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Analytical chemistry

For

First Year Student

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Chemistry: is the study of matter, including its composition, structure, physical properties, and reactivity. It is divided into five fields: organic, inorganic, physical, biochemical, and analytical.

What Is Analytical Chemistry?

"Analytical chemistry is what analytical chemists do."

Analytical chemistry is often described as the area of chemistry responsible for characterizing the composition of matter, both qualitatively (what is present) and quantitatively (how much is present). It was dealing with the identification and determination of compound. , it is convenient for our purposes to treat it as a five-step process:

1. Identify and define the problem.
2. Design the experimental procedure.
3. Conduct an experiment, and gather data.
4. Analyze the experimental data.
5. Propose a solution to the problem.

Typical problems on which analytical chemists work include qualitative analyses (what is present?), quantitative analyses (how much is present?), characterization analyses (what are the material's chemical and physical properties?), and fundamental analyses (how does this method work and how can it be improved?).

Analytical chemistry consists of:

Qualitative analysis which deals with the identification of elements, ions, or compounds present in a sample (tell us what chemicals are present in a sample).

Quantitative analysis, which is dealing with the determination of how much of one or more constituents is present (tells how much amounts of chemicals are present in a sample).

This analysis can be divided into three branches:

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

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

Instrumental analysis: They are based on the measurement of a physical property of the sample, for example, an electrical property or the absorption of electromagnetic radiation.

Volumetric analysis was divided to:

A: Titration analysis.
B: Gas analysis.

Well, we are speaking about the volumetric analysis, we shall consider, what the solutions are:

Solution: Homogeneous mixture of two or more substances produces from dissolved (disappeared) solute particle (ions, atoms, molecules) (lesser amount) between solvent particle (larger amount).

Solute (lesser amount) + Solvent (larger amount) → Solution

$$NaCl_{(s)} + H_2O_{(l)} \rightarrow \text{Salt Solution}$$

Concentrated Solution has a large amount of solute, and **Dilute Solution** has a small amount of solute.

Classification of solutions according to amount of solute:

Unsaturated solutions: if the amount of solute dissolved is less than the solubility limit, or if the amount of solute is less than the capacity of the solvent.

Saturated solutions: is one in which no more solute can dissolve in a given amount of solvent at a given temperature, or if the amount of solute equal to capacity of solvent.

Super saturated solutions: solution that contains a dissolved amount of solute that exceeds the normal solubility limit (saturated solution). Or a solution contains a larger amount of solute than the capacity of solvent at high temperature.

Classification of solution based on solute particle size:

True solution.

Suspension solution: heterogeneous mixtures which settle on standing and its components can be separated by filtrating (Amoxicillin, Antibiotics), particle of solute visible to the naked eye.

Colloidal solution: homogeneous mixture which does not settle nor are their components filterable, solute particle visible with an electron microscope (milk).

We are now considered the standard solution which was defined as:

Standard solution: It is a reagent of known concentration that is used to carry out a titrimetric analysis.

The properties of standard solution are:

1 – Be sufficiently stable so that it is only necessary to determine its concentration once.

2 – React rapidly with the analyte so that the time required to complete the analysis is minimized.

3 – React completely with the analyte so that satisfactory end point is realized.

4 – Undergo a selective reaction with the analyte.

5 – The reaction with the analyte can be described by a balanced equation.

A titration was performed by adding a standard solution from a burette or other liquid – dispensing device to a solution of the analyte until the reaction between the two solutions is judged complete. The volume of the reagent needed to complete the titration is determined from the difference between the initial and final volume.

Titrimetric methods include a large and powerful group of quantitative procedures based on measuring the amount of a reagent of known concentration that is consumed by an analyte.

There are many types of titrimetry:

- Volumetric titrimetry: Involves measuring the volume of a solution of known concentration that is needed to react essentially completely with analyte.
- Gravimetric titrimetry: Differs only in that the mass of the reagent is measured instead of volume.
- Coulometric titrimetry: The reagent is a constant direct electrical current of known magnitude that consumes the analyte; here, the time required to complete the electrochemical reaction is measured.

Titrimetric methods are widely used for routine determination because they are:

Rapid, convenient, accurate and readily automated.

Classification of volumetric or titrimetric methods:

(1) Neutralization (acid-base) titrations.
(2) Precipitation titrations.
(3) Complexation titrations.
(4) Reduction-Oxidation titrations.

Equivalent point: The point in titration in which the amount of added standard reagent is equivalent to the amount of the analyte (theoretical point). That means the amounts are chemically equivalent.

End point: The point in titration in which the physical change occurs, that is associated with the condition of chemical.

The difference in volume or mass between equivalent and end points is called the titration error.

$\mathbf{E_t = V_{ep} - V_{eq}}$
$\mathbf{E_t}$ = titration error
$\mathbf{V_{eq}}$ = theoretical volume (volume at equivalent point)
$\mathbf{V_{ep}}$ = actual volume (volume at end point)

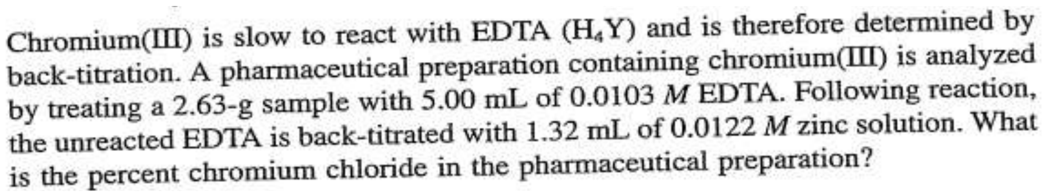
Primary standard material:

It is a highly purified compound that serves as a reference material in all volumetric and mass titrimetric methods.

