Analytical chemistry

Lecture № 2

General concepts of chemical equilibrium

$CaCO_3(s) + CO_2(g) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

Reversible Reactions and Chemical Equilibria

In 1798, the chemist ***Claude Berthollet*** (1748–1822) accompanied a French military expedition to Egypt. While visiting the Natron Lakes, a series of salt water lakes carved from limestone, Berthollet made an observation that contributed to an important discovery. Upon analyzing water from the Natron Lakes, Berthollet found large quantities of common salt, NaCl, and soda ash, Na_2CO_3, a result he found surprising. Berthollet "knew" that a reaction between Na_2CO_3 and $CaCl_2$ goes to completion, forming NaCl and a precipitate of $CaCO_3$ as products.

$$\mathrm{Na_2CO_3 + CaCl_2 \longrightarrow 2NaCl + CaCO_3}$$

Understanding this, Berthollet expected that large quantities of NaCl and Na_2CO_3 could not coexist in the presence of $CaCO_3$. Since the reaction goes to completion, adding a large quantity of $CaCl_2$ to a solution of Na_2CO_3 should produce NaCl and $CaCO_3$, leaving behind no unreacted Na_2CO_3. In fact, this result is what he observed in the laboratory. The evidence from Natron Lakes, where the coexistence of NaCl and Na_2CO_3 suggests that the reaction has not gone to completion, ran counter to Berthollet's expectations. Berthollet's important insight was recognizing that the chemistry occurring in the Natron Lakes is the reverse of what occurs in the laboratory.

$$\mathrm{CaCO_3 + 2NaCl \longrightarrow Na_2CO_3 + CaCl_2}$$

Using this insight Berthollet reasoned that the reaction is ***reversible***, and that the relative amounts of "reactants" and "products" determine the direction in which the reaction occurs, and the final composition of the reaction mixture. We recognize a reaction's ability to move in both directions by using a double arrow when writing the reaction.

$$\mathrm{Na_2CO_3 + CaCl_2 \rightleftharpoons 2NaCl + CaCO_3}$$

Berthollet’s reasoning that reactions are reversible was an important step in understanding chemical reactivity. When we mix together solutions of Na_2CO_3 and $CaCl_2$, they react to produce NaCl and $CaCO_3$.

The reaction reaches a point after which no further changes occur in the amounts of these species. Such a condition is called a state of **equilibrium.** Although a system at equilibrium appears static on a macroscopic level, it is important to remember that the forward and reverse reactions still occur. A reaction at equilibrium exists in a “steady state,” in which the rate at which any species forms equals the rate at which it is consumed.

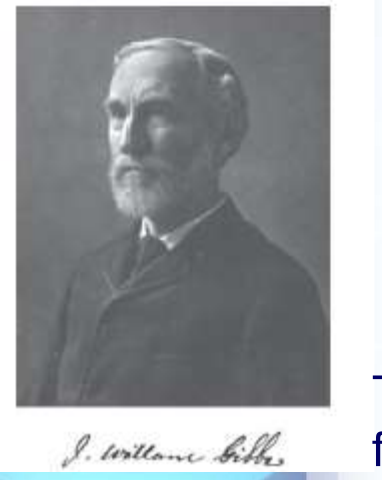
! A system is at equilibrium when the concentrations of reactants and products remain constant.

Thermodynamics and Equilibrium Chemistry

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

By convention, species to the left of the arrows are called reactants, and those on the right side of the arrows are called products. As Berthollet discovered, writing a reaction in this fashion does not guarantee that the reaction of A and B to produce C and D is favorable. Depending on initial conditions, the reaction may move to the left, to the right, or be in a state of equilibrium. Understanding the factors that determine the final position of a reaction is one of the goals of chemical thermodynamics.

The tendency for a reaction to occur is defined thermodynamically from its change in **enthalpy (*H*) *and entropy (S).***



J. Willard Gibbs (1839–1903) was the founder of chemical thermodynamics. He introduced the concept of free energy, now universally called Gibbs free energy in his honor.

Gibb's free energy

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

A thermodynamic function for systems at constant temperature and pressure that indicates whether or not a reaction is favorable ($\Delta G < 0$), *unfavorable* ($\Delta G > 0$), *or at equilibrium* ($\Delta G = 0$).

Enthalpy is a measure of the net flow of energy, as heat, during a chemical reaction. Reactions in which heat is produced have a negative ΔH *and are called* exothermic. Endothermic reactions absorb heat from their surroundings and have a positive ΔH. ***Entropy*** is a measure of randomness, or disorder.

The sign of ΔG *can be used to predict the direction in which a reaction moves* to reach its equilibrium position. A reaction is always thermodynamically favored when enthalpy decreases and entropy increases. Substituting the inequalities $\Delta H < 0$ and $\Delta S > 0$ *into equation shows that* ΔG *is negative when a reaction is thermodynamically* favored. When ΔG *is positive, the reaction is unfavorable as written* (although the reverse reaction is favorable). Systems at equilibrium have a ΔG of zero. As a system moves from a nonequilibrium to an equilibrium position, ΔG *must* change from its initial value to zero. At the same time, the species involved in the reaction undergo a change in their concentrations. The Gibb's free energy, therefore, must be a function of ***the concentrations*** of reactants and products.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

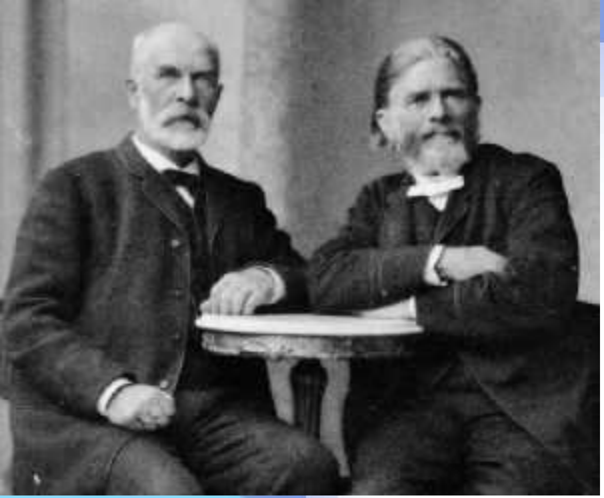
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

ΔG°, *is the change in Gibb's free energy under* ***standard-state conditions;*** defined as a temperature of 298 K, all gases with partial pressures of 1 atm, all solids and liquids pure, and all solutes present with 1 M concentrations. The reaction quotient, *Q, accounts for nonstandard-state pressures* or concentrations.

