Aqueous Solutions and Chemical Equilibria

Aqueous Solutions and Chemical Equilibria

- At equilibrium, the rate of a forward process or reaction and that of the reverse process are equal.
- the strong electrolytes listed are acids, bases, and salts. A salt is produced in the reaction of an acid with a base. Ex., NaCl, Na2SO4, and NaOOCCH3 (sodium acetate).

- Acids and bases

According to the Brønsted-Lowry theory, an acid is a proton donor, and a base is a proton acceptor. For a molecule to behave as an acid, it must encounter a proton acceptor (or base) and vice versa.

- Conjugate Acids and Bases

A conjugate base is formed when an acid loses a proton.

For example, acetate ion is the conjugate base of acetic acid.

A conjugate acid is formed when a base accepts a proton.

$$acid_1 \leftrightarrow base_1 + proton$$

$$base_2 + proton \leftrightarrow acid_2$$

$$Acid_1 + base_2 \leftrightarrow base_1 + acid_2$$

- Acid1 and base1 act as a conjugate acid/base pair, or just a conjugate pair.

- Similarly, every base accepts a proton to produce a conjugate acid.
- When these two processes are combined, the result is an acid/base, or
- neutralization reaction.
- This reaction proceeds to an extent that depends on the relative tendencies
- of the two bases to accept a proton (or the two acids to donate a proton).

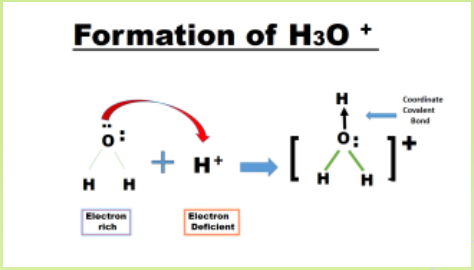
- In an aqueous solution of ammonia, water can donate a proton and acts as an
- acid with respect to the solute NH3.

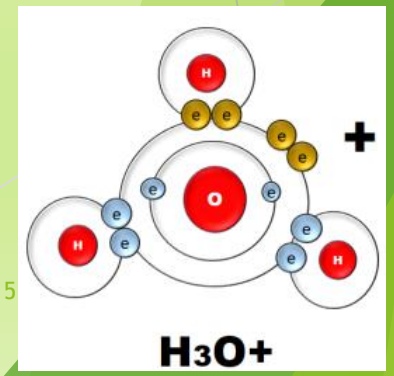
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

- Ammonia (base1) reacts with water (acid2) to give the conjugate acid ammonium ion
- (acid1) and hydroxide ion (base2) of the acid water.
- On the other hand, water acts as a proton acceptor, or base, in an aqueous
- solution of nitrous acid.

$$H_2O + HNO_2 \leftrightarrow H_3O^+ + NO_2^-$$

- The conjugate base of the acid HNO_2 is nitrite ion.
- The conjugate acid of water is the hydrated proton written as H_3O^+.
- This species is called the hydronium ion, and it consists of a proton covalently bonded to a single water molecule.





Amphiprotic species

- Species that have both acidic and basic properties are amphiprotic.
- Ex., dihydrogen phosphate ion, $H_2PO_4^-$, which behaves as a base in the presence of a proton donor such as H_3O^+.
-

$$H_2PO_4^- + H_3O^+ \leftrightarrow H_3PO_4 + H_2O$$

- Here, H_3PO_4 is the conjugate acid of the original base.
- - In the presence of a proton acceptor, such as hydroxide ion, however, $H_2PO_4^-$ behaves as an acid and donates a proton to form the conjugate base HPO_4^{2-}

$$H_2PO_4^- + OH^- \leftrightarrow HPO_4^{2-} + H_2O$$

- The simple amino acids are an important class of amphiprotic compounds that contain both a weak acid and a weak base functional group.

