Thermodynamics, Kinetics, and the Control of Chemical Reactions

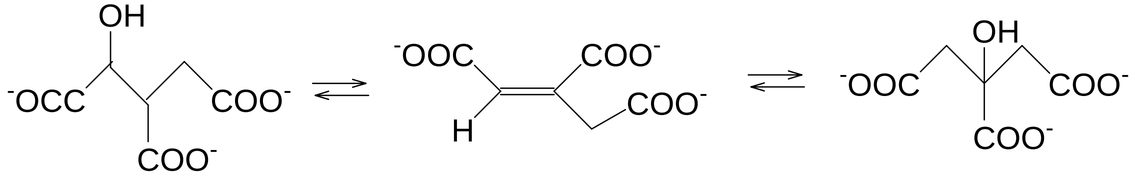
Suppose that a reactant, A, has two possible pathways for its reaction, producing the product B by one pathway, and the product C by a second, independent pathway. Suppose, as well, that these reactions are each in equilibrium. We can represent this as

$$B \leftrightarrows A \leftrightarrows C$$

The final concentrations of A, B, and C are, of course, determined by the system's thermodynamic parameters (the two equilibrium constants). The concentrations of A, B, and C as the reaction takes place, however, are determined by the system's kinetic parameters (the rate constants for the two forward and the two reverse reactions). The goal of this worksheet, therefore, is to explore the relative importance of thermodynamics and kinetics in controlling the progress and outcome of a chemical reaction.

The Chemical System

One of the many reactions taking place in your cells is the catalytic conversion of *cis*-aconitic acid to citric acid and isocitric acid



isocitric acid (B) — *cis*-acontic acid (A) — citric acid (C)

For the purpose of this exercise, we will initially treat the system as one in which all three species remain in equilibrium with the following thermodynamic and kinetic parameters:

Equilibrium Constants (where K_{XY} is for the reaction $X \leftrightarrows Y$)

$K_{AB} = 1.49$ $\qquad$ $K_{AC} = 22.73$

Rate Constants (where $k_{X\rightarrow Y}$ is for the reaction $X \rightarrow Y$ which is first-order in X)

$k_{A\rightarrow B} = 0.1$ $\qquad$ $k_{B\rightarrow A} = 0.067$ $\qquad$ $k_{A\rightarrow C} = 0.1$ $\qquad$ $k_{C\rightarrow A} = 0.0044$

Task 1. For a simple system at equilibrium, the rate of the forward reaction is the same as the rate of the reverse reaction. Write rate laws for the reactions $A \rightarrow B$ and $B \rightarrow A$, assuming pseudo-first order kinetics in A or B for each, and show that the equilibrium constant K_{AB} and the rate constants $k_{A\rightarrow B}$ and $k_{B\rightarrow A}$ are self consistent. Repeat for the interconversion of A and C.

A Thermodynamic Analysis of the Chemical System

Thermodynamics and equilibrium chemistry allow us to predict the relative favorability of competing chemical reactions.

Task 2. Based on the equilibrium constants, which product, isocitric acid or citric acid, is the favored product. Clearly explain your reasoning.

Equilibrium chemistry also allows us to predict the composition of a system when it reaches equilibrium.

Task 3. Assume that you start with 100 units of A. Considering only the equilibrium between A and C, what is the expected composition of the system (units of A and units of C) when equilibrium is reached?