At equilibrium the Gibb's free energy is zero

$$\Delta G^\circ = -RT \ln K$$

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



In 1863 Guldberg and Waage described what we now call the *law of mass action*

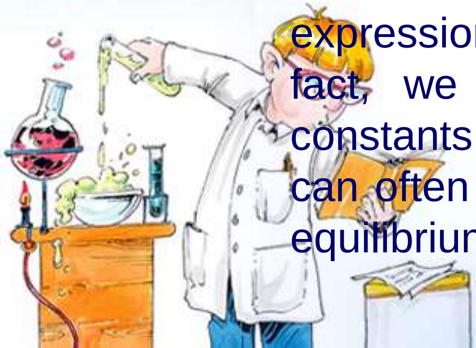
$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}[B]^b_{eq}}$$

Equilibrium-Constant
Expressions

The constant *K is a temperature-dependent numerical quantity* called the ***equilibrium constant****. By convention, the concentrations of the products, as the equation is written, are always placed in the numerator and the concentrations of* the reactants are always in the denominator.

The influence of concentration or pressure (if the participants are gases) on the position of a chemical equilibrium is conveniently described in quantitative terms by means of an equilibrium-constant expression. These expressions are derived from thermodynamics. They are important because they allow us to predict the direction and completeness of chemical reactions. An equilibrium-constant expression, however, yields no information concerning the rate of a reaction. In fact, we sometimes find reactions that have highly favorable equilibrium constants but are of little analytical use because they are so slow. This limitation can often be overcome by the use of a catalyst, which speeds the approach to equilibrium without changing its position.



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Assume 0.10 mol of A is reacted with 0.20 mol of B in a volume of 1000 mL; $K = 1.0 \times 10^{10}$*. What are the equilibrium concentrations of A, B, and C?*

$$\mathrm{A} + 2\mathrm{B} \rightleftharpoons 2\mathrm{C} \qquad K = \frac{[\mathrm{C}]^2}{[\mathrm{A}][\mathrm{B}]^2}$$

$$\begin{array}{ccccc} \mathrm{A} & + & 2\mathrm{B} & \rightleftharpoons & 2\mathrm{C} \\ x & & 2x & & 0.20 - 2x \approx 0.20 \end{array}$$

For each mole of A that either reacts (or is produced), we produce (or remove) two moles of C, and consume (or produce) two moles of B. Substituting into the equilibrium constant expression,

$$\frac{(0.20)^2}{(x)(2x)^2} = 1.0 \times 10^{10}$$

$$\frac{0.040}{4x^3} = 1.0 \times 10^{10}$$

$$x = [\mathrm{A}] = \sqrt[3]{\frac{4.0 \times 10^{-2}}{4.0 \times 10^{10}}} = \sqrt[3]{1.0 \times 10^{-12}} = 1.0 \times 10^{-4} M$$

$$\mathrm{B} = 2x = 2.0 \times 10^{-4} M$$

$$A + B \rightleftharpoons C + D \qquad K = \frac{[C][D]}{[A][B]}$$

The initial concentration of A is 0.20 *M and that of B is 0.50 M, while C and D* are initially 0 *M. After the reaction has reached equilibrium, the concentrations of A* and B will be decreased and those of C and D will be increased. Let *x represent the* equilibrium concentration of C or the moles/liter of A and B reacting. Since we get one mole of D with each mole of C, the concentration of D will also be *x.* We may represent the *initial concentration of A and B as the* ***analytical concentrations,*** C_A and C_B*. The* ***equilibrium concentrations are [A] and [B].*** The concentrations of A and B will each be diminished by *x, that is,* $[A] = C_A - x$ *and* $[B] = C_B - x$*.*

! The equilibrium concentration is the initial (analytical) concentration minus the amount reacted.

Chemical Reactions: The Rate Concept

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

According to Guldberg and Waage, the rate of the forward reaction is equal to a constant times the concentration of each species raised to the power of the number of molecules participating in the reaction: that is

$$\text{Rate}_{fwd} = k_{fwd}[A]^a[B]^b$$

where rate$_{fwd}$ *is the rate of the forward reaction and* k_{fwd} *is the* ***rate constant,*** *which* is dependent on such factors as the temperature and the presence of catalysts.

