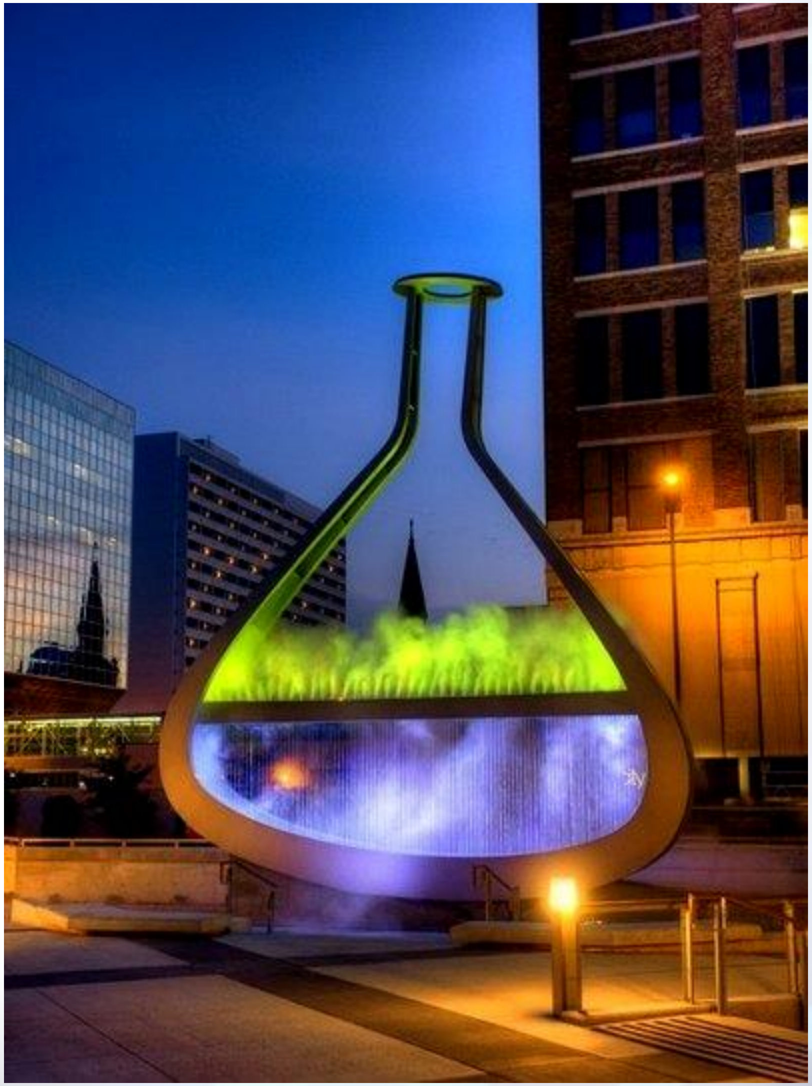
Analytical chemistry

Lecture № 5

Complexation equilibria
Part I



General Definitions Concerning Complexes

$[Co(NH_3)_6]Cl_3$

1893 year

Alfred Werner

According to the IUPAC, a *coordination entity, or complex, is composed of a central* atom, usually a metal atom, to which is attached a surrounding array of other atoms or groups of atoms, each of which is called a *ligand. The central atom is also called* the *nucleus.*

A complex (or coordination compound) is a compound, which consist either of complex ions with other ions of opposite charge or a neutral complex species.

Werner postulates

1. Complexes are built around a central element called the ***coordinator*** *element .*

2. Coordinator elements exhibit two kinds of valences: the principal or usual valence, which is ionic, and a secondary valence that is nonionic. The notion of principal ionic valence has been replaced by that of oxidation number. The oxidation number of the central element is defined as being the electrical charge it should bring if the electrons it shared with the ligands (within the complex) had been assigned to the more electronegative atom constituting a bond with the central element.

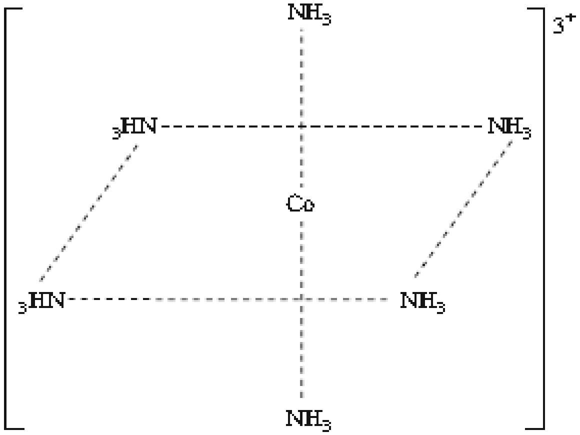
3. In a complex, the sum of the numbers of the principal and secondary valences is constant. This number is the coordination number, or the *coordinence, of the* metallic ion. It is the maximum number of monodentate ligands that can be bound to it.