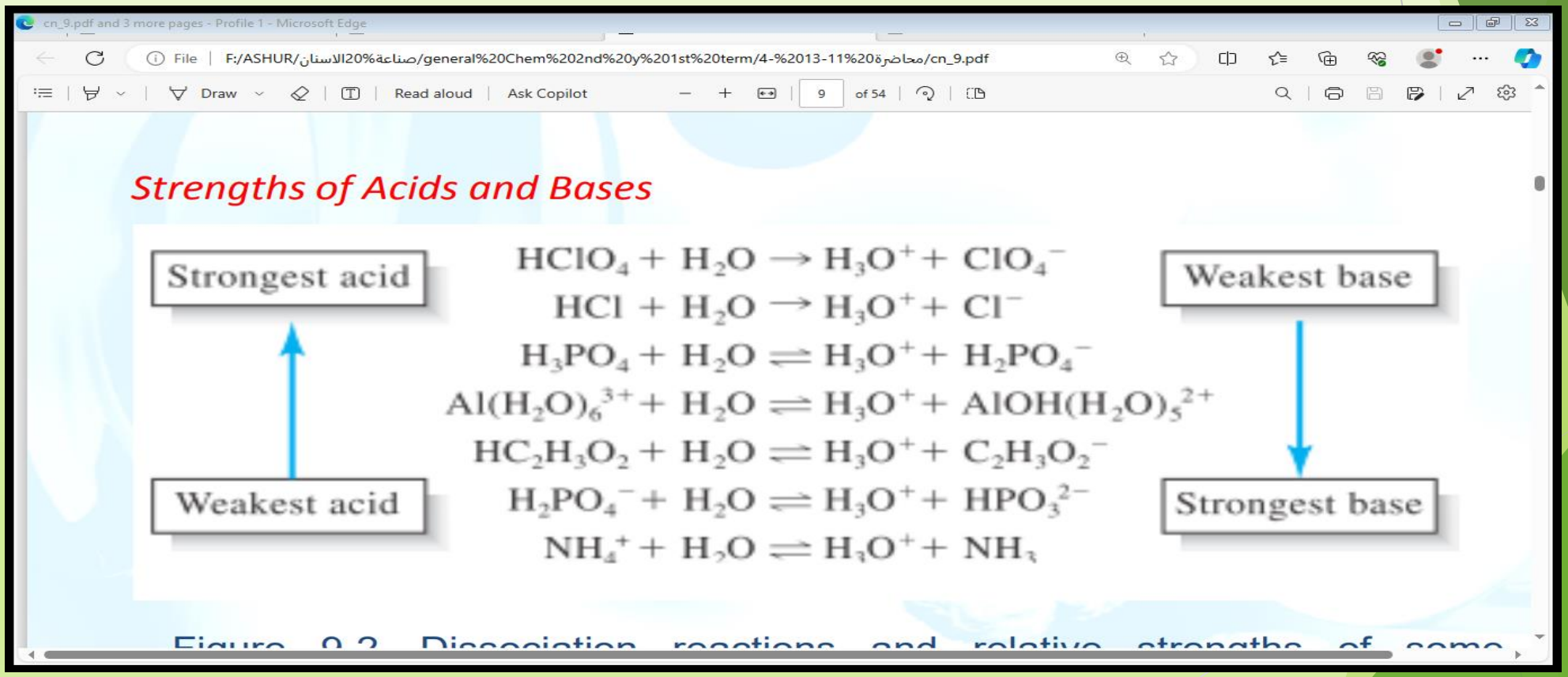
- When dissolved in water, an amino acid, such as glycine, undergoes a kind of internal acid/base reaction to produce a *zwitterion—a species that has both a positive and a negative charge*

$$NH_2CH_2COOH \leftrightarrow NH_3^+ CH2COO^-$$

- Common amphiprotic solvents include Water, methanol, ethanol, and anhydrous acetic acid.