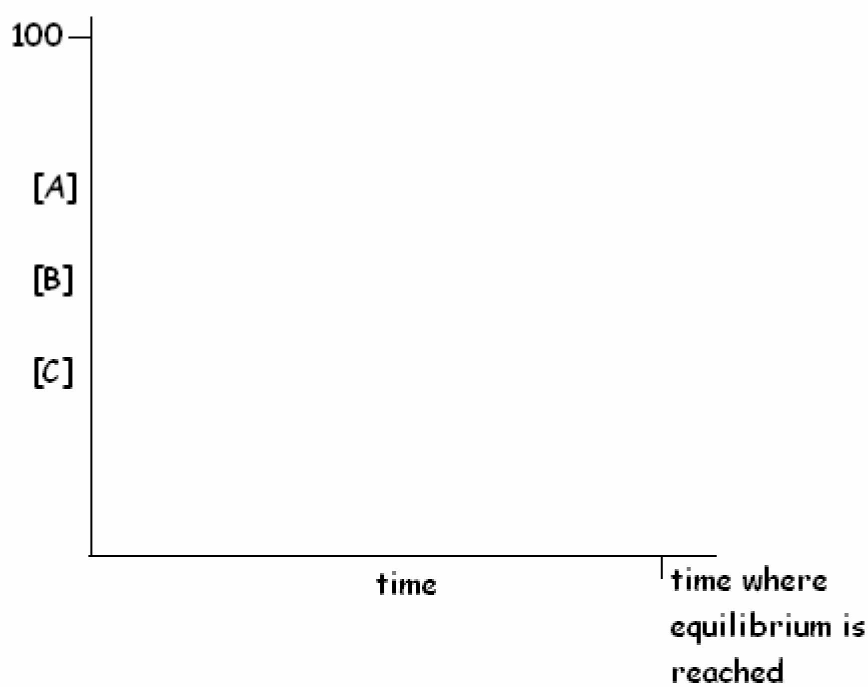
Task 4. In a system of linked equilibria, such as the system you are exploring in this worksheet, the equilibrium concentration of a species involved in multiple equilibria must be the same in each equilibrium constant expression. Your answer from Task 3, therefore, must also be the amount of A in equilibrium with B. How many units of B, therefore, are present in this system at equilibrium?

Task 5. The results of the previous two tasks leaves you with three absolute numbers representing the amounts of A, B and C at equilibrium. Of more interest to us is the relative abundance of each species. Add together the units of A, B, and C at equilibrium to get the total units. Next, calculate the percentage of A, B, and C present at equilibrium (to the nearest one's place); these should add up to 100%. The result of this calculation tells you the relative amount of each species at equilibrium. Check your answers with the instructor before continuing.

A Kinetic Analysis of the Chemical System

Thermodynamics informs us of a chemical reaction's equilibrium position, but does not provide information about how the reaction progresses toward equilibrium. The reaction's kinetics, however, as expressed by a rate law, provides all the information necessary to predict the concentrations of reactants and products as the reaction proceeds toward equilibrium.

Task 6. Begin by making your best guess as to the progress of the chemical system as it moves from an initial condition (100 units of A, 0 units of B and 0 units of C) to its equilibrium condition as determined in Task 5. Use the axes below and draw predicted concentration vs. time profiles for each component.



Task 7. In class, we learned how to calculate the concentration of a reactant at time, t, when the kinetics followed simple zero-order, first-order or second-order kinetics. We also learned how more complicated kinetics could be simplified using pseudo-order conditions. The kinetics in this system, due to the presence of both forward and reverse reactions, are too complicated for us to treat in this course. There are software packages, however, that will do all the necessary calculations for you. One such program is KinBat, which we will use to calculate the actual amount of A, B and C as the chemical system moves toward equilibrium. Do the following:

1. Find the icon for KinBat on your computer's desktop and launch the program.

2. Click on the button labeled "Edit Kinetic Scheme" which opens an editor for specifying the reaction's mechanism. In the row labeled Reaction 1 enter a 1 in the reactant's box for A and a 1 in the product's box for B (this specifies the reaction's stoichiometry), a 0.1 in the box for the rate constant k and a 1 in the reaction order box for A. These values specify the following information about one step in the overall mechanism

   Reaction: $A \rightarrow B$; Rate Law: $R = k[A]$; Rate Constant: 0.1

   In the same fashion, enter information for the remaining steps in the mechanism; that is

   $B \rightarrow A$ with a rate law of $R = k[B]$ where k is 0.067

   $A \rightarrow C$ with a rate law of $R = k[A]$ where k is 0.1

   $C \rightarrow A$ with a rate law of $R = k[C]$ where k is 0.0044

   Click OK to return to the program's main screen.

3. In the box labeled Reactor Volume, enter a value of 1 (this value has no effect on our simulation). In the box labeled reaction time, enter 200; this is the length of the simulation. Finally, in the box for the Initial Concentration of Component A, enter 100. Leave the remaining boxes empty.

4. From the Settings menu select Accuracy-Speed. Adjust the slider to its far right position (slower/more accurate). If necessary, make this window bigger and click OK.

5. Click on the button labeled Start Calculation and, if a graph doesn't appear, then click on the button for Show Graph. The graph will display concentrations of A, B, and C as they are calculated.

Observe the results from this calculation and compare to your predictions. Briefly discuss the similarities and differences between your predictions and the model's results. Examine, in particular, the profile for the concentration of B over time and convince yourself that this makes sense. What does it mean for a reaction to be under kinetic control and to be under thermodynamic control?