Sections 16.1-2
Equilibrium and the Equilibrium Constant

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Equilibrium and the Equilibrium Constant

In these sections…

a. Microscopic reversibility
b. The equilibrium state
c. Equilibrium expressions
d. Nature of the equilibrium constant
e. Manipulating equilibrium expressions

Microscopic Reversibility

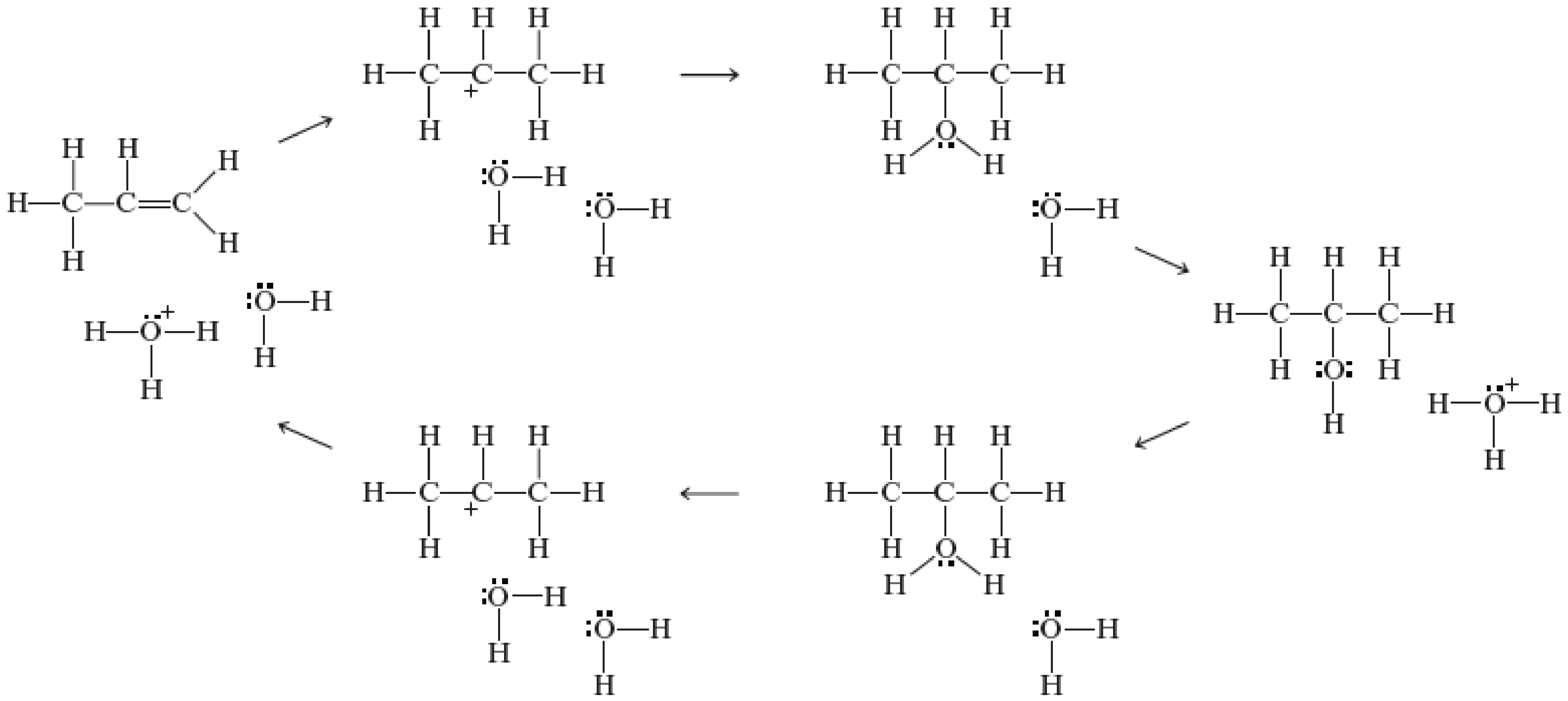
Any elementary step can proceed in either the forward direction or the reverse direction.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightarrow FeSCN^{2+}(aq)$$

$$FeSCN^{2+}(aq) \rightarrow Fe^{3+}(aq) + SCN^{-}(aq)$$

Microscopic Reversibility

alkenes → alcohols



alcohols ← alkenes

The Equilibrium State

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightarrow FeSCN^{2+}(aq)$$

$$FeSCN^{2+}(aq) \rightarrow Fe^{3+}(aq) + SCN^{-}(aq)$$

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{2+}(aq)$$

The Equilibrium Constant, K (also written K_{eq})