Similarly, for the reverse reaction

$$\text{Rate}_{rev} = k_{rev}[C]^c[D]^d$$

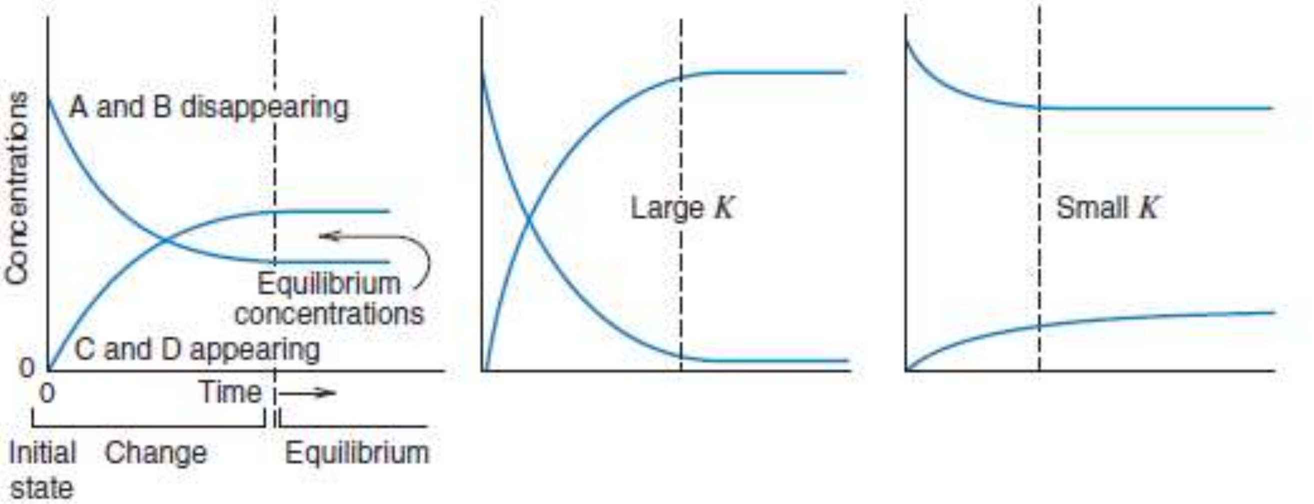
At equilibrium, the rate of the reverse reaction equals the rate of *the forward reaction.*

$$k_{fwd}[A]^a[B]^b = k_{rev}[C]^c[D]^d$$

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

The rate of chemical reaction is proportional to the product of active masses (concentrations) of reacting substances raised to a power of respective stoichiometrical coefficients at any moment in time

When the reaction between A and B is initiated, the rate of the forward reaction is large because the concentrations of A and B are large, whereas the backward reaction is slow because the concentrations of C and D are small (that rate is initially zero). As the reaction progresses, concentrations of A and B decrease and concentrations of C and D increase, so that the rate of the forward reaction diminishes while that for the backward reaction increases (Figure 6.1). Eventually, the two rates become equal, and the system is in a state of equilibrium. At this point, the individual concentrations of A, B, C, and D remain constant.



The larger the equilibrium constant, the farther to the right is the reaction at equilibrium.

A large equilibrium constant does not assure the reaction will proceed at an appreciable rate.

Types of equilibria:

I. A *homogeneous* equilibrium is an equilibrium that involves reactants and products in a single phase (in solution, particle):

- solutions of electrolytes;
- protolytic equilibrium (hydrolysis, buffer systems);
- complex compounds;
- red-ox systems.

II. *A heterogeneous* equilibrium is an equilibrium involving reactants and products in more than one phase:

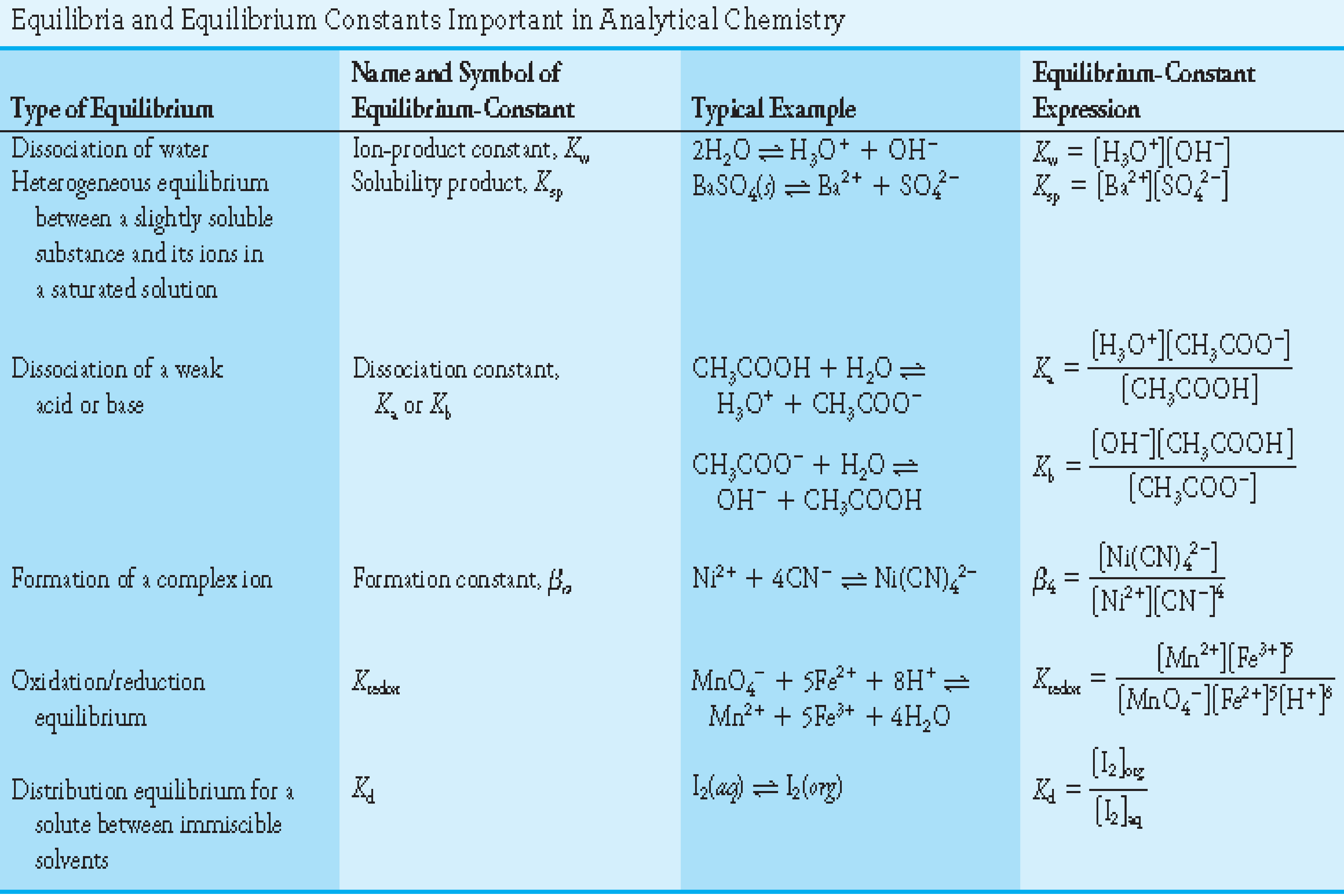
a) liquid–solid systems:

