Fundamentals of

Analytical Chemistry

Eighth Edition

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Analytical Chemistry

References:

1- Skoog (Fundamentals of Analytical Chemistry) 8edition (Thomson, 2004)

2- Daniel harris (Quantitative chemical analysis) (2006)

3- Gary D. Christian (Analytical Chemistry) 7th Ed, 2014

Introduction to Analytical Chemistry

- ***What is analytical chemistry?***

- Analytical chemistry is a scientific discipline that develops and applies methods, instruments and strategies to obtain information on the composition and nature of matter. It deals with methods for the identification of one or more of the components in a sample of matter and the determination of the relative amounts of each. Accordingly, it is divided in to two main parts:

1- Qualitative analysis: an analysis in which we determine the identity of the constituent species in a sample. (i.e. shows what elements, compounds and ions a given sample).

2- Quantitative analysis: An analysis in which we determine how much of a constituent species is present in a sample. (i.e. the assessments the quantity or percentage of the individual elements, compounds and ions in the sample).

- **For example**, if the water of such river is contaminated and leads to die fishes and other aquatic organism the aim of qualitative analyses is to identify the reasons of this contamination. Is the reason, the transfer of heavy metals (such as Pb, Hg, Cd) to the water river? If the answer is positive, how much the quantity or concentration of contaminated element is? (This is quantitative analysis job).

- The roles of analytical chemistry

1- It plays a vital role in the development of science. It has evolved from an art to a science with application throughout industry, medicine and all science. To illustrate, consider a few examples:

a- The concentration of O_2 and CO_2 are determined in millions of blood samples every day and used to diagnose and treat illnesses.

b- Quantitative measurement of ionized Ca in blood serum help diagnose parathyroid disease in human.

c- Quantitative determination of N_2 in food establishes their protein content and thus their nutritional value.

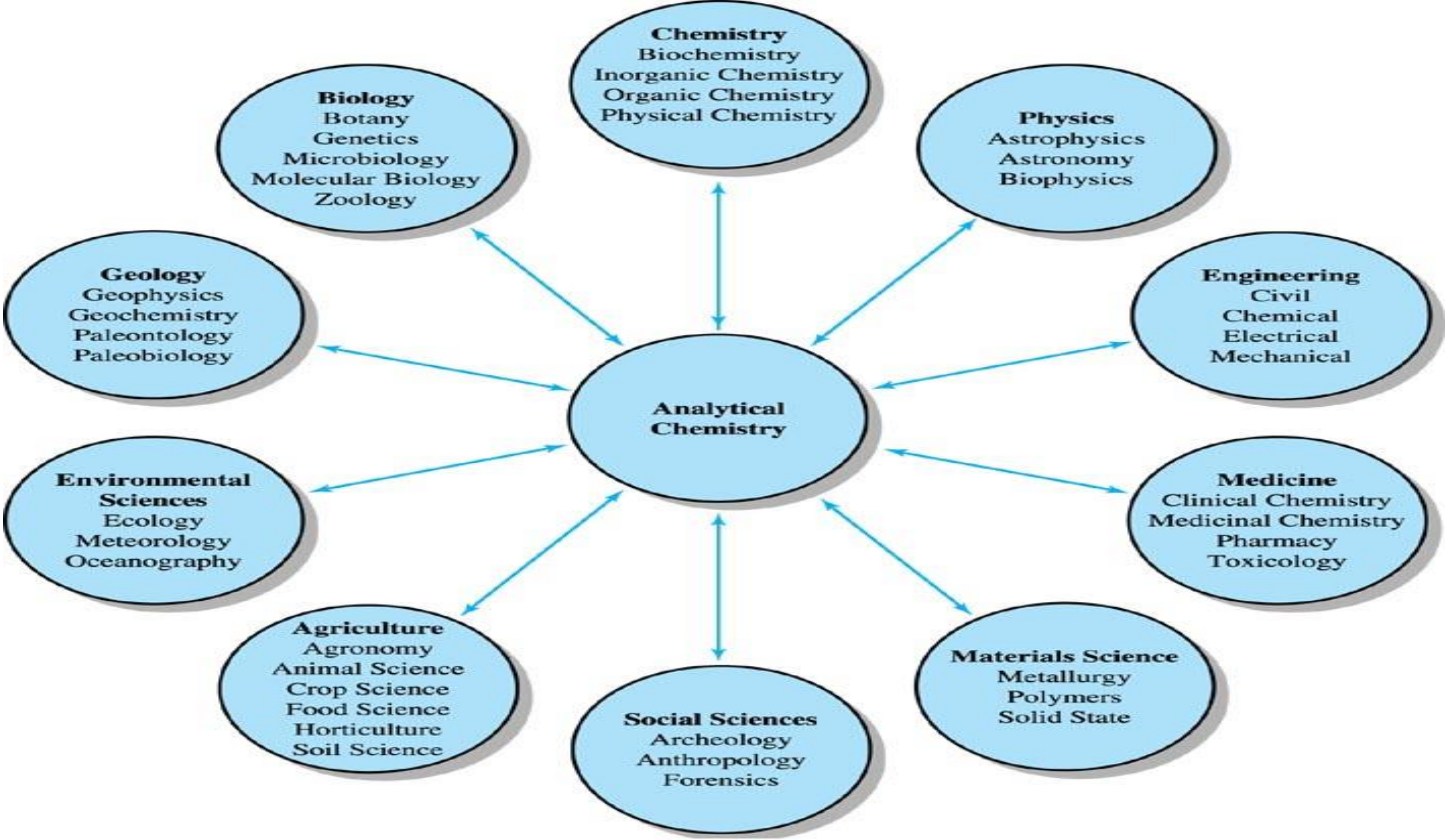
d- Quantitative analysis of raw materials and final product in the industrial production lines.

2- Quantitative analytical measurements also play a vital role in many research areas in chemistry, biochemistry, biology, geology and the other sciences, for example:

a- Quantitative measurements of K, Ca and Na ions in the body fluids of animals permit physiologists to study the role of these ions in the nerve-signal conduction as well as muscle contraction and relaxation.

b- Materials scientists rely heavily on quantitative analyses of crystalline germanium and silicon in their studies of semiconductor devices.

- Many chemists, biochemists, and medicinal chemists devote much time in the laboratory gathering quantitative information about system of interest to them. The central role of analytical chemistry in this enterprise and many others is illustrated in Figure (1). All branches of chemistry draw on the ideas and techniques of analytical chemistry. Chemistry is often termed the **central science**; and the top center position of chemistry as well as the center position of analytical chemistry in the figure symbolizes the importance of chemistry sciences. Analytical chemistry serves an essential tool in the entire field depicted in the figure.



Chemistry
Biochemistry
Inorganic Chemistry
Organic Chemistry
Physical Chemistry

Biology
Botany
Genetics
Microbiology
Molecular Biology
Zoology

Physics
Astrophysics
Astronomy
Biophysics

Geology
Geophysics
Geochemistry
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Crop Science
Food Science
Horticulture
Soil Science

Social Sciences
Archeology
Anthropology
Forensics

Materials Science
Metallurgy
Polymers
Solid State

General steps in a chemical analysis

- 1- Define the problem.
- 2- Selecting analytical procedures (method).
- 3- Sampling (obtain sample).
- 4- Sample preparation (prepare sample for analysis).
- 5- Perform any necessary chemical separations.
- 6- Analysis (perform the measurement).
- 7- Calculate the results and report

Classifying Analytical Techniques

- **A- Classical techniques**

Mass, **volume**, and **charge** are the most common signals for classical techniques, and the corresponding techniques are:

1- **Volumetric techniques** **(Titrimetric analysis)**: The analyte reacts with a measured volume of reagent of known concentration, in a process called titration.

2- **Gravimetric techniques:** usually involves the selective separation of the analyte by precipitation, followed by the very non-selective measurement of mass (of the precipitate).

3- **Coulometeric techniques**.

B- Instrumental techniques

1- Spectroscopic methods - measuring the interaction between the analyte and electromagnetic radiation (or the production of radiation by an analyte).

2- Electroanalytic methods - measure an electrical property (i.e., potential, current, resistance, amperes, etc.) chemically related to the amount of analyte.

Analytes: The constituents of interest in a sample.

Matrix: All other constituents in a sample except for the analytes.

Table 1.1

Comparison of Different Analytical Methods

Method	Approx. Range (mol/L)	Approx. Precision (%)	Selectivity	Speed	Cost	Principal Uses
Gravimetry	10^{-1}–10^{-2}	0.1	Poor–moderate	Slow	Low	Inorg.
Titrimetry	10^{-1}–10^{-4}	0.1–1	Poor–moderate	Moderate	Low	Inorg., org.
Potentiometry	10^{-1}–10^{-6}	2	Good	Fast	Low	Inorg.
Electrogravimetry, coulometry	10^{-1}–10^{-4}	0.01–2	Moderate	Slow–moderate	Moderate	Inorg., org.
Voltammetry	10^{-3}–10^{-10}	2–5	Good	Moderate	Moderate	Inorg., org.
Spectrophotometry	10^{-3}–10^{-6}	2	Good–moderate	Fast–moderate	Low–moderate	Inorg., org.
Fluorometry	10^{-6}–10^{-9}	2–5	Moderate	Moderate	Moderate	Org.
Atomic spectroscopy	10^{-3}–10^{-9}	2–10	Good	Fast	Moderate–high	Inorg., multielement
Chromatography	10^{-3}–10^{-9}	2–5	Good	Fast–moderate	Moderate–high	Org., multicomponent
Kinetic methods	10^{-2}–10^{-10}	2–10	Good–moderate	Fast–moderate	Moderate	Inorg., org., enzymes

Example: What is the mass in grams of Na^+ (22.99 g/mol) in 25.0 g of Na_2SO_4 (142.0 g/mol)?

$$\text{amount } Na^+ = \text{No. mole } Na_2SO_4 \times \frac{2\text{mol } Na^+}{\text{mol } Na_2SO_4}$$

$$\text{No. mole } Na_2SO_4 = 25.0\text{g } Na_2SO_4 \times \frac{1\text{mole } Na_2SO_4}{142.0\text{g } Na_2SO_4}$$

$$= 0.176 \text{ mol}$$

$$\text{amount } Na^+ = 0.176 \text{ mol } Na_2SO_4 \times \frac{2\text{mol } Na^+}{\text{mol } Na_2SO_4}$$

$$= 0.352 \text{ mol}$$

To find the mass of sodium, we multiply the number of moles of Na^+ by the molar mass of Na^1 (22.99 g/mol).

$$\text{Mass } Na^+ = 0.352 \text{ mol } Na^+ \times \frac{22.99 \text{ g/mol}}{\text{mol } Na^+} = \mathbf{8.10\ g\ Na^+}$$

Units for Expressing Concentration.

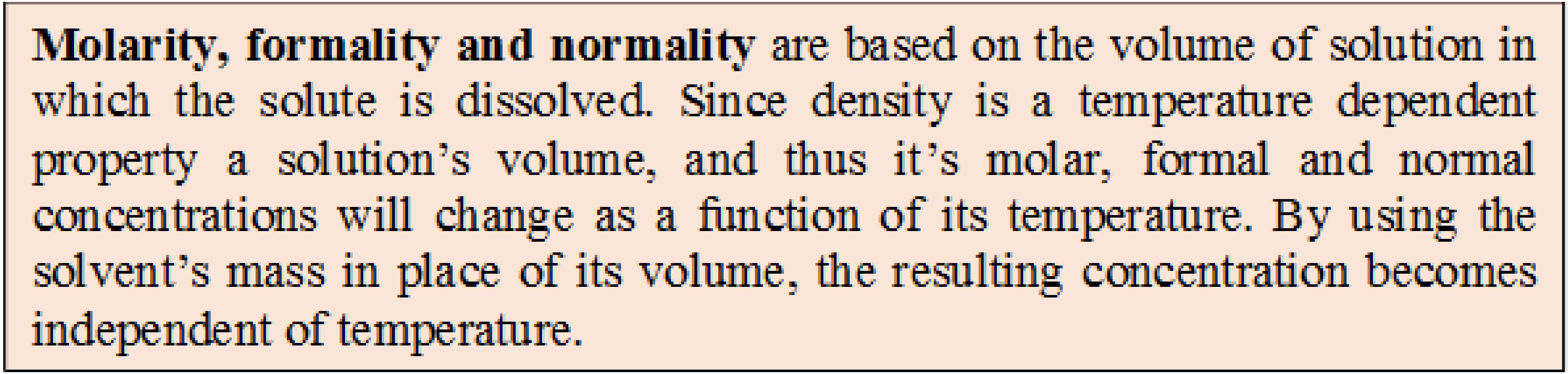
1- Molarity: is the number of moles of chemical species that is contained in one liter of the solution.

2- Formality: is a substance's total concentration in solution without regard to its specific chemical form.

- Both Molarity and Formality express concentration as moles of solute per liter of solution. There is a subtle difference between molarity and formality there is no difference between a substance's molarity and formality if it dissolves without dissociating into ions. The molar concentration of a solution of glucose, for example, is the same as its formality. For substances that ionize in solution, such as NaCl, molarity and formality are different. For example, dissolving 0.1 mol of NaCl in 1 L of water gives a solution containing 0.1 mol of Na^+ and 0.1 mol of Cl. The molarity of NaCl, therefore, is zero since there is essentially no undissociated NaCl in solution. The solution instead, is 0.1 M in Na^+ and 0.1 M in $Cl^–$.

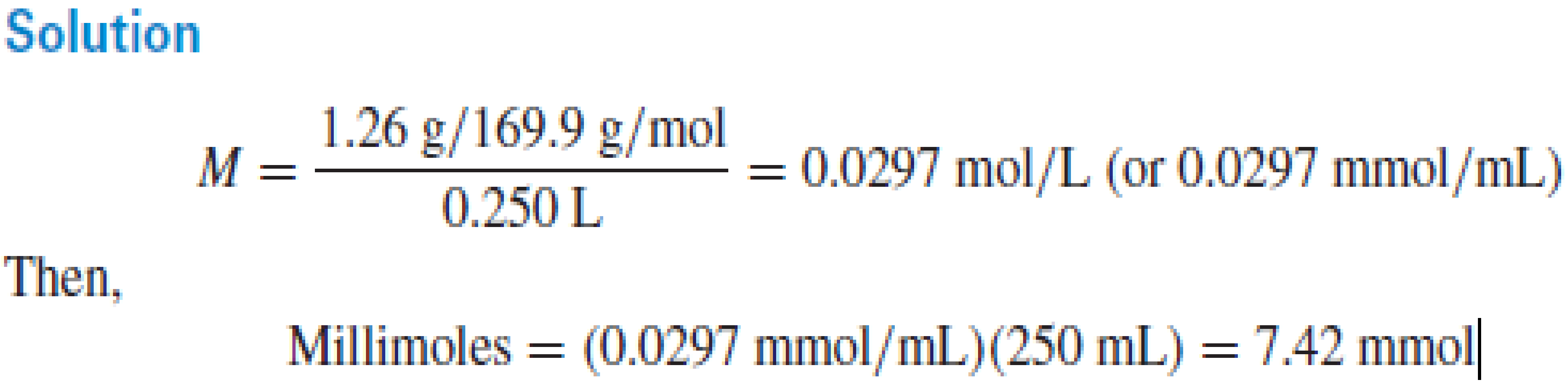
3- Normality: it is the number of equivalent weight of substance in solution has one liter volume.

