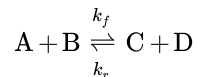


## 5.17: Chemical Equilibrium as the Equality of Rates for Opposing Reactions

Suppose that the bimolecular reaction



occurs as an elementary process. From our conclusions about the concentration dependencies of elementary reactions, the rate of the net reaction is

$$\begin{aligned} R &= \frac{1}{V} \frac{d\xi}{dt} \\ &= -\frac{1}{V} \frac{dn_A}{dt} \\ &= k_f[A][B] - k_r[C][D] \end{aligned}$$

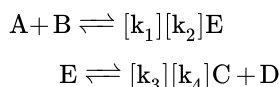
at any time. In particular, this rate equation must remain true at arbitrarily long times—times at which the reaction has reached equilibrium and at which  $dn_A/dt = 0$ . Therefore, at equilibrium we have

$$K = \frac{k_f}{k_r} \quad (5.17.1)$$

$$= \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}} \quad (5.17.2)$$

where the concentration-term subscripts serve to emphasize that the concentration values correspond to the reaction being in a state of equilibrium. We see that the ratio of rate constants,  $k_f/k_r$ , characterizes the equilibrium state. This constant is so useful we give it a separate name and symbol, the **equilibrium constant**,  $K$ .

Now, let us consider the possibility that the reaction is not an elementary process, but instead proceeds by a two-step mechanism involving an intermediate,  $E$ :



The sum of these elementary processes yields the same overall reaction as before. This mechanism implies the following differential equations:

$$\begin{aligned} \frac{1}{V} \frac{dn_A}{dt} &= -k_1[A][B] + k_2[E] \\ \frac{1}{V} \frac{dn_D}{dt} &= k_3[E] - k_4[C][D] \end{aligned}$$

At equilibrium, both  $n_A$  and  $n_D$  must be constant, so both differential equations must be equal to zero. Hence, at equilibrium,

$$\begin{aligned} \frac{k_1}{k_2} &= \frac{[E]_{eq}}{[A]_{eq}[B]_{eq}} \\ \frac{k_3}{k_4} &= \frac{[C]_{eq}[D]_{eq}}{[E]_{eq}} \end{aligned}$$

Multiplying these, we have

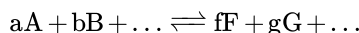
$$K = \frac{k_1 k_3}{k_2 k_4} \quad (5.17.3)$$

$$= \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}} \quad (5.17.4)$$

The concentration dependence of the equilibrium constant for the two-step mechanism (Equation 5.17.4) is the **same** as for case that the reaction is an elementary process (Equation 5.17.2). As far as the description of the equilibrium system is concerned, the

only difference is that the equilibrium constant is interpreted as a function of different rate constants (Equation 5.17.1 vs. Equation 5.17.3).

For the general reaction



we see that any sequence of elementary reactions will give rise to the same concentration expression for the equilibrium system. Whatever the mechanism, reactant  $A$  must appear  $a$  times more often on the left side of elementary reactions than it does on the right. Product  $F$  must appear  $f$  times more often on the right side of elementary reactions than it does on the left. Any intermediates must appear an equal number of times on the left and on the right in the various elementary reactions. As a result, when we form the ratio of forward to reverse rate constants for each of the elementary reactions and multiply them, the concentration of reactant  $A$  must appear in the product to the  $-a$  power, the concentration of product  $F$  must appear to the  $+f$  power, and the concentrations of the intermediates must all cancel out. We conclude that the condition for equilibrium in the general case is

$$K = \frac{[F]^f [G]^g \dots}{[A]^a [B]^b \dots}$$

where we drop the “eq” subscripts, trusting ourselves to remember that the equation is valid only when the concentration terms apply to the equilibrated system.

## Pure Phases

When the reaction involves a pure phase as a reactant or product, we observe experimentally that the amount of the pure phase present in the reaction mixture does **NOT** affect the position of equilibrium. The composition of the reaction solution is the same so long as the solution is in contact with a finite amount of the pure phase. This means that we can omit the concentration of the substance that makes up the pure phase when we write the equilibrium-constant expression. In writing the equilibrium constant expression, we can take the concentration the substance to be an arbitrary constant. Unity is usually the most convenient choice for this constant.

To rationalize this experimental observation within our kinetic model for equilibrium, we postulate that the rate at which molecules leave the pure phase is proportional to the area,  $S$ , of the phase that is in contact with the reaction solution; that is,

$$R_{\text{leaving}} = k_1 S.$$

We postulate that the rate at which molecules return to the pure phase from the reaction solution is proportional to both the area and the concentration of the substance in the reaction solution. If the pure phase consists of substance  $A$ , we have

$$R_{\text{returning}} = k_2 S[A].$$

At equilibrium, we have  $R_{\text{leaving}} = R_{\text{returning}}$ , so that  $k_1 S = k_2 S[A]$ , and  $[A] = k_1/k_2 = \text{constant}$

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