The most important requirements for the primary standard materials are:
1 – High purity.
2 – Atmospheric stability.
3 – Absence of hydrated water so that the composition of the solid does not change with variations in relative humidity.
4 – Ready availability at modest cost.
5 – Reasonable solubility in the titration medium.
6 – Reasonable large molar mass, so that the relative error association with weighing the standard is minimized.

Back titration:- sometimes a reaction is slow to go to completion, and a sharp end point cannot be obtained. A back titration will often yield useful results. In this technique, a measured amount of the reagent, which would normally be the tritrant, is added to the sample so that there is a slight excess. After the reaction with the analyte is allowed to go to completion, the amount of excess (unreacted) reagent is determined by titration with another standard solution. In back-titration, a known number of millimoles of reaction it is taken, in excess of the analyte. The unreacted portion is titrated.

mmol reagent reacted = mmol taken – mmol back-titrated
mg analyte = mmol reagent reacted x factor (mmol analyte/mmol reagent)



Chromium(III) is slow to react with EDTA (H_4Y) and is therefore determined by back-titration. A pharmaceutical preparation containing chromium(III) is analyzed by treating a 2.63-g sample with 5.00 mL of 0.0103 *M* EDTA. Following reaction, the unreacted EDTA is back-titrated with 1.32 mL of 0.0122 *M* zinc solution. What is the percent chromium chloride in the pharmaceutical preparation?

Solution

Both Cr^{3+} and Zn^{2+} react in a 1 : 1 ratio with EDTA:

$$Cr^{3+} + H_4Y \rightarrow CrY^- + 4H^+$$
$$Zn^{2+} + H_4Y \rightarrow ZnY^2 + 4H^+$$

The millimoles of EDTA taken is

$$0.0103 \text{ mmol EDTA/mL} \times 5.00 \text{ mL EDTA} = 0.0515 \text{ mmol EDTA}$$

The millimoles of unreacted EDTA is

$$0.0112 \text{ mmol } Zn^{2+}\text{/mL} \times 1.32 \text{ mL } Zn^{2+} = 0.0148 \text{ mmol unreacted EDTA}$$

The millimoles of reacted EDTA is

$$0.0515 \text{ mmol taken} - 0.0148 \text{ mmol left} = 0.0367 \text{ mmol EDTA} \equiv \text{mmol } Cr^{3+}$$

The milligrams of $CrCl_3$ titrated is

$$0.0367 \text{ mmol } CrCl_3 \times 158.4 \text{ mg/mmol} = 5.81 \text{ mg } CrCl_3$$

$$\% \; CrCl_3 = \frac{5.81 \text{ mg } CrCl_3}{2630\text{-mg sample}} \times 100\% = 0.221\% \; CrCl_3$$

Expressing Amount of solute:

Mole: is the number of Avogadro number of atom, molecule, electron and proton (6.022×10^{23}).

1 mole of C = 12 gram of carbon (molar mass) = 6.022×10^{23} atoms of C

1 mole of H = 2 gram of hydrogen (molar mass) = 6.022×10^{23} atoms of H

1 mole of O = 16 grams of oxygen (molar mass) = 6.022×10^{23} atoms of O

The number of moles of a substance is calculated from

$$\text{Moles} = \frac{\text{grams}}{\text{formula weight (g/mol)}}$$

where formula weight represents the atomic or molecular weight of the substance. Thus,

$$\text{Moles } Na_2SO_4 = \frac{g}{\text{f wt}} = \frac{g}{142.04 \text{ g/mol}}$$

$$\text{Moles } Ag^+ = \frac{g}{\text{f wt}} = \frac{g}{107.870 \text{ g/mol}}$$

$$\text{Millimoles} = \frac{\text{milligrams}}{\text{formula weight (mg/mmol)}}$$

Weight / M.wt. = M. x V (L)

wt. g = M. x V (L) x F.wt. (M. wt.)

wt. mg = M. x V (ml) x F.wt. (M. wt.).

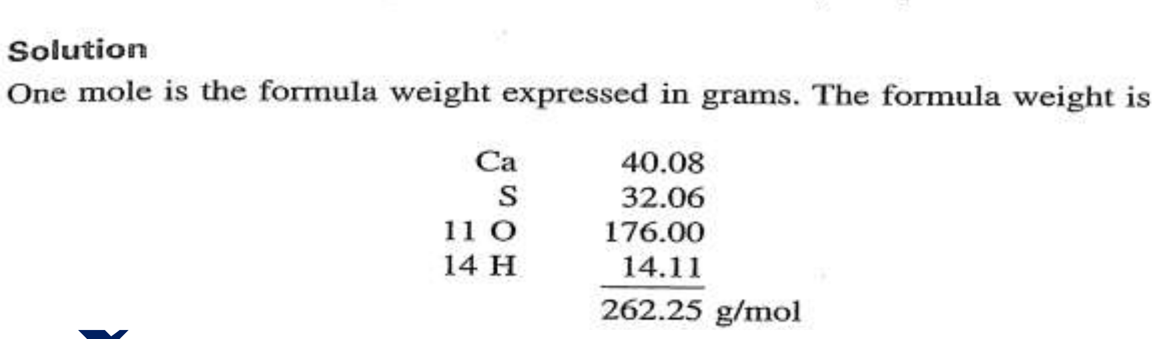
Find millimole of the following:

1 – 200 ml of 0.1 M NaCl. (F. wt. = 58 g / mole)

2 – 2 L 0f 0.1 M NaCl.
3 – 5.85 g of NaCl.