- saturated solution–precipitate (sediment);
- colloids;

b) liquid–liquid system:

- extraction.

Types of Equilibria Constants in Analytical Chemistry



Equilibria and Equilibrium Constants Important in Analytical Chemistry

Type of Equilibrium	Name and Symbol of Equilibrium-Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water	Ion-product constant, K_w	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	$K_w = [H_3O^+][OH^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, K_{sp}	$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ $CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$ $K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
Formation of a complex ion	Formation constant, β_n	$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$	$\beta_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$	$K_{redox} = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$

Le Chˆatelier’s Principle

The equilibrium concentrations of reactants and products can be altered by applyingstress to the system, for example, by changing the temperature, the pressure, or the concentration of one of the reactants. The effects of such changes can be predicted from **Le Chˆatelier’s principle,** which states that 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.

1. **Temperature Effects** on Equilibrium Constants

temperature has a pronounced effect on the rates of the forward and backward reactions involved in the equilibrium, and so it influences the *rate at which equilibrium is approached. This is* because the number and the energy of collisions among the reacting species increase with increasing temperature.

2. **Pressure Effects** on Equilibria

Pressure can have a large influence on the position of chemical equilibrium for reactions occurring in the gaseous phase. An increase in pressure favors a shift in the direction that results in a reduction in the volume of the system. But for reactions occurring in solutions, normal pressure changes have a negligible effect on the equilibrium because liquids cannot be compressed the way gases can.

3. Concentration Effects on Equilibria

The value of an equilibrium constant is independent of the concentrations of the reactants and products. However, the *position of equilibrium is very definitely influenced* by the concentrations. The direction of change is readily predictable from Le Chˆatelier’s principle. Consider the reaction of iron(III) with iodide:

$$3I^- + 2Fe^{3+} \rightleftharpoons I_3^- + 2Fe^{2+}$$

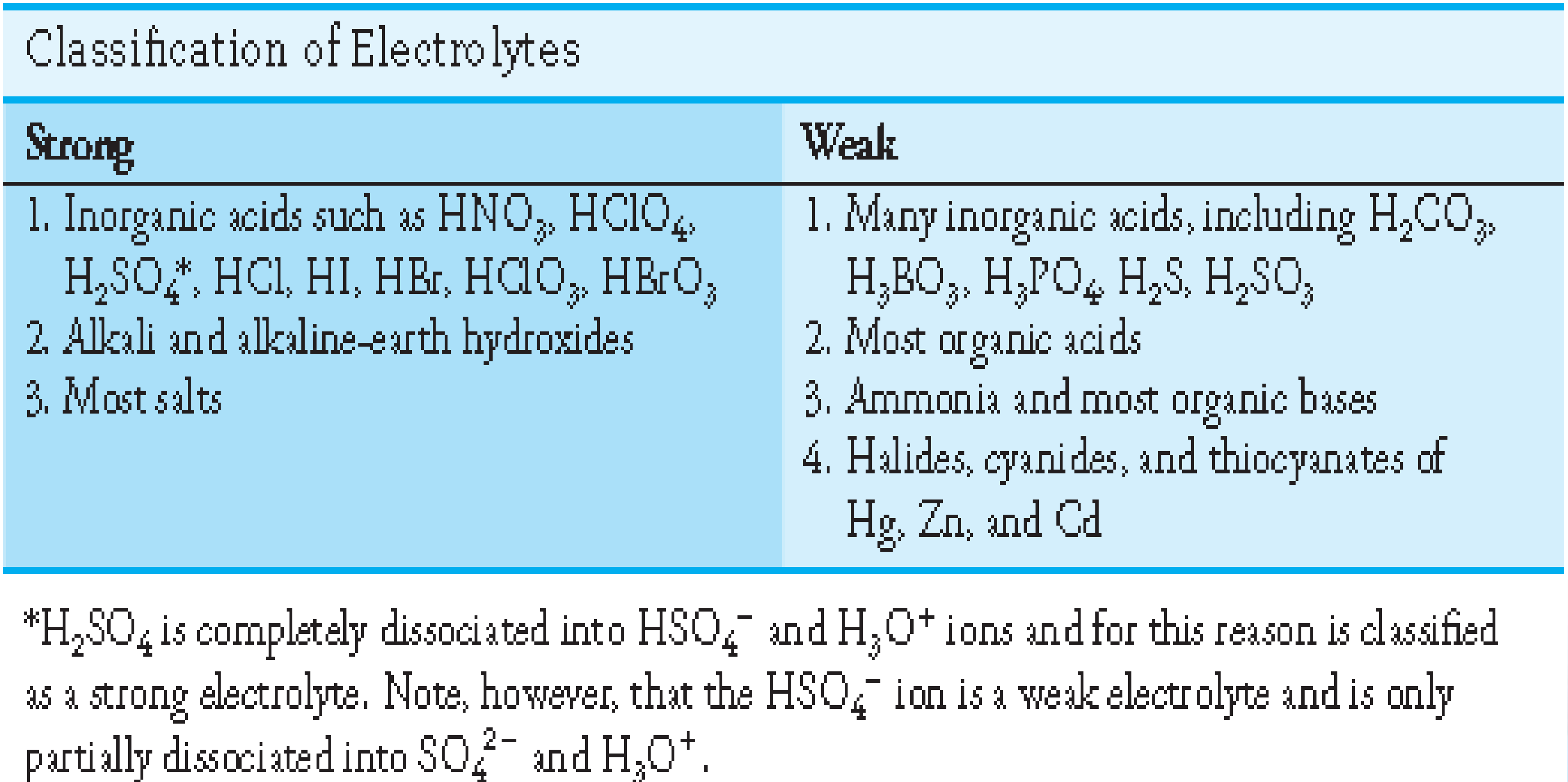
If the four components are in a state of equilibrium, as determined by the equilibrium constant, addition or removal of one of the components would cause the equilibrium to reestablish itself. For example, suppose we add more iron(II) to the solution. According to Le Chˆatelier’s principle, the reaction will shift to the left to relieve the stress. Equilibrium will eventually be reestablished, and its position will still be defined by the same equilibrium constant.