4- Molality: is the number of moles of chemical species per kilogram of solvent, is used in thermodynamic calculations where a temperature independent unit of concentration is needed. While molarity changes with temperature because the volume of a solution usually increases when it is heated.



Molarity, formality and normality are based on the volume of solution in which the solute is dissolved. Since density is a temperature dependent property a solution's volume, and thus it's molar, formal and normal concentrations will change as a function of its temperature. By using the solvent's mass in place of its volume, the resulting concentration becomes independent of temperature.

- **Example**: A solution is prepared by dissolving 1.26 g $AgNO_3$ in a 250 mL volumetric flask and diluting to volume. Calculate the molarity of the silver nitrate solution. How many millimoles $AgNO_3$ were dissolved?



Solution

$$M = \frac{1.26\ \text{g}/169.9\ \text{g/mol}}{0.250\ \text{L}} = 0.0297\ \text{mol/L (or 0.0297 mmol/mL)}$$

Then,

$$\text{Millimoles} = (0.0297\ \text{mmol/mL})(250\ \text{mL}) = 7.42\ \text{mmol}$$

- **Example:** Calculate the analytical and equilibrium molar concentrations of the solute species in an aqueous solution that contains 285 mg of trichloroacetic acid, Cl_3CCOOH (163.4 g/mol), in 10.0 mL (the acid is 73% ionized in water).
- **Solution:** we calculate the number of moles of Cl_3CCOOH, which we symbolize, as HA, and divide by the volume of the solution, 10.0 mL, or 0.0100 L. Therefore,

$$\text{amount HA} = n_{\text{HA}} = 285\ \cancel{\text{mg HA}} \times \frac{1\ \cancel{\text{g HA}}}{1000\ \cancel{\text{mg HA}}} \times \frac{1\ \text{mol HA}}{163.4\ \cancel{\text{g HA}}}$$
$$= 1.744 \times 10^{-3}\ \text{mol HA}$$

The molar analytical concentration, c_{HA}, is then

$$c_{\text{HA}} = \frac{1.744 \times 10^{-3}\ \text{mol HA}}{10.0\ \cancel{\text{mL}}} \times \frac{1000\ \cancel{\text{mL}}}{1\ \text{L}} = 0.174\ \frac{\text{mol HA}}{\text{L}} = 0.174\ \text{M}$$

In this solution, 73% of the HA dissociates, giving H^+ and A^-:

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$

The equilibrium concentration of HA is then 27% of c_{HA}. Thus,

$$[\text{HA}] = c_{\text{HA}} \times (100 - 73)/100 = 0.174 \times 0.27 = 0.047\ \text{mol/L}$$
$$= 0.047\ \text{M}$$

The equilibrium concentration of A^- is equal to 73% of the analytical concentration of HA, that is,

$$[\text{A}^-] = \frac{73\ \text{mol A}^-}{100\ \cancel{\text{mol HA}}} \times 0.174\ \frac{\cancel{\text{mol HA}}}{\text{L}} = 0.127\ \text{M}$$

Because 1 mole of H^+ is formed for each mole of A^-, we can also write

$$[\text{H}^+] = [\text{A}^-] = 0.127\ \text{M}$$

and

$$c_{\text{HA}} = [\text{HA}] + [\text{A}^-] = 0.047 + 0.127 = 0.174\ \text{M}$$

- **Example:** Describe the preparation of 2.00 L of 0.10 M Na_2CO_3 (106g/mol) from the solid?

mol Na_2CO_3 needed = 0.1mol/L x 2L= 0.2 mol

mass Na_2CO_3 = 0.2 mol x 106 g/mol =**21.2g**

Dissolve 21.2g of Na_2CO_3 in distilled water and dilute to 2L.

Dilution

- Dilute solutions can be prepared from concentrated solutions. A volume of the concentrated solution is transferred to a fresh vessel and diluted to the desired final volume. The number of moles of reagent in *V* liters containing M moles per liter is the product **M.V = mol/L. L**, so we equate the number of moles in the concentrated (conc) and dilute (dil) solutions:

- **Dilution Law:**

$$(\mathbf{M}_{\mathbf{conc}} \ \mathbf{x}\ \mathbf{V}_{\mathbf{conc}}) = (\mathbf{M}_{\mathbf{dil}} \ \mathbf{x}\ \mathbf{V}_{\mathbf{dil}})$$

$$(\mathbf{N}_{\mathbf{conc}} \ \mathbf{x}\ \mathbf{V}_{\mathbf{conc}}) = (\mathbf{N}_{\mathbf{dil}} \ \mathbf{x}\ \mathbf{V}_{\mathbf{dil}})$$

- **Example:** Describe how you would prepare the following three solutions: (a) 500 mL of approximately 0.20 M NaOH using solid NaOH; (b) 1 L of 150.0 ppm Cu^{2+} using Cu metal; and (c) 2 L of 4% v/v acetic acid using concentrated glacial acetic acid.

- **Solution:**

(a) Since the concentration only needs to be known to two significant figures, the mass of NaOH and volume of solution do not need to be measured exactly. The desired mass of NaOH is

$$M= \frac{mass(g)}{M.mass\ (g.mol)} \times \frac{1}{V(l)}$$

$$0.20\ \text{mol/L} = \frac{mass(g)}{40g/mol} \times \frac{1000}{500mL} = \mathbf{4.0g}$$

To prepare the solution we place 4.0 g of NaOH, in a bottle or beaker and add approximately 500 mL of water.

(b) Since the concentration of Cu^{2+} needs to be exact, the mass of Cu metal and the final solution volume must be measured exactly. The desired mass of Cu metal is

$$\text{mass (mg)} = \frac{150\ mg}{L} \times 1.000\ \text{L} = 150.0\ \text{mg} = \mathbf{0.1500\ g}$$

To prepare the solution we measure out exactly 0.1500 g of Cu into a small beaker. To dissolve the Cu we add a small portion of concentrated HNO_3 and gently heat until it completely dissolves. The resulting solution is poured into a 1 L volumetric flask. The beaker is rinsed repeatedly with small portions of water, which are added to the volumetric flask.

(c) The concentration of this solution is only approximate, so volumes do not need to be measured exactly. The necessary volume of glacial acetic acid is

$$\frac{4.0\ \mathrm{mL\ CH3\ COOH}}{100 mL} \times 2000\ mL = \mathbf{80mL}\ \mathrm{CH_3COOH}$$

To prepare the solution we use a graduated cylinder to transfer 80 mL of glacial acetic acid to a container that holds approximately 2 L, and we then add sufficient water to bring the solution to the desired volume.

Stock solution: A solution of known concentration from which other solutions are prepared.
Quantitative transfer: The process of moving a sample from one container to another in a manner that ensures all material is transferred.

- **Example:** The molarity of “concentrated” HCl is approximately 12.1 M. How many milliliters of this reagent should be diluted to 1.000 L to make 0.100 M HCl?

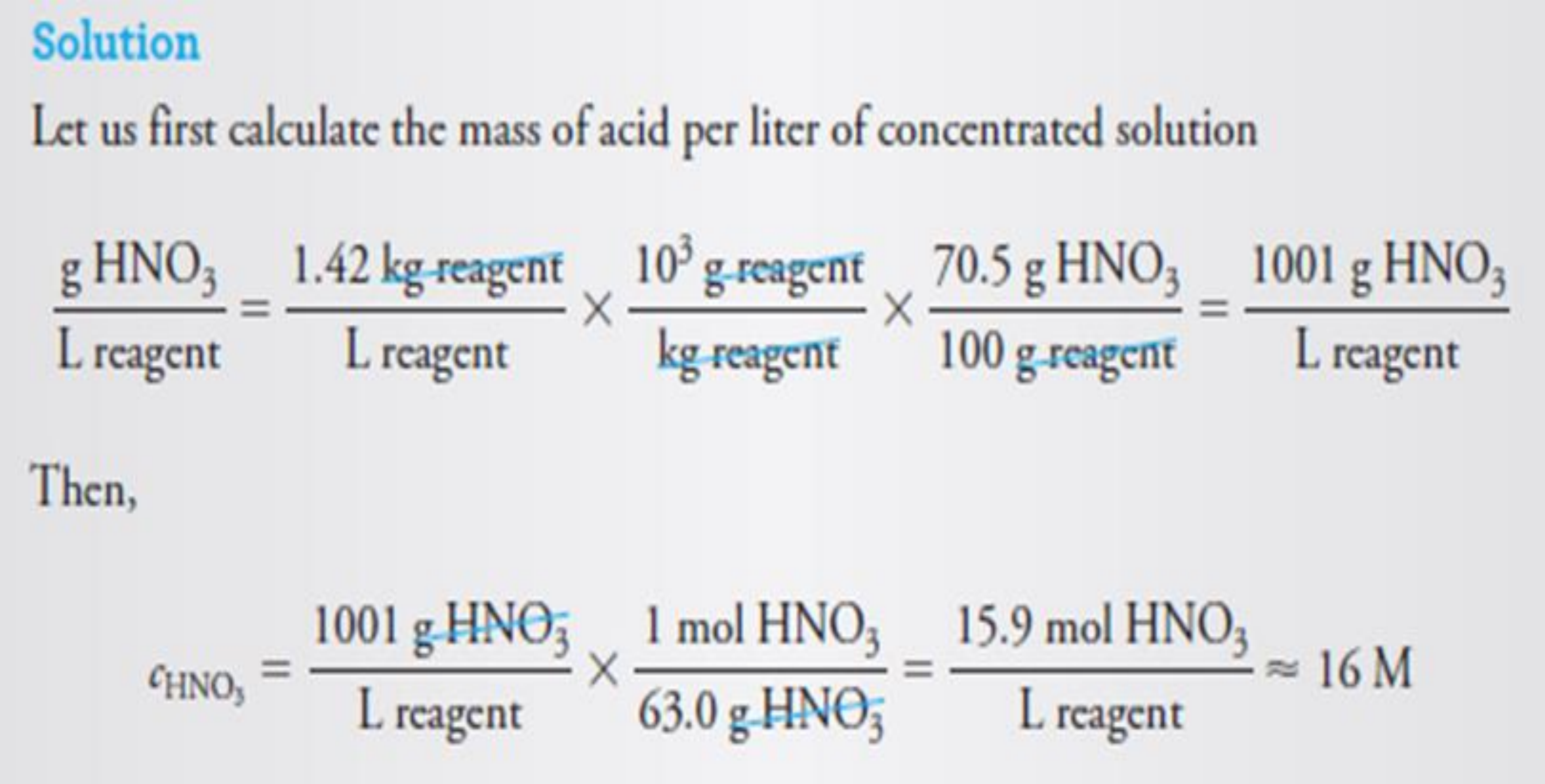
- **Solution**: The dilution formula handles this problem directly:

$$\mathbf{M}_{\mathbf{conc}} \cdot \mathbf{V}_{\mathbf{conc}} = \mathbf{M}_{¿\,\mathbf{dil}} \cdot \mathbf{V}_{\mathbf{dil}}$$

(12.1 M).(x mL) = (0.100 M).(1 000 mL) → x = **8.26 mL**

To make 0.100 M HCl, we would dilute 8.26 mL of concentrated HCl up to 1.000 L. The concentration will not be exactly 0.100 M, because the reagent is not exactly 12.1 M. A table inside the cover of this book gives volumes of common reagents required to make 1.0 M solutions.

- **Example:** Calculate the molar concentration of HNO_3 (63.0 g/mol) in a solution that has a specific gravity of 1.42 Kg and is 70.5% HNO_3 (w/w).



Solution

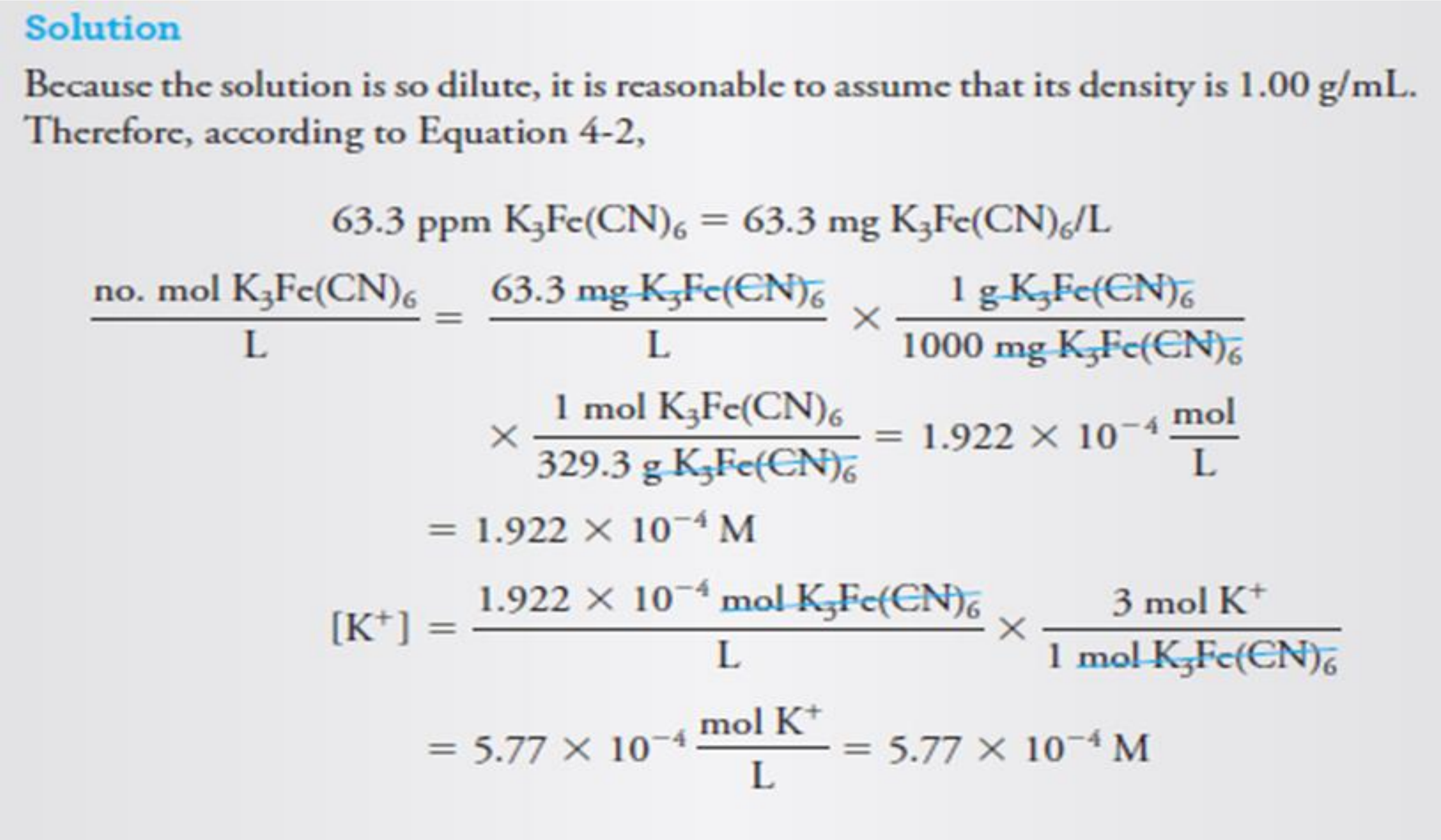
Let us first calculate the mass of acid per liter of concentrated solution

$$\frac{\text{g HNO}_3}{\text{L reagent}} = \frac{1.42\ \cancel{\text{kg reagent}}}{\text{L reagent}} \times \frac{10^3\ \cancel{\text{g reagent}}}{\cancel{\text{kg reagent}}} \times \frac{70.5\ \text{g HNO}_3}{100\ \cancel{\text{g reagent}}} = \frac{1001\ \text{g HNO}_3}{\text{L reagent}}$$

Then,

$$c_{\text{HNO}_3} = \frac{1001\ \text{g}\ \cancel{\text{HNO}_3}}{\text{L reagent}} \times \frac{1\ \text{mol HNO}_3}{63.0\ \text{g}\ \cancel{\text{HNO}_3}} = \frac{15.9\ \text{mol HNO}_3}{\text{L reagent}} \approx 16\ \text{M}$$

Example: What is the molar concentration of K^+ in a solution that contains 63.3 ppm of $K_3Fe(CN)_6$ (329.3 g/mol)?