Autoprotolysis Autoprotolysis (also called autoionization)

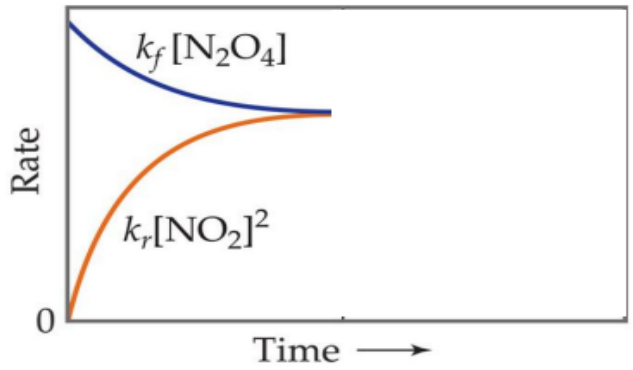
- is the spontaneous reaction of molecules of a substance to give a pair of ions.
- The hydronium and hydroxide ion concentrations in pure water are only about 10^{-7} M.



Chemical equilibrium

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The Concept of Equilibrium



$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

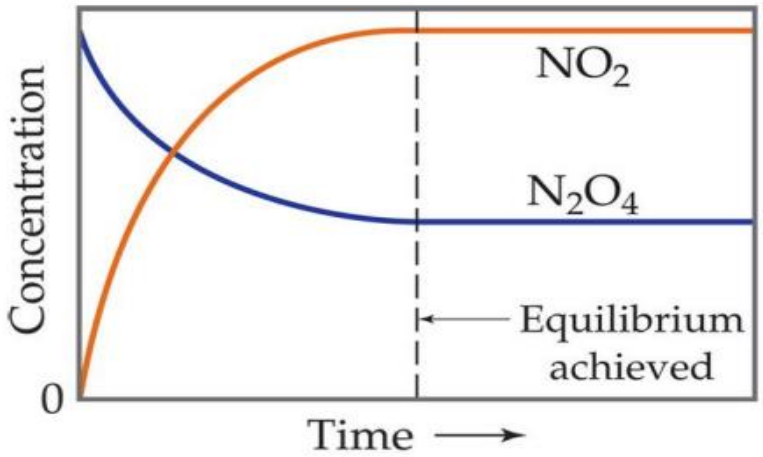
- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding at the same rate.



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A System at Equilibrium

Once equilibrium is achieved, the *amount* of each reactant and product remains constant.