- Gram – atomic weight: the weight of element in gram. Example :C = 12 gram
- Gram – Molecular weight: the weight of compound in gram.
  Exp: $CH_3COOH = 2C + 4H + 2O$
  $= 2x12 + 4x1 + 2x16$
  $= 60$ g.
- Gram – Ion: the weight of ion which was contented in the compound.
  Exp: $NH_4Cl \longrightarrow NH_4^+ + Cl^-$
  35.5 g/mol. 14 + 4 35.5 g/ mol.
  18 g/ mol.
- Gram – equivalent weigh: the equivalent weight of element or compound in gram.
  Eq. wt. = M.wt. / n n = number of (H^+, OH^-, electron, ion group……….etc.).
  1 – Equivalent weight for element:
  Eq.wt. = At.wt. / Valance.Exp : eq.wt. for Cl^- = At.wt. of Cl^-/ valance = 35.5/1= 35.5 g. eq
  2 – Equivalent weight for acid:
  It was equal the formula weight (molecular weight) for the compound divided by number of H^+can be replaced by other ions.
  Eq.wt. of acid = M.wt. / no. of H^+
  Examples:
  $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$ n = 2
  $H_2SO_4 + NaOH \longrightarrow NaHSO4 + H_2$

Example:



Calculate the number of grams in one mole of $CaSO_4 \cdot 7H_2O$.

Solution

One mole is the formula weight expressed in grams. The formula weight is

Ca	40.08
S	32.06
11 O	176.00
14 H	14.11
	262.25 g/mol

Units for Expressing Concentration

Concentration is a general measurement unit stating the amount of solute present in a known amount of solution.

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}}$$

Molarity and Formality

Molarity: number of solute moles dissolved in solution volumes in liter.

Formality: number of formula weight in liter of solution, is a substance’s total concentration in solution without regard to its specific chemical form. 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^-. The formality of NaCl, however, is 0.1 F because it represents the total amount of NaCl in solution.

Normality: it is the number of equivalent weights of a substance in solution have one letter volume.

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.

Molality: is used in thermodynamic calculations where a temperature independent unit of concentration is needed**.**

Weight, Volume, and Weight-to-Volume Ratios:

Weight percent (% w/w), **volume percent** (% v/v) and **weight-to-volume percent** (% w/v) express concentration as units of solute per 100 units of sample. A solution in which a solute has a concentration of 23% w/v contains 23 g of solute per 100 ml of solution.

Parts per million (ppm) and **parts per billion** (ppb) are mass ratios of grams of solute to one million or one billion grams of sample, respectively. For example, a steel that is 450 ppm in Mn contains 450 mg of Mn for every gram of steel. If we approximate the density of an aqueous solution as 1.00 g/ml, then solution concentrations can be expressed in parts per million or parts per billion using the following relationships.

$$\text{ppm} = \frac{\text{mg}}{\text{liter}} = \frac{\mu\text{g}}{\text{mL}}$$

$$\text{ppb} = \frac{\mu\text{g}}{\text{liter}} = \frac{\text{ng}}{\text{mL}}$$

For gases a part per million usually is a volume ratio. Thus, a helium concentration of 6.3 ppm means that one liter of air contains 6.3 ml of He.

The relationship between ppm with M and N:

ppm = M x M.wt. x1000

ppm = N x Eq.wt. x 1000

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

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

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

$$\text{ppm (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}}\right] \times 10^6 \text{ (ppm/g solute/mL sample)}$$

$$\text{ppb (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}}\right] \times 10^9 \text{ (ppb/g solute/mL sample)}$$

$$\text{ppt (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}}\right] \times 10^{12} \text{ ppt/g solute/mL sample)}$$

$$\text{meq} = \frac{\text{mg}}{\text{eq wt (mg/meq)}} = \frac{\text{mg}}{\text{f wt (mg/mmol)}/n \text{ (meq/mmol)}}$$

n = charge on ion

The concentration of zinc ion in blood serum is about 1 ppm. Express this as meq/L.

Solution

$$1 \text{ ppm} = 1\ \mu\text{g/mL} = 1 \text{ mg/L}$$

The equivalent weight of Zn^{2+} is 65.4 (mg/mmol)/2 (meq/mmol) = 32.7 mg/meq. Therefore,

$$\frac{1 \text{ mg Zn/L}}{32.7 \text{ mg/meq}} = 3.06 \times 10^{-2} \text{ meq/L Zn}$$

This unit is actually used for the major electrolyte constituents as in Table 5.3 rather than the trace constituents, as in the example here.