Solution

Because the solution is so dilute, it is reasonable to assume that its density is 1.00 g/mL. Therefore, according to Equation 4-2,

$$63.3\text{ ppm } K_3Fe(CN)_6 = 63.3\text{ mg } K_3Fe(CN)_6/\text{L}$$

$$\frac{\text{no. mol } K_3Fe(CN)_6}{\text{L}} = \frac{63.3\ \cancel{\text{mg } K_3Fe(CN)_6}}{\text{L}} \times \frac{1\ \cancel{\text{g } K_3Fe(CN)_6}}{1000\ \cancel{\text{mg } K_3Fe(CN)_6}}$$

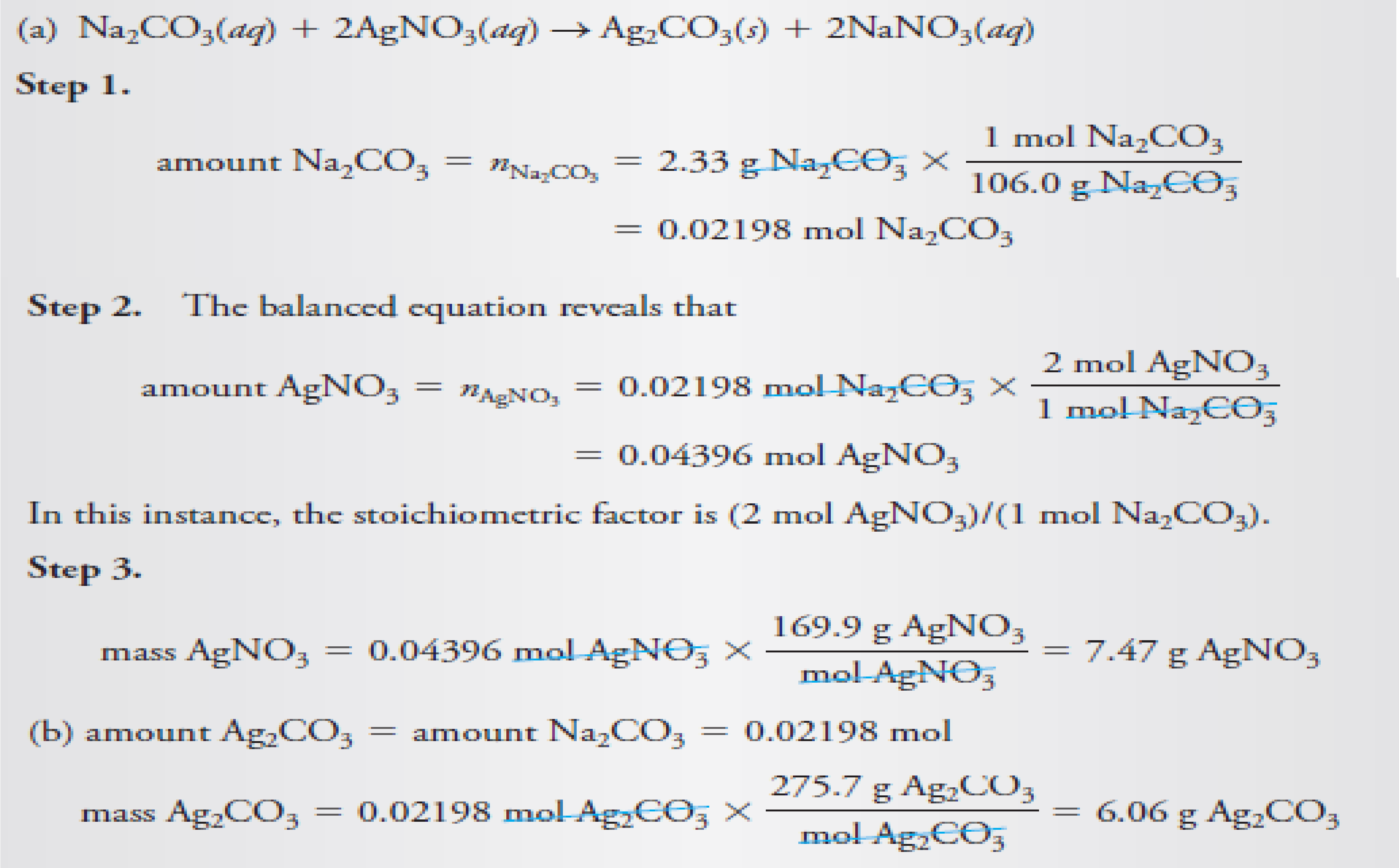
$$\times \frac{1\text{ mol } K_3Fe(CN)_6}{329.3\ \cancel{\text{g } K_3Fe(CN)_6}} = 1.922 \times 10^{-4}\ \frac{\text{mol}}{\text{L}}$$

$$= 1.922 \times 10^{-4}\text{ M}$$

$$[K^+] = \frac{1.922 \times 10^{-4}\ \cancel{\text{mol } K_3Fe(CN)_6}}{\text{L}} \times \frac{3\text{ mol } K^+}{1\ \cancel{\text{mol } K_3Fe(CN)_6}}$$

$$= 5.77 \times 10^{-4}\ \frac{\text{mol } K^+}{\text{L}} = 5.77 \times 10^{-4}\text{ M}$$

- **Example:** (a) What mass of $AgNO_3$ (169.9 g/mol) is needed to convert 2.33 g of Na_2CO_3 (106.0 g/mol) to Ag_2CO_3? (b) What mass of Ag_2CO_3 (275.7 g/mol) will be formed?
- **Solution:**



(a) $Na_2CO_3(aq) + 2AgNO_3(aq) \rightarrow Ag_2CO_3(s) + 2NaNO_3(aq)$

Step 1.

$$\text{amount } Na_2CO_3 = n_{Na_2CO_3} = 2.33\ \cancel{g\ Na_2CO_3} \times \frac{1\ mol\ Na_2CO_3}{106.0\ \cancel{g\ Na_2CO_3}}$$
$$= 0.02198\ mol\ Na_2CO_3$$

Step 2. The balanced equation reveals that

$$\text{amount } AgNO_3 = n_{AgNO_3} = 0.02198\ \cancel{mol\ Na_2CO_3} \times \frac{2\ mol\ AgNO_3}{1\ \cancel{mol\ Na_2CO_3}}$$
$$= 0.04396\ mol\ AgNO_3$$

In this instance, the stoichiometric factor is (2 mol $AgNO_3$)/(1 mol Na_2CO_3).

Step 3.

$$\text{mass } AgNO_3 = 0.04396\ \cancel{mol\ AgNO_3} \times \frac{169.9\ g\ AgNO_3}{\cancel{mol\ AgNO_3}} = 7.47\ g\ AgNO_3$$

(b) amount Ag_2CO_3 = amount Na_2CO_3 = 0.02198 mol

$$\text{mass } Ag_2CO_3 = 0.02198\ \cancel{mol\ Ag_2CO_3} \times \frac{275.7\ g\ Ag_2CO_3}{\cancel{mol\ Ag_2CO_3}} = 6.06\ g\ Ag_2CO_3$$

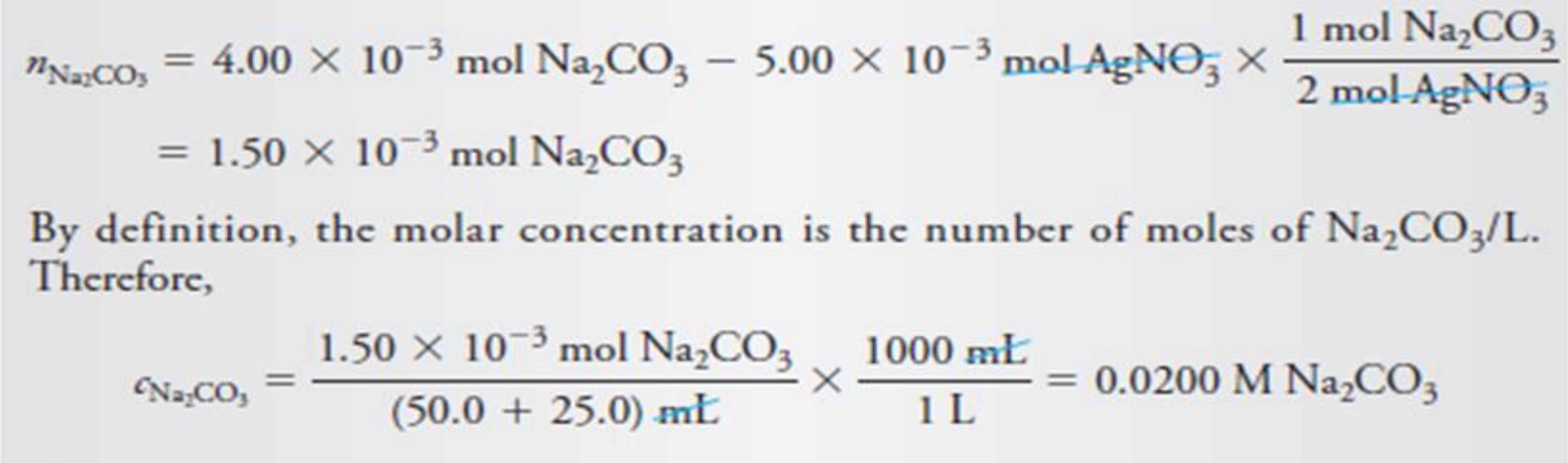
- **Example:** What will be the molar analytical concentration of Na_2CO_3 in the solution produced when 25.0 mL of 0.200 M $AgNO_3$ is mixed with 50.0 mL of 0.0800 M Na_2CO_3?

- **Solution:**

$$\mathbf{2AgNO_3 + Na_2CO_3 \rightarrow Ag_2CO_3 + 2NaNO_3}$$

$n_{AgNO3} = 0.20\ mol/L \times 25mL \times 1L/1000mL = 5x10^{-3}\ mol$

$n_{Na2CO3} = 0.080\ mol/L \times 50\ mL \times 1L/1000mL = 4x10^{-3}\ mol$



$$n_{Na_2CO_3} = 4.00 \times 10^{-3}\ \text{mol Na}_2\text{CO}_3 - 5.00 \times 10^{-3}\ \cancel{\text{mol AgNO}_3} \times \frac{1\ \text{mol Na}_2\text{CO}_3}{2\ \cancel{\text{mol AgNO}_3}}$$

$$= 1.50 \times 10^{-3}\ \text{mol Na}_2\text{CO}_3$$

By definition, the molar concentration is the number of moles of Na_2CO_3/L. Therefore,

$$c_{Na_2CO_3} = \frac{1.50 \times 10^{-3}\ \text{mol Na}_2\text{CO}_3}{(50.0 + 25.0)\ \cancel{\text{mL}}} \times \frac{1000\ \cancel{\text{mL}}}{1\ \text{L}} = 0.0200\ \text{M Na}_2\text{CO}_3$$

- **Importance of equilibrium constant**
- 1- It permits us to perform computation that relate the concentrations of reactants and products in an equilibrium system.
- 2- The magnitude of K_e provides us with useful qualitative information about the extent to which a reaction proceeds toward completion.
- **a-** When K_e is large, the position of equilibrium lies far to the right (i.e. the forward reaction will go to near completion).
- **b-** When K_e is small only relatively small amounts of the products are present in the system at equilibrium (i.e. the equilibrium is found to be strongly shifted to the left.).
- 3- In analytical chemistry the following table (1) shows the types of chemical equilibrium and equilibrium constants that are of importance in analytical chemistry.

TABLE

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	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$

Equilibria involving weak electrolytes

- All substances that dissociate in water into ions are called **electrolytes or ionic substance,** those do not dissociate are termed **non-electrolytes or nonionic substance**.

- Aqueous solutions of electrolytes conduct an electric currant, but those of non-electrolytes do not. Electrolytes are classified as **Strong or Weak.**

- Most of the solutes we will discuss are electrolytes, which form ions when dissolved in water (or certain other solvents) and thus produce solutions that conduct electricity. **Strong electrolytes** ionize essentially completely in a solvent. **Weak electrolytes** ionize only partially. This means that a solution of a weak electrolyte will not conduct electricity as well as a solution containing an equal concentration of a strong electrolyte.

Strong Electrolytes	strong acids	HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and H_2SO_4
	strong bases	NaOH, KOH, LiOH, $Ba(OH)_2$, and $Ca(OH)_2$
	salts	NaCl, KBr, $MgCl_2$, and many more
Weak Electrolytes	weak acids	HF, H_2SO_3, H_2S, $HC_2H_3O_2$ (acetic acid), H_2CO_3 (carbonic acid), H_3PO_4 (phosphoric acid), and many more
	weak bases	NH_3 (ammonia), C_5H_5N (pyridine), and several more, all containing "N"

- Aqueous solutions of electrolytes are characterized by certain physical properties:

1- Lowering of vapor pressure.

2- Lowering of freezing point

3- Elevation of boiling point

4- Development of osmotic pressure.

Strong electrolytes are considered to be completely ionized in a solvent. There ionization may be presented as follows:

$$\text{Solute} \xrightarrow{H_2O} \text{Solute ions}$$

Weak electrolytes are considered to be partially dissociated, where a dynamic equilibrium will be established between the solute ions and its undissociated molecules.

$$\text{Solute} + H_2O \rightleftharpoons \text{Solute ions}$$

The degree of electrolytic dissociation or ionization of weak electrolyte become great when the solution is made more dilute.