4. Catalysts

Catalysts either speed up or retard the rate at which an equilibrium is attained by affecting the rates of both the forward and the backward reactions. But catalysts affect both rates to the same extent and thus have ***no effect*** on the value of an equilibrium constant.

5. Equilibrium Constants for Dissociating or Combining Species—Weak Electrolytes

When a substance dissolves in water, it will often partially or completely dissociate or ionize. Electrolytes that tend to dissociate only partially are called ***weak electrolytes***, and those that tend to dissociate completely are ***strong electrolytes***. For example, acetic acid only partially ionizes in water and is therefore a weak electrolyte. But hydrochloric acid is completely ionized and is therefore a strong electrolyte.



Classification of Electrolytes

Strong	Weak
1. Inorganic acids such as HNO_3, $HClO_4$, H_2SO_4*, HCl, HI, HBr, $HClO_3$, $HBrO_3$	1. Many inorganic acids, including H_2CO_3, H_3BO_3, H_3PO_4, H_2S, H_2SO_3
2. Alkali and alkaline-earth hydroxides	2. Most organic acids
3. Most salts	3. Ammonia and most organic bases
	4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

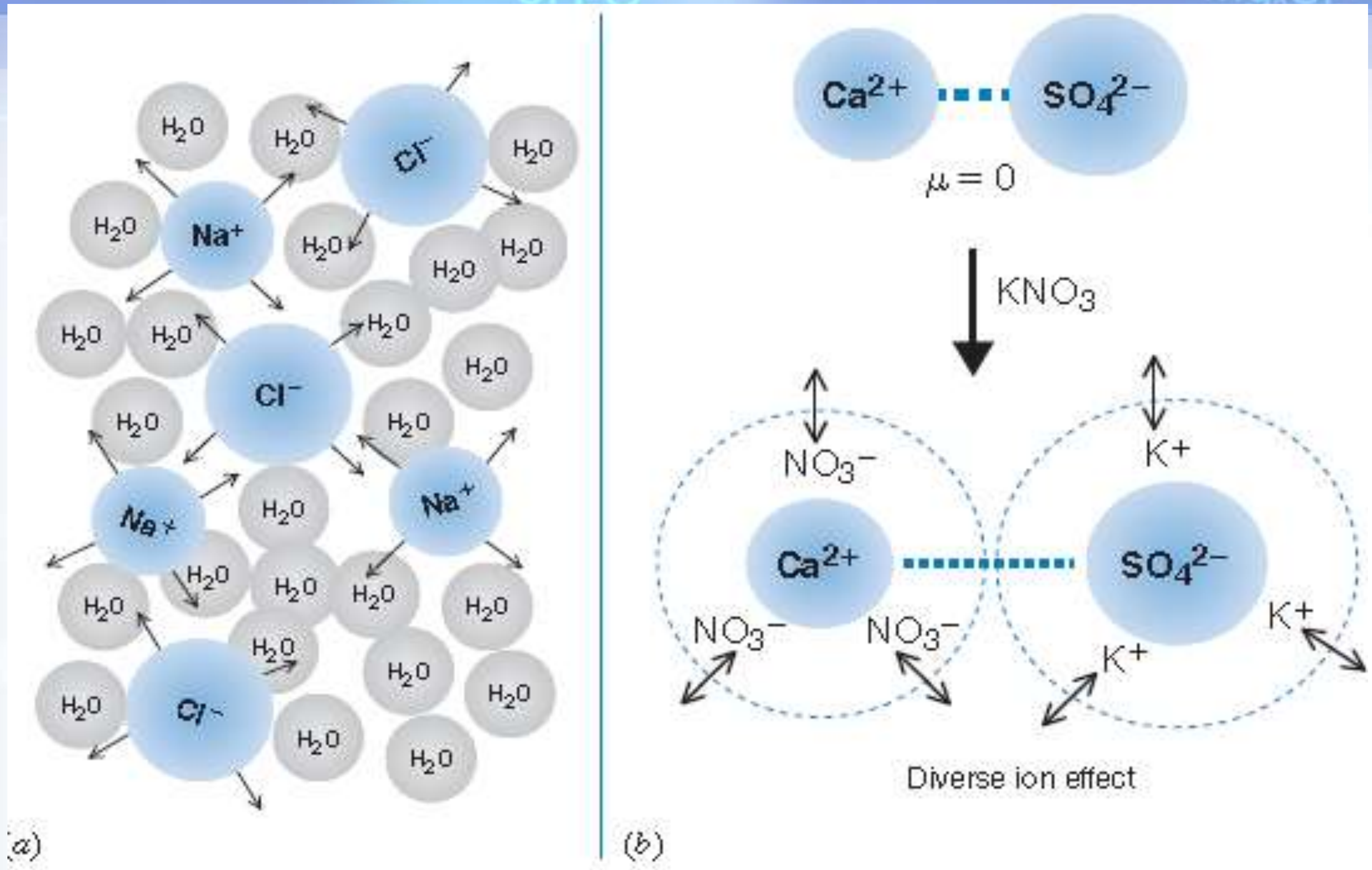
*H_2SO_4 is completely dissociated into HSO_4^- and H_3O^+ ions and for this reason is classified as a strong electrolyte. Note, however, that the HSO_4^- ion is a weak electrolyte and is only partially dissociated into SO_4^{2-} and H_3O^+.