<u>Forward reaction</u>:
$Fe^{3+}(aq) + SCN^{-}(aq) \rightarrow FeSCN^{2+}(aq)$ Rate = $K_f[Fe^{3+}][SCN^-]$

<u>Reverse reaction</u>:
$FeSCN^{2+}(aq) \rightarrow Fe^{3+}(aq) + SCN^{-}(aq)$ Rate = $K_r[FeSCN^{2+}]$

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at equilibrium, forward rate = reverse rate

so

$K_f[Fe^{3+}][SCN^-] = K_r[FeSCN^{2+}]$

We rewrite this: K =

The Equilibrium Constant, K

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]}$$

All solutions at equilibrium will have this ratio of concentrations.

- It doesn’t matter if you start with reactants or with products.
- It doesn’t matter which is the limiting reactant.
- All equilibrium solutions will have the same *ratio of concentrations*.
- But, not all solutions have the *same concentrations*.
- Solutions *can* have a different ratio of concentrations, but they’re not at equilibrium.

The Meaning of K

Overall reaction: sum of all the elementary steps

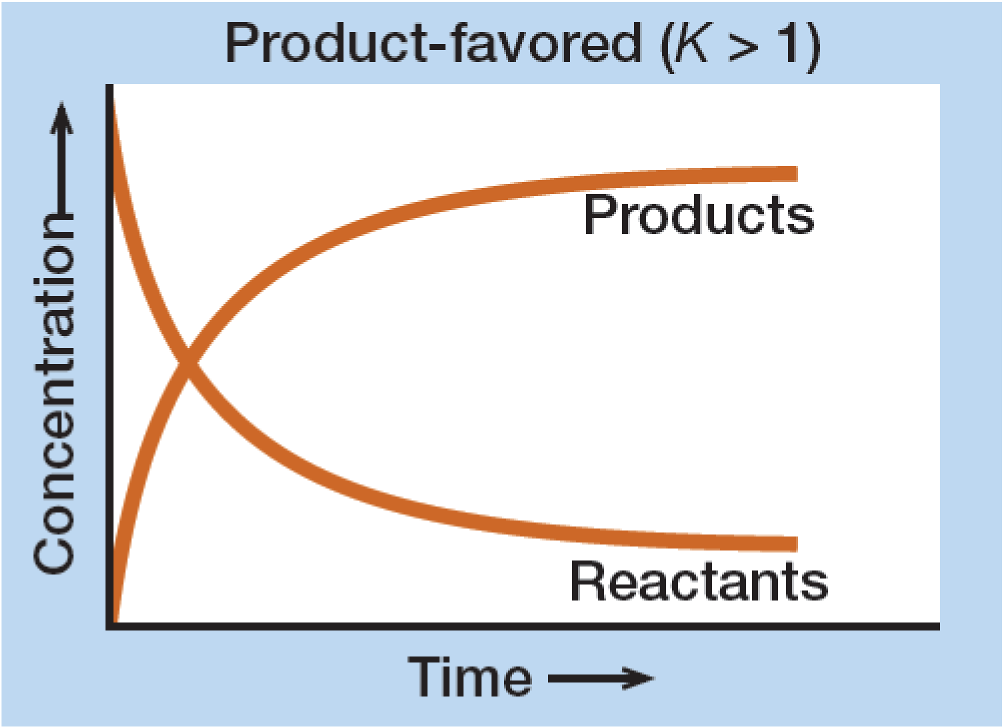
Intermediate: Formed in one step, and then used in a later step