Example:

Calculate the equivalent weight and normality for a solution of 6.0 M H_3PO_4 given the following reactions:

(a) $H_3PO_4(aq) + 3OH^-(aq) \rightleftharpoons PO_4^{3-}(aq) + 3H_2O(\ell)$

(b) $H_3PO_4(aq) + 2NH_3(aq) \rightleftharpoons HPO_4^{2-}(aq) + 2NH_4^+(aq)$

(c) $H_3PO_4(aq) + F^-(aq) \rightleftharpoons H_2PO_4^-(aq) + HF(aq)$

(a) $\text{EW} = \frac{\text{FW}}{n} = \frac{97.994}{3} = 32.665 \qquad \text{N} = n \times \text{M} = 3 \times 6.0 = 18 \text{ N}$

(b) $\text{EW} = \frac{\text{FW}}{n} = \frac{97.994}{2} = 48.997 \qquad \text{N} = n \times \text{M} = 2 \times 6.0 = 12 \text{ N}$

(c) $\text{EW} = \frac{\text{FW}}{n} = \frac{97.994}{1} = 97.994 \qquad \text{N} = n \times \text{M} = 1 \times 6.0 = 6.0 \text{ N}$

Calculate the normality of the solutions containing the following: (a) 5.300 g/L Na_2CO_3 (when the CO_3^{2-} reacts with two protons). (b) 5.267 g/L $K_2Cr_2O_7$ (the Cr is reduced to Cr^{3+}).

Solution

(a) CO_3^{2-} reacts with $2H^+$ to H_2CO_3:

$$N = \frac{5.300 \text{ g/L}}{(105.99/2) \text{ g/eq}} = 0.1000 \text{ eq/L}$$

(b) Each Cr(VI) is reduced to Cr^{3+}, a total change of $6e^-$/molecule $K_2Cr_2O_7$:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^3 + 7H_2O$$

$$N = \frac{5.267 \text{ g/L}}{(294.19/6) \text{ g/eq}} = 0.1074 \text{ eq/L}$$

$$\text{Eq . wt . for acid} = \frac{\text{M .wt .of acid}}{\text{no .of } H^{+}}$$

$$\text{Eq .wt . for base} = \frac{\text{M .wt .of base}}{\text{no .of } OH^{-}}$$

$$\text{Eq . wt . for salt} = \frac{\text{M .wt .of salt}}{\text{no . of metal a tom} * \text{no . of oxidation number}}$$

$$\text{Eq . wt . for oxidant regent} = \frac{\text{M .wt .for oxidant}}{\text{no .of accept e-}}$$

$$\text{Eq . wt . for reductant regent} = \frac{\text{M .wt .for reductant}}{\text{no .of loss e-}}$$

$$\text{Eq . wt . for precipitation reaction} = \frac{\text{M .wt .of salt}}{\text{Ion valance}}$$

$$\text{Eq . wt . for complexation reaction} = \frac{\text{M .wt .for possative ion}}{\text{valance of possative ion}}$$

$$\text{Molality (m)} = \frac{\text{no .of mole (solute)}}{\text{one kg of solution}}$$

$$m = \frac{\text{wt.}}{\text{M .wt .}} * \frac{1}{\text{wt .(kg)solution}}$$

$$\text{Formality (F)} = \frac{d * \% * 1000}{\text{F .wt .}} \quad \text{for liquid} \quad \text{(d or sp. g)}$$

$$F = \frac{\text{wt.}}{\text{f .wt .}} \times \frac{1000}{\text{V (ml)}} \quad \text{for solid}$$

$$\text{Molarity (M)} = \frac{\text{wt.}}{\text{M .wt .}} * \frac{1000}{\text{V (ml)}} \quad \text{for solid}$$

$$M = \frac{d * \% * 1000}{\text{M .wt .}} \quad \text{for liquid} \quad \text{(d or sp.g)}$$

$$\text{Normality (N)} = \frac{\text{wt.}}{\text{Eq .wt .}} * \frac{1000}{\text{V (ml)}} \quad \text{for solid}$$

$$N = \frac{sp.g * \% * 1000}{\text{Eq .wt .}} \quad \text{for liquid (sp.g or d)}$$

$\text{Wt .}_{(g)} = \text{M . * M. wt . * V (L)}$

$\text{Wt .}_{(mg)} = \text{M . * M. wt . * V (ml)}$

$\text{Wt}_{(g)} = \text{N * Eq . wt * V (L)}$

$\text{Wt}_{(mg)} = \text{N * Eq . wt . * V (ml)}$

ppm = M . * M . wt * 1000

ppm = N * Eq . wt * 1000

no . of mole . = M * V

$N_1V_1 = N_2V_2 \quad M_1V_1 = M_2V_2 \quad F_1V_1 = F_2V_2$

A solution of sodium carbonate is prepared by dissolving 0.212 g Na_2CO_3 and diluting to 100 mL. Calculate the normality of the solution (a) if it is used as a monoacidic base, and (b) if it is used as a diacidic base.

Solution

$$\text{(a)}\quad N = \frac{\text{mg}_{Na_2CO_3}/(Na_2CO_3/1)}{\text{mL}} = \frac{212\ \text{mg}/(106.0/1\ \text{mg/meq})}{100\ \text{mL}} = 0.0200\ \text{meq/mL}$$

$$\text{(b)}\quad N = \frac{\text{mg}_{Na_2CO_3}/(Na_2CO_3/2)}{\text{mL}} = \frac{212\ \text{mg}/(106.0/2\ \text{mg/meq})}{100\ \text{mL}} = 0.0400\ \text{meq/mL}$$

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,

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

A 2.6-g sample of plant tissue was analyzed and found to contain 3.6 µg zinc. What is the concentration of zinc in the plant in ppm? In ppb?

Solution

$$\frac{3.6\ \mu\text{g}}{2.6\ \text{g}} = 1.4\ \mu\text{g/g} = 1.4\ \text{ppm}$$

$$\frac{3.6 \times 10^3\ \text{ng}}{2.6\ \text{g}} = 1.4 \times 10^3\ \text{ng/g} = 1400\ \text{ppb}$$

One ppm is equal to 1000 ppb. One ppb is equal to 10^{-7}%.

Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million	ppm	mg/kg	mg/L	µL/L
(1 ppm = 10^{-4}%)		µg/g	µg/mL	nL/mL
Parts per billion	ppb	µg/kg	µg/L	nL/L
(1 ppb = 10^{-7}% = 10^{-3} ppm)		ng/g	ng/mL	pL/mL[a]
Milligram percent	mg%	mg/100 g	mg/100 mL	

[a] pL = picoliter = 10^{-12} L.

A 25.0-µL serum sample was analyzed for glucose content and found to contain 26.7 µg. Calculate the concentration of glucose in ppm and in mg/dL.

Solution

$$25.0\ \cancel{\mu\text{L}} \times \frac{1\ \text{mL}}{1000\ \cancel{\mu\text{L}}} = 2.50 \times 10^{-2}\ \text{mL}$$

$$26.7\ \cancel{\mu\text{g}} \times \frac{1\ \text{g}}{10^5\ \cancel{\mu\text{g}}} = 2.67 \times 10^{-5}\ \text{g}$$

$$\text{ppm} = \frac{2.67 \times 10^{-5}\ \text{g glucose}}{2.50 \times 10^{-2}\ \text{mL serum}} \times 10^6\ \mu\text{g/g} = 1.07 \times 10^3\ \mu\text{g/mL}$$

or

$$\frac{26.7\ \mu\text{g glucose}}{0.0250\ \text{mL serum}} = 1.07 \times 10^3\ \mu\text{g/mL} = \text{ppm}$$

$$\text{mg/dL} = \frac{26.7\ \mu\text{g glucose} \times 10^{-3}\ \text{mg}/\mu\text{g}}{0.025\ \text{mL serum}} \times 100\ \text{ml/dL} = 107\ \text{mg/dL}$$

[Note the relationship between ppm (wt/vol) and mg/dL.]

p - Functions:

p - Function: The p-function of a number X is written as pX and is defined as:

$$pX = -\log(X)$$

Thus, the pH of a solution that is 0.10 M H^+ is

$$pH = -\log[H^+] = -\log(0.10) = 1.00$$

and the pH of 5.0×10^{-13} M H^+ is

$$pH = -\log[H^+] = -\log(5.0 \times 10^{-13}) = 12.30$$

Example:

What is the $[H^+]$ in a solution that has a pH of 5.16?

SOLUTION

The concentration of H^+ is

$$pH = -\log[H^+] = 5.16$$

$$\log[H^+] = -5.16$$

$$[H^+] = \text{antilog}(-5.16) = 10^{-5.16} = 6.9 \times 10^{-6}\ M$$

Example:

What is pNa for a solution of 1.76×10^{-3} M Na_3PO_4?

SOLUTION

Since each mole of Na_3PO_4 contains three moles of Na^+, the concentration of Na^+ is

$$[Na^+] = \frac{3\ \text{mol}\ Na^+}{\text{mol}\ Na_3PO_4} \times 1.76 \times 10^{-3}\ M = 5.28 \times 10^{-3}\ M$$

and pNa is

$$pNa = -\log[Na^+] = -\log(5.28 \times 10^{-3}) = 2.277$$

Example: A solution is prepared by dissolving 1.26 gm $AgNO_3$ in a 250 ml volumetric flask and diluting to volume. Calculate the molarity of the $AgNO_3$ solution. How many millmoles $AgNO_3$ were dissolved?

Solution:

$$M = \frac{wt.(g)}{M.wt.(g/mole)} * \frac{1000}{V(ml)}$$

$$M = \frac{1.26}{169.9} * \frac{1000}{250}$$

$$= 0.0297 \text{ mol / L}$$

Example: How many grams per milliliter of NaCl are contains in a 0.250 M solution.

Solution :

$$M = \frac{wt.}{M.wt.} * \frac{1000}{V(ml)}$$

$$0.250 = \frac{wt.}{58.4} * \frac{1000}{1}$$

$wt._{(g)} = 0.0146$ g / ml

Example: How many grams of Na_2SO_4 should be weight out to prepare 500 ml of a 0.2 M solution?

Solution:

$$M = \frac{wt.}{M.wt.} * \frac{1000}{V(ml)}$$

$$0.1 = \frac{wt.}{142} * \frac{1000}{500}$$

wt. = 7.1 gm

Example: Calculate the concentration of potassium ion in gram per liter after mixing 100 ml of 0.250 M KCl and 200 ml of 0.1 M K_2SO_4 .

Solution:

no. of mmol (K^+) = mmol (KCl) + 2 mmol (K_2SO_4)

$= (M * V)_{KCl} + (M * V)_{K2SO4}$

$= (0.25 * 100)_{KCl} + (0.1 * 200)_{K2SO4}$

= 25 + 40 = 65 mmol. KCl in 300 ml

wt. = mmole * M.wt.

= 65 * 39.1 = 2541.5 mg

= 2.541 gm in 300 ml mg = 10^{-3} gm

$$\text{Conc .} = \frac{2.541 \text{ mg} * 100 \text{ ml}}{300 \text{ ml}} = 8.47 \text{ gm / l}$$

$$N = \frac{\text{wt.(g)}}{\text{eq.wt}} * \frac{1000}{V(\text{ml})} \quad \text{for solid}$$

$$N = \frac{\text{sp.g (d)} * \% * 1000}{\text{eq.wt}} \quad \text{for liquid}$$

Example: How many milliliters of 0.25 M solution of H_2SO_4 will react with 10 ml of 0.25 M solution of NaOH?