The dissociation or ionization of weak electrolytes is quantitatively described by equilibrium constant. Suppose the dissociation of AB.

$$\mathbf{AB \rightleftharpoons A + B}$$

The equilibrium constant K_e of the dissociation is generally written as:

$$\mathbf{K_e = \frac{[A]\,[B]}{[AB]}}$$

- When Ke, large this means that the compound is highly dissociation. For example, if Ke for acid is large, it would be strong.
- Some substances are dissociation in sequence steps, so the equilibrium constant may be written for each step. Suppose the dissociation of A_2B;

$$A_2B \rightleftharpoons AB + B \qquad K_1 = \frac{[A]\,[AB]}{[A_2B]} \qquad \text{-------} \ (1)$$

$$AB \rightleftharpoons A + B \qquad K_1 = \frac{[A]\,[B]}{[AB]} \qquad \text{-------} \ (2)$$

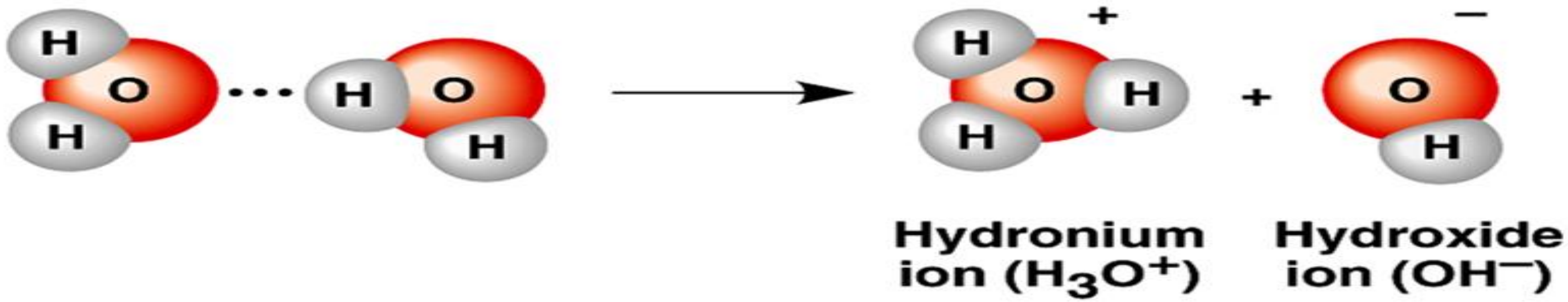
By multiplication of eq. (1) & eq. (2), we get the overall equilibrium constant for the reaction;

$$A_2B \rightleftharpoons 2A + B$$

$$K_e = K_1 \,.\, K_2 = \frac{[A][AB]}{[A_2B]} \times \frac{[A][B]}{[AB]} = \frac{[A]^2\,[B]}{[A_2B]} \qquad \text{------} \ (3)$$

Ionization of Water

- Water may be regarded as an extremely weak, since it undergo self- dissociation to vary slight extent into hydronium (H_3O^+) and hydroxide (OH^-) as follow;



$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \text{------ (4)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{------ (5)}$$

An equilibrium constant for this reaction can be formulated as shown in equation bellow:

$$K_e = \text{constant} = \frac{[H^+]\,[OH^-]}{[H_2O]} = 1.8\text{x}10^{-16} \qquad \text{------- (6)}$$

The molar concentration of water at 25°C is constant and equal to 55.5M

{1000g/L} /(18 g/mol) = 55.5mol/L. eq.(6) lead to

$$\mathbf{\frac{[H^+]\,[OH^-]}{55.5} = 1.8\text{x}10^{-16} \quad \text{-------} \ (7)}$$

And, $\mathbf{[H^+]\,[OH^-] = (55.5)\,(1.8\text{x}10^{-16}) = 1\text{x}10^{-14} = K_w}$

Where K_w is known as the ion product of water or the water constant.

If the eq(4) is used, its equilibrium expression will be,

$$\frac{\mathbf{[H_3O^+]\,[OH^-]}}{[H_2O]^2} = \mathbf{K_e} = \frac{\mathbf{[H_3O^+]\,[OH^-]}}{(55.5)^2} \quad \text{----------} \ \mathbf{(8)}$$

$$\mathbf{[H_3O^+]\,[OH^-] = (K_e)\,(55.5)^2 = K_w}$$

$$[H_3O^+]\,[OH^-] = K_w = 1x10^{-14} \text{ -------- } (9)$$

$$[H_3O^+]\,[OH^-] = \sqrt{K_w} = 1x10^{-7}$$

A useful relationship is obtain by taken negative logarithm of equation (9);

$$-\text{Log } K_w = -\text{Log } [H_3O^+] \;\; -\text{Log } [OH^-]$$

$$pK_w = pH + pOH$$

In pure water two molecules of H_2O give one H_3O^+ and one OH^- ions therefore;

$$[H_3O^+] = [OH^-] = \sqrt{K_w} = \sqrt{1x10^{-14}} = 1x10^{-7}\,M$$

$$pK_w = 14 = pH + pOH$$

$$pH = pOH = 7$$

- At 25°C, the ion-product constant for water is 1.008 x 10^{-14}. For convenience, we use the approximation that at room temperature K_w < 1.00 x 10^{-14}. **Table 1** shows how K_w depends on temperature. The ion-product constant for water permits us to easily find the hydronium and hydroxide ion concentrations of aqueous solutions.

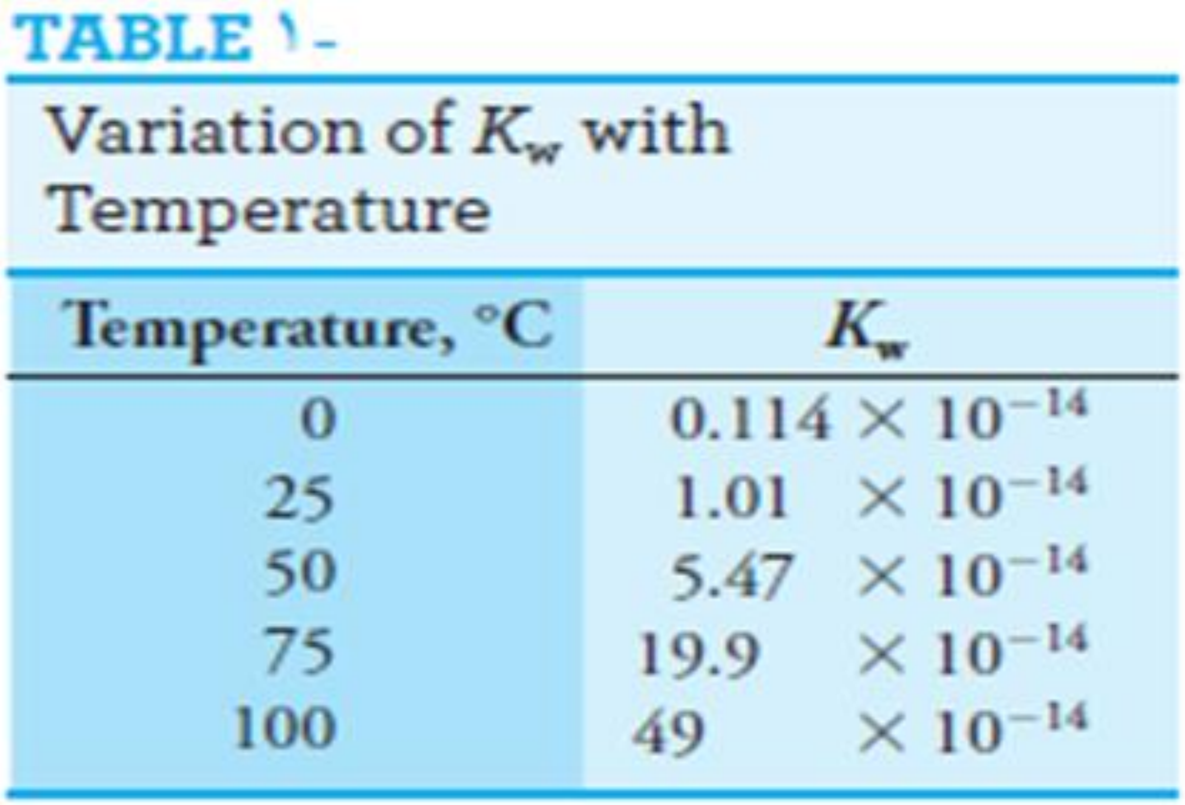


TABLE 1 -

Variation of K_w with Temperature

Temperature, °C	K_w
0	0.114×10^{-14}
25	1.01×10^{-14}
50	5.47×10^{-14}
75	19.9×10^{-14}
100	49×10^{-14}

- In most labs, the answer is “No.” Pure water at should have a pH of 7.00. Distilled water from the tap in most labs is acidic because it contains CO_2 from the atmosphere. CO_2 is an acid by virtue of the reaction

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

- CO_2 can be largely removed by boiling water and then protecting it from the atmosphere.

pH and body chemistry

- Normal pH 7.3 to 7.5
- Acidic pH < 7.3
- Alkalosis > 7.45
- Body chemistry is buffered with carbonates and phosphates which reduce the acid/alkalinity change. These reduce the pH effect.

$$[OH^-] \approx 0.200$$

$$pOH = -\log 0.200 = 0.699$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.200} = 5.00 \times 10^{-14}\ M$$

$$pH = -\log 0.500 \times 10^{-14} = 13.301$$

Note that the approximation

$$[OH^-] = 0.200 + 5.00 \times 10^{-14} \approx 0.200\ M$$

causes no significant error in our answer.

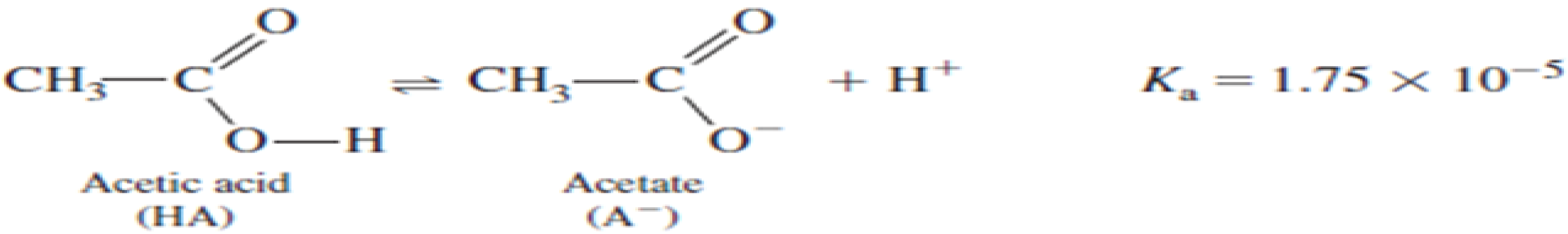
Equilibrium constant for acids and bases

- All weak acids, denoted HA, react with water by donating a proton to H_2O
- *Dissociation of weak acid:* **$HA + H_2O \rightleftharpoons H_3O^+ + A^-$**
- Which means exactly the same as;

Dissociation of weak acid: **$HA \rightleftharpoons H^+ + A^-$** $\quad$ $$K_a = \frac{[H^+][A^-]}{[HA]}$$

The equilibrium constant is called the **acid dissociation constant**. By definition, a weak acid is one that is only partially dissociated in water. This definition means that is “small“ for a weak acid.

- Common classes of weak acid Acetic acid is a typical weak acid;



And most **carboxylic acids** are weak acids, and most **carboxylate anions** are weak bases.

R-COOH	$R\text{-}COO^-$, where R is an organic substituent
A carboxylic acid	A carboxylate anion
(Weak acid, HA)	(Weak base, A^-)

- Weak acid has Ka < 1 leads to small $[H3O^+]$ and pH of 2-7
- Similarly, weak base, B react with water by abstracting a proton from H_2O:

Base hydrolysis: $\mathbf{B + H_2O \rightleftharpoons BH^+ + OH^-}$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

The equilibrium constant is called the **base hydrolysis constant.** By definition, a weak base is one for which is K_b "small."

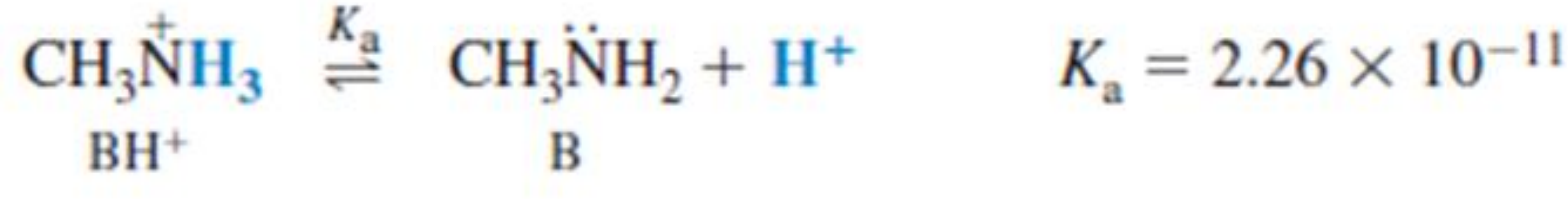
Methylamine is a typical weak base.

$$\mathbf{CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-}$$

Amines are nitrogen-containing compounds:

RNH_2	a primary amine}	RNH_3^+	
R_2NH	a secondary amine}	$R_2NH_2^+$	**ammonium ions**
R_3N	a tertiary amine}	R_3NH^+	

- **Amines** are weak bases, and **ammonium ions** are weak acids. The “parent” of all amines is ammonia, NH_3. When a base such as methylamine reacts with water, the product is the conjugate acid. That is, ammonium ion produced in the above reaction is a weak acid:



$$\underset{BH^+}{CH_3\overset{+}{N}H_3} \overset{K_a}{\rightleftharpoons} \underset{B}{CH_3\ddot{N}H_2} + H^+ \qquad K_a = 2.26 \times 10^{-11}$$

- Weak base has $K_b < 1$ leads to small [OH^-] and pH of 12-7
- Although we will usually write a **base** as **B** and an **acid** as **HA,** it is important to realize that **BH^+** is also an **acid** and **A^-** is also a **base.**

Challenge: Phenol (C_6H_5OH) is a weak acid. Explain why a solution of the ionic compound potassium phenolate ($C_6H_5O^-K^+$) is basic?

Solubility of a precipitation in pure water

With the solubility-product expression, we can calculate the solubility of a sparingly soluble substance that ionizes completely in water.

Example: How many grams of $Ba(IO_3)_2$ (487 g/mol) can be dissolved in 500 mL of water at 25°C? $K_{sp} = 1.57\times10^{-9}$

Solution A:

$$Ba(IO_3)_{2(s)} \rightleftharpoons Ba^{2+} + 2IO_3^-$$

$$[Ba^{2+}]\,[IO_3^-]^2 = K_{sp} = 1.57\times10^{-9}$$

1 mol of Ba^{2+} is formed for each mole of $Ba(IO_3)_2$ that dissolves. Therefore,

$$\text{molar solubility of } Ba(IO_3)_2 = [Ba^{2+}]$$

Since two moles of iodate are produced for each mole of barium ion, the iodate concentration is twice the barium ion concentration:

$$[IO_3^-] = 2[Ba^{2+}]$$

Substituting this last equation into the equilibrium-constant expression gives:

$$[Ba^{2+}]\,(2[Ba^{2+}])^2 = K_{sp} = 1.57\text{x}10^{-9}$$

$$[Ba^{2+}] = \left(\frac{1.57\text{x}10^{-9}}{4}\right)^{1/3} = 7.32\text{x}10^{-4}$$

Since 1 mol Ba^{2+} is produced for every mole of $Ba(IO_3)_2$,

$$\text{Solubility} = 7.32 \text{ x } 10^{-4}\text{ M}$$

To compute the number of millimoles of $Ba(IO_3)_2$ dissolved in 500 mL of solution, we write;

$$\text{No. mmol } Ba(IO_3)_2 = 7.32 \text{ x } 10^{-4}\text{ (mmol/mL) x } 500\text{ mL} = 0.366\text{ mmol}$$

mass $Ba(IO_3)_2$ = 0.366 mmol x 0.487 (g/mmol) = **0.178 g**

$$[Ba^{2+}] = 0.0200 + \tfrac{1}{2}[IO_3^-]$$

By substituting these quantities into the solubility-product expression, we find that:

$$\left(0.0200 + \tfrac{1}{2}[IO_3^-]\right)[IO_3^-]^2 = 1.57 \times 10^{-9}$$

Since $\frac{1}{2}[IO_3^-] <<< 0.0200$,

$$1.57x10^{-9} = 0.02\ [IO_3^-]^2$$

$$[IO_3^-]= 2.80x10^{-4}\ M$$

$$\text{Solubility of } Ba(IO_3)_2 = \tfrac{1}{2} \text{ x } 2.80x10^{-4} = 1.40\ x10^{-4} M$$

If we compare the solubility of barium iodate in the presence of a common ion (Example B), with the solubility pure water (Example A), we see that the presence of a small concentration of the common ion has decreased the molar solubility of $Ba(IO_3)_2$ by a factor of about 5.