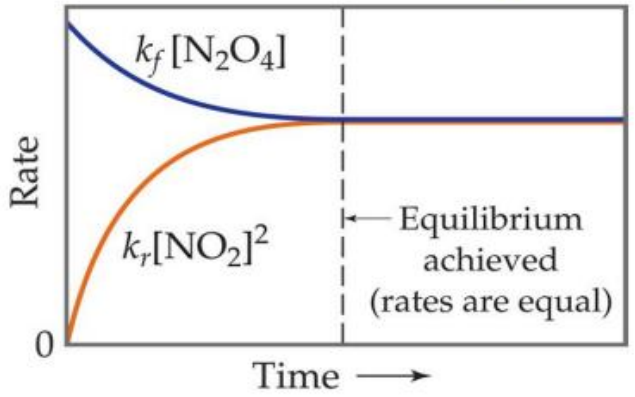


$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

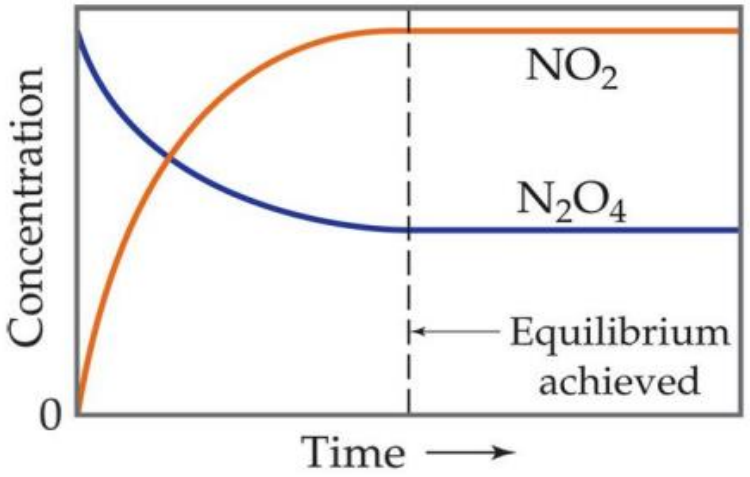


A System at Equilibrium

Rates become equal



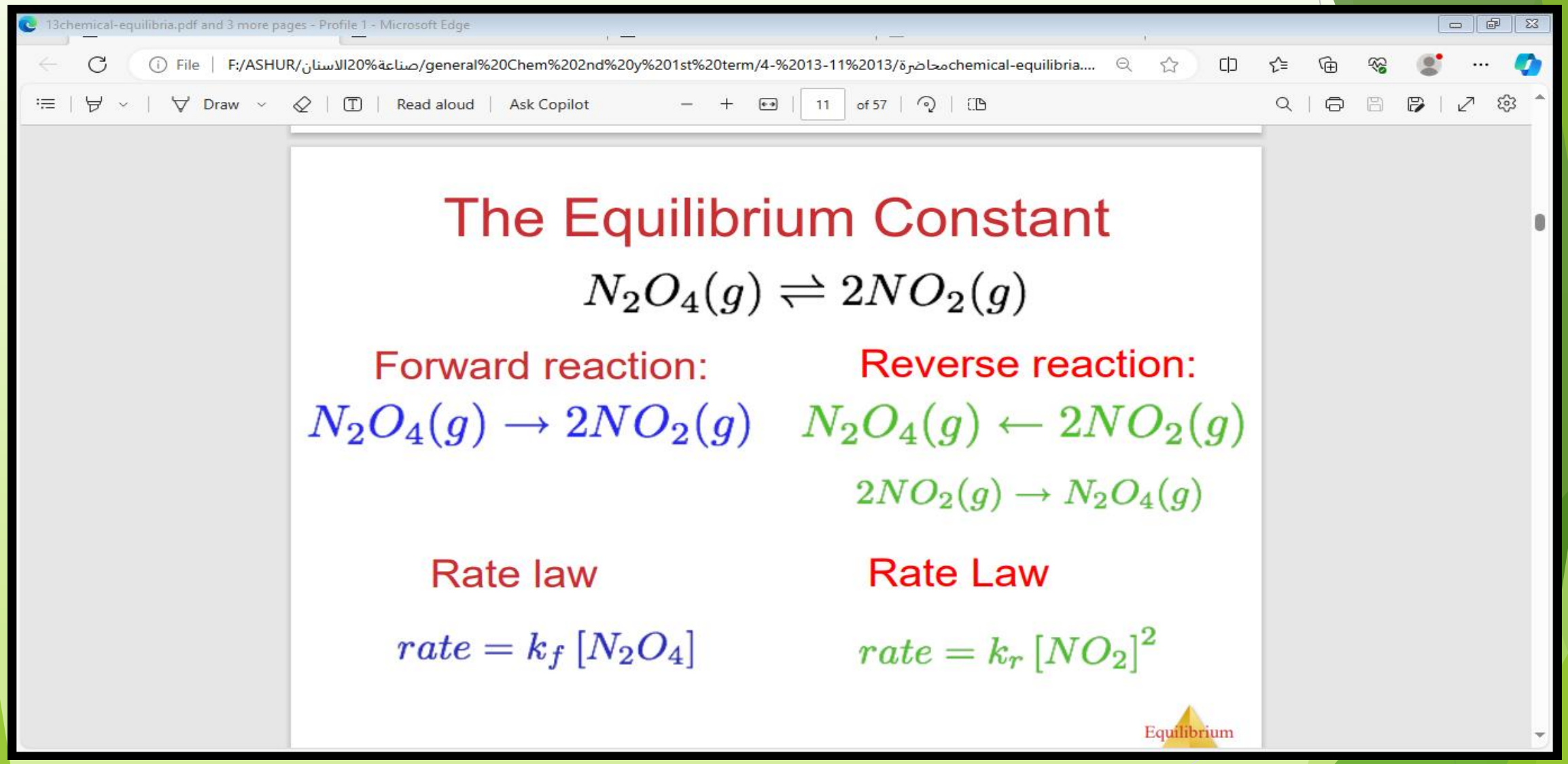
Concentrations become constant



$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$



The Equilibrium Constant



The Equilibrium Constant

At equilibrium

$$rate_f = rate_b$$

$$k_f\,[N_2O_4] = k_r\,[NO_2]^2$$

Rearranging gives:

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$



The Equilibrium Constant

The ratio of the rate constants is a constant (as long as T is constant).