4. According to Werner, ligands are spatially distributed around the metallic ion.

$$[Co^{III}(NH_3)_6]^{3+}$$

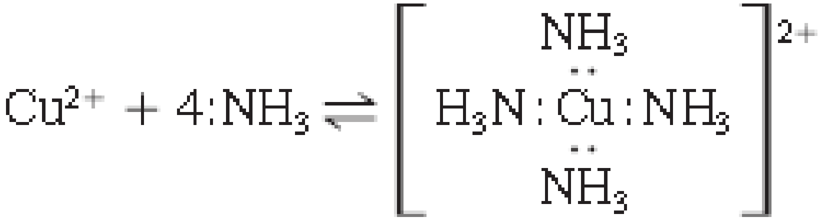
$$[Co^{III}(NH_3)_5Cl]^{2+}$$

Hg_2Cl_2



$$M^{n+} + \ddot{L}^{-} \rightleftharpoons ML^{(n-1)+}$$

Central atoms ligands
electron-acceptor electron-donor



$$Cu^{2+} + 4{:}NH_3 \rightleftharpoons \left[\begin{array}{c} NH_3 \\ \ddot{} \\ H_3N : Cu : NH_3 \\ \ddot{} \\ NH_3 \end{array}\right]^{2+}$$

The central atom of a complex is a Lewis acid and the ligands are Lewis bases. In otherwords, to use the language of organic chemists, we can say that central atoms are *electrophilic and ligands nucleophilic species.*

so ligands may be neutral molecules (such as H_2O or NH_3) or anions (such as CN^- or Cl^-) that have at least one atom with alone pair of electrons.

Rules of Nomenclature and Writing

The metal must be written first in the formula of a complex. It must be followed by the symbols of the ligands ranked according to their *electrical charges*, which must decrease in negativity from left to right. The entire complex must be enclosed in square brackets. The global electrical charge of the complex must be indicated outside the brackets as a right superscript, with the number before the sign.

Roman numerals indicate the oxidation state of the metal in the complex. To simplify the writing, some ligands may be represented by standard symbols in the formula. The symbol “en” represents the ligand ethylenediamine: ${}_2HN - CH_2 - CH_2 - NH_2$.

The rule concerning the names of the complexes is as follows: We must begin by listing the ligands in alphabetic order before writing the name of the central atom. The prefixes *mono, bi, tri, tetra, and so on are used in expressions of complexes. The* central nucleus is designated next. When the complex is an anion, the name of the central element must be terminated with the ending “ate,” whereas no distinguishing termination is used for cationic or neutral coordination entities. The oxidation number of the central atom is indicated by appending a Roman numeral to the central atom’s name. This number is enclosed in parentheses next to the name of the central atom. The net electrical charge must be written in Arabic figures outside the brackets. The neutral ligands must be designated by their usual names, and the anionic ones must have their usual names with the suffix “o.” Therefore, the ligands H_2O, NH_3, CO, NO, and OH^- are respectively named *aqua, ammine, carbonyl, nitroxyl, and hydroxo.*

$[Pt^{IV}(NH_3)_6]^{4+}$ hexammineplatinum(IV) cation

$[Pt^{II}(Cl_2)(NH_3)(H_2O)]$ ammineaquadichloroplatinum(II) complex
$[Al(H_2O)_6]^{3+}$ hexaaquaaluminium(III) cation,

$[Fe^{III}(CN)_5(NO)]_2^{-}$ pentacyanonitrosylferrate(III) anion,

$[Cu^{II}(en)_3]^{2+}$ tris-(ethylenediamine)copper(II) cation,

$[Cr^{III}(NCS)_4(NH_3)_2]^{-}$ diamminetetraisothiocynatochromate(III).

$[Cd^{II}I_3]^{-}$ triiodocadmiate(II)

Electrical Charge of an Ion Complex

The electrical charge of an ion complex is equal to the algebraic sum of the charges of the central ion and the ligands. For example, in the case of the hexacyanoferrate(III) complex

$[Fe(CN)_6]^{3-}$

the iron atom is supposed to be at oxidation state +III and the cyanide at the state −I, as in potassium cyanide.

