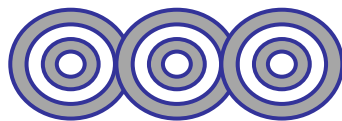# Fundamentals of Analytical Chemistry

Chemical Equilibrium

Ahmad Aqel Ifseisi
Assistant Professor of Analytical Chemistry
College of Science, Department of Chemistry
King Saud University
P.O. Box 2455 Riyadh 11451 Saudi Arabia
Building: 05, Office: 2A/149 & AA/53
Tel. 014674198, Fax: 014675992
Web site: http://fac.ksu.edu.sa/aifseisi
E-mail: ahmad3qel@yahoo.com
**   aifseisi@ksu.edu.sa**

Chemical equilibrium occurs when opposing reactions are proceeding at equal rates: The rate at which the products are formed from the reactants equals the rate at which the reactants are formed from the products. As a result, concentrations cease to change, making the reaction appear to be stopped.

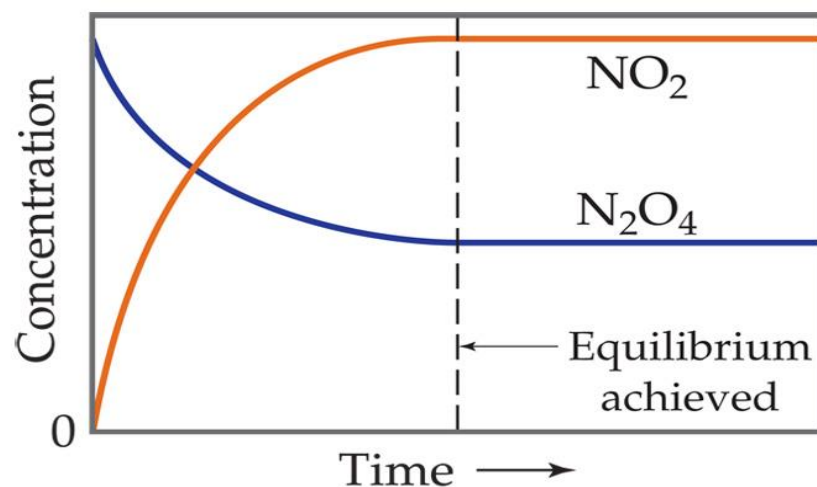$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
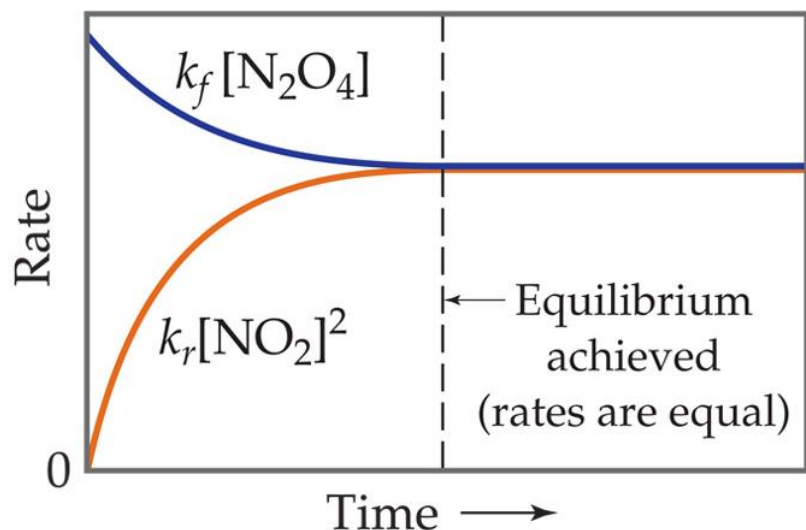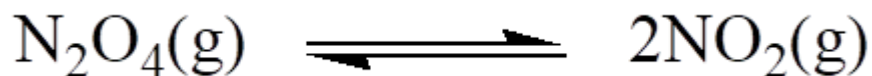
As a system approaches equilibrium, both the forward and reverse reactions are occurring.

At equilibrium, the forward and reverse reactions are proceeding at the same rate.

Once equilibrium is achieved, the amount of each reactant and product (concentrations) remains constant.

Since, in a system at equilibrium, both the forward and reverse reactions are being carried out, we write its equation with a double arrow.

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

Colorless   **Brown**

The equilibrium mixture results because the reaction is **reversible**.

Forward reaction: $N_2O_4(g) \longrightarrow 2\,NO_2(g)$ $Rate_f = k_f[N_2O_4]$

Reverse reaction: $2\,NO_2(g) \longrightarrow N_2O_4(g)$ $Rate_r = k_r[NO_2]^2$

Where k_f and k_r are the rate constants for the forward and reverse reactions. At equilibrium, the rate at which products are produced from reactants equals the rate at which reactants are produced from products:

$$\underset{\text{Forward reaction}}{k_f[N_2O_4]} = \underset{\text{Reverse reaction}}{k_r[NO_2]^2}$$

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

At equilibrium the ratio of the concentration terms involving N_2O_4 and NO_2 equals a constant (called equilibrium constant).

Consider the following general chemical reaction:

$$aA + bB \rightarrow cC + dD$$

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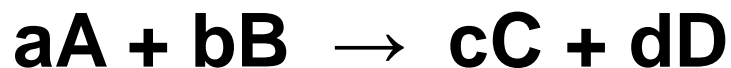$$\text{Rate}_{rev} = k_{rev} [C]^c [D]^d$$

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

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

Rearranging these equations gives the molar equilibrium constant (which holds for dilute solutions) for the reaction, K:

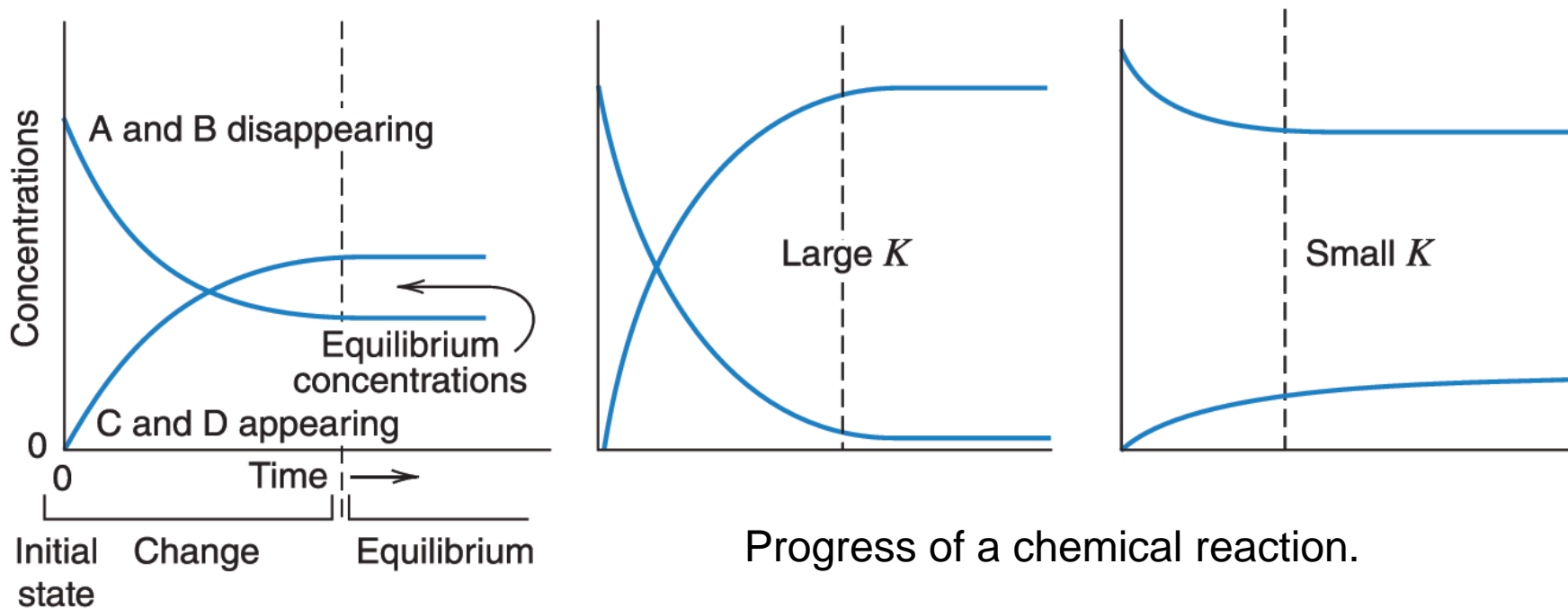$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{k_{fwd}}{k_{rev}} = K$$

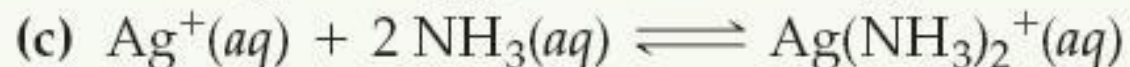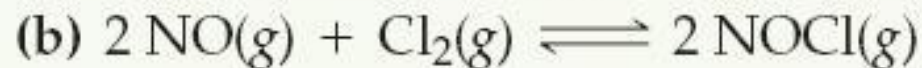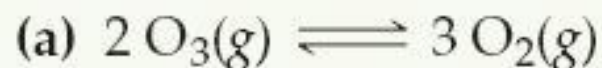$$aA + bB \rightarrow cC + dD \qquad K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The value of K can be calculated empirically by measuring the concentrations of A, B, C, and D at equilibrium.

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

Progress of a chemical reaction.

Example

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

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

Types of Equilibria

We can write equilibrium constants for virtually any type of chemical process.

Some common equilibria are listed in the Table. The equilibria may represent **dissociation** (acid/base, solubility), **association** or formation of products (complexes), **reactions** (redox), a **distribution** between two phases (water and nonaqueous solvent-solvent extraction; adsorption from water onto a surface, as in chromatography, etc.).

Types of Equilibria

Equilibrium	Reaction	Equilibrium Constant
Acid–base dissociation	$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_a, acid dissociation constant
Solubility	$MA \rightleftharpoons M^{n+} + A^{n-}$	K_{sp}, solubility product
Complex formation	$M^{n+} + aL^{b-} \rightleftharpoons ML_a^{(n-ab)+}$	K_f, formation constant
Reduction–oxidation	$A_{red} + B_{ox} \rightleftharpoons A_{ox} + B_{red}$	K_{eq}, reaction equilibrium constant
Phase distribution	$A_{H_2O} \rightleftharpoons A_{organic}$	K_D, distribution coefficient

Equilibrium Constants and Units

Equilibrium constants are reported without units. Equilibrium constants derived from thermodynamic measurements are defined in terms of **activities** rather than **concentrations** or **partial pressures**.

$$a_i = C_i f_i$$

a_i: activity of an ion
C_i: the concentration of the ion i
f_i: activity coefficient

The activity of any substance is the ratio of the concentration or pressure of the substance to a reference concentration (1 M) or a reference pressure (1 atm).

For pure solids and pure liquids, the situation is even simpler because the activities then merely equal 1 (again with no units).

In real systems, activities are also ratios that have no units. As a result, the thermodynamic equilibrium constant derived from them also has no units. Therefore, the equilibrium constants without units as well.

Heterogeneous Equilibria

The concentrations of **solids** and **liquids** are essentially **constant**

The concentration of both solids and liquids can be obtained by multiplying the density of the substance by its molar mass, and both of these are constants at constant temperature. Therefore, the concentrations of **solids** and **liquids** do not appear in the equilibrium expression.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$$

$$K_c = [Pb^{2+}]\,[Cl^-]^2$$

The omission of pure solids and liquids from equilibrium-constant expressions can be explained by the activity, which is a ratio of the concentration to a reference value. For a pure substance, the reference value is the concentration of the pure substance itself, so that the activity of any pure solid or liquid is always simply 1.
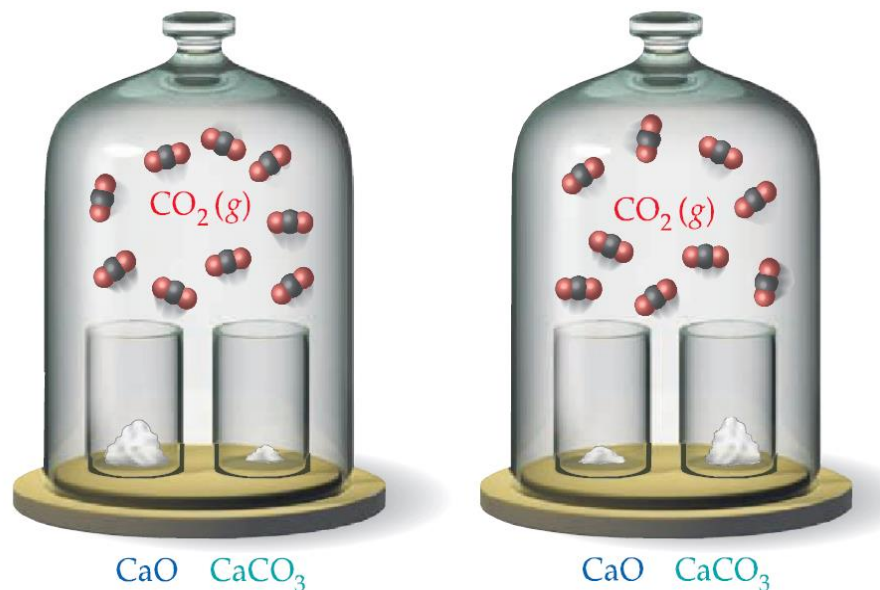
As a further example of a heterogeneous reaction, consider the decomposition of calcium carbonate:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

As long as some $CaCO_3$ or CaO remain in the system, the amount of CO_2 above the solid will remain the same.

The equilibrium-constant expression for the reaction is

$$K_c = [CO_2] \quad \text{and} \quad K_p = P_{CO_2}$$

CaO   CaCO₃   CaO   CaCO₃

The equilibrium involving $CaCO_3$ or CaO and CO_2 is a heterogeneous equilibrium. The equilibrium pressure of CO_2 is the same in the two bell jars as long as the two systems are at the same temperature, even though the relative amounts of pure $CaCO_3$ and CaO differ greatly.

When a solvent is involved as a reactant or product in an equilibrium, its concentration is also excluded from the equilibrium-constant expression, provided the concentrations of reactants and products are low, so that the solvent is essentially a pure substance.
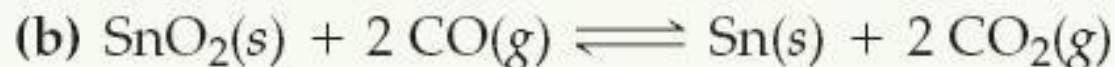
$$H_2O(l) + CO_3{}^{2-}(aq) \rightleftharpoons OH^-(aq) + HCO_3{}^-(aq)$$

Gives an equilibrium-constant expression in which $[H_2O]$ is excluded:

$$K_c = \frac{[OH^-][HCO_3{}^-]}{[CO_3{}^{2-}]}$$

Example

Write the equilibrium-constant expression for K_c for each of the following reactions:

(a) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$

(b) $SnO_2(s) + 2\,CO(g) \rightleftharpoons Sn(s) + 2\,CO_2(g)$

Solution

(a) The equilibrium-constant expression is

$$K_c = \frac{[CO]}{[CO_2][H_2]}$$

Because H_2O appears in the reaction as a pure liquid, its concentration does not appear in the equilibrium-constant expression.

(b) The equilibrium-constant expression is

$$K_c = \frac{[CO_2]^2}{[CO]^2}$$

Because SnO_2 and Sn are both pure solids, their concentrations do not appear in the equilibrium-constant expression.

Calculating Equilibrium Constants

A closed system initially containing 1.00×10^{-3} M H_2 and 2.00×10^{-3} M I_2 at 448 °C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M. Calculate K_c at 448 °C for the reaction taking place, which is :

$$H_{2\ (g)} + I_{2\ (g)} \rightleftharpoons 2\ HI_{(g)}$$

What Do We Know?

