BE 25 Winter 2025
Homework #1
Due at 9 AM, January 14, 2025

Problem 1.1 (From chemical reactions to ODEs, 30 pts).
For each chemical reaction scheme below, write down a system of ordinary differential equations describing the dynamics assuming mass action kinetics. Please use c_X to denote the concentration of species X.

a) Simple enzyme catalysis.

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k_\mathrm{cat}} \mathrm{E} + \mathrm{P} \tag{1.1}$$

b) Competitive binding.

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AB} \tag{1.2}$$

$$\mathrm{A} + \mathrm{C} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{AC} \tag{1.3}$$

c) Active/inactive switching with binding.

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* \tag{1.4}$$

$$\mathrm{A}^* + \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{A}^*\mathrm{B} \tag{1.5}$$

d) The Lindemann mechanism is used to describe reactions that take place in the gas phase. In the Lindemann mechanism, a unimolecular species, A, is converted into a product, but may only do so from an "activated" configuration. The molecule gets activated or deactivated upon collision with another molecular species, M.

$$\mathrm{A} + \mathrm{M} \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{1.6}$$

$$\mathrm{A}^* \xrightarrow{\mathrm{k}_2} \mathrm{P} \tag{1.7}$$

While there are plenty of gas-phase reactions that are important to biology, we will focus almost exclusively on reactions in solution. The Lindemann mechanism has interesting consequences in the gas phase as pressure is varied, but here, we will just use the chemical reaction scheme as an interesting example for reaction in solution. Write ODEs for the above scheme.

e) Multiple routes to the same place.

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AB} \tag{1.8}$$

$$\mathrm{A} + \mathrm{C} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{AC} \tag{1.9}$$

$$\mathrm{AB} + \mathrm{C} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{ABC} \tag{1.10}$$

$$\mathrm{AC} + \mathrm{B} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{ABC} \tag{1.11}$$

We will show that there are restrictions on the values that the rate constants may take later in the term.

Problem 1.2 (Conservation laws, 20 pts).
For each example reaction in Problem 1.1, state how many conserved quantities there are and write down that many conserved quantities. As an example, if we consider reversible dimerization, $\mathrm{AA} \rightleftharpoons \mathrm{A}+\mathrm{A}$, there is one conserved quantity, which can be identified as the total amount of A, $c_\mathrm{A} + 2c_\mathrm{AA}$. That is, as the reaction proceeds, the quantity $c_\mathrm{A} + 2c_\mathrm{AA}$ remains constant. So, if the initial concentrations of the respective species are c_A^0 and c_AA^0, then $c_\mathrm{A}^0 + 2c_\mathrm{AA}^0 = c_\mathrm{A} + 2c_\mathrm{AA}$. So, your response to this problem for the reaction $\mathrm{AA} \rightleftharpoons \mathrm{A}+\mathrm{A}$ would be that there is one conserved quantity, $c_\mathrm{A} + 2c_\mathrm{AA}$.

Problem 1.3 (Empirical rate laws, 25 pts).
This problem is based on problem 9.5 of Tinoco, et al., Physical Chemistry: Principles and Applications in Biological Sciences. Imagine you are studying a biochemical reaction $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C}$.

a) You suspect it follows a simple mechanism as dictated by mass action. Write an expression for the rate of production of C; that is write an expression for $\mathrm{d}c_\mathrm{C}/\mathrm{d}t$ in terms of the concentrations of A and B.

b) You perform an experiment where you mix A and B together with known concentrations and measure the initial rate of production of C. You get the following results.

c_A^0 (µM)	c_B^0 (µM)	initial rate of production of C (µM/s)
1	1	1
2	1	4
1	2	1

Is the rate expression you proposed in part (a) consistent with the experiment? If not, write down a new expression for $\mathrm{d}c_\mathrm{C}/\mathrm{d}t$ that is.

c) What is the value of rate constant for the reaction based on the experimental data?

d) If you found that the mass action-based mechanism is not consistent with the observations, propose a set of elementary reactions that is and explain why it works.

Problem 1.4 (The Langmuir adsorption isotherm, 25 pts).
Chemical reactions often happen on surfaces. This is true certainly in industrial catalysis, but also in the living world in which reactants need to be localized to membranes prior to reacting.

Imagine a surface containing N sites to which a molecule A may bind. (Each site can bind either zero or one A molecules.) Denote by S an unoccupied site on the surface. Then, the reversible binding reaction is $\mathrm{A} + \mathrm{S} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{AS}$, where the subscripts on the rate constants stand for "adsorption" and "desorption." (Adsorption is a term meaning adherence to a surface.)

a) Write the rate expression for $\mathrm{d}c_\mathrm{A}/\mathrm{d}t$ based on mass action and any conservation laws. You do not need to consider conservation of A, since in the next part, we seek an expression not in terms of the total amount of A, but rather the steady state concentration.

b) Steady state is when the time derivatives vanish. Derive an expression for the steady-state fraction of surface sites that are bound as a function of the steady-state concentration of A. Sketch the function. This expression is called the **Langmuir adsorption isotherm**. Its functional form is ubiquitous, and this is one of many approaches to deriving it.