The number of covalent bonds that a cation tends to form with electron donors is its **coordination number. Typical values for coordination numbers are two, four,** and six.

Dentate - the number of coordination points with the central ion (the number of electron-donating groups). If there is only one coordination point, the ligand is said to be *monodentate; otherwise,* it is called *bidentate ("two-toothed"), etc. More generally, it is described as polydentate.*

$[Ag(NH_3)_2]^+$

Cn = 2

$[Ag(S_2O_3)_2]^{3-}$

cn = 4

Some Monodentate Ligands

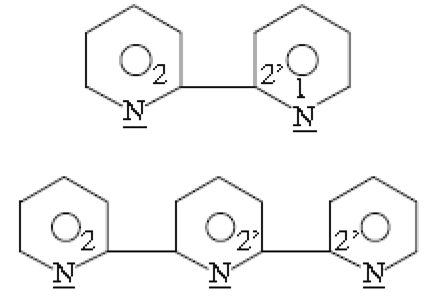
- **mineral anions, such as cyanide CN^-, thiocyanate SCN^-, fluoride F^-, chloride Cl^-, bromide Br^-, iodide I^-, azide N_3^-, isocyanate NCO^-, hydroxide OH^-, nitrite NO_2^-, nitrate NO_3^-, isothiocyanate NCS^-, sulfide S^{2-}, carbonate CO_3^{2-},sulfate SO_4^{2-}, and thiosulfate $S_2O_3^{2-}$ ions;**

- **organic anions, such as amidure NR_2^-, alcoolate RO^-, carboxylate $RCOO^-$, and thiolate RS^- ions;**

- **mineral molecules, such as ammoniac NH_3 and water H_2O;**

- **organic molecules, such as pyridine, aniline, phosphines PR_3, phosphites $P(OR)_3$, and arsines AsR_3.**

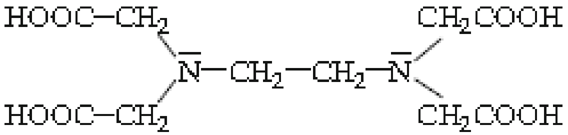
Some Polydentate Ligands



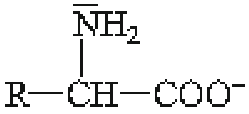
- dipyridine and terpyridine, which coordinate to the central atom through the electron pairs of the nitrogen atoms:
- ethylenediamine (en), which is bidentate:

$$_2HN - CH_2 - CH_2 - NH_2;$$

- ethylenediaminetetraacetic acid (H_4EDTA) and its derivatives. hexadentate (four pairs brought by carboxylate groups and two brought by nitrogen atoms).



- α-amino acids, which are bidentate through the lone electron pair of the nitrogen atom and through the carboxylate rest;

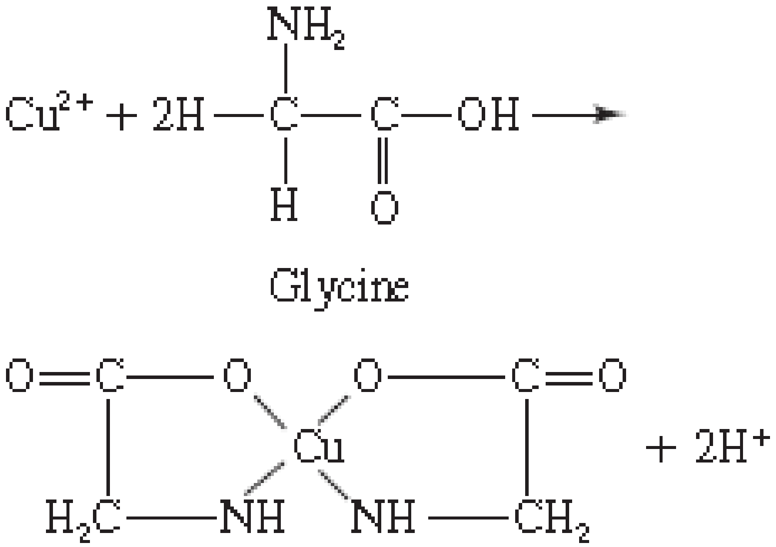


$$R-\overset{\overset{\overline{N}H_2}{|}}{C}H-COO^-$$

- acids-alcohols, such as tartaric acids COOH–CHOH–CHOH–COOH, citric acid COOH–CH2–C(OH) (COOH)–CH2–COOH, and malic acid COOH–CH2–CH(OH)–COOH;