Equilibrium constant of formation of complex

- An analytical important class of reactions involves the formation of soluble complex;

$$M + nX \rightleftharpoons MX_n$$

$$K_f = \frac{[MX_n]}{[M][X]^n}$$

Where K_f is the formation constant.

Oxidation –Reduction equilibra

- Equilibrium constant for redox. Reaction can be formulated in the usual way for example,

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H_3O^+ \rightleftharpoons 6Fe^{3+} + 2Cr^{3+} + 21H_2O$$

$$K = \frac{[Fe^{3+}]^6\,[Cr^{3+}]^2}{[Fe^{2+}]^6\,[Cr_2O_7^{2-}]\,[H_3O^+]^{14}}$$

Calculation using equilibria and equilibrium constants

- To illustrate the type of computations that one might perform either to evaluate an equilibrium constant for measured concentration or to use the equilibrium constant to calculate the concentration of the reactants and products in a particular equilibrium mixture.
- These equilibria are fundamentally the same as any other type of equilibrium , but the calculations do not usually get as messy as other types of calculations.

i. Write the balanced equation and use the stoichiometry to express the concentration of all species in terms of the initial concentration of one of the species and a variable.

ii. Write the equilibrium constant expressions from the balanced equation and substitute the equilibrium concentrations into it.

iii. Solve the expression for x and determine all equilibrium concentrations.

- **Example:** Suppose the following reaction: **A+B ↔ C+D** The primary concentration of A= 0.2M, B= 0.5M and Keq= 0.3 calculate the concentration of A, B, C and D at equilibrium?

- **Solution**

The first step in the solution is to write down the equilibrium expression.

$$Ke = \frac{[C]\,[D]}{[A][B]}$$

- The second step is to construct the concentration table in order to find out how the concentrations of the reactants and products are changed and become at equilibrium. Before starting the reaction the [A] = 0.2 and [B]= 0.5 present initially and the [C] and [D] are equal zero. But when the reaction is reached to equilibrium, the concentration of A and B decrease while the concentration of C and D.

Ionization constant of weak monotropic acids (Ka) and pH of solution:

Let us consider of a weak monobasic acid HA which reacts with water to give:

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

Applying the law of mass action;

$$Ka = \frac{[H_3O^+][A^-]}{[HA]}$$

In pure aqueous solution of HA,

$$\mathbf{[H_3O^+] = [A^-]}$$

and the concentration of molecular acid [HA] is $C_a - [H_3O^+]$ where C_a is the original concentration of HA, thus at equilibrium, we have;

$$\begin{array}{ccccccc} HA & + & H_2O & \leftrightarrow & H_3O^+ & + & A^- \\ C_a - [H_3O^+] & & & & [H_3O^+] & & [H_3O^+] \\ C_a - [A^-] & & & & [A^-] & & [A^-] \end{array}$$

$$K_a = \frac{[H_3O^+]^2}{C_a - [H_3O^+]} = \frac{[A^-]^2}{C_a - [A^-]} \qquad \text{-------} \ (i)$$

Solving equation this for H_3O^+ gives;

$$[H_3O^+] = \frac{1}{2} K_a + \frac{1}{4} K_a + K_a . C_a$$

If the degree of ionization of weak acid is less than 5% the value of $[H_3O^+]$ is very small compared to Ca, hence it can be discarded from the denominator of equation (i) which then be written in the approximated form.

$$K_a = \frac{[H_3O^+]^2}{C_a}$$

$$\{ [H_3O^+] = \sqrt{K_a C_a} \} -\log$$

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \text{Log } C_a$$

Degree of ionization (α) of weak acid

- It is known that an acid is any substance capable of yielding H^+ in water solution (Arrhenius definition). The strength of an acid is therefore, determined by the extent to which it is ionized giving hydronium ions.
- In of the **Brønsted-Lowry** sense the tendency of an acid to lose or donate protons is a measure of its strength.
- The extent or degree of ionization (α) of an acid at equilibrium is given as:

$$\alpha = \frac{[H_3O^+]}{C_a}$$

Where C_a is molar concentration of the acid.

Percent ionization

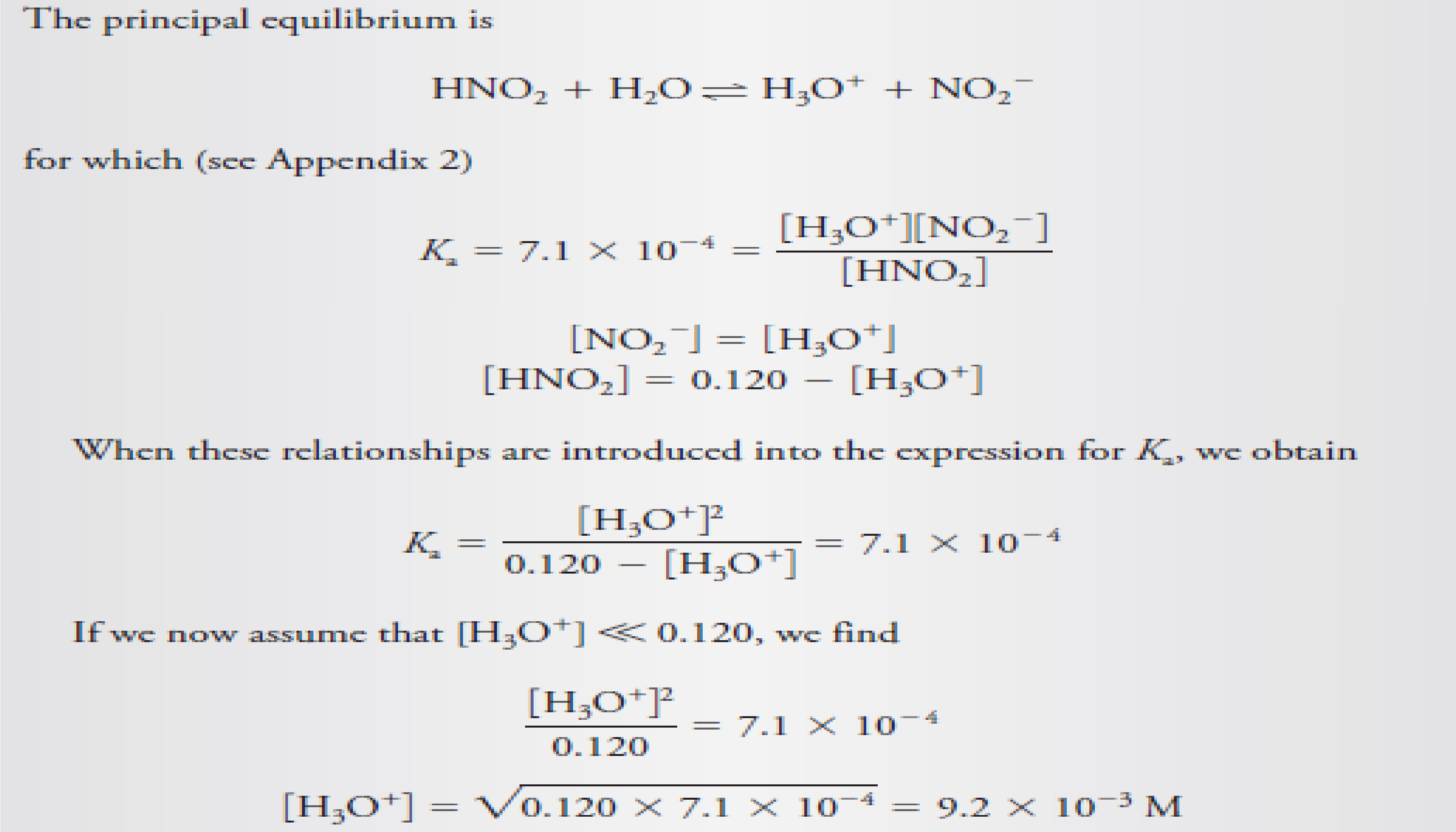
$$\alpha\% = \frac{[H_3O^+]}{C_a} \times 100$$

The equation which combine three factors, the ionization constant (K_a), the molarity (M) and degree of ionization (α) is;

$$K_a = \frac{(M\alpha)\,(M\alpha)}{M\,(1-\alpha)}$$

Where ($M\alpha$) refer to the molar concentration of H_3O^+ ions and also for molarity of the anion, while $M\,(1-\alpha)$ is the conc. of the unionized molecules of the acid.

Example: Calculate the hydronium ion concentration in 0.120 M nitrous acid?



The principal equilibrium is

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

for which (see Appendix 2)

$$K_a = 7.1 \times 10^{-4} = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$[NO_2^-] = [H_3O^+]$$
$$[HNO_2] = 0.120 - [H_3O^+]$$

When these relationships are introduced into the expression for K_a, we obtain

$$K_a = \frac{[H_3O^+]^2}{0.120 - [H_3O^+]} = 7.1 \times 10^{-4}$$

If we now assume that $[H_3O^+] \ll 0.120$, we find

$$\frac{[H_3O^+]^2}{0.120} = 7.1 \times 10^{-4}$$

$$[H_3O^+] = \sqrt{0.120 \times 7.1 \times 10^{-4}} = 9.2 \times 10^{-3}\ M$$

$$K_a = \frac{X^2}{0.3} = 7.2\text{x}10^{-10}$$, solving for x

$$X = [H_3O^+] = (0.30)\,(7.2\text{x}10^{-10}) = \mathbf{1.47\text{x}10^{-5}\ M}$$

$$\mathbf{pH=}\ \text{-Log}\,[H_3O^+] = \text{-Log}\ 1.47\text{x}10^{-5}\ \mathbf{= 4.83}$$

The percent ionization is: $[HCN]_o = C_a$;

Percent ionization = $\alpha\% = \frac{[H_3O^+]}{[HCN]_o}\text{x}100 = \frac{1.47\text{x}10^{-5}}{0.30}\text{ x }100 = 4.9\text{x }10^{-3}$

$$K_b = \frac{[OH^-]^2}{[BOH]} = \frac{[OH^-]^2}{C_b}$$

Where C_b is the conc. of the base in mole per liter.

Since; $[\mathbf{OH^-}] = \mathbf{K_w / [H_3O^+]}$

$$\mathbf{[OH^-] = \sqrt{K_b.C_b}.}$$

Then;

$$\frac{K_w}{[H_3O^+]} = \sqrt{K_b.C_b}$$

And

$$\mathbf{pH = pK_w - \frac{1}{2}pK_b + \frac{1}{2}\,Log\ C_b}$$

In term of Arrhenious definition, the strength of a base is determined by its degree of ionization in solution to give OH^- ions thus;

$$\boldsymbol{\alpha = \frac{[OH^-]}{C_b}}$$

$$\boldsymbol{\%\alpha = \frac{[OH^-]}{C_b} \times 100}$$

Make approximation $[C_5H_5N] = 0.010\text{-}x = 0.010M$. Substituting

$$K_b = \frac{X^2}{(0.01-x)} = 1.7\times10^{-9}$$

$$X = [OH^-] = 4.1\times10^{-6}M$$

Testing the assumption that the approximation is reasonable;

$$\frac{X}{C_b} \times 100 = \frac{4.1\times10^{-6}}{0.010} \times 100 = 0.041\%$$

Since x is less than 5% of initial concentration of pyridine, then the assumption is valid. At equilibrium, $x = [OH^-] = 4.1\times10^{-6}$ M, to find the pH, first calculate the pOH and then use the relationship; pH + pOH = 14

$$pOH = -\text{Log } 4.1\times10^{-6} = 5.38$$

$$pH = 14 - 5.38 = 8.62$$

Polyprotic acids

- Acids which in their reaction with water yield more than one hydronium ion per one molecule are called polyprotic acids. Acids which can produce two hydronium ions, such as H_2S, H_2CO_3, H_2SO_3, $H_2C_2O_4$ and H_2SO_4 are called dibasic (diprotic). If an acid has three hydronium ions (producing three H^+) then it is called tribasic (triprotic) acid, such as H_3PO_4, H_3ASO_4.
- If we take oxalic acid as an example for dibasic acid $H_2C_2O_4$, the ionization reactions occur in two steps; the conjugate base in the first step becomes the acid in the second step of ionization:

$$\mathbf{H_2C_2O_4 \leftrightarrow H^+ + HC_2O_4^- \qquad K_{a1} = 6.5x10^{-2}}$$

$$\mathbf{HC_2O_4^- \leftrightarrow H^+ + C_2O_4^{2-} \qquad K_{a2} = 6.1x10^{-5}}$$

This example is typical in that $K_{a1} >> K_{a2.}$ .It is always more difficult to remove an H^+ ion from a negative ion such as $HC_2O_4^-$ than from neutral molecule such as $H_2C_2O_4$.

When H_2S reacts with water, it undergoes tow step of ionization, where each step has its own value of ionization constant.

$$\mathbf{H_2S + H_2O \leftrightarrow H_3O^+ + HS^-} \text{ -------- } \mathbf{(a)}$$

$$\mathbf{HS^- + H_2O \leftrightarrow H_3O^+ + S^{2-}} \text{ -------- } \mathbf{(b)}$$

The overall reaction of H2S with water is:

$$\mathbf{H_2S + 2H_2O \leftrightarrow 2H_3O^+ + S^{2-}} \text{ --------} \mathbf{(c)}$$

The ionization constant expression for the primary and secondary ionizations as presented in the equations (a and b) are as follows;

$$\frac{[H_3O^+][HS^-]}{[H_2S]} = K_{a1} = 5.7 \times 10^{-8} \qquad \text{---------}\ (d)$$

$$\frac{[H_3O^+]\,[S^{2-}]}{[HS]} = K_{a2} = 1.2 \times 10^{-15} \qquad \text{--------}\ (e)$$

For the overall reaction (c)

$$\frac{[H_3O^+]^2\,[S^{2-}]}{[H_2S]} = K_a = 6.8 \times 10^{-23} \qquad \text{---------}\ (f)$$

The overall ionization constant K_a shown in (f) is actually obtained by multiplying the equations (d) and (e).

It can be observed that K_{a1} is almost 5 x10^7 times greater than K_{a2} thus H_2S is much stronger acid than HS^- ion. Therefore, the molar concentration of hydronium ion of H_2S is calculated as if it is derived from the primary ionization alone. Hence equation (d) is applied for calculation $[H_3O^+]$ when the solution contains only H_2S and H_2O, it is obvious, that $[HS^-] = [H_3O^+]$ and then;

$$\frac{\mathbf{[H_3O^+]^2}}{\mathbf{[H_2S]}} = K_{a1} = 5.7 \times 10^{-8} \quad \text{---------} \text{ (d)}$$

So, the general equation for calculating $[H_3O^+]$ of a solution of dibasic acid is therefore;

$$\mathbf{[H_3O^+] = \sqrt{K_{a1}.C_a}}$$

Another point of interest in calculations involving weak dibasic acid is that the numerical value of the molar concentration of the divalent anion in a saturated solution of the acid is practically equal to K_{a2}. Thus the actual value of the sulphide ion conc. is a saturated solution of H_2S is;

$$\mathbf{[S^{2-}] = K_{a2} = 1.2x10^{-15}}$$

Because of the large difference between the value of K_{a1} and K_{a2} and the very low of the latter, the conc. of H_3O^+ ions produced by the ionization of HS^- is so small ,that $[HS^-]$ has the same value as that due to the first ionization. Hence $[H_3O^+] = [HS^-]$. In a saturated aqueous solution of H_2S. When the second ionization is applied;

Example: A saturated solution of H_2S is approximately 0.1 M. Calculate:

A: The pH of the saturated solution and degree of ionization.

