The Approach to Equilibrium
CHEM 361A: Introduction to Physical Chemistry

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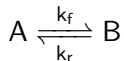Lecture 17

Table of contents

Learning Objective: To quantify how long it takes to reach equilibrium.

References:

- Atkins and de Paula Focus 6E
- Chang §12.10

The Approach to Equilibrium

All forward reactions are accompanied with backwards reactions.
Consider the following reaction:

$$A \xrightleftharpoons[k_r]{k_f} B$$

The rate expressions for both directions are:

1

$$\text{rate}_f = k_f[A]$$

2

$$\text{rate}_r = k_r[B]$$

Then we can write the net consumption of A to be:

$$\frac{d[A]}{dt} = k_r[B] - k_f[A]$$

Integrated Rate Law Example
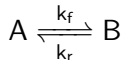
Given the rate law expression

$$\frac{d[A]}{dt} = k_r[B] - k_f[A]$$

determine the integrated rate law expression for [A] if $[B]_0=0$.

Hint: Let $[B] = [A]_0-[A]$

Integrated Rate Law Example (cont.)

Given that the integrated rate law expressions for

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

are

$$[A] = \frac{(k_r + k_f e^{-(k_f+k_r)t})[A]_0}{k_f + k_r}$$

$$[B] = \frac{k_f(1 - e^{-(k_f+k_r)t})[A]_0}{k_f + k_r}$$

determine $[B]_{eq}$ and $[A]_{eq}$

Hint: Let $t \to \infty$
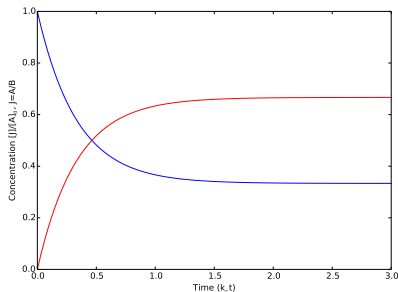
Plotting [A] and [B] as a Function of Time

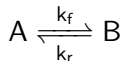Given that

$$[A]_{eq} = \frac{k_r [A]_0}{k_f + k_r}$$

and

$$[B]_{eq} = \frac{k_f [A]_0}{k_f + k_r}$$

if $k_f = 2k_r$, determine $[A]_{eq}$ and $[B]_{eq}$ in terms of $[A]_0$.

(Re)Introduction of Equilibrium Concepts

The equilibrium expression for

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

is

$$K = \frac{[B]_{eq}}{[A]_{eq}}$$

An equilibrium expression can also be calculated starting from the rate law expression. At equilibrium:

$$\frac{d[A]}{dt} = 0 = k_r[B]_{eq} - k_f[A]_{eq}$$

Rearranging gives

$$\frac{k_f}{k_r} = \frac{[B]_{eq}}{[A]_{eq}}$$

How Equilibrium Changes with Temperature

Given that:

$$K = \frac{k_f}{k_r}$$

we can gain insight into how the equilibrium changes with temperature

Equilibrium Constant, K

- Use van't Hoff Equation

$$\ln \frac{K'}{K} = \frac{\Delta H^{\ominus}}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$
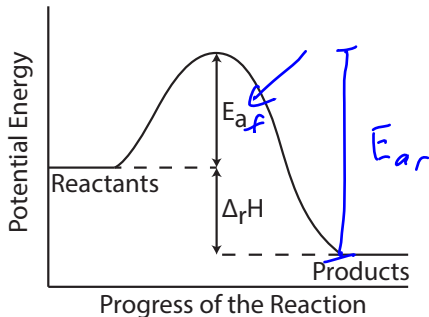
Ratio of rate constants, k_f/k_r

- Use Arrhenius Equation

$$\ln \frac{k'}{k} = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

Demonstration that Equilibrium and Kinetics Show the Same Shift
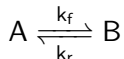

$$E_{a_r} - E_{a_s} = \Delta H$$

Given the following reaction profile rationalise that you get the same equilibrium shift looking at how the equilibrium constant, K, and the ratio of rate constants, change with an increase in temperature.

Calculating the Shift in Concentration Due to a Temperature Change

Continuing to work with the reaction:

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

before a temperature shift the net rate of change of [A] is

$$\frac{d[A]}{dt} = k_{r,ini}[B] - k_{f,ini}[A]$$

and at equilibrium

$$k_{r,ini}[B]_{eq,ini} = k_{f,ini}[A]_{eq,ini}$$

When the temperature shifts, based on the rate law equation, the new equilibrium is determined by:

$$k_f[A]_{eq} = k_r[B]_{eq}$$

Finding the Rate of the Shift

We can write the deviation from [A] and [B] from their respective equilibrium values as x, so

$$[A] = [A]_{eq} - x$$
$$[B] = [B]_{eq} + x$$

Substituting this into the rate law expression

$$\frac{d[A]}{dt} = k_r[B] - k_f[A]$$

We find that the deviation from the new equilibrium is found by:

$$x = x_0 e^{-t/\tau} \quad \text{where} \quad \tau = (k_r + k_f)^{-1}$$

where τ is the time constant of the relaxation

Equilibrium Shift

Consider the previous established equilibrium where the steady state $[A] = [A]_0/3$ and $[B] = 2[A]_0/3$. If the temperature were to shift suddenly such that K is now equal to 1, determine the time constant, τ and the new equilibrium concentrations of the two species.

Plot of Concentration Shift
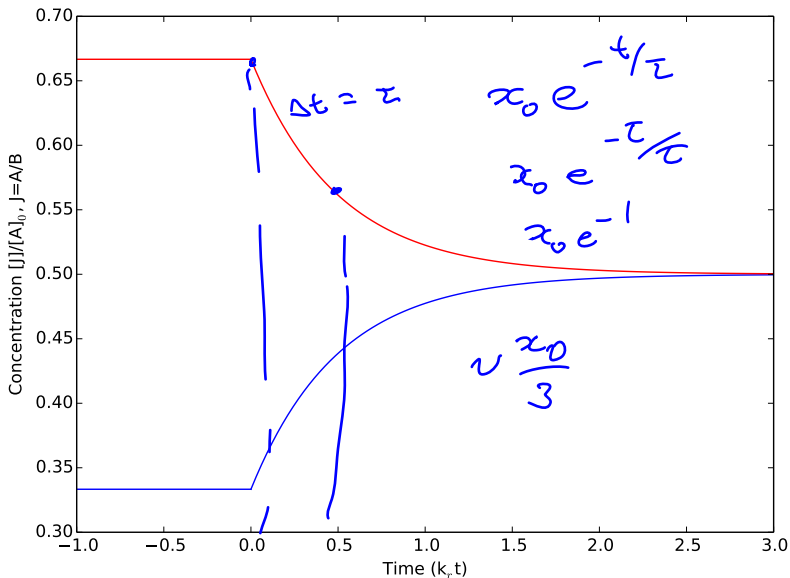
Summary

- Many reactions have both backwards and forwards reactions. Both should be included in the rate law expression
- The equilibrium constant, K, can be related to the rate constants for a process.
- As systems move to equilibrium, one metric that quantifies the time it takes to reach equilibrium is the time constant, τ, which depends on the rate constants for the reaction.