An organic agent that has two or more groups capable of complexing with a metal ion is called a **chelating agent. The complex formed is called a chelate. The chelating** agent is called the *ligand.*

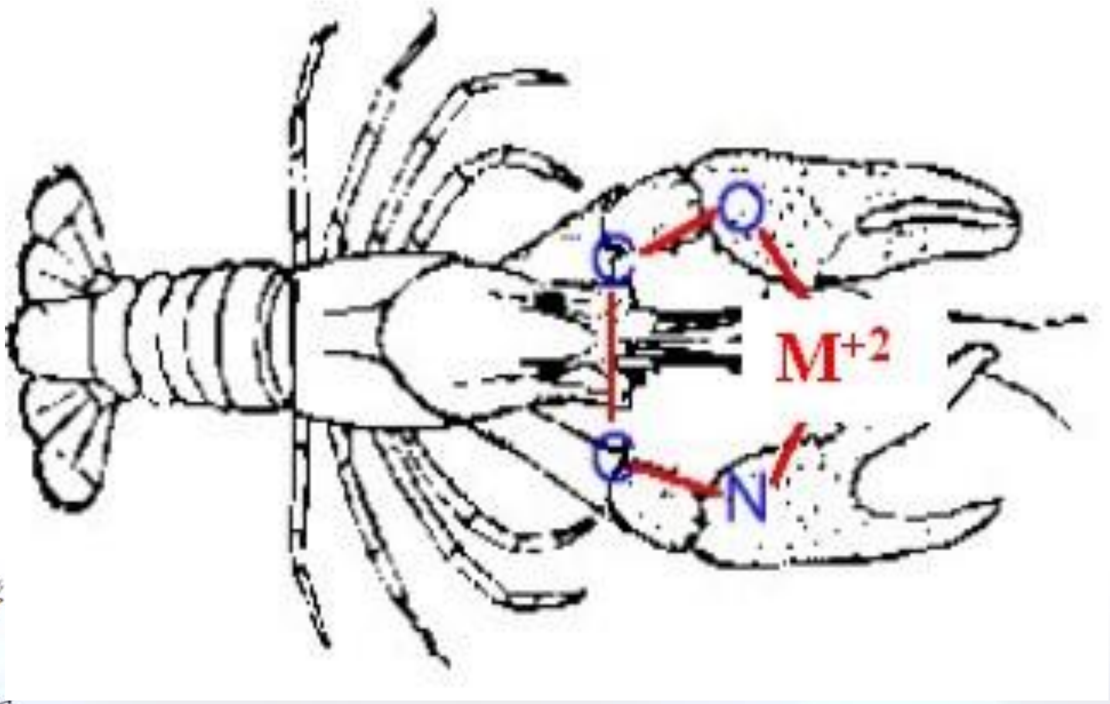
A chelate is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five- or six-membered heterocyclic ring.



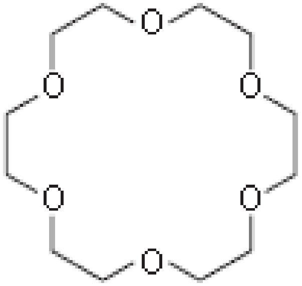
Cu^{2+} complex with glycine.

Species with two or more nuclei that are good Lewis bases are potential chelate ligands.

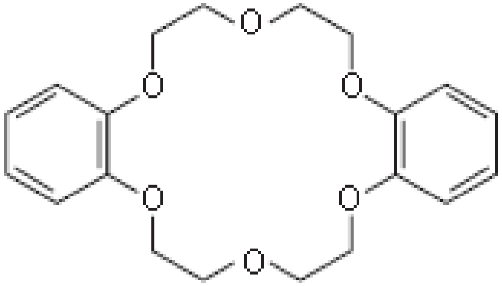
The term *chelate* was first applied in 1920 by Sir Gilbert T. Morgan and H.D.K. Drew, who stated: "The adjective chelate, derived from the great claw or chela (*Greek:* chely) of the lobster or other crustaceans, is suggested for the caliper-like groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings." This term is generic for all ligands which have at least two atoms



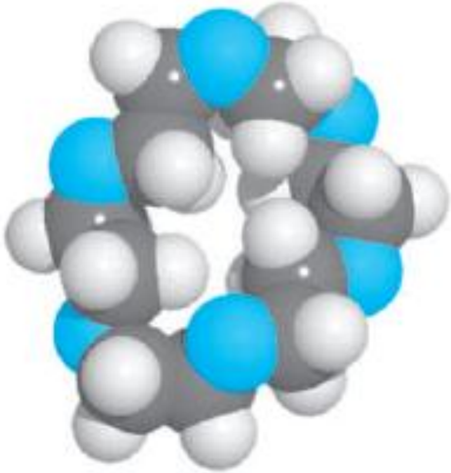
Macrocycles - type of complex is formed between metal ions and cyclic organic compounds**. These molecules contain nine or** more atoms in the cycle and include at least three heteroatoms, usually oxygen, nitrogen or sulfur. Crown ethers, such as 18-crown-6 and dibenzo-18-crown-6 are examples of organic macrocycles.