B: The sulphide ion concentration of the saturated solution.

C: The sulphide ion concentration of the solution when a strong acid is added to make the solution 0.20M with respect to H_3O^+ ion .$K_{a1} = 5.7 \times 10^{-8}$, $K_{a2} = 1.2 \times 10^{-15}$.

Solution:

A- The hydronium ion conc. here is calculated as follow:

$$\frac{\mathbf{[H_3O^+][HS^-]}}{\mathbf{[H_2S]}} = K_{a1} = 5.7 \text{ x } 10^{-8}$$

Let $x = [H_3O^+] = [HS^-]$

Then $0.1 - x = [H_2S]$

And

$$\frac{(x)\,(x)}{0.1 - x} = 5.7 \text{ x } 10^{-8} \qquad x = 7.5 \text{x} 10^{-5}\text{ M} = [H_3O^+]$$

$$\text{Degree of ionization} = \frac{[H_3O^+]}{[H_2S]} = \frac{7.5\text{x}10^{-5}}{0.1} = 1.2\text{x}10^{-15}$$

B- $[S^{2-}] = K_{a2} = 1.2\text{x}10^{-15}\text{M}$

C- In this the overall ionization reaction of hydrogen sulphide and water must be used.

$$\mathbf{H_2S + 2H_2O \leftrightarrow 2H_3O^+ + S^{2-}}$$

$[H_3O^+] = 0.2M$, and $[S^{2-}] = 0.1M$

In equilibrium;

$$\frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = K_a \quad \text{and} \quad \frac{(0.2)^2[S^{2-}]}{0.1} = 6.8 \times 10^{-23}$$

$[S^{2-}] = \mathbf{1.7X10^{-22}\ M}$

Systematic treatment of equilibrium

- The study of chemical equilibrium provides a basis for most techniques in analytical chemistry, such as titrations, and chromatography, and for the application of chemistry to other disciplines, such as geology and biology.
- The systematic treatment of equilibrium gives us tools to deal with all types of chemical equlilibria, regardless of their complexity.
- For example, if we want the solubility of barium sulfate in an acidic solution, we must calculate the concentrations of all the species in the solution. In this example, there are five species: $[Ba^{2+}]$, $[SO_4^{2-}]$, $[HSO_4^-]$, $[H_3O^+]$, and $[OH^-]$. To calculate the solubility of barium sulfate in this solution rigorously, it is necessary to create five independent algebraic equations that can be solved simultaneously to give the five concentrations.

We use three types of algebraic equations to solve multiple-equilibrium problems:

(1) Equilibrium-constant expressions.

(2) Mass-Balance Equations (MBE), and

(3) Charge-Balance Equation (CBE).

The mass balance states the quantity of dissociated and undissociated acetic acid in the solution must equal the amount of acetic acid put into the solution.

MBE:

$$0.050M = C_{CH3COOH} = [CH_3COOH] + [CH_3COO^-]$$

What we put into the solution undissociated dissociated

When a compound dissociate in several ways, the MB must include all the products.

e,g. phosphoric acid H_3PO_4 dissociate to $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}

MB; $C_{H3PO4} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

Mass balance when the total concentration is known

Example: Write mass balance for K^+ and for phosphate in a solution prepared by mixing 0.025 mol KH_2PO_4 plus 0.030 mol KOH and diluting to 1.00 L.

Solution:

The total K^+ is 0.025 M + 0.030M. So one trivial mass balance is

$$[K^+] = 0.055\ M$$

The total concentration of all forms of phosphate is 0.025M. So the mass balance for phosphate is;

$$[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = 0.025\ M$$

That is, the number of atoms of Ag^+ must equal three times the total number of atoms of phosphorus, regardless of how many species contain phosphorus.

In a mass balance, the analytical concentration is equal to the sum of the concentrations of the equilibrium species derived from the parent compound (or an appropriate multiple).

CHARGE BALANCE EQUATION (CBE)

It is an algebraic statement of electroneutraliy: *CBE means the sum of positive charges in solution equals the sum of the negative charges in solution.*

Suppose the solution contains the following species:

$$H^+, OH^-, K^+, H_2PO_4^-, HPO_4^{2-}, PO_4^{3-}$$

The charge balance is;

$$[H^+] + [K^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

Charge balance equation is based on the equality in molar charge concentrations and that to obtain the charge concentration of an ion, you must multiply the molar concentration of the ion by its charge.

Example: Calculate the solubility of $Mg(OH)_2$ in water ?

Solution:

Step1. Pertinent Equation;

Two equilibria that need to be considered are:

$$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$$

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

Step 2. Definition of Unknown

Since 1 mol of Mg^{2+} is formed for each mole of $Mg(OH)_2$ dissolved,

$$\text{Solubility of } Mg(OH)_2 = [Mg^{2+}]$$

Step 3. Equilibrium-Constant Expression

$$K_{sp} = [Mg^{+2}][OH^-]^2 = 7.1x10^{-12} \text{ ---------- } (1)$$

$$K_w = [H_3O^+]\,[OH^-] = 1.0x10^{-14} \text{ --------- } (2)$$

Step 4. Mass-Balance Equation

There are two sources of OH^- ions: $Mg(OH)_2$ and H_2O as shown in step 1.

The OH^- ions resulting from dissociation of $Mg(OH)_2$, is twice the Mg^{2-} ion conc. and that from dissociation of H_2O is equal to the H_3O^+ ion conc. Thus;

$$[OH^-] = 2[Mg^{2+}] + [H_3O^+] \text{ ----------- } (3)$$

Step 5. Charge-Balance equation;

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

Note that this equation is identical to equation in step 4. Often a MBE and a CBE are the same.

Step 6. Number of independent Equations and Unknowns

We have developed three independent algebraic equations (Equations 1, 2 and 3) and have three unknowns ($[Mg^{2+}]$, $[OH^-]$ and $[H_3O^+]$). Therefore, the problem can be solved rigorously.

Step 7. Approximation

We can make approximations only in Equation 3. Since the solubility product constant for $Mg(OH)_2$ is relatively large, the solution will somewhat basic. Therefore, it is reasonable to assume that $[H_3O^+] << [OH^-]$. Equation 3 then simplifies to;

$$[OH^-] = 2[Mg^{2+}] \text{ --------- } (4)$$

Step 8. Solving the Equations

Substitution of Equation 4 into equation 1 gives;

$$[Mg^{+2}]\,(2[Mg^{+2}])^2 = 7.1x10^{-12}$$

$$[Mg^{+2}]^3 = \frac{7.1x10^{-12}}{4} = 1.78x10^{-12}$$

$$[Mg^{+2}] = \text{Solubility} = 1.21X10^{-4}\ M$$

Step 9. Check of assumption

Substitution into equation 4 yields;

$$[OH^-] = 2\ x1.21x10^{-4} = 2.42x10^{-4}\ M$$

$$[H^+] = \frac{1x10^{-14}}{2.42x10^{-4}} = 4.1x10^{-11}\ M$$

Thus, our assumption that $4.1x10^{-11} << 1.6x10^{-4}$ is certainly valid.

Step 2. Definition of the Unknown;

CaC_2O_4 is a strong electrolyte so that its molar analytical concentration is equal to the equilibrium $[Ca^{2+}]$.That is;

$$\text{Solubility} = [Ca^{2+}] \text{ --------- } (5)$$

Step 3. Equilibrium-Constant Expression;

$$[Ca^{2+}]\,[C_2O_4^{2-}] = K_{sp} = 1.7\text{x}10^{-9} \qquad \text{-------------} \ (6)$$

$$\frac{[H_3O^+]\,[HC_2O_4^-]}{[H_2C_2O_4]} = K_1 = 5.60\text{x } 10^{-2} \text{ ----------- } (7)$$

$$\frac{[H_3O^+]\,[C_2O_4^{2-}]}{[HC_2O_4^-]} = K_2 = 5.42\text{x } 10^{-5} \text{ ----------- } (8)$$

$$K_w = [H_3O^+]\,[OH^-] = 1.0\text{x}10^{-14} \qquad \text{---------} \ (9)$$

Step 4. **MBE;**

Because CaC_2O_4 is the only source of Ca^{2+} and the three oxalate species;

$$[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^{-}] + [H_2C_2O_4] \text{ ------------ } (10)$$

Moreover, the problem states that the pH is 4.0. Thus;

$$[H_3O^+] = 1.00\text{x}10^{-4}$$

and

$$[OH^-] = \frac{1.00\text{x}10^{-14}}{1.00\text{x}10^{-4}} = 1.00\text{x}10^{-10}$$

$$[H_2C_2O_4] = \frac{[H_3O^+]\,[C_2O_4^{2-}]\ 1.85}{K_1}$$

Substituting numerical values for $[H_3O^+]$ and K_1 yields;

$$[H_2C_2O_4] = \frac{[C_2O_4^{2-}]\ 1.85\text{x}10^{-4}}{5.60\text{x}\ 10^{-2}} = 3.3\text{x}10^{-3}\,[C_2O_4^{2-}]$$

Substituting these expressions for $[HC_2O_4^{-1}]$ and $[H_2C_2O_4]$ into equation 10 gives;

$$\begin{aligned}[Ca^{2+}] &= [C_2O_4^{2-}] + 1.85[C_2O_4^{2-}] + 3.30\ \text{x}10^{-3}\,[C_2O_4^{2-}] \\ &= 2.85\ [C_2O_4^{2-}]\end{aligned}$$

$$[C_2O_4^{2-}] = \frac{[Ca^{2+}]}{2.85}$$

Substituting into equation 6 gives;

$$1.7\text{x}10^{-9} = \frac{[\text{Ca}^{2+}]\,[\text{Ca}^{2+}]}{2.85}$$

$$\text{Solubility} = [\text{Ca}^{2+}] = 1.7\text{x}10^{-9} \text{ x } 2.85 = 7.1\text{x}10^{-5}\ \text{M}$$

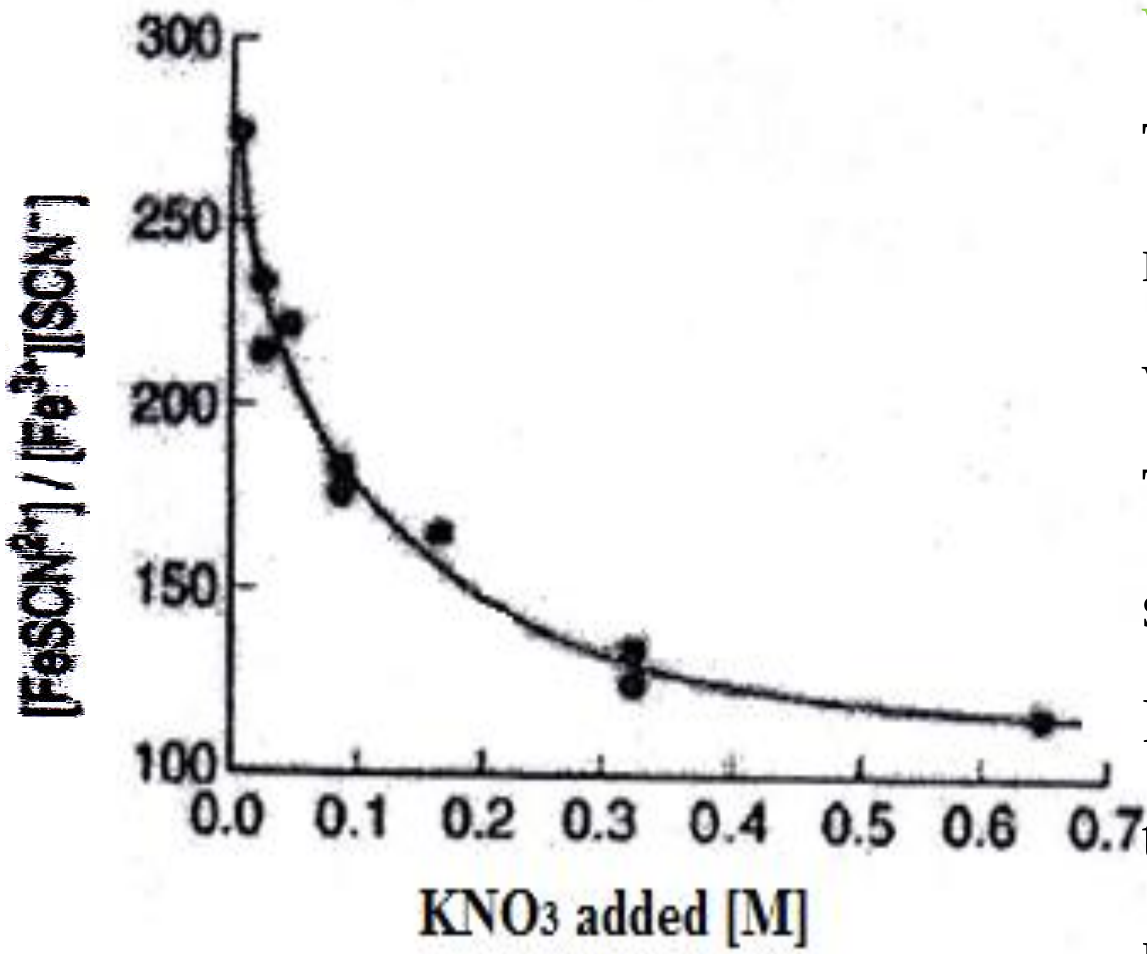
Suppose the following reaction between ferric ion and thiocyanate ion;

$$\underset{\text{Pale yellow}}{Fe^{3+}} + \underset{\text{colorless}}{SCN^-} \leftrightarrow \underset{\text{red}}{Fe(SCN)^{2+}}$$

The equilibrium constant is:

$$K = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}]\,[SCN^-]} \qquad \text{--------} \ (1)$$

- If an "inert" salt_ (we mean a salt whose ions do not react with other ions), such as KNO_3 electrolytic solution is added to the above equilibrium reaction. Experimental evidences show that the color of the ferrothiocyante ion become less intense which indicate its concentration has decreased and that the equilibrium has been shift to the left by the electrolyte, thereby, the concentration equilibrium constant is decreased as shown in the following figure. That is, the equilibrium "constant "is not really constant.



Why the equilibrium constant is really decreased?

The addition of an electrolyte to the reaction mixture, the ionic strength of the solution increases which promotes dissociation of Fe(SCN)$^{2+}$ into ions. Thus, the above reaction is driven to the left if ionic strength is raised, say, 0.01 to 0.1 M (see the Figure). Increasing ionic strength Fe(SCN)$^{2+}$ therefore reduces the attraction-between ,any particular Fe^{3+} ion and any SCN$^-$ ion, relative to their attraction for each other in distilled water. The effect reduce their tendency to come together, thereby increasing the dissociation of Fe(SCN)$^{2+}$.

Example: What is the ionic strength of a solution that is 0.05 M in KNO_3 and 0.1M in Na_2SO_4?