The expression becomes

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$



The Equilibrium Constant

To generalize, the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

Has the equilibrium expression:

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

This expression is true even if you don't know the elementary reaction mechanism.

Equilibrium

SAMPLE EXERCISE 15.1 **Writing Equilibrium-Constant Expressions**

Write the equilibrium expression for K_c for the following reactions:

(a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$

(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

(a) $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$,

(b) $Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4{}^{2-}(aq)$.



SAMPLE EXERCISE 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:

(a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$
(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$
(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

Solution

Analyze: We are given three equations and are asked to write an equilibrium-constant expression for each.

Plan: Using the law of mass action, we write each expression as a quotient having the product concentration terms in the numerator and the reactant concentration terms in the denominator. Each term is raised to the power of its coefficient in the balanced chemical equation.

Solve:

$$\textbf{(a)}\ K_c = \frac{[O_2]^3}{[O_3]^2},\ \textbf{(b)}\ K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]},\ \textbf{(c)}\ K_c = \frac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$$

PRACTICE EXERCISE

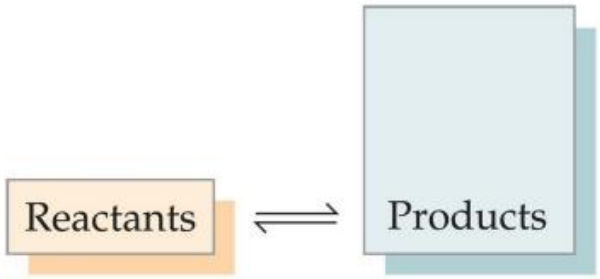
Write the equilibrium-constant expression, K_c for

(a) $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$,
(b) $Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4{}^{2-}(aq)$.

Answers: **(a)** $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$; **(b)** $K_c = \dfrac{[CdBr_4{}^{2-}]}{[Cd^{2+}][Br^-]^4}$

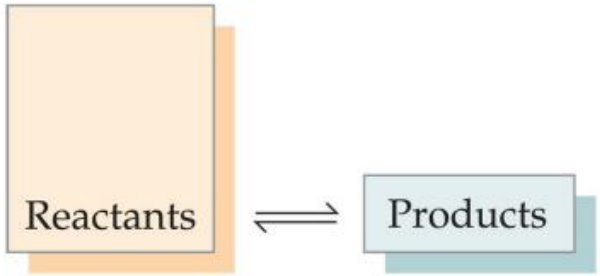
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What Does the Value of *K* Mean?



(a) $K \gg 1$

- If $K >> 1$, the reaction is *product-favored*; product predominates at equilibrium.



(b) $K \ll 1$

- If $K << 1$, the reaction is *reactant-favored*; reactant predominates at equilibrium.



- The mass-action effect is a shift in the position of an equilibrium caused by adding one of the reactants or products to a system.

- Equilibrium is a dynamic process. At equilibrium, the amounts of reactants and products are constant because the rates of the forward and reverse processes are exactly the same.

- Chemical thermodynamics is a branch of chemistry that concerns the flow of heat and energy in chemical reactions. The position of a chemical equilibrium is related to these energy changes.