18-crown-6



dibenzo-18-crown-6



Molecular model of 18-crown-6. This crown ether can form strong complexes with alkali metal ions. The formation constants of the Na^+, K^+, and Rb^+ complexes with 18-crown-6 are in the 10^5 to 10^6 range.

The most important complex compounds with inorganic ligands, used in analysis

1. Ammonia:

– selection (colourless complex): $[Ag(NH_3)_2]^+$, $[Zn(NH_3)_4]^{2+}$, $[Cd(NH_3)_4]^{2+}$;

– detection (coloured complex): $[Cu(NH_3)_4]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Ni(NH_3)_4]^{2+}$.

2. Halogen and rhodanide:

– selection with extraction in inorganic solvents;

– detection (coloured complex): $[Fe(SCN)_3]^{3-}$, $[BiJ_4]^-$, $[CoCl_4]^{2-}$.

3. Fluor – separation and masking (colourless complex): $[FeF_6]^{3-}$.

4. Cyanide – determination (coloured complex): $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{2-}$.

Complexation Equilibria

$$\begin{aligned} M + L &\rightleftharpoons ML \\ ML + L &\rightleftharpoons ML_2 \\ ML_2 + L &\rightleftharpoons ML_3 \\ \vdots \quad & \quad \vdots \\ ML_{n-1} + L &\rightleftharpoons ML_n \end{aligned}$$

$$M + L \rightleftharpoons ML \qquad \beta_1 = \frac{[ML]}{[M][L]} = K_1$$

$$M + 2L \rightleftharpoons ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2} = K_1K_2$$

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3} = K_1K_2K_3$$

$$\vdots \qquad \vdots$$

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n} = K_1K_2 \cdots K_n$$

The equilibrium constants for complex formation reactions are generally written as formation constants.

K1 - K4 -* Stepwise formation constant*.

***K_1 = [ML]/[M][L], K_2 = [ML2]/[ML][L], and so on. We can also write* the equilibria as the sum of individual steps. These have overall formation constants designated by the symbol β_n.**

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+ \quad K_{f1} = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} = 2.5 \times 10^3$$

$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2{}^+ \quad K_{f2} = \frac{[Ag(NH_3)_2{}^+]}{[Ag(NH_3)^+][NH_3]} = 1.0 \times 10^4$$

The overall reaction is the sum of the two steps, and the overall formation constant is the product of the stepwise formation constants

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2{}^+ \quad \beta_2 = K_1K_2 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 2.5 \times 10^7$$

$$\lg\beta_2 = \lg K_1 + \lg K_2 = 7{,}23$$

The formation constant is also called the **stability constant** ***Ks, or Kstab.*** We could write the equilibria in the opposite direction, as dissociations. If we do this, the concentration terms are inverted in the equilibrium constant expressions. The equilibrium constants then are simply the reciprocals of the formation constants, and they are called **instability constants** ***Ki, or dissociation constants Kd***

$$Ag(NH_3)_2{}^+ \rightleftharpoons Ag^+ + 2NH_3 \quad K_d = \frac{1}{K_f} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2{}^+]} = 4.0 \times 10^{-8}$$

	$[Co(NH_3)_4]^{2+}$	$[Cd(NH_3)_4]^{2+}$	$[Ni(NH_3)_4]^{2+}$	$[Zn(NH_3)_4]^{2+}$	$[Cu(NH_3)_4]^{2+}$
$\lg\beta_4$	5,07	6,56	7,47	9,08	12,03

→

Stability of complexes

$$\beta_n^0 = \frac{a_{ML_n}}{a_M\, a_L^n}$$

$$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

$$\beta'_n = \frac{[ML_n]}{C_M C_L^n}$$

thermodynamic formation constant

conditional formation constant, or effective formation constant

$$\beta_n = \beta_n^0 \frac{y_M \cdot y_L^n}{y_{ML_n}}$$

$$\beta'_n = \beta_n \cdot \alpha_M \cdot \alpha_L^n$$

$$\alpha_M = \frac{[M]}{c_M}; \quad \alpha_{ML} = \frac{[ML]}{c_M};$$

$$\alpha_{ML_2} = \frac{[ML_2]}{c_M}; \quad \alpha_{ML_n} = \frac{[ML_n]}{c_M}$$

alpha value of Me is the fraction of the total metal concentration in that form. Thus, α_M is the fraction of the total metal present at equilibrium in the free metal form, α_{ML} is the fraction in the ML form.