Solution:

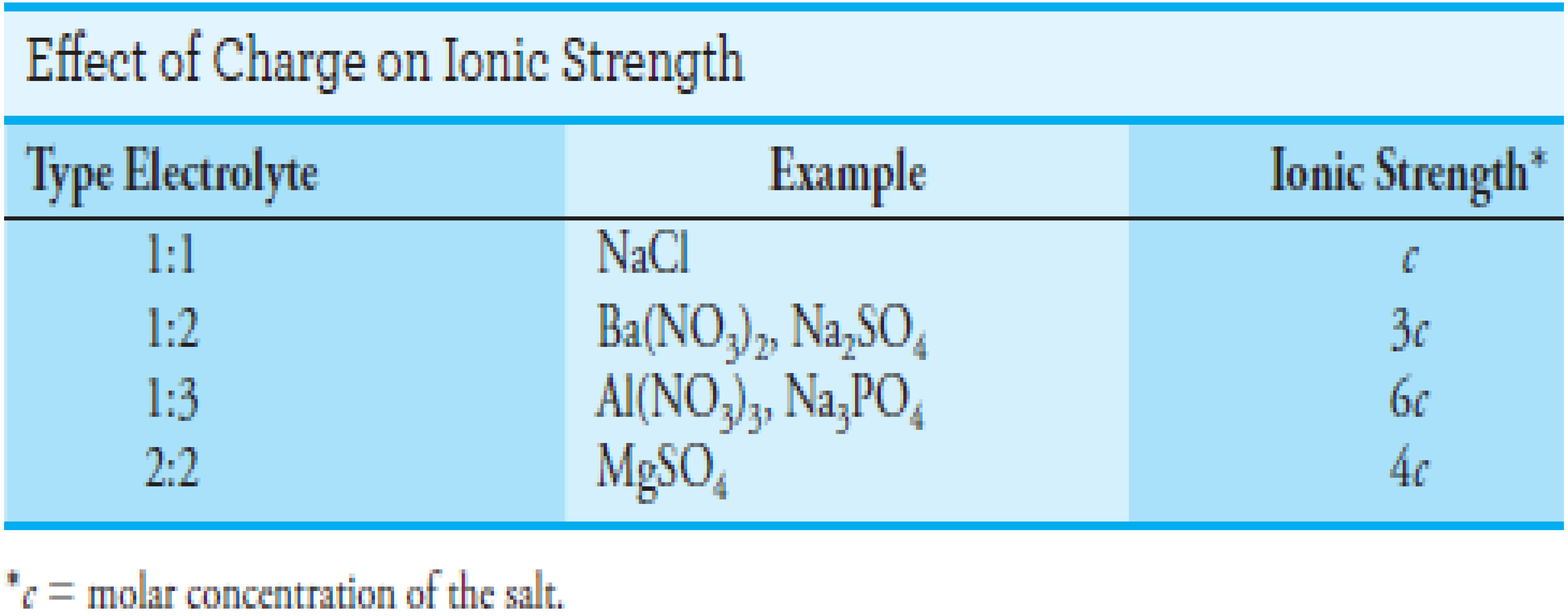
$$\mu = ½ \{[K^+] \text{ x } (+1)^2 + [NO_3^-] \text{ x } (-1)^2 + [Na^+] \text{ x } (+1)^2 + [SO_4^{2-}] \text{ x } (-2)^2\}$$

$$= ½ \{0.05 \text{ x } 1 + 0.05 \text{ x } 1 + 0.2 \text{ x } 1 + 0.1 \text{ x } 4\} = 0.35M$$

It is apparent from these examples that for a 1:l electrolyte (KNO_3), the ionic strength equals the molarity. For any other stoichiometry (such as the 2:1 electrolyte Na_2SO_4), ionic strength is greater than the molarity.

The Salt Effect

- Salts containing cations or anions with a charge ≥ 2 are much less dissociated, even in dilute solution. For example, for $MgSO_4$, 35% is present as an ion pair, not free ion. A solution of 0.025M $MgSO_4$ contains 0.016M Mg^{2+}, 0.016M $SO_4^{=}$ and 0.009M $MgSO_4(aq)$. The ionic strength of (0.025M) $MgSO_4$ is not 0.025X4= 0.1M, but just 0.065M. This salt is not strong electrolyte. While, the salts composed of cations with a charge of +1 and anions with a charge of -1 dissociate almost completely when dissolved at low concentration (< 0.1M) .We have calling such salts strong electrolytes.



Effect of Charge on Ionic Strength

Type Electrolyte	Example	Ionic Strength*
1:1	NaCl	c
1:2	$Ba(NO_3)_2$, Na_2SO_4	$3c$
1:3	$Al(NO_3)_3$, Na_3PO_4	$6c$
2:2	$MgSO_4$	$4c$

*c = molar concentration of the salt.

Activity and Activity Coefficients

Equation (1) does not predict any effect of ionic strength on a chemical reaction. To account for the effect of ionic strength, concentrations are replaced by activities. The activity, or effective concentration, of species X depends on ionic strength of the medium and is defined as:

$a_x = [X] . f_x$

The activity a_x of species X is its concentration [X] multiplied by its activity coefficient f_x.

The activity coefficient and thus the activity of X species vary with ionic strength such that substitution of a_x for [X] in any equilibrium-constant expression frees the numerical value of the constant from dependence on ionic strength.

Activity is used to express the true (ideal) concentration of an electrolyte and usually the activity is not equal the molar concentration of an electrolyte, i.e. $a_x \neq [X]$.

The activity coefficient is a measure the extent of attraction and repulsion forces between ions i.e. is a measure the deviation of behavior from ideality.

1. If the $f_x=1$, $a_x = [X]$ for dilute solution ($< 10^{-4}$M) where the interionic distance are so large that forces between ions are of no practical significance, then the behavior would be ideal and the equation (5) would be correct.

2. If the $f_x < 1$, $a_x \neq [X]$, this means that the ions is restricted in its movements by interionic forces i.e. when the concentration of such electrolytes increase or by addition of external salt, the activity coefficient is depressed and the activity becomes less than concentration.

How to calculate the activity coefficients?

Using the extended Debye- Hṻckel, we can calculate the activity coefficients which related to ionic strength,

$$\log f = \frac{-0.51z^2\sqrt{\mu}}{1 + (3.3\alpha\sqrt{\mu})} \text{(at 25°C)}$$

f is the activity coefficient of an ion of charge ±z and ἀ diameter ion (nm,; 1nm=10^{-9} nm) in an aqueous solution if ionic strength μ. The equation work fairly well for $\mu \leq 0.1$M.

Example: calculate the activity coefficient of H^+ ion when $\mu = 0.025M$, use the hydrated radius $\alpha = 0.900nm$.

Solution:

$$\text{Log } f_{H+} = \frac{(-0.51)(1)^2 . \sqrt{0.025}}{1 + (3.3 \times 0.900 \sqrt{0.025})} = - 0.05486$$

$$f_{H+} = 10^{-0.05486} = 0.881$$

Example: calculate the activity coefficient for K^+ and $SO_4^=$ for the solution 0.002 of K_2SO_4 use ion size for K^+ = 300pm and $SO_4^=$ = 400pm.

Solution:

$$\mu = \tfrac{1}{2}\left(C_1Z_1^2 + C_2Z_2^2\right)$$

$$= \tfrac{1}{2}\left\{2x\,(0.002)\,(+1)^2 + (0.002)\,(-2)^2\right\}$$

$$=0.006\ M$$

$$\log\ f = \frac{-0.51z^2\sqrt{\mu}}{1 + (3.3\alpha\sqrt{\mu})}$$

$$\log\ f_{K+} = \frac{-0.51\ (+1)^2\ \sqrt{0.006}}{1+ (3.3x\ 0.300\ \sqrt{0.006})} = -\ 0.0367$$

$$f_{K+} = 10^{-0.0367} = 0.919$$

$$\log f_{SO4=} = \frac{-0.51\ (-2)^2\sqrt{0.006}}{1+ (3.3x\ 0.400\ \sqrt{0.006})} = -\ 0.14343$$

$$f_{SO4=}\quad 10^{-0.14343} = 0.719$$

Example: Use activities to calculate the solubility of $Ba(IO_3)_2$ in a solution containing 0.033F of $MgCl_2$, $K_{sp} = 1.57x10^{-9}$. Use ion size for Ba^{2+}= 600pm and IO^{3-} =500pm.

Solution:

	$Ba(IO_3)_2 \rightleftharpoons$	Ba^{2+} +	$2IO_3^-$	$K_{sp} = 1.57x10^{-9}$
Initial conc.	solid	0	0	
Final conc.	solid	x	2x	

$$K_{sp} = a_{\ Ba2+} \ . \ a^2_{\ IO3-} = [Ba^{2+}]\ f_{\ Ba2+} \ . \ [IO_3^-]^2\ f^2_{IO3}{}^-$$

$$\mathbf{K_{sp} = [Ba^{2+}]\ [IO_3^-]^2 \ .\ f_{\ Ba2+}\ f^2_{IO3-}}$$

$$1.57x10^{-9} = (x)\ (2x)^2 \ .\ f_{\ Ba2+}\ f^2_{IO3-}$$

$$1.57x10^{-9} = 4x^3 \ .\ f_{\ Ba2+}\ f^2_{IO3-}$$

We have to find the activity coefficients for each ion. Find the ionic strength of 0.033F of $MgCl_2$ solution.

$MgCl_2 \rightleftharpoons$	Mg^{2+} +	$2Cl^-$
0.033	0.033	2x0.033=0.066

$\mu = \frac{1}{2} (C_1Z_1^2 + C_2Z_2^2)$

$= \frac{1}{2}\{(0.033) (+2)^2 + (0.066) (-1)^2\}$

$=0.099 = 0.1\ M$

$$\log f_{Ba2+} = \frac{-0.51\ (+2)^2 \sqrt{0.1}}{1+(3.3x0.600 \sqrt{0.1}} = -0.3977$$

f_{Ba2+} = 0.400

$$\log f_{IO3-} = \frac{-0.51\ (-1)^2 \sqrt{0.1}}{1+(3.3x0.500 \sqrt{0.1}} = -0.1062$$

f_{IO3-} = 0.783

- We substitute these values in solubility expression to find the solubility of;

$Ba(IO_3)_2$

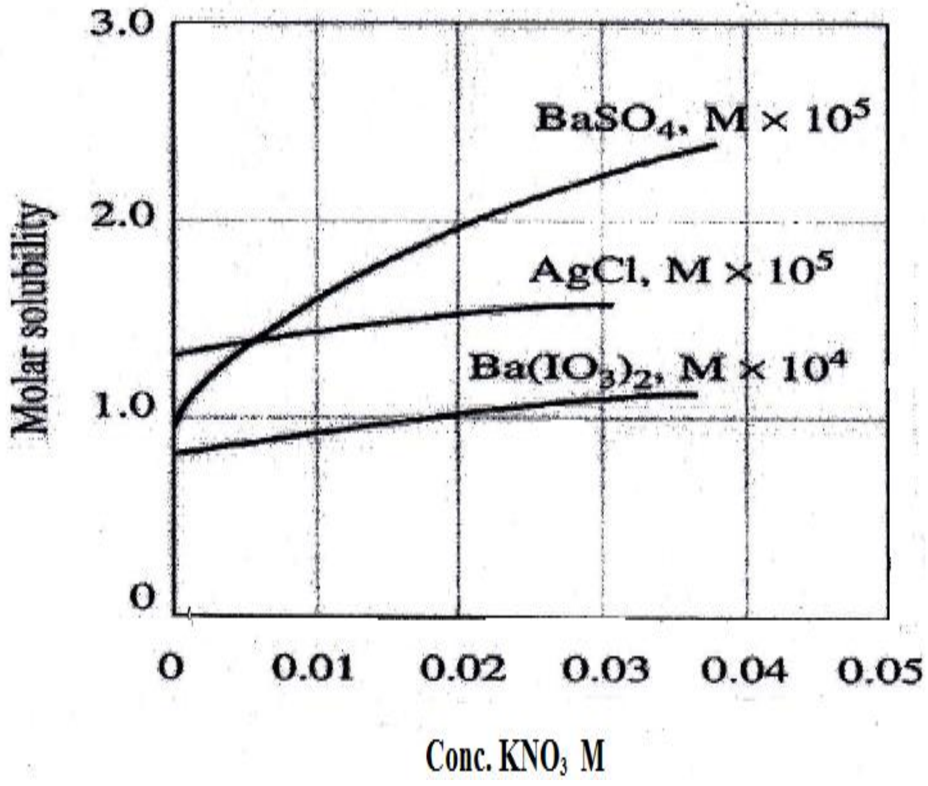
$$1.57x10^{-9} = 4x^3 \textbf{ . } f_{Ba2+}\ f^2_{IO3-}$$

$$= 0.981\ X^3$$

$$X^3 = \frac{1.57x10^{-9}}{0.981} = 1.17x10^{-3}\ M$$

Effect of ionic strength on Solubility

The solubility of the precipitates increases (in general) in electrolyte solutions.



The above Figure shows that the magnitude of this effect for three precipitates present in the solutions of different concentrations of KNO_3.

i. The solubility of $BaSO_4$ increase two-folds when the KNO_3 concentration is increased from 0 to 0.02 M.

ii. The same change in electrolyte concentration increases the solubility of $Ba(IO_3)_2$ by a factor of only 1.25 and of AgCl by 1.20.

iii. The effect of electrolyte on solubility is due to the attraction of solute ions by electrolyte dissolved in solution. This attraction leads to the displacement in the direction of chemical equilibrium.

Example: Calculate the solubility of AgCl in 0.1 M Na_2SO_4 take into account the activities. Compare the results without activities and comment. K_{sp} (AgCl) =$1.0x10^{-10}$, ion size for Ag^+ and Cl^- are 0.250 and 0.300 nm respectively.

Solution:

$$K_{sp} = a_{Ag+} \, . \, a_{Cl-} = [Ag^+] \, f_{Ag+} \, . \, [Cl^-] \, f_{Cl^-}$$

$$\mu = ½\{[Na^+] \text{ x } (+1)^2 + [SO_4^{=}] \text{ x } (-2)^2\}$$

$$= ½\{(0.2) \text{ x } (+1)^2 + (0.1) \text{ x } (4)\} = 0.3M$$

$$\log f_{Ag+} = \frac{-0.51 \, (+1)^2 \sqrt{0.3}}{1+(3.3x0.250 \sqrt{0.3})} = -0.200$$

$$\mathbf{f_{Ag+} = 0.63}$$

It is wrong to imagine that dissolving the solid material in solvent only produces the solutions, but they could be obtained by dissolving the solute of different states (gas, liquid, and solid) in solvent of different states of gaseous, liquid, and solid i.e. there are liquid-liquid (for example, ethylene glycol in water-antifreeze solution), gas-liquid (for example, carbonated beverages, which contains dissolved CO2), solid-liquid (Na_2CO_3 in water), gas-gas (for example, the atmosphere that surrounds the earth etc.

Classification of solutions

Solutions are classified into:

According to the concentration of solute in solution as follows;

1. Saturated solution; the solution in which the solute in dynamic equilibrium state with solution at certain temperature. i.e. dissolve amount of solute= amount precipitated of it.

The concentration of saturated solution at certain temperature is represented by solubility of solute in solvent at that temperature. e.g. 35.7g NaCl /100mL H_2O at 0°C.

2. Unsaturated solution; the solution in which the amount of solute less than is needed for saturation, thus, no dynamic equilibrium exist between the solute and solvent .g. 20g of NaCl in 100 mL of water at 0°C.

3- Supersaturated solutions; the solutions that contain more solute than ordinary required for saturation, at 0°C. Sodium acetate dissolves in water to extent of 119g/100mL, but its solubility increases with increasing temperature.