	$[H_2]$, M	$[I_2]$, M	$[HI]$, M
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At equilibrium			1.87×10^{-3}

[HI] Increases by 1.87×10^{-3} M

	$[H_2]$, M	$[I_2]$, M	$[HI]$, M
Initially	1.00×10^{-3}	2.00×10^{-3}	0
Change			$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half as much.

	$[H_2]$, M	$[I_2]$, M	$[HI]$, M
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-0.935×10^{-3}	-0.935×10^{-3}	$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

We can now calculate the equilibrium concentrations of all three compounds

	$[H_2]$, M	$[I_2]$, M	$[HI]$, M
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-0.935×10^{-3}	-0.935×10^{-3}	$+1.87 \times 10^{-3}$
At equilibrium	0.065×10^{-3}	1.065×10^{-3}	1.87×10^{-3}

and, therefore, the equilibrium constant

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})} = 51$$

Example

A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at 472 °C. The equilibrium mixture of gases was analyzed and found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data, calculate the equilibrium constant K_p for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
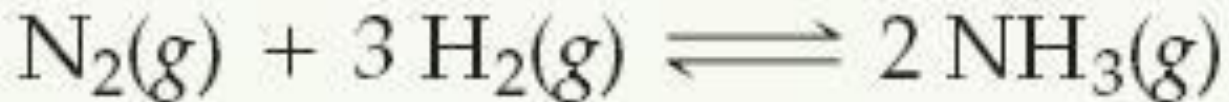
Solution

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$

Example

The chemicals A and B react as follows to produce C and D:

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

The equilibrium constant K has a value of 0.30. Assume 0.20 mol of A and 0.50 mol of B are dissolved in 1.00 L, and the reaction proceeds. Calculate the concentrations of reactants and products at equilibrium.

	[A]	[B]	[C]	[D]
Initial	0.20	0.50	0	0
Change (x = mmol/mL reacting)	$-x$	$-x$	$+x$	$+x$
Equilibrium	$0.20 - x$	$0.50 - x$	x	x

Substitute these values in the equilibrium constant expression and solve for x:

$$\frac{(x)(x)}{(0.20 - x)(0.50 - x)} = 0.30$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x^2 = (0.10 - 0.70x + x^2)0.30$$

$$= \frac{-0.21 \pm \sqrt{(0.21)^2 - 4(0.70)(-0.030)}}{2(0.70)}$$

$$0.70x^2 + 0.21x - 0.030 = 0$$

$$= \frac{-0.21 \pm \sqrt{0.044 + 0.084}}{1.40} = 0.11\ M$$

[A] = 0.20−x = 0.09 M
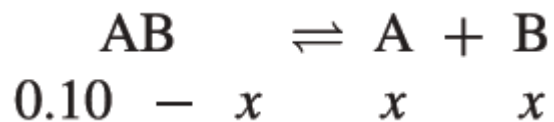[B] = 0.50−x = 0.39 M
[C] = [D] = x = 0.11 M

Example

Calculate the equilibrium concentrations of A and B in a 0.10 M solution of a weak electrolyte AB with an equilibrium constant of 3.0×10^{-6}.

Solution

$$AB \rightleftharpoons A + B \qquad K_{eq} = \frac{[A][B]}{[AB]}$$

Both [A] and [B] are unknown and equal. Let x represent their equilibrium concentrations. [AB] at equilibrium is equal to its initial analytical concentration minus x.

$$AB \rightleftharpoons A + B$$
$$0.10 - x \qquad x \qquad x$$

The value of K_{eq} is quite small, so we are probably justified in neglecting x compared to 0.10.

$$\frac{(x)(x)}{0.10} = 3.0 \times 10^{-6}$$

$$x = [A] = [B] = \sqrt{3.0 \times 10^{-7}} = 5.5 \times 10^{-4} M$$

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	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ $CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_a = \dfrac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$ $K_b = \dfrac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
Formation of a complex ion	Formation constant, β_n	$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$	$\beta_4 = \dfrac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$	$K_{redox} = \dfrac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \dfrac{[I_2]_{org}}{[I_2]_{aq}}$