$$\alpha_{\mathrm{M}} = \frac{1}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2 + \beta_3[\mathrm{L}]^3 + \cdots + \beta_n[\mathrm{L}]^n}$$

$$\alpha_{\mathrm{ML}} = \frac{\beta_1[\mathrm{L}]}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2 + \beta_3[\mathrm{L}]^3 + \cdots + \beta_n[\mathrm{L}]^n}$$

$$\alpha_{\mathrm{ML_2}} = \frac{\beta_2[\mathrm{L}]^2}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2 + \beta_3[\mathrm{L}]^3 + \cdots + \beta_n[\mathrm{L}]^n}$$

$$\alpha_{\mathrm{ML}_n} = \frac{\beta_n[\mathrm{L}]^n}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2 + \beta_3[\mathrm{L}]^3 + \cdots + \beta_n[\mathrm{L}]^n}$$

Kinetics of Complexes' Formation: Labile and Inert Complexes

The rate with which a given complex exchanges its ligands with other complexes present in the solution is a mark of the *lability property.*

Those for which these reactions are fast are said to be *labile.* *Those for which they are* slow are said to be *inert.*

Hexamminecobalt (III) complex $[Co(NH_3)_6]^{3+}$. It can survive for several days in acidic aqueous solution although it is not stable. (The fact that a compound is not stable is purely and simply in the realm of thermodynamics.) This is because it is inert. Its instability is proved by the equilibrium constant value of the following reaction

$$[Co(NH_3)_6]^{3+} + 6H^+ + 6H_2O \rightleftharpoons [Co(H_2O)_6]^{3+} + 6NH_4^+, \quad K = 10^{25}.$$

the tetracyanonickelate(II) complex $[Ni(CN)_4]^{2-}$ is very stable. The exchange rate of the ligand CN^- with its counterpart radiolabeled on the carbon ($^*CN^-$) is extremely fast

$$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}, \quad \beta_4 = 10^{22}.$$

labile complex is a complex that forms in the time interval necessary to carry out the mixture of reagents, that is, immediately. For example, the hexamminecopper(II) complex $[Cu(NH_3)_6]^{2+}$ is immediately formed by mixing ammonia with a copper(II) solution. An inert complex is a complex whose half-life is around several hours and even, sometimes, several days, at usual temperatures. $[Cr(NH_3)_6]^{3+}$

Calculations Used in Analytical Chemistry

Units

SI is the acronym for the French “Système International d’Unités.”

- The International System of Units (SI) is based on 7 fundamental base units.
- Numerous other useful units, such as volts, hertz, coulombs, and joules, are derived from these base units.
- To express small or large measured quantities in terms of a few simple digits, prefixes are used with these base units and other derived units.