Solution:

N = nM

$N_{H2SO4} = 2 * M = 2 * 0.25 = 0.5$ eq/l

$N_{NaOH} = 1 * M = 1 * 0.25 = 0.25$ eq/l

$(N * V)_{H2SO4} = (N * V)_{NaOH}$

$(0.5 * V)_{H2SO4} = (0.25 * 10)_{NaOH}$

$V_{H2SO4} = 5.0$ ml

Example: Calculate the weight percentage of solution prepare by mixing 5.0 gm $AgNO_3$ with 100 ml water (density l g/cm^3).

Solution:

$$\left(\frac{\text{wt.}}{\text{wt.}}\ \%\right) = \frac{\text{wt.solute (g)}}{\text{wt.solution (g)}} * 100$$

$$= \frac{\text{wt.}(AgNO_3)\ \text{(g)}}{\text{wt.solute} + \text{wt.solvent}} * 100$$

$$\left(\frac{\text{wt.}}{\text{wt.}}\ \%\right) = \frac{5}{5+(100*1)} * 100$$

$$= \frac{5}{105} * 100 = 4.76\ \%$$

Example: Calculate number of grams in 500 ml silane solution (wt / v % = 0.859 %).
Solution:

$$\left(\frac{\text{wt.}}{\text{v}}\ \%\right) = \frac{\text{wt.solute (g)}}{\text{V solution (ml)}} * 100$$

$$0.859\ \% = \frac{\text{wt.NaCl}}{500} * 100$$

$$\text{wt. NaCl} = \frac{0.859*500}{100} = 4.25\ \text{g NaCl}$$

Example: Calculate the molarity of 28% NH_3 (17g/mol.), sp.g 0.898
Solution:

$$M = \frac{\text{sp.g}*\%*1000}{\text{M.wt}} = \frac{0.989*28*1000}{17} = 14.79\ \text{mol/L}$$

Example: how many milliliters of concentrated H_2SO_4 have 94%, density 1.831 g/cm^3 are required to prepare liter of 0.1 M solution.(M.wt. 98 g/mole)
Solution: The first step we should calculate the molarity of concentrated H_2SO_4

$$M = \frac{d * \% * 1000}{M.wt} = \frac{1.831 * 94 * 1000}{98} = 17.5\ \text{mol/L}$$

The second step we should calculate the volume needed to prepare the diluted solution.

$$(M1 \times V1)\text{conc.} = (M2 \times V2)\text{diluted}$$

$$(17.5 \times V1) = (0.1 \times 1000)$$

$$V1 = 5.71\ \text{ml}$$

So 5.71 ml of concentrated H_2SO_4 must be diluted to prepared 0.1 M solution .

Example: prepare 500 ml of 0.01 solution of Na^+ from Na_2CO_3 (106 g/mol)

$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{-2}$ M of $Na_2CO_3 = \frac{0.01}{2} = 0.005$

$$\text{M of } Na_2CO_3 = \frac{wt.}{M.wt} \times \frac{1000}{500}$$

$$0.005 = \frac{wt.}{106} \times \frac{1000}{500}$$

$$wt. = \frac{0.005 \times 106}{2} = 0.265\ gm\ \text{Na2CO3}$$

So 0.265 g of Na_2CO_3 must be dissolved in 500 ml of water.

Example: calculate the volume percentage of solution preparing by mixing 50 m methyl alcohol with 200 ml water.

$$(V/V\ \%) = \frac{\text{V solute (ml)}}{\text{V solution or sample (ml)}} \times 100$$

$$= \frac{50\ \text{ml}}{(50+200)\text{ml}} \times 100 = 20\%$$

Example: calculate the molality for solution preparing by mixing 4 gm NaOH (40 g/mol.) with 500 g water.

$$\textbf{Molality (m)} = \frac{wt}{M.wt} \times \frac{1000}{wt.(g)} = \frac{4}{40} \times \frac{1000}{500} = 0.2\ \text{m}$$

Mole fraction (x):

$$X = \frac{\text{no.mole solute (n1)}}{\text{no.mole solute (n1)+no.mole solvent (n2)}}$$

Example: One liter of acetic and solution contain 80.8g of acetic acid, the solution density 1.00978 g/cm3

Solution:- n = no. of mole

$$X_1 = \frac{n1}{n1+n2}$$

$$X_1 = \frac{\left(\frac{wt}{M.wt.}\right)CH3COOH}{\left(\frac{wt}{M.wt.}\right)CH3COOH + \left(\frac{(\text{density} \times \text{volume}) - \text{weight of acid}}{M.wt}\right)}$$

$$X_1 = \frac{80.8/60}{\frac{80.8/60}{60} + (\frac{(1.00978 \times 1000) - 80.8}{18})} = 0.025$$

$$X_2 = \frac{(\frac{(1.00978 \times 1000) - 80.8}{18})}{\frac{80.8}{60} + (\frac{(1.00978 \times 1000) - 80.8}{18})} = 0.975$$

Example: 4.57 gm of $BaCl_2.2H_2O$ (244 g/mol.) are dissolved in sufficient water to give 250 ml of solution. Calculate the formal concentration of $BaCl_2$ and Cl^- in this solution.

$$F_{BaCl\,2} = \frac{wt.}{F.wt.} * \frac{1000}{v\,(ml)} = \frac{4.57}{244} * \frac{1000}{250} = 0.0749\ F$$

$$BaCl_2 \longrightarrow Ba^{+2} + 2Cl^-$$

$0.0749\ F \quad (2*0.0749) = 0.149 F Cl^-$

Example: Describe the preparation of 5 L of 0.1 M Na_2CO_3 (105.99) from the primary standard solid.

