

# Principle of Detailed Balance in Kinetics

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In 1975 Mahan (1) wrote a very nice article entitled “Microscopic Reversibility and Detailed Balance” that emphasized molecular collisions and the use of partition functions in chemical kinetics. One of the things that has happened since then is the development of computer programs for personal computers that make it possible to solve rather complicated sets of simultaneous differential equations (2). The concentrations of reactants as a function of time can be calculated for reaction systems that show the effects of detailed balance on chemical kinetics. In this article calculations are used to show what would happen in the chemical monomolecular triangle reaction for cases where the principle of detailed balance is violated.

A discussion of the principle of detailed balance has to start with the principle of microscopic reversibility in mechanics. It was recognized in classical mechanics that when time  $t$  occurs in an equation, changing  $t$  to  $-t$  does not invalidate the equation. A simple example of this time-reversal invariance is a movie of a collision between two billiard balls. This movie appears to be in accord with classical mechanics whether the film is run forwards or backwards. When quantum mechanics was developed, it was found to be time-reversal invariant as well. This means that for every type of interaction between particles the exact reverse is also possible. When a system is at equilibrium this means that the forward rate of a molecular process has to be equal to the reverse rate of that process. Applying this to a chemical reaction observed on a macroscopic scale means that at equilibrium, the forward rate of each step is equal to the reverse rate of that step; this is the principle of detailed balance. This jump from the molecular scale to the macroscopic scale requires a leap of faith, but it is based on research that led Onsager (3) to his treatment of reciprocal relations, which is discussed in more advanced textbooks (4). Here we examine three simple cases that help clarify consequences of the principle of detailed balance in chemical kinetics and its relation to thermodynamic equilibrium, steady states, and oscillating reactions.

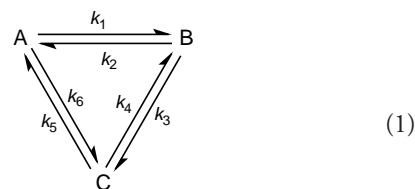
The first question that should be discussed is “What do we mean by equilibrium?” We know that when a thermodynamic system is at equilibrium, it is not changing with time and the temperature and concentration are uniform throughout the system. But that is not enough. Callen (5) writes, “Operationally, a system is in an equilibrium state if its properties are consistently described by thermodynamic theory.” He recognized that this criterion is circular, but gives a good defense. In addition the principle of detailed balance has to be obeyed. Here we consider a system at specified temperature and pressure, and so the thermodynamic equilibrium state is the one that minimizes the Gibbs energy,  $G$ . When we study a reaction system, we know a lot about how changes in the temperature and pressure affect equilibrium constants.

In some cases it is not easy to decide whether a system is at equilibrium or in a steady state, and so we need to ask “What is a steady state or stationary state?” Actually the state

of the system is not literally steady or stationary, but the concentrations of one or more species are approximately constant while the concentrations of other species are changing much more rapidly. The rate of change of the concentration of one or more intermediates may be so close to zero that the steady-state approximation is useful in treating the kinetics of the reaction system.

Usually chemical reactions approach equilibrium without oscillations, but sometimes oscillations are observed. However, these oscillations always appear far from equilibrium, and reactions never oscillate around the equilibrium composition. Thermodynamics does not allow a reaction system to go through an equilibrium state to a state of higher Gibbs energy. Equilibrium at constant temperature and pressure is reached at the lowest Gibbs energy. Reactions that show oscillations usually involve autocatalysis, and they eventually reach equilibrium if the system is closed.

To clarify the application of the principle of detailed balance, calculations are presented here on the interconversion of three isomers A, B, and C. The general case is represented by:



This reaction system is used because it is the simplest that can be used to illustrate the principle of detailed balance. The simultaneous rate equations are

$$\frac{d[A]}{dt} = -(k_1 + k_6)[A] + k_2[B] + k_5[C] \quad (2)$$

$$\frac{d[B]}{dt} = k_1[A] - (k_2 + k_3)[B] + k_4[C] \quad (3)$$

$$\frac{d[C]}{dt} = k_6[A] + k_3[B] - (k_4 + k_5)[C] \quad (4)$$

The following three cases are discussed when A is initially present at 1 M:

$$\text{Case I: } k_1 = k_3 = k_5 = 1 \text{ and } k_2 = k_4 = k_6 = 0$$

$$\text{Case II: } k_1 = k_2 = k_3 = k_4 = k_5 = k_6 = 1$$

$$\text{Case III: } k_1 = 2 \text{ and } k_2 = k_3 = k_4 = k_5 = k_6 = 1$$

We will find that only one of these cases can be a real molecular system.

The Mathematica software (2) makes it possible to solve systems of simultaneous differential equations for given values of rate constants and initial concentrations and to obtain the concentrations of A, B, and C as a function of time (2). The operations in the solution of the equations for the three cases are given in the Supplemental Material.<sup>W</sup>

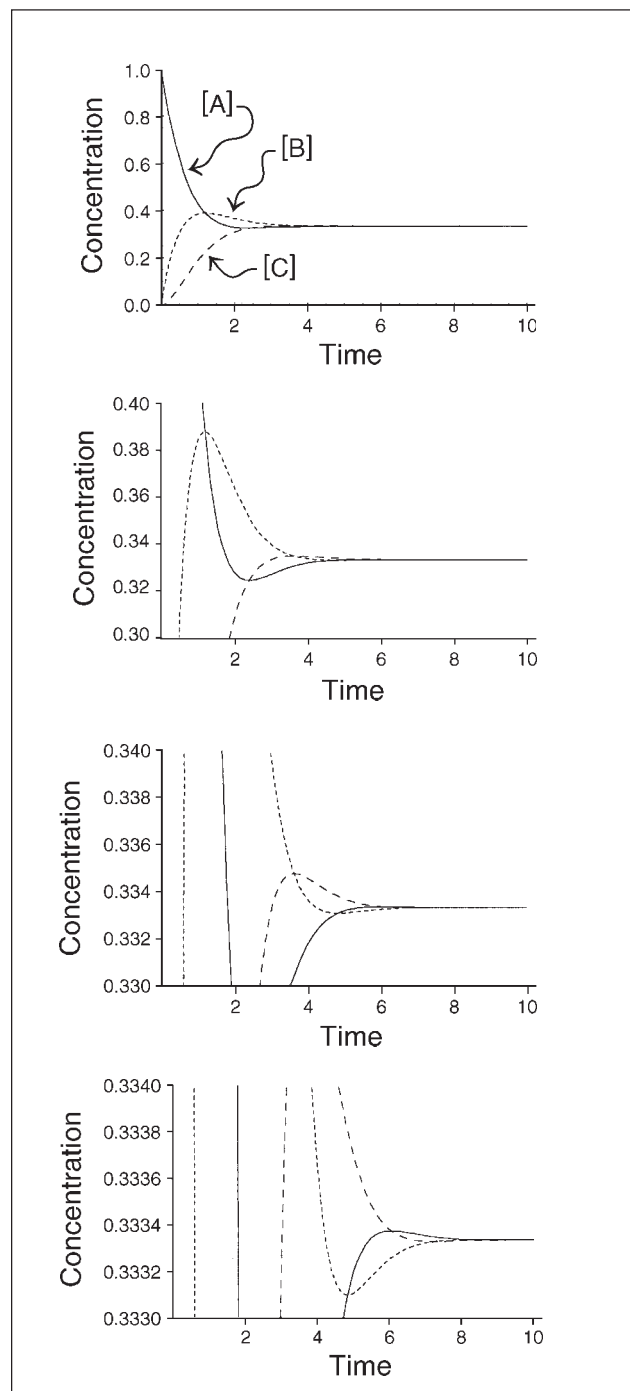


Figure 1. Plots of concentrations of A (solid line), B (small dashed line), and C (larger dashed line) versus time when  $k_1 = k_3 = k_5 = 1$  and  $k_2 = k_4 = k_6 = 0$ . The vertical scale is expanded in three steps by a factor of 10 in each step to show what happens at longer times.

### Case I: $k_1 = k_3 = k_5 = 1$ and $k_2 = k_4 = k_6 = 0$

This reaction system is represented by the following three differential equations:

$$\frac{d[A]}{dt} = -k_1[A] + k_5[C] \quad (5)$$

$$\frac{d[B]}{dt} = k_1[A] - k_3[B] \quad (6)$$

$$\frac{d[C]}{dt} = k_3[B] - k_5[C] \quad (7)$$

When  $[A]_0 = 1$  M and the three rate constants are each set at unity, Mathematica yields the plots of concentration versus time that are given in Figure 1. In the early part of the reaction the concentration of A decreases, the concentration of B rises immediately, but there is an induction period in the appearance of C because it is formed from B. The second plot shows more clearly that both B and C overshoot their long-term values, and A undershoots. The last two plots show that these oscillations continue at longer times. The oscillations diminish with time, and eventually the reaction system reaches a steady state in which the concentrations of A, B, and C are equal. However, the circulation around the cycle never stops, and this circulation violates the principle of detailed balance. Since this case violates the principle of detailed balance, it cannot occur in a real molecular system. From a thermodynamic point of view, the equilibrium constants for  $[B]/[A]$ ,  $[C]/[B]$ , and  $[A]/[C]$  are all infinite, which does not make any sense. So we conclude that this hypothetical system does not satisfy the principle of detailed balance or the requirements of thermodynamics. The monomolecular triangle reaction with  $k_2 = k_4 = k_6 = 0$  is treated by Starzak (6) for the general case, which shows that for some choices of the three rate constants, there are no oscillations.