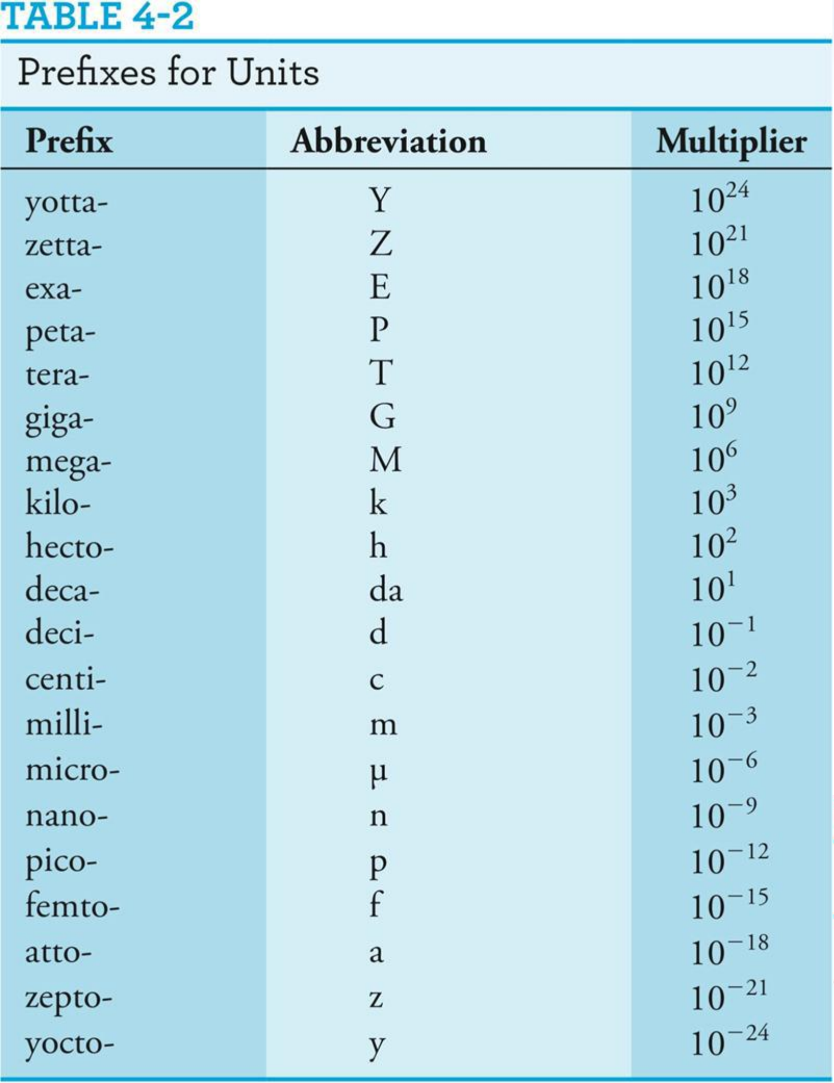


TABLE 4-2

Prefixes for Units

Prefix	Abbreviation	Multiplier
yotta-	Y	10^{24}
zetta-	Z	10^{21}
exa-	E	10^{18}
peta-	P	10^{15}
tera-	T	10^{12}
giga-	G	10^{9}
mega-	M	10^{6}
kilo-	k	10^{3}
hecto-	h	10^{2}
deca-	da	10^{1}
deci-	d	10^{-1}
centi-	c	10^{-2}
milli-	m	10^{-3}
micro-	µ	10^{-6}
nano-	n	10^{-9}
pico-	p	10^{-12}
femto-	f	10^{-15}
atto-	a	10^{-18}
zepto-	z	10^{-21}
yocto-	y	10^{-24}

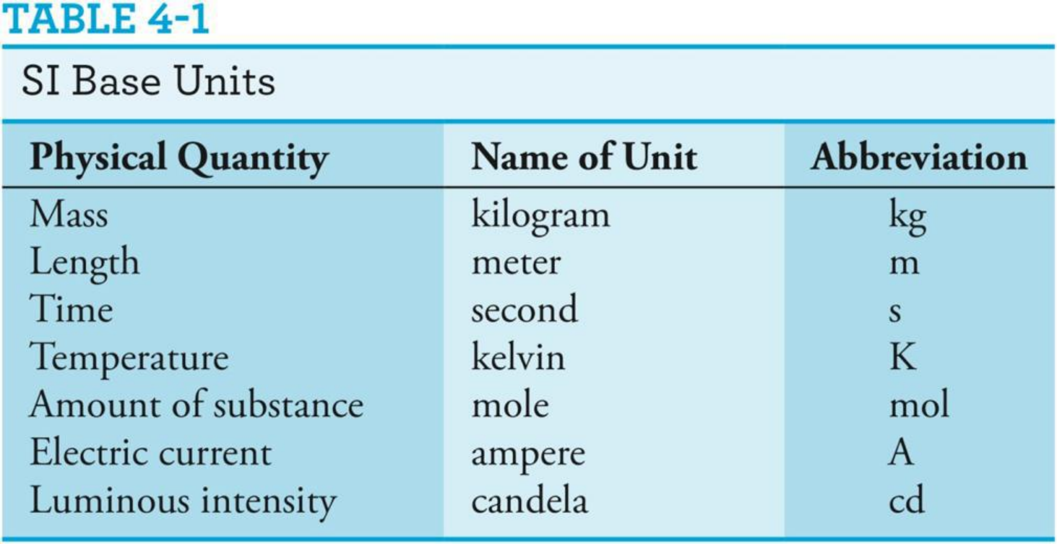


TABLE 4-1

SI Base Units

Physical Quantity	Name of Unit	Abbreviation
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	cd

The Mole

- The mole (abbreviated mol) is the SI unit for the amount of a chemical substance.
- It is always associated with specific microscopic entities such as atoms, molecules, ions, electrons, other particles, or specified groups of such particles as represented by a chemical formula.
- It is the amount of the specified substance that contains the same number of particles as the number of carbon atoms in exactly 12 grams of ^{12}C.
- This is Avogadro's number $N_A = 6.022 \times 10^{23}$.
- The **molar mass M of a substance is the mass in grams of 1 mole of that substance.**
- The Millimole

1 millimole = 1/1000 of a mole 1 millimolar mass (mM) = 1/1000 of the molar mass.