The Effect of Electrolytes on Chemical Equilibria

Extensive studies have revealed that the magnitude of the electrolyte effect is highly dependent on the charges of the participants in an equilibrium. When only neutral species are involved, the position of equilibrium is essentially independent of electrolyte concentration. With ionic participants, the magnitude of the electrolyte effect increases with charge.

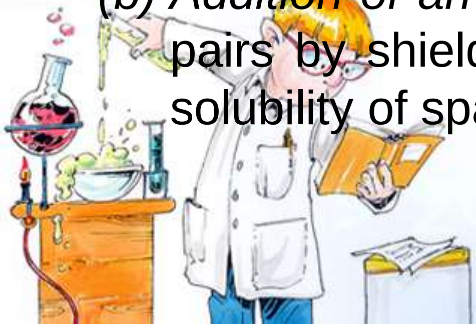
Generally, the presence of diverse salts (not containing ions common to the equilibrium involved) will cause an increase in dissociation of a weak electrolyte or in the solubility of a precipitate. Cations attract anions, and vice versa, and so the cations of the analyte attract anions of the diverse electrolyte and the anions of the analyte are surrounded by the cations of the diverse electrolyte. The attraction of the ions participating in the equilibrium of interest by the dissolved electrolyte effectively shields them, *decreasing their effective concentration and shifting the equilibrium. We say that an* “ion atmosphere” is formed about the cation and anion of interest. As the charge on either the diverse salt or the ions of the equilibrium reaction is increased, the diverse salt effect generally increases. This effect on the equilibrium is not predicted by Le Chˆatelier’s principle; but it is readily understood if you think in terms of the effective concentrations being changed.

This “effective concentration” of an ion in the presence of an electrolyte is called the **activity of the ion.**



(a) *In solution, Na^+ and* Cl^- from salt form an ion atmosphere where each ion type has ore of the oppositely charged ions as nearest neighbors. The structure is very dynamic in nature (all species are rapidly shifting).

(b) *Addition of an inert salt, such as* KNO_3, decreases the attraction between ion pairs by shielding and reducing the effective charge and thus increases the solubility of sparingly soluble salts such as $CaSO_4$



a - activities, or effective concentrations, of the ions are less than their actual concentrations as a result of the electrical interaction of the ions in solution.

$$a_X = [X]\gamma_X$$

a_X - the activity of the species X, [X] - its molar concentration, and γ_X is a dimensionless quantity called the **activity coefficient.**

The concentration is usually expressed as molarity, and the activity has the same units as the concentration. The activity coefficient is dimensionless. The activity coefficient varies with the total number of ions in the solution and with their charge, and it is a correction for interionic attraction. *In dilute solution, less than 10^{-4}M, the activity coefficient of a simple electrolyte is near unity, and activity is approximately equal to* the concentration. As the concentration of an electrolyte increases, or as an extraneous salt is added, the activity coefficients of ions decrease, and the activity becomes less than the concentration. Note, however, that at much higher concentrations a different effect comes into play. Ions, especially cations, are hydrated in aqueous solution and the associated water of solvation becomes unavailable to function as solvent. This causes the activity coefficient to reach a minimum as a function of concentration and at very high concentrations; it has a value greater than unity.

1. The activity coefficient of a species is a measure of the effectiveness with which that species influences an equilibrium in which it is a participant. In very dilute solutions in which the ionic strength is minimal, this effectiveness becomes constant, and the activity coefficient is unity. Under these circumstances, the activity and the molar concentration are identical (as are thermodynamic and concentration equilibrium constants). As the ionic strength increases, however, an ion loses some of its effectiveness, and its activity coefficient decreases.

2. In solutions that are not too concentrated, the activity coefficient for a given species is independent of the nature of the electrolyte and dependent only on the ***ionic strength***.

3. For a given ionic strength, the activity coefficient of an ion decreases more dramatically from unity as the charge on the species increases.

4. The activity coefficient of an uncharged molecule is approximately unity, no matter what the level of ionic strength.

5. At any given ionic strength, the activity coefficients of ions of the same charge are approximately equal. The small variations among ions of the same charge can be correlated with the effective diameter of the hydrated ions.

The mean activity coefficient of the electrolyte A*mBn is defined as*

$$\gamma_{\pm} = \text{mean activity coefficient} = (\gamma_A^m \gamma_B^n)^{1/(m+n)}$$

The mean activity coefficient can be measured in any of several ways, but it is impossible experimentally to resolve this term into the individual activity coefficients for γ_A and γ_B.