Catalyst: Used in one step, and then reproduced in a later step

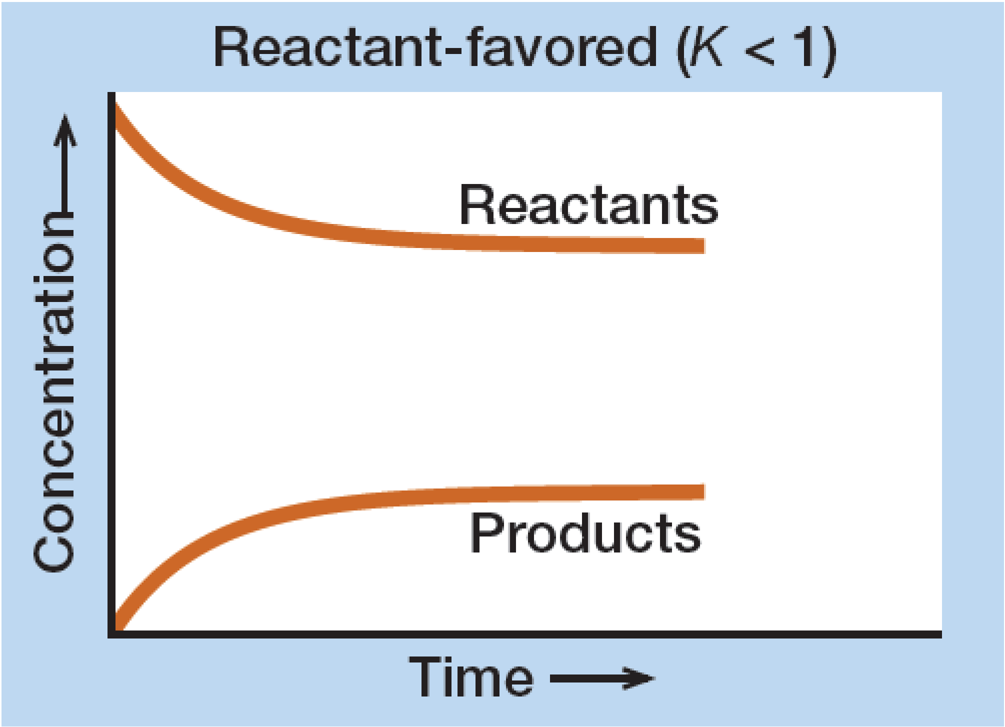
Overall Reactions:

Step 1.	Unimolecular	$O_3(g) \rightarrow O_2(g) + O(g)$
Step 2.	Bimolecular	$O_3(g) + O(g) \rightarrow 2\ O_2(g)$
Overall Reaction:		

The Meaning of K



System 1: Large K;
Product Favored



System 2: Small K;
Reactant Favored

Writing Equilibrium Expressions

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftarrows c\,\mathrm{C} + d\,\mathrm{D}$$

$$K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

Rules:

- Products over reactants, raised to stoichiometric powers
- Solids and bulk solvents not included in the equilibrium expression

Writing Equilibrium Expressions: Examples

$$H_2(g) + Cl_2(g) \rightleftarrows 2\ HCl(g)$$

$$C(s) + H_2O(g) \rightleftarrows H_2(g) + CO(g)$$

$$CH_3CO_2H(aq) + H_2O(\ell) \rightleftarrows H_3O^+(aq) + CH_3CO_2^-(aq)$$

Equilibrium Constants for Gases: K_p vs. K_c

$$K_p = K_c(RT)^{\Delta n}$$

Calculate K_p for the following reaction:

$2\ NOBr(g) \rightleftarrows 2\ NO(g) + Br_2(g)$ $K_c = 6.50 \times 10^{-3}$ at 298 K

Manipulating Equilibrium Constants

Rules:

- Multiply reaction by a constant, raise K to the power of that constant
- Reverse a reaction, take inverse of K
- Add two reactions, K is the product of the K's of those reactions

Example: $2\ NOBr(g) \rightleftarrows 2\ NO(g) + Br_2(g)$ $K_c = 6.50 \times 10^{-3}$ at 298 K

What is K for: $NOBr(g) \rightleftarrows NO(g) + \frac{1}{2}\ Br_2(g)$

Manipulating Equilibrium Constants

- Reverse a reaction, take inverse of K

Example: $2\ NOBr(g) \rightleftarrows 2\ NO(g) + Br_2(g)$ $K_c = 6.50 \times 10^{-3}$ at 298 K

What is K for $2\ NO(g) + Br_2(g) \rightleftarrows NOBr(g)$

Manipulating Equilibrium Constants

- Add two reactions, K is the product of the K's of those reactions

(1) $Cu^{2+}(aq) + 4\ NH_3(aq) \rightleftarrows Cu(NH_3)_4^{2+}(aq)$ $\quad K_1 = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4}$ $= 6.8 \times 10^{12}$

(2) $Cu(OH)_2(s) \rightleftarrows Cu^{2+}(aq) + 2\ OH^-(aq)$ $\quad K_2 = [Cu^{2+}][OH^-]^2$ $= 1.6 \times 10^{-19}$

Net reaction:

$$Cu(OH)_2(s) + 4\ NH_3(aq) \rightleftarrows Cu(NH_3)_4^{2+}(aq) + 2\ OH^-(aq) \quad K_{net} = \frac{[Cu(NH_3)_4^{2+}][OH^-]^2}{[NH_3]^4}$$

K_{net} =