### Case II: $k_1 = k_2 = k_3 = k_4 = k_5 = k_6 = 1$

We might think that we can give the six rate constants in reaction system 1 any values we wish, and indeed we can use Mathematica to calculate the concentrations of A, B, and C as functions of time for any values of the six rate constants. However, when the reaction system comes to equilibrium, the principle of detailed balance requires that for each of the three steps, the rate of the forward reaction must be equal to the rate of the backward reaction at equilibrium. This leads to the following expressions for the equilibrium constants of the three steps:

$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_1}{k_2} \quad (8)$$

$$\frac{[C]_{\text{eq}}}{[B]_{\text{eq}}} = \frac{k_3}{k_4} \quad (9)$$

$$\frac{[A]_{\text{eq}}}{[C]_{\text{eq}}} = \frac{k_5}{k_6} \quad (10)$$

Multiplying the left-hand sides of these three equations yields unity, and so

$$\frac{k_1 k_3 k_5}{k_2 k_4 k_6} = 1 \quad (11)$$

Thus according to the principle of detailed balance, the six rate constants in reaction system 1 are not independent.

Figure 2 shows that there are no oscillations when the rate constants are all equal to unity. The concentrations of B

and C are always equal. This case is in accord with the principle of detailed balance because eq 11 is satisfied, and the expectations of thermodynamics are fulfilled.

### Case III: $k_1 = 2$ and $k_2 = k_3 = k_4 = k_5 = k_6 = 1$

In order to see what happens when eq 11 is not satisfied, the value of  $k_1$  is doubled. The first plot in Figure 3 shows that as A decreases at short times, the concentration of B rises and the concentration of C rises more slowly to a

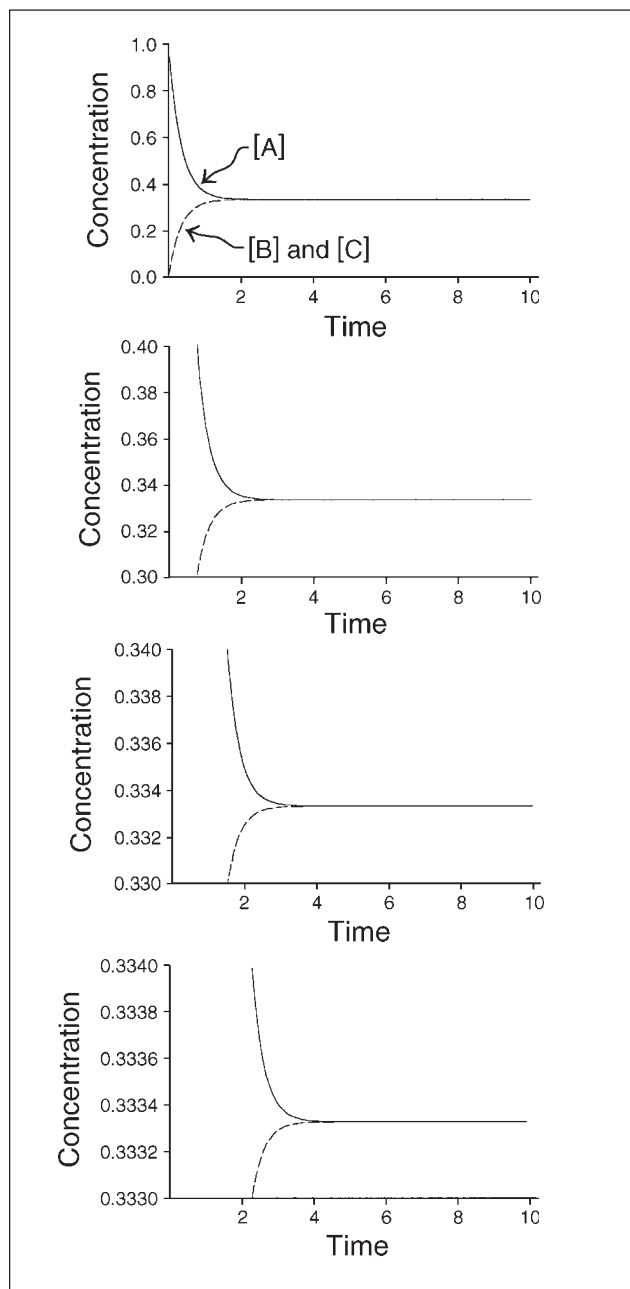


Figure 2. Plots of concentrations of A (solid line), B (small dashed line), and C (larger dashed line) versus time when  $k_1 = k_2 = k_3 = k_4 = k_5 = k_6 = 1$ . The vertical scale is expanded in three steps by a factor of 10 in each step to show what happens at longer times. Note that the concentrations of B and C are always equal.