Solubility

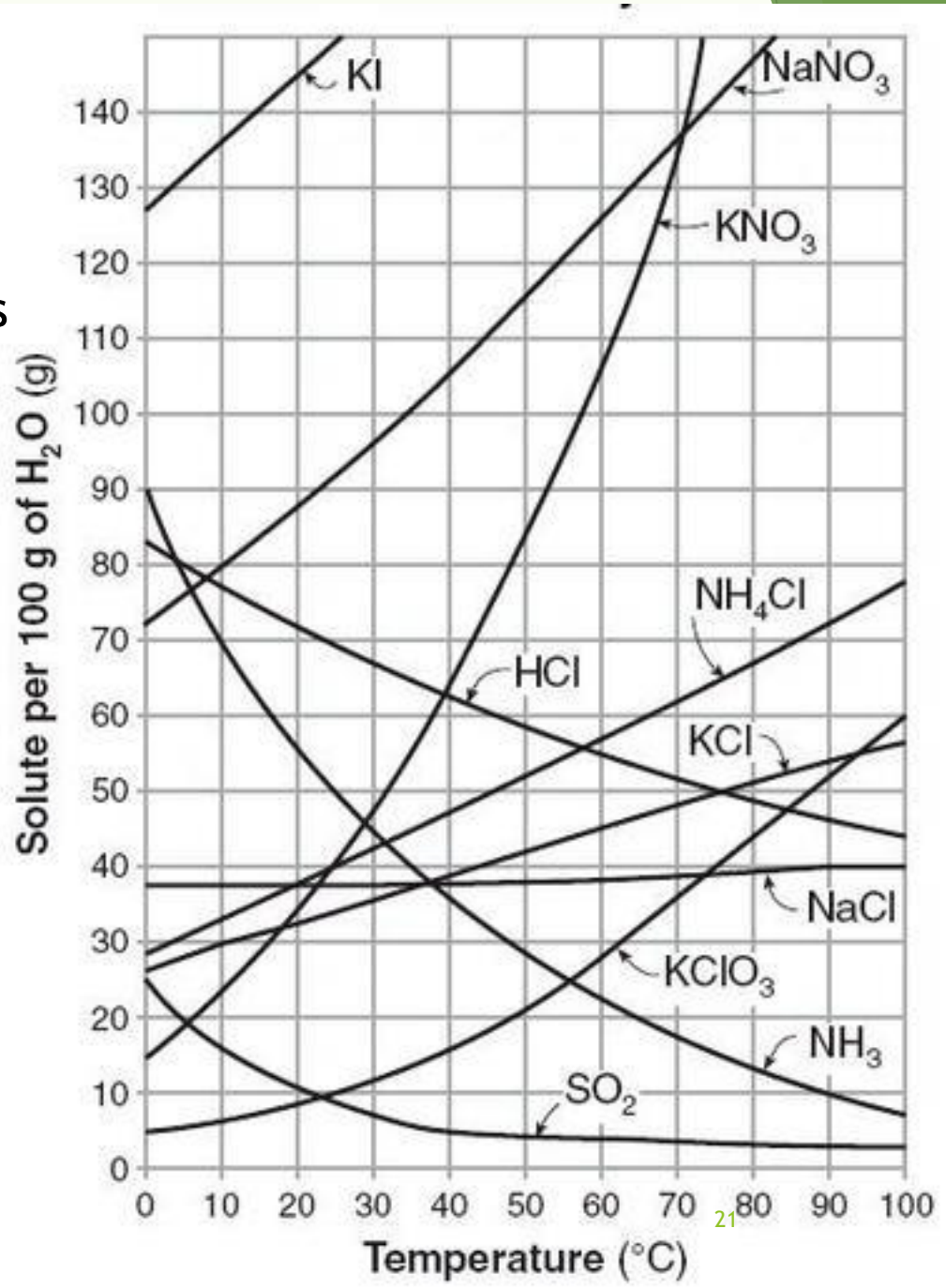
Definition of Solubility

- Solubility is the ability of a solid, liquid, or gaseous chemical substance (referred to as the solute) to dissolve in solvent (usually a liquid) and form a solution. The solubility of a substance

- fundamentally depends on the solvent used, as well as temperature and pressure. The solubility of a substance in a particular solvent is measured by the concentration of the saturated solution. A solution is considered saturated when adding additional solute no longer increases the concentration of the solution.

Factors Affecting Solubility

1. Temperature: The solubility of a given solute in a given solvent typically depends on temperature. For many solids dissolved in liquid water, solubility tends to correspond with increasing temperature
2. Pressure: Pressure has a negligible effect on the solubility of solid and liquid solutes, but it has a strong effect on solutions with gaseous solutes
3. Polarity:a polar solute such as sugar is very soluble in polar water, less soluble in moderately polar methanol, and practically insoluble in non-polar solvents



End