Systematic studies have shown that the effect of added electrolyte on equilibria is *independent* of the chemical nature of the electrolyte but depends on a property of the solution called the ***ionic strength*****.**

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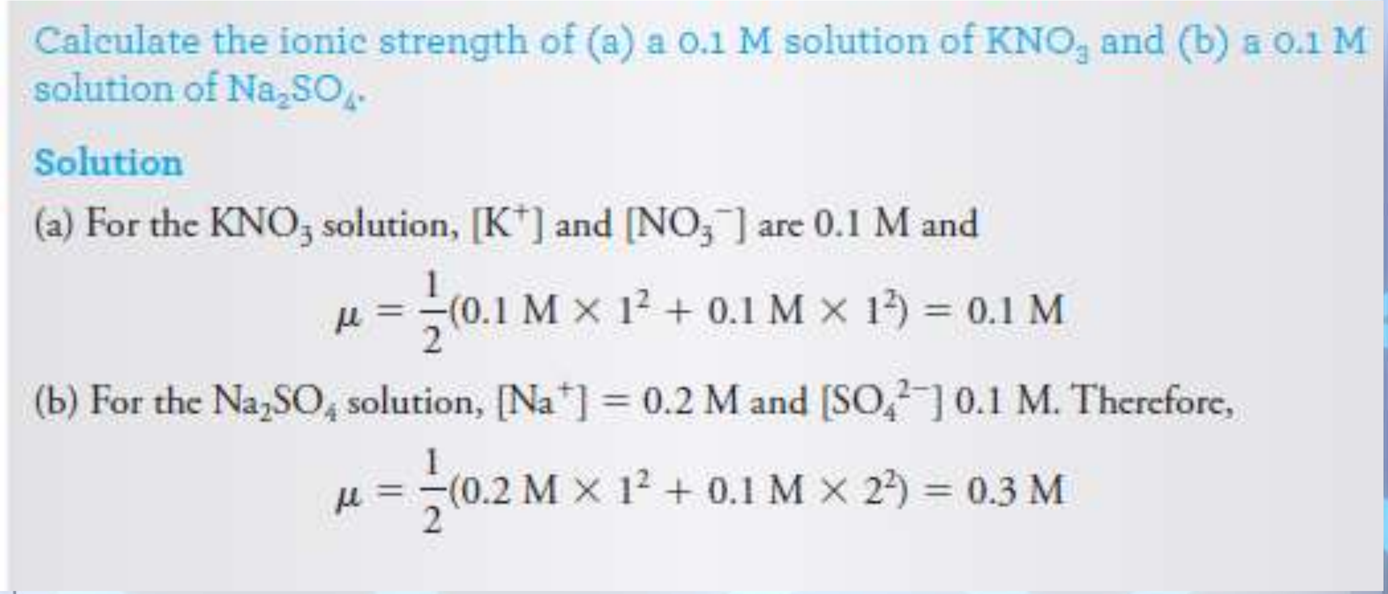
$$\mu = \frac{1}{2}\sum_i c_i z_i^2$$

where *μ is the ionic strength and Z_i is the charge on each individual ion. All cations* and anions present in solution are included in the calculation.

In 1921 Lewis and Randall first introduced the empirical concept of ionic strength and showed that in dilute solution, the logarithm of the activity coefficient is proportional to the square root of the ionic strength.

Higher charged ions contribute more to the ionic strength.



Calculate the ionic strength of (a) a 0.1 M solution of KNO_3 and (b) a 0.1 M solution of Na_2SO_4.

Solution

(a) For the KNO_3 solution, $[K^+]$ and $[NO_3^-]$ are 0.1 M and

$$\mu = \frac{1}{2}(0.1\ \mathrm{M} \times 1^2 + 0.1\ \mathrm{M} \times 1^2) = 0.1\ \mathrm{M}$$

(b) For the Na_2SO_4 solution, $[Na^+] = 0.2$ M and $[SO_4^{2-}]$ 0.1 M. Therefore,

$$\mu = \frac{1}{2}(0.2\ \mathrm{M} \times 1^2 + 0.1\ \mathrm{M} \times 2^2) = 0.3\ \mathrm{M}$$

If more than one salt is present, then the ionic strength is calculated from the total concentration and charges of all the different ions. For any given electrolyte, the ionic strength will be proportional to the concentration. Strong acids that are completely ionized are treated in the same manner as salts. If the acids are partially ionized, then the concentration of the ionized species must be estimated from the ionization constant before the ionic strength is computed. Very weak acids can usually be considered to be nonionized and do not contribute to the ionic strength.

In 1923, Dutch physicist Petrus (Peter) Debye (1884–1966), together with his assistant Erich Huckel (1896–1980), developed the Debye-Huckel theory of electrolyte solutions, an improvement of Svante Arrhenius's theory of electrical conductivity in electrolytic solutions. Peter Debye (1884–1966) was born and educated in Europe but became professor of chemistry at Cornell University in 1940. He was noted for his work in several distinct areas of chemistry, including electrolyte solutions, X-ray diffraction, and the properties of polar molecules. He received the 1936 Nobel Prize in Chemistry.


Erich A. A. J. Huckel


Peter J. W. Debye

CALCULATION OF ACTIVITY COEFFICIENTS

1. The Debye-Huckel Limiting Law

When m is less than 0.01 M

$$-\log \gamma_X = 0.51\, Z_X^2 \sqrt{\mu}.$$

2. Extended Debye–Huckel equation

When μ is 0.1-0.01 M

$$-\log \gamma_X = \frac{0.51 Z_X^2 \sqrt{\mu}}{1 + 3.3 \alpha_X \sqrt{\mu}}$$

A=0.51 and B = 0.33 are constants; a_x is the ion size parameter, which is the effective diameter of the hydrated ion in angstrom units, A°, γ_X - activity coefficient of the species X,*Z_X - charge on the species X,* μ - ionic strength of the solution

3. Davies modification

For higher ionic strengths

0.2–0.5

$$-\log f_i = 0.51 Z_i^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\, \mu \right)$$