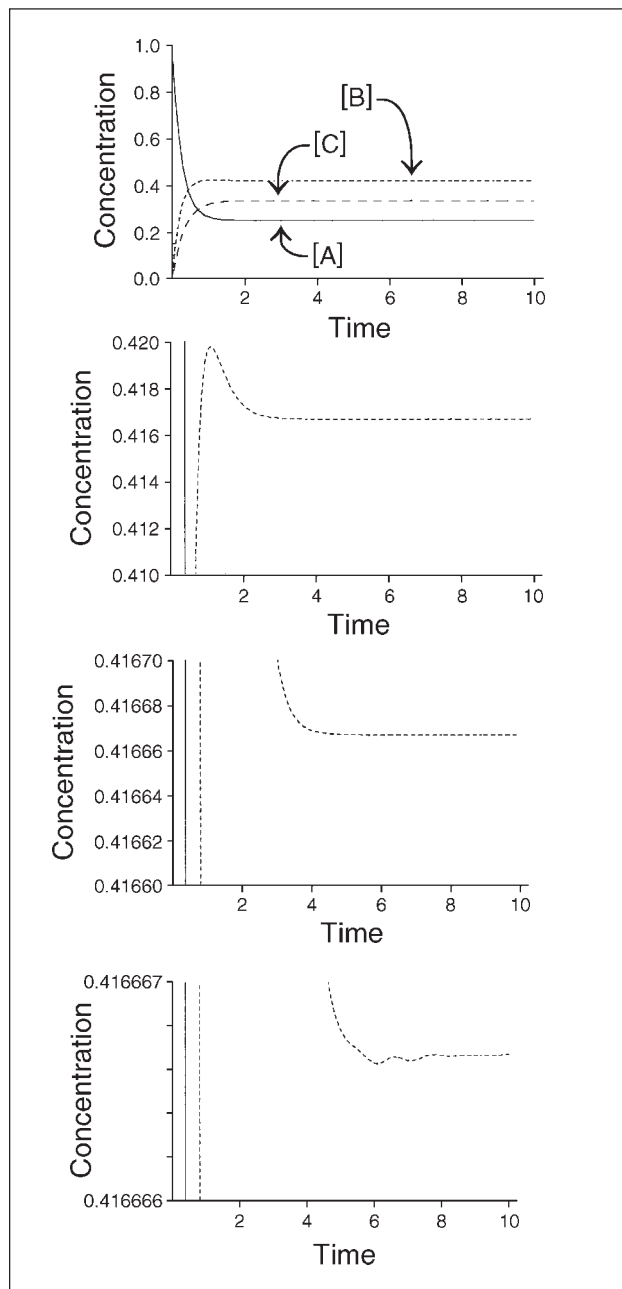


Figure 3. Plots of concentrations of A (solid line), B (small dashed line), and C (larger dashed line) versus time when  $k_1 = 2$  and  $k_2 = k_3 = k_4 = k_5 = k_6 = 1$ . The vertical scale is expanded in each of three steps by a factor of 100 in each step to show what happens at longer times. Attention is focused on B.

lower level than B. In the other plots the vertical scale is expanded by a factor of 100 in each step. Note that B overshoots and approaches its long-time value with oscillations that go above and below the long-time value. Since the equilibrium constant for  $A = B$  is 2, we might expect that the long-time value of  $[B]/[A]$  would be 2, but this ratio is 1.67. This case violates the principle of detailed balance since  $(k_1k_3k_5)/(k_2k_4k_6) = 2$ . At longer times the oscillations diminish and a steady state is reached, but there is still circulation around the cycle that is not consistent with the principle of detailed balance. This is the second system that is physically unrealistic because it violates the principle of detailed balance.

## Discussion

These calculations are like the tip of an iceberg in the sense that they provide visual information about the effect of the principle of detailed balance on a simple reaction system. But the principles of detailed balance and microscopic reversibility are very deep subjects and the literature (the rest of the iceberg) is interesting and challenging. In addition to the references that have already been given, Strizhak and Menzinger (7) discuss a simple experiment that illustrates oscillations, limit cycles, chaos, bifurcations, and noise, and Gray and Scott (8) provide an overview of oscillating reactions.

## Supplemental Material

This program and others used in preparing the figures for this article are available in this issue of *JCE Online*.

## Acknowledgments

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