when this reaction reaches its chemical equilibrium:

$$\sum_{k=1}^{n} \nu_k \mu_{X_k} = \sum_{k=1}^{n} \kappa_k \mu_{X_k} \iff \sum_{k=1}^{n} \big(\nu_k - \kappa_k\big)\Big(\mu^o_{X_k} + k_B T \ln x_k^{eq}\Big) = 0. \tag{1.2}$$

One can write the kinetic equations in terms of the Law of Mass Action as

$$\frac{\mathrm{d}x_k}{\mathrm{d}t} = \big(\kappa_k - \nu_k\big)\Big(R^+(\mathbf{x}) - R^-(\mathbf{x})\Big), \tag{1.3}$$

in which

$$R^+(\mathbf{x}) = k_+ \prod_{j=1}^{n} x_j^{\nu_j}, \quad R^-(\mathbf{x}) = k_- \prod_{j=1}^{n} x_j^{\kappa_j}. \tag{1.4}$$

(a) Find a relationship between the “constant term”

$$\sum_{k=1}^{n} \big(\nu_k - \kappa_k\big)\mu^o_{X_k}$$

in Eq. 1.2 and the rate constants k_+ and k_- in Eq. 1.4.

(b) Show that, in equilibrium or not, the $\Delta\mu$ for the reaction:

$$\Delta\mu \equiv \sum_{k=1}^{n} \big(\nu_k - \kappa_k\big)\mu_{X_k} = k_B T \ln\left(\frac{R^+(\mathbf{x})}{R^-(\mathbf{x})}\right).$$

4. Consider the Lotka-Volterra system with all reactions reversible:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X, \quad X + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2Y, \quad Y \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} B. \tag{1.5}$$

We again follow the notations as in Problem 1. However, we assume all A, B, X and Y are in a closed system, which means A and B, as well as X and Y, are all changing with time following the Law of Mass Action.

(a) Write the *four* ordinary differential equations for the chemical reaction system.

(b) Let the chemical potentials for species A, X, Y, and B be:

$$\mu_A = \mu_A^o + k_B T \ln a, \quad \mu_X = \mu_X^o + k_B T \ln x, \quad \mu_Y = \mu_Y^o + k_B T \ln y, \quad \mu_B = \mu_B^o + k_B T \ln b.$$

Find the relationship between difference $\mu_A^o - \mu_X^o$, $\mu_X^o - \mu_Y^o$, $\mu_Y^o - \mu_B^o$, and the kinetic parameters k's in (1.5).

(c) Consider the total "chemical free energy" of the system (Gibbs function):

$$\begin{aligned} G(a,x,y,b) &= a(t)\mu_A + x(t)\mu_X + y(t)\mu_Y + b(t)\mu_B \\ &= a(t)\Big(\mu_A^o + k_B T \ln a(t)\Big) + x(t)\Big(\mu_X^o + k_B T \ln x(t)\Big) + y(t)\Big(\mu_Y^o + k_B T \ln y(t)\Big) \\ &\quad + b(t)\Big(\mu_B^o + k_B T \ln b(t)\Big). \end{aligned}$$

G is a function of time t since a, x, y, and b are all changing with time according to the system of differential equations from part (a). Show that

$$\frac{\mathrm{d}G\big(a(t), x(t), y(t), b(t)\big)}{\mathrm{d}t} = \sum_{\sigma = a,x,y,b} \left(\frac{\partial G}{\partial \sigma}\right) \frac{\mathrm{d}\sigma}{\mathrm{d}t} \leq 0. \tag{1.6}$$

(d) Based on Eq. 1.6, what can you say about the kinetics of this reversible Lotka-Volterra system?