Ion Size Parameters for Common Ions

Ion	Ion size parameter Å (Angstroms)
H^+	9
$(C_3H_7)_4N^+$	8
$(C_3H_7)_3NH^+$, $\{OC_6H_2(NO_3)_3\}^-$	7
Li^+, $C_6H_5COO^-$, $(C_2H_5)_4N^+$	6
$CHCl_2COO^-$, $(C_2H_5)_3NH^+$	5
Na^+, IO_3^-, HSO_3^-, $(CH_3)_3NH^+$, $C_2H_5NH_3^+$	4–4.5
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	3
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	2.5
Mg^{2+}, Be^{2+}	8
Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}	6
Sr^{2+}, Ba^{2+}, Cd^{2+}, $H_2C(COO)_2^{2-}$	5
Hg_2^{2+}, SO_4^{2-}, CrO_4^{2-}	4
Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}	9
$Citrate^{3-}$	5
PO_4^{3-}, $Fe(CN)_6^{3-}$, $\{CO(NH_3)_6\}^{3+}$	4
Th^{4+}, Zr^{4+}, Ce^{4+}	11
$Fe(CN)_6^{4-}$	5

Calculate the activity coefficients for K^+ and $SO_4{}^{2-}$ in a 0.020 *M* solution of potassium sulfate.

Solution

The ionic strength is 0.060, so we would use Equation 6.19b. From Table 6.2, we find that $a_{K^+} = 3$ Å and $a_{SO_4{}^{2-}} = 4.0$ Å. For K^+, we can use Equation 6.20:

$$-\log f_{K^+} = \frac{0.51(1)^2\sqrt{0.060}}{1+\sqrt{0.060}} = 0.10_1$$

$$f_{K^+} = 10^{-0.101} = 10^{-1} \times 10^{0.899} = 0.79_4$$

For $SO_4{}^{2-}$, use Equation 6.19b:

$$-\log f_{SO_4{}^{2-}} = \frac{0.51(2)^2\sqrt{0.060}}{1+0.33 \times 4.0\sqrt{0.060}} = 0.37_8$$

$$f_{SO_4{}^{2-}} = 10^{-1} \times 10^{0.62_2} = 0.41_9$$

Solving Multiple-Equilibrium Problems

(1) equilibrium-constant expressions,
(2) *mass-balance equations, and*
(3) a single charge-balance equation.

Mass-balance equations relate the *equilibrium concentrations of various species in* a solution to one another and to the *analytical concentrations of the various solutes.*

An equation stating that matter is conserved, and that the total amount of a species added to a solution must equal the sum of the amount of each of its possible forms present in solution.

Charge-balance equation **-** solutions are neutral because the *molar concentration of positive charge in an electrolyte solution always equals the molar concentration of negative charge.*

An equation stating that the total concentration of positive charge in a solution must equal the total concentration of negative charge.

Write the equations of mass balance for $[Ag(NH_3)_2]Cl$ *solution*

The equilibria are

$$[Ag(NH_3)_2]Cl \rightarrow Ag(NH_3)_2^+ + Cl^-$$

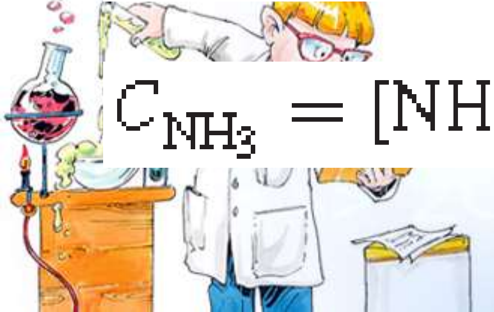
$$Ag(NH_3)_2^+ \rightleftharpoons Ag(NH_3)^+ + NH_3$$

$$Ag(NH_3)^+ \rightleftharpoons Ag^+ + NH_3$$

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

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$C_{Ag} = [Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+]$$



$$C_{NH_3} = [NH_4^+] + [NH_3] + [Ag(NH_3)^+] + 2[Ag(NH_3)_2^+]$$

Write a charge-balance equation for solution of sodium chloride.

$$[Na^{+}] + [H_3O^{+}] = [Cl^{-}] + [OH^{-}]$$

Consider a solution that has magnesium chloride

$$2[Mg^{2+}] + [H_3O^{+}] = [Cl^{-}] + [OH^{-}]$$

Write a mass balance and charge balance equations for a 0.10 M solution of $NaHCO_3$.

It is easier to keep track of what species are in solution if we write down the reactions that control the solution’s composition. These reactions are the dissolution of a soluble salt

$NaHCO_3(s)$ ® $Na^+_{(aq)} + HCO_3^-{}_{(aq)}$

and the acid–base dissociation reactions of HCO_3^- and H_2O

$HCO_3^- + H_2O$ □ $H_3O+(aq) + CO_3^{2-}$

$HCO_3^- + H_2O$ □ $OH^- + H_2CO_3$

$2\ H_2O$ □ $H_3O^+ + OH^-$

The mass balance equations are

$0.10\ M = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

$0.10\ M = [Na^+]$

The charge balance equation is

$[Na^+] + [H_3O^+] = [OH^-] + [HCO_3^-] + 2$ ´ $[CO_3^{2-}]$

The thermodynamic equilibrium constant:

Thermodynamic equilibrium constants hold at all ionic strengths.

$$K^\circ_{eq} = \frac{a_A \cdot a_B}{a_{AB}} = \frac{[A]f_A \cdot [B]f_B}{[AB]f_{AB}}$$

$$K^\circ_{eq} = K_{eq}\frac{f_A \cdot f_B}{f_{AB}}$$

The concentration equilibrium constant:

Concentration equilibrium constants must be corrected for ionic strength.

$$K_{eq} = K^\circ_{eq}\frac{f_{AB}}{f_A \cdot f_B}$$

K_{eq} = K°_{eq} at zero ionic strength, but at appreciable ionic strengths, a value for K_{eq} *must be calculated for each ionic strength.*