1 mmol = 10^{-3} mol, and 10^{3} mmol = 1 mol

Solutions and their concentrations

Concentration of Solutions

The molar concentration c_x of a solution of a solute species X is the number of moles of that species that is contained in 1 liter of the solution (not 1 L of the solvent).

$$c_x = \frac{n_x}{V}$$

n, number of moles of solute

V, the volume of solution

The unit of molar concentration is **molar, symbolized by M, which has the dimensions of mol/L, or mol L^{-1}.**

Molar concentration is also the number of millimoles of solute per milliliter of solution.

There are two ways of expressing molar concentration:

Molar analytical concentration is the total number of moles of a solute, regardless of its chemical state, in 1 L of solution. The molar analytical concentration describes how a solution of a given concentration can be prepared. The **molar equilibrium concentration,** or just equilibrium concentration, refers to the molar concentration of a particular species in a solution at equilibrium.

To specify the molar equilibrium concentration of a species, it is necessary to know how the solute behaves when it is dissolved in a solvent. They are usually symbolized by placing square brackets around the chemical formula for the species.

Ex., $[H_2SO_4] = 0.00$ M; $[H^+] = 1.01$ M.

The IUPAC recommends the general term “concentration” to express the composition of a solution with respect to its volume, with four sub terms: amount concentration, mass concentration, volume concentration, and number concentration.

Molar concentration, molar analytical concentration, and molar equilibrium concentration are all amount concentrations by this definition.

The molar analytical concentration of H_2SO_4 is given by

$c\ H_2SO_4 = [SO_4^{2-}] + [HSO_4^{2-}]$

because SO_4^{2-} and HSO_4^{2-} are the only two sulfate-containing species in the solution.

The molar equilibrium concentrations are $[SO_4^{2-}]$ and $[HSO_4^{2-}]$.

Percent Concentration

- In IUPAC terminology, weight percent is mass concentration and volume percent is volume concentration.
- Weight percent is often used to express the concentration of commercial aqueous reagents. Volume percent is commonly used to specify the concentration of a solution prepared by diluting a pure liquid compound with another liquid.
- Weight or volume percent is often used to indicate the composition of dilute aqueous solutions of solid reagents.

$$\text{weight percent}(w/w) = \frac{\text{weight solute}}{\text{weight solution}} \times 100\%$$

$$\text{volume percent}(v/v) = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

$$\text{weight / volume percent}(w/v) = \frac{\text{weight solute, g}}{\text{volume solution, mL}} \times 100\%$$

Parts per million and parts per billion

In IUPAC terminology, parts per billion, parts per million, and parts per thousand are mass concentrations.

For very dilute solutions, **parts per million (ppm) is a convenient way to express concentration:**

$$c_{ppm} = \frac{massofsolute}{massofsolution} \times 10^{6}\ ppm$$

For even more dilute solutions, 109 ppb rather than 106 ppm is used in the previous equation to give the results in **parts per billion (ppb).**

The term **parts per thousand (ppt)** is also used, especially in oceanography.

Solution-Diluent Volume Ratios

The composition of a dilute solution is sometimes specified in terms of the volume of a more concentrated solution and the volume of solvent used in diluting it.

Thus, a 1:4 HCl solution contains four volumes of water for each volume of concentrated hydrochloric acid.

This method of notation is frequently ambiguous.

p-Functions

The concentration of a species is expressed as its p-function, or p-value. The best-known p-function is pH, which is the negative logarithm of [H+].

The p-value is the negative logarithm (to the base 10) of the molar concentration of that species. Thus, for the species X,

$$pX = -\log [X]$$

$$\boxed{V_{concd} \times c_{concd} = V_{dil} \times c_{dil}}$$

The two terms on the left are the volume and molar concentration of a concentrated solution that is being used to prepare a diluted solution having the volume and concentration given by the corresponding terms on the right.

This equation is based on the fact that the number of moles of solute in the diluted solution must equal the number of moles in the concentrated reagent.

This equation can be used with L and mol/L or mL and mmol/mL.