Solubility of precipitates

Solubility *is the amount of solute needed to give a saturated solution with a given amount of solvent*. Thus, the solubility of NaCl in water at 0°C is 37g/100mL. Usually solute's solubility changes with temperature. For example at 100°C the solubility of NaCl is 39.1g/100mL of H_2O.this means that we should always specify the temperature when stating the solubility. We can classify the materials according to their solubilities in certain solution into:

Reactions that yield products of limited solubility find application in three important analytical processes:

1. The separation of an analyte as a precipitate from soluble substances that would otherwise interfere with ultimate measurement.

2. Gravimetric analysis, in which the precipitate is formed whose weight is chemically related to the amount of analyte.

3. Titrimetric analysis, based on the determination of volume of a standard reagent required precipitating the analyte essentially completely.

The success of each of these applications requires that the solids produced have a relatively low solubility, be reasonably pure, and have a suitable particle size.

The Solubility- product Constant (K_{sp})

It is the equilibrium constant for the dissociation of solid salts gives its ions in solution.

Solid is omitted from equilibrium constant because it is in its standard state. As an example, consider the dissociation of mercury (1) chloride (Hg_2Cl_2) in water. In saturated solution of Hg_2Cl_2, equilibrium exists between the solid salt and its dissolved ions. The reaction is;

$$Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$$

$$K_e = \frac{[Hg_2^{2+}]\,[Cl^-]^2}{[Hg_2Cl_{2(s)}]}$$

$$K_e\,[Hg_2Cl_{2(s)}] = K_{sp} = [Hg_2^{2+}]\,[Cl^-]^2$$

Example What are the molar concentrations of Ag^+ and CrO_4^{2-} in a saturated solution of Ag_2CrO_4 at 25°C? For Ag_2CrO_4 $K_{sp} = 1.9x10^{-12}$.

Solution:

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

Initial conc.	solid	0	0
Final conc.	solid	2x	x

$$K_{sp} = [Ag^+][\ CrO_4^{2-}]$$

$$1.9x10^{-12} = (2x)^2\ (x)$$

$$[CrO_4^{2-}] = x = 7.8x10^{-5}\ M$$

$$[Ag^+] = 2x = 2\ (7.8x10^{-5}) = 1.6x10^{-4}\ M$$

If NaCl solution is now added to this solution, the Cl- ion concentration will increase and drive this equilibrium to the left, thereby causing some of AgCl to precipitate. In other word, AgCl is less soluble in aqueous NaCl than in pure water.

Example: What will be the concentration of Hg_2^{2+} in a solution containing 0.03M NaCl saturated with Hg2Cl2? $K_{sp}(Hg_2Cl_2)=1.2\times10^{-18}$.

$$Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$$

Initial conc.	solid	0	0.030
Final conc.	solid	x	2x+0.030

The initial conc. of Cl^- is from the dissolved NaCl, which dissociates completely into Na^+ and Cl^-. The final conc. of Cl^- has contribution from NaCl and Hg_2Cl_2. The proper solubility equation is;

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (x)\,(2x+0.030) = 1.2x10^{-18}$$

since, $2x \ll 0.030$, the equation simplifies to $(x)\,(0.30)^2 = 1.2x10^{-18}$ ·

in the absence of Cl^-, the solubility of Hg_2^{2+} was $2.6x10^{-7}$ M. in the presence of 0.030 M Cl^- , the solubility of Hg_2^{2+} is reduced to $1.3x10^{-15}$ M.

Example: Calculate the molar solubility of $Ba(IO_3)_2$ in a solution that result when 200 mL of 0.01 M $Ba(NO_3)_2$ is mixed with 100 mL of 0.1M $NaIO_3$ .K_{sp} $Ba(IO_3)_2$ = $1.57x10^{-9}$

Solution:

$$Ba(NO_3)_2 + 2NaIO_3 \rightleftharpoons Ba(IO_3)_2 + 2NaNO_3$$

no.mmol Ba^{2+} = 200 mL x 0.010mmol/mL= 2.0 mmol

no.mmol IO_3^- = 100 mL x 0.10 mmol/mL =10.0mmol

If formation of $Ba(IO_3)_2$ is complete,

no.mmol excess $NaIO_3$ = 10.0 - 2(2.0) = 6.0

$$[IO_3^-] = \frac{6.0\ \text{mmol}}{200\text{mL}+100\text{mL}} = \frac{6.0\ \text{mmol}}{300\text{mL}} = 0.020\text{M}$$

Molar solubility $Ba(IO_3)_2$ = $[Ba^{2+}]$

$[IO_3^-]$ = 0.020 = $2[Ba^{2+}]$ +

where $2[Ba^{2+}]$ represents the IO_3^- contributed by the sparingly soluble $Ba(IO_3)_2$; if $[IO_3^-] = 0.020$

$$\text{Solubility } Ba(IO_3)_2 = [Ba^{2+}] = \frac{Ksp}{[IO_3^-]^2} = \frac{1.57\times10^{-9}}{(0.020)^2}$$

$$= 3.93\times10^{-6}\ M$$

2- The effect of pH on solubility

The solubilities of many precipitates are affected by the presence of $[H_3O^+]$ in solution. Precipitates that exhibit this behavior contain an **anion with basic properties, a cation with acidic properties, or both.** An example of a precipitate containing an anion with basic properties is barium sulphate:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+} + SO_4^{=}$$

$$SO_4^{=} + H_3O^{+} \rightleftharpoons HSO_4^{-} + H_2O$$

Thus, its solubility increases with increases in acidity.

On other hand precipitates with acidic cation, become less soluble as the acid concentration becomes greater. For example, when water is saturated with bismuth iodide, the following equilibria are established:

$$BiI_3 \rightleftharpoons Bi^{3+} + 3I^{-}$$

$$Bi^{3+} + 2H_2O \rightleftharpoons Bi(OH)^{2+} + H_3O^{+}$$

Addition of acid to this system decreases the concentration of Bi $(OH)^{2+}$, resulting increases in Bi^{3+} shift the first equilibrium to the left and cause the formation of additional precipitate.

(A) Solubility calculations at constant pH

The calculation of solubility under this circumstance is illustrated in **(lecture 7pp.54).**

(B) Solubility calculations at variable pH

If a salt of weak acid, H_2A, is represented by the formula **MA**, it will do so according to the reaction;

$$MA + 2\,H_3O^+ \rightleftharpoons M^{2+} + H_2A + 2H_2O \text{ --------- } (1)$$

The solubility product expression of the salt is;

$$K_{sp} = [M^{2+}]\,[A^=] \qquad \text{---------} \ (2)$$

For weak dibasic acid, the overall dissociation constant is;

$$K_a = \frac{[H_3O^+]^2[A^=]}{[H_2A]} \qquad \text{---------} \ (3)$$

By dividing the expression (2 & 3) in one gives (4);

$$\frac{[M^{2+}]\,[A^{=}]}{\dfrac{[H_3O^{+}]^2[A^{=}]}{[H_2A]}} = \frac{K_{sp}}{K_a} \qquad \text{---------} \; (4)$$

Simplifying equation (4) lead to;

$$\frac{[M^{2+}]\,[H_2A]}{[H_3O^{+}]^2} = \frac{K_{sp}}{K_a} \qquad \text{---------} \; (5)$$

For slightly soluble salts such as those of the sulfide (ZnS, CuS, etc.)

$$\frac{[M^{2+}]\,[H_2S]}{[H_3O^+]^2} = \frac{K_{sp}}{6.8\ \times 10^{-23}}$$

For slightly soluble Carbonate Salts:

$$\frac{[M^{2+}]\,[H_2CO_3]}{[H_3O^+]^2} = \frac{K_{sp}}{6.8\ \times 10^{-17}}$$

Example: From the data, show calculations as to whether one or both sulfide salts are soluble or insoluble in 1M HCl?

K_{sp} (PbS)= $3.4\mathrm{x}10^{-28}$ K_{sp} (MnS) =$1.4\mathrm{x}10^{-15}$

$K_a(H_2S)$ = $6.8\mathrm{x}10^{-23}$ $[H_2S]$= 0.1M in saturated

Solution: For lead,

$$\frac{[Pb^{2+}]\,[H_2S]}{[H_3O^+]^2} = \frac{3.4\mathrm{x}10^{-28}}{6.8\ \mathrm{x}10^{-23}}$$

$$\frac{[Pb^{2+}]\,(0.10)}{(1)^2} = \frac{3.4\mathrm{x}10^{-28}}{6.8\ \mathrm{x}10^{-23}}$$

$$[Pb^{2+}] = 5.0\mathrm{x}10^{-5}\ M$$

This low concentration indicates that the PbS is slightly soluble in 1M HCl.

For MnS,

$$\frac{[Mn^{2+}]\,[H_2S]}{[H_3O^+]^2} = \frac{1.4x10^{-15}}{6.8\ x10^{-23}}$$

$$\frac{[Mn^{2+}]\,(0.10)}{(1)^2} = \frac{1.4x10^{-15}}{6.8\ x10^{-23}}$$

$$[Mn^{2+}] = 2.1x10^{-8}\ M$$

This theoretical concentration of Mn^{2+} ions shows that the MnS is readily soluble in 1M HCl.

By simplification,

1. For moderately soluble precipitate, the $[H_3O^+]$ will be small and can be neglected.
2. For precipitate of low solubility, the $[OH^-]$ and $[H_3O^+]$ are identical.

In the first case,

$$2[M^{2+}] = [OH^-] \quad \text{------------------} \ (4)$$

Substitute (4) in (1) gives;

$$[M^{2+}] = \left(\frac{K_{sp}}{4}\right)^{1/3} = S \qquad S = \text{solubility} \ \text{-------} \ (5)$$

In the second case, $2[M^{2+}] << [OH^-]$ then equation (3) becomes;

$$[H_3O^+] = [OH^-] = 1x10^{-7}$$

Substitute this in equation (1) gives;

$$[M^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{K_{sp}}{1x10^{-14}} = S \qquad \text{-------} \ (6)$$

Example: Calculate the solubility of $Fe(OH)_3$ in water. $K_{SP}(Fe(OH)_3)$=4x1 0^{-38}

$$Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+} + 3OH^-$$

$$2H_2O \rightleftharpoons H_3O^+ + 2OH^-$$

Let's assume the charge-balance expression

$3[Fe^{3+}] + [H_3O^+] = [OH^-]$, then $[H_3O^+]$ is very small

$$\mathbf{3[Fe^{3+}] = [OH^-]}$$

$$Ksp = [Fe^{3+}]\ [OH^-]^3$$

$$= [Fe^{3+}]\{3[Fe^{3+}]\}^3$$

$$= 27[Fe^{3+}]^4$$

$$[Fe^{3+}] = \sqrt[4]{\frac{Ksp}{27}} = \sqrt[4]{\frac{4\times10^{-38}}{27}}$$

$$= \mathbf{1.96x10^{-10}\ M \approx 2x10^{-10}\ M}$$

We have assumed, however, that $[OH^-] = 3[Fe^{3+}] = 3 \times 2 \times 10^{-10} = 6 \times 10^{-10}$ M this means that,

$$[H_3O^+] = \frac{1 \times 10^{-14}}{6 \times 10^{-10}} = 1.7 \times 10^{-5} \text{ M}$$

Clearly, $[H_3O^+]$ is not much smaller than $3[Fe^{3+}]$; indeed, the reverse appears to be;

$$3[Fe^{3+}] << [H_3O^+]$$

and the charge-balance equation reduces to

$$[H_3O^+] = [OH^-] = 1 \times 10^{-7}$$

substitution for $[OH^-]$ in the solubility product expression gives,

$$[Fe^{3+}] = \frac{4 \times 10^{-38}}{(1 \times 10^{-7})^3} = \mathbf{4 \times 10^{-17}\ M = S}$$

The assumption that $3[Fe^{3+}] << [H_3O^+]$ is clearly valid. Note the large error in the first assumption where the faulty assumption was made.

Example: A solution is 0.20 M in each Al^{3+} and Ni^{2+} .At what pH value each metal begins to precipitate? K_{sp} {$Al(OH)_3$} = $2.20x10^{-32}$ and K_{sp} {$Ni(OH)_2$} = $2.00x10^{-14}$.

For Al^{3+}

$K_{sp} = [Al^{3+}] [OH^-]^3$

$2.20x10^{-32} = (0.20) [OH^-]^3$

$[OH^-]^3 = 11x10^{-32}$

$-log [OH^-]^3 = 32 – log 11$

$3pOH = 32- 1.0414$

$pOH = 10.32$

$pH = 14- 10.32 = \mathbf{3.68}$

For Ni^{2+}

$K_{sp} = [Ni^{2+}] [OH^-]^2$

$2.00x10^{-14} = (0.20) [OH^-]^3$

$[OH^-]^2 = 1x10^{-13}$

$-log [OH^-]^2 = –log 1x10^{-13}$

$2pOH = 13$

$pOH = 6.5$

$pH = 14- 6.5 = \mathbf{7.5}$

4- Effect of Complex Ion Formation on Solubility

The solubility of a precipitate may increase dramatically in the presence of reagents that form complexes with anion or the cation of the precipitate. For example, fluoride ions prevent the precipitation of $Al(OH)_3$ even though the K_{sp} of this precipitate is very small ($2x10^{-32}$). The cause of this increase in solubility is shown by;

$$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$$

$$Al^{3+} + 6F^- \rightleftharpoons AlF_6^{3-}$$

The fluoride complex is sufficiently stable to permit fluoride ions to compete successfully with hydroxide ions for aluminium ions.

- **Example:** Calculate the solubility of AgCl in 0.01 M NH_3. K_{sp} (AgCl = $1x10^{-18}$, K_{f1}= $2.3x10^3$, K_{f2}= $6.9x10^3$.

Solution:

$$AgCl \rightleftharpoons Ag^+ + Cl^- \qquad K_{sp} = [Ag^+]\,[Cl^-] \text{ -------- } (1)$$

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+ \qquad K_{f1} = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} \text{ ----}(2)$$

$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad K_{f2} = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+][NH_3]} \text{ --- } (3)$$

Mass-balance expression is;

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

$$= [Ag^+]+ K_{f1}\,[Ag^+][NH_3]+K_{f2}\,K_{f1}\,[Ag^+][NH_3]^3$$

$$\frac{C_{Ag^+}}{[Ag^+]} = 1 + K_{f1}\,[NH_3] + K_{f2}\,K_{f1}[NH_3]^2$$

$$\frac{[Ag^+]}{C_{Ag^+}} = \frac{1}{1 + K_{f1}\,[NH_3] + K_{f2}\,K_{f1}[NH_3]^2}$$

$$\frac{{}^{Ksp}/_{[Cl]^-}}{C_{Ag^+}} = \frac{1}{1 + K_{f1}\,[NH_3] + K_{f2}\,K_{f1}[NH_3]^2}$$

$$K_{sp} = C_{Ag^+}\,[Cl^-] = \frac{1}{1 + K_{f1}\,[NH_3] + K_{f2}\,K_{f1}[NH_3]}$$

$$= \frac{1}{1 + (2.3x10^3)(0.01) + (2.3x10^3)(\,6.9x10^3)(0.01)^2}$$

$$= 7.1x10^{-4}$$

$$S = C_{Ag^+} = [Cl^-]$$

$$K_{sp} = 7.1x10^{-4}\ S^2$$

$$1x10^{-10} = 7.1x10^{-4}\ S^2$$

$$S = \mathbf{3.7x10^{-4}\ M}$$