$105.99 \cong 106$

$Wt._{(g)} = M * V\,(L) * M.\,wt.$

$= 0.1 * 5 * 106 = 53$ gram

There for the solution is prepared by dissolving 53 g of Na_2CO_3 in water and diluting the volume to 5

Example: Describe how you prepared 0.01 M solution (500 ml) of Na^+ from Na_2CO_3 .

$mmole\ Na^+ = \frac{1}{2}\ mmole\ Na_2CO_3$

$mmole\ Na^+ = 500 * 0.01 = 5 = \frac{1}{2}\ mmole\ Na_2CO_3$

$mmole\ Na_2CO_3 = \frac{1}{2} * 5 = 2.5$

$wt._{(mg)}\ Na_2CO_3 = M * V\,(ml).\ F.\,wt.$ → **(M * V) = 2.5**

$= 2.5 * 106 = 265$ mg

The solution was prepared by weighing 0.265 g (265 mg) of Na_2CO_3 and dissolved in 500 ml.

Example: From the solution in Ex. how you can prepared 50 ml of 0.005 M Na^+.

$M_1V_1 = M_2V_2$ → dilution low

$V * 0.01 = 50 * 0.05$

$V = 25$ ml

Thus 25 ml of conc. solution will dilute to 50 ml.

Example: What is the normality of HCl if 500 ml of acid contain 37.413 g from HCl gas.

$$N = \frac{wt.}{Eq.wt.} * \frac{1000}{V\,(ml)} \qquad Eq.\ wt.\ HCl = \frac{M.wt}{n} = \frac{M.wt}{1}$$

$$N = \frac{37.413}{36.5} * \frac{1000}{500} = 2.05$$

Example: calculate the concentration (M) for the solution of NaCl (M. wt. 58.51) that has w/ v% equal 0.85 %.

$\frac{w}{v}$ % = 0.85 that mean each 100 ml contain 0.85 and that yield each 1000 ml contain:

$$\frac{0.85}{100} * 1000 = 8.5\ g$$

$$M = \frac{wt.}{M.wt.} * \frac{1000}{V\,(ml)}$$

$$= \frac{0.85}{58.5} * \frac{1000}{100} = 0.145\ M$$

Example: Describe how you can prepare 250 ml solution of H_2SO_4 has (0.1 N and 0.1 M) if you know the sp.g is1.099 g, the percentage of acid is % 98 and M.wt. 98 g/mole.

$$Eq.\ wt. = \frac{98}{2} = 49$$

$$N = \frac{sp.g * \% * 1000}{Eq.wt.} = \frac{1.09 * \frac{98}{100} * 1000}{49} = 21.8\ N$$

$$N = n\,M \rightarrow M = \frac{21.8}{2} = 10.9$$

Now we calculate the N and M for 250 ml by using dilution low

A: $N_1V_1 = N_2V_2 \rightarrow 21.8 * V = 250 * 0.1 \qquad V_1 = 1.147$ ml

This volume will diluted to 250 ml

B: $M_1V_1 = M_2V_2 \rightarrow 10.9 * V_1 = 250 * 0.1 \qquad V_1 = 2.294$ ml

This volume will diluted to 250 ml

Example: How many gram of Na_2CO_3 was found in 250 ml of 0.2 N solution?

$\text{wt.}_{(g)} = N \ast V\,(L) \ast \text{Eq. wt.}$ $\qquad$ $\text{Eq. wt.} = \frac{106}{n} = \frac{106}{2} = 53$

$\text{wt.}_{(g)} = 0.2 \ast \frac{250}{1000} \ast 53 = 2.65\ g$

Example: What is the molarity of K^+ in solution that contain 63.3 ppm of $K_3Fe\,(CN)_6$ (F.wt.329.3)

63.3 ppm $K_3Fe\,(CN)_6$ = 63.3 mg $K_3Fe(CN)_6$

$mg = M \ast V \ast F.\ wt.$

$63.3 = M \ast 10^3 \ast 329.3 \rightarrow M = 1.922 \ast 10^{-4}$

Here:

Each mole $K_3Fe\,(CN)_6$ = 3 mole K^+

$1.922 \ast 10^{-4}$ $\qquad$ $3 \ast 1.922 \ast 10^{-4} = 5.77 \ast 10^{-4}\ M$

Example: calculate **p – value** for each ion in solutions that is $2 \ast 10^{-3}$ M NaCl and $5.4 * 10^{-4}$ M. HCl

$pH = -\,Log\,[\,H_3O^+\,] = -\,Log\,[\,5.4 \ast 10^{-4}\,] = 4.268$

$pNa = -\,Log\,[\,Na^+\,] = -\,Log\,[\,2 \ast 10^{-3}\,] = 3.699$

$pCl = -\,Log\,[\,Cl^-\,] = -\,Log\,[2 \ast 10^{-3} + 5.4 \ast 10^{-4}\,]$

$= -\,Log\,[2.54 \ast 10^{-3}] = 2.595$

Example: Calculate the molar concentration of Ag^+ in a solution has **pAg** of 6.372.

