

Chapter 4



General Concepts of Chemical Equilibrium

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- The reactions never go in only one direction, but actually reach an equilibrium in which the rates of reactions in both directions are equal.

4.1 Chemical Reactions: The Rate Concept

molar equilibrium constant : $\frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{k_f}{k_b} = K$

for $aA + bB \leftrightarrow cC + dD$ rxn

The order of the reaction: the sum of the exponents in the rate constant.

The larger will be the equilibrium constant and the farther to the right the reaction will be at equilibrium.

Fig 4.1

4.2 Types of Equilibria

Table 4.1

- Acid-base dissociation;
solubility;
complex formation;
reduction-oxidation;
phase distribution.

4.3 Gibbs Free Energy and the Equilibrium Constant

endothermic reaction:

enthalpy (ΔH) is positive

exothermic reaction:

enthalpy (ΔH) is negative

Gibbs free energy: $G = H - TS$

$$G = H - T \Delta S$$

at a constant temperature

A process will be spontaneous when ΔG is negative, will be spontaneous in the reverse direction when ΔG is positive, and will be at equilibrium when ΔG is zero.

A reaction is favored by heat given off (negative ΔH), as in exothermic reactions, and by increased entropy (positive ΔS).

Standard state:

1atm, 298K, unit concentration

$$G^{\circ} = -RT \ln K = -2.303RT \log K$$

R: gas constant

4.4 LE CHÂTELIER' s Principle

When stress is applied to a system at chemical equilibrium, the equilibrium will shift in a direction that tends to relieve or counteract that stress.

Ex: T, P, [C].

4.5 Temperature Effects on Equilibrium Constants

An endothermic forward reaction which absorbs heat will be displaced to the right with an increase in the equilibrium constant.

Temperature influences the rate at which equilibrium is approached.

The rates of many reactions increase about two-to threefold for every 10 rise in temperature.

4.6 Pressure Effects on Equilibria

Pressure can have a large influence on the position of chemical equilibrium for reactions occurring in the gaseous phase.

But for reactions occurring in solutions, normal pressure changes have a negligible effect on the equilibrium.

4.7 Effect of Concentrations on Equilibria

The direction of change is predictable from Le châtelier's principle.

4.8 Catalysts

Catalysts alter the rate at which an equilibrium is attained, but have no effect on the value of an equilibrium constant.

4.9 Completeness of Reactions

The remaining amount of the substance being determined is too small to be measured by the measurement technique.

- 1) increase the concentration of a reactant
 - 2) decrease the concentration of a product
- } shift to right

Product may be decreased

- 1) By allowing a gaseous product to escape.
- 2) By precipitating the product.
- 3) By forming a stable ionic complex of the product in solution.
- 4) By preferential extraction.

4.10 Equilibrium Constants for Dissociating or Combining Species

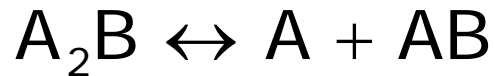
Weak electrolytes: partially dissociated electrolytes Ex: HOAc

Strong electrolytes: completely dissociated electrolytes Ex: HCl

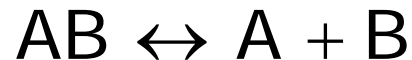


The larger K_{eq} , the greater will be the dissociation.

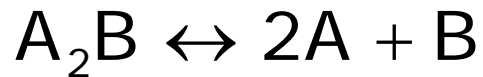
4.10-2



$$K_1 = \frac{[A][AB]}{[A_2B]}$$



$$K_2 = \frac{[A][B]}{[AB]}$$

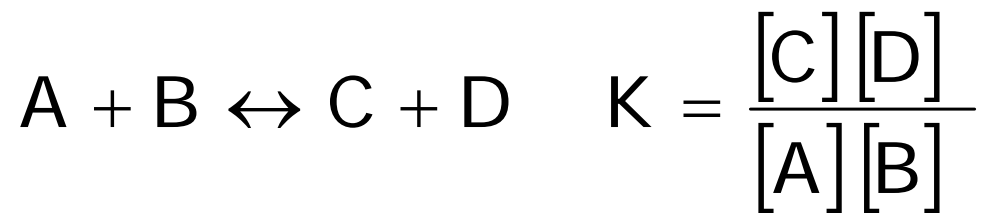


$$K_{eq} = \frac{[A]^2[B]}{[A_2B]} = K_1 K_2$$



$$K_{eq(\text{reverse})} = \frac{[AB]}{[A][B]} = \frac{1}{K_{eq}}$$

4.11 Calculation Using Equilibrium Constants



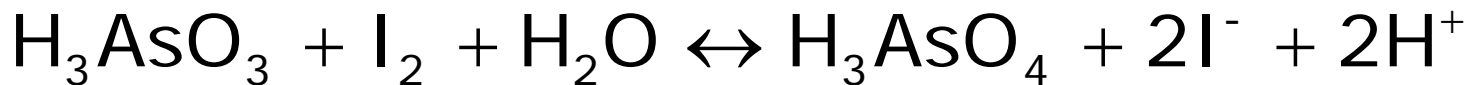
if analytical concentration $\geq 100 K_{\text{eq}}$

$$\Rightarrow C - x \approx C$$

4.12 The Common Ion Effect

Predicted from Le châtelier' s principle

Ex :



are usually done in slightly alkaline solution

4.13 Systematic Approach to Equilibrium Calculations

- the law of mass conservation
- the law of charge conservation

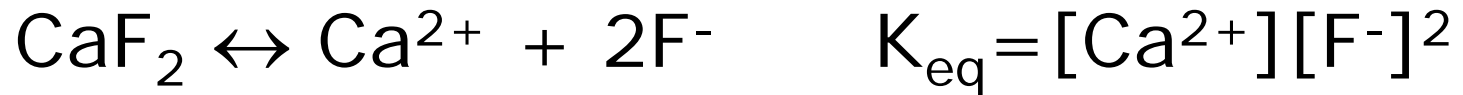
- Equilibrium calculations using the systematic approach
 1. Write the chemical reactions appropriate for the system.
 2. Write the equilibrium constant expressions for these reactions.
 3. Write all the mass balance expressions.
 4. Write the charge balance expression.

5. Count the number of chemical species involved and the number of independent equations.
6. Make simplifying assumptions concerning the relative concentrations of chemical species.
7. Calculate the answer.
8. Check the validity of your assumptions.

4.14 Heterogeneous Equilibria

dissolution of a solid

formation of a precipitate



4.15 Activity and Activity Coefficients

The presence of diverse salts (not containing ions common to the equilibrium involved) will cause an increase in dissociation of a weak electrolyte or in the solubility of a precipitate.

□ Activity:

the “effective concentration” of an ion in the presence of an electrolyte.

□ Activity coefficient:

$$a_i = C_i f_i \quad f_i: \text{ activity coefficient}$$

when $C < 10^{-4} \text{M}$ $\Rightarrow C \approx a; f_i = 1$

□ Ionic strength:

$$\mu = \frac{1}{2} \sum C_i Z_i^2$$

□ Calculation of activity coefficients:

Debye - Hückel equation :

$$-\log f_i = \frac{0.51 Z_i^2 \sqrt{\mu}}{1 + 0.33 a_i \sqrt{\mu}} \quad \text{when } \mu < 0.2$$

a_i : ion size parameter

$$-\log f_i = \frac{0.51 Z_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad \text{when } \mu < 0.01$$

Davies equation :

$$-\log f_i = \frac{0.51 Z_i^2 \sqrt{\mu}}{1 + 0.33 a_i \sqrt{\mu}} - 0.10 Z_i^2 \mu \quad \text{when } 0.2 < \mu < 0.6$$

- General conclusions about activity coefficients:
 1. The activity coefficients of ions of a given charge type are approximately the same in solutions of a given ionic strength.
 2. The behavior of ions become less ideal as the charge type increase.

3. The calculated activity coefficient of an ion in a mixed electrolyte solution will be less accurate than in a single-electrolyte solution.
4. The activity coefficient of nonelectrolytes (uncharged molecules) can generally be considered equal to unity in ionic strengths up to 0.1.

4.16 The Diverse Ion Effect: The Thermodynamic Equilibrium Constant

Thermodynamic equilibrium constants (K_{eq}°) hold at all ionic strengths.



$$K_{\text{eq}}^{\circ} = \frac{a_A \cdot a_B}{a_{AB}} = \frac{[A] f_A \times [B] f_B}{[AB] f_{AB}}$$

$$= K_{\text{eq}} \frac{f_A \cdot f_B}{f_{AB}}$$

or $K_{\text{eq}} = K_{\text{eq}}^{\circ} \frac{f_{AB}}{f_A \cdot f_B}$