$pAg = -\,Log\,[Ag^+] = 6.372$

$Log\,[Ag^+] = -\,6.372 \rightarrow [Ag^+] = 10^{-6.372} = 1.709 \ast 10^{-3}$

Example: How many gram of NaCl was needed to prepare 250 ml of solution contain 100 ppm Na^+ if you know At. wt. (Cl = 35.5) and (Na = 23)?

$ppm = \frac{mg}{L} \quad \rightarrow 100\ ppm = 100\ \frac{mg}{L} \quad = 0.1\ g/L$

Na^+ in 250 ml $= \frac{0.1 \ast 250}{1000} = 0.025\ g$

$NaCl_{\ (g)} = \frac{Na^+(g) \ast M.wt.\ of\ NaCl}{At.wt.\ of\ Na^+}$

$\text{wt. NaCl}_{\ (g)} = \frac{0.025 \ast 58.5}{23} = 0.0636\ g\ NaCl$

Example: If the gallon is (3800 ml) of solution contain 10 ppm of C_2H_5OH. How many mg in one litter?

$$\text{ppm} = \frac{\text{mg}}{\text{L}} \quad \rightarrow \frac{\text{mg}}{1000 \text{ ml}}$$

$$\text{mg} = \frac{\text{ppm} * 3800}{1000} \quad = 38$$

Example: What is the volume of HCl which is needed to prepare 100 ml of solution has 6 M conc. if you know the % of HCl equal 37 % sp.g was 1.18 g /ml.

$$M = \frac{\text{sp.g} * \% * 1000}{\text{M.wt.}} = \frac{1.18 * \frac{37}{100} * 1000}{36.5} = 11.96$$

$M_1V_1 = M_2V_2 \quad \rightarrow \quad 6 * 100 = 11.96 * V_2 \qquad V_2 = 50.17$ ml

The volume will dilute to 100 ml

Example: How many gram of $AgNO_3$ (169.9) was needed to prepare 500 ml solution of 0.125 M?

$$M = \frac{\text{wt.}}{\text{M.wt.}} * \frac{1000}{V\,(\text{ml})} = \frac{\text{wt.}}{169.9} * \frac{1000}{500}$$

$$\text{wt.} = 0.125 * 169.9 * \frac{1000}{500} = 10.62 \text{ g}$$

Example: Calculate the volume percentage for the solution prepared by added 50 ml of C_2H_5OH to 200 ml water.

$V_{\text{product}} = V_1 + V_2 = 50 + 200 = 250$ ml

$\% \frac{V}{V} = \frac{50}{250} * 100 = 20$ % for C_2H_5OH

$\% \frac{V}{V} = \frac{200}{250} * 100 = 80$ % for water

Example: Calculate the w/w% for the solution prepared by dissolving 5 g of $AgNO_3$ in 100 ml of water.

Assumed of water equal 1 g/ml.

$\text{wt.}_{\text{solvent}} = d \times V = 1 \times 100 = 100$ g

$\text{wt.}_{\text{solution}} = 100 + 5 = 105$ g

$\%\, w/w = \frac{5}{105} * 100 = 4.76$ % for $AgNO_3$

Example: How many gram of NaCl was founded in 500 ml of solution has w/v % = 0.859?

$$\% \frac{wt.}{V} = 0.859 \rightarrow \frac{wt.}{V} = \frac{0.859}{100}$$

$$wt. = \frac{0.859}{100} * V_{ml} = \frac{0.859}{100} * 500 = 4.25 \text{ g}$$

Example: How many gram of sugar was found in 1 L of solution have w/v = 5 %?

$$\% \frac{wt.}{V} = 5 \rightarrow wt. = \frac{5}{100} * V = \frac{5}{100} * 1000 \qquad wt. = 50 \text{ g}$$

Example: Calculate the M for $Al_2(SO_4)_3$ solution has 0.3 N and $Bi(NO_3)_2$ has 0.2 M.

$$N = n\,M \rightarrow M = \frac{N}{n} = \frac{0.3}{6} = 0.05 \text{ molar } Al_2(SO_4)_3$$

$$N\ Bi(NO_3)_2 = n\,M = 3 * 0.2 = 0.6$$

Example: If you know that the density of CH_3COOH solution which contains 80.8 g/L of acid was 1.0097 g/ml what is the M, m, wt % and mole fraction?

$$M = \frac{wt.}{M.wt.} * \frac{1000}{V\,(ml)} = \frac{80.8}{60} * \frac{1000}{1000} = 1.35 \text{ M}$$

$$\text{Molality (m)} = \frac{\text{no. of mole (solute)}}{Wo} * 1000$$

$$W_o = W_{solvent} = W_{solution} - W_{acetic\ acid}$$

$$= (1000 * 1.0097) - 80.8 = 928.9 \text{ g}$$

$$\text{Molality} = \frac{\frac{wt.}{M.wt.}\text{ acetic acid}}{Wo} * 1000$$

$$= \frac{\frac{80.8}{60}}{928.9} * 1000 = 1.45$$

$$\% \text{ acetic acid} = \frac{W_{solute}}{W_{solution}} * 100 = \frac{80.8}{1000 * 1.0097} * 100 = 8\ \%$$

$$X_{SL} = \frac{n_{solute}}{\text{total } n} \qquad \text{total } n = n_{solvent} + n_{solute}$$

$$= \frac{\frac{80.8}{60}}{\frac{928.9}{18} + \frac{80.8}{60}} = 0.025$$

$$X_{sol.} = \frac{n_{solvent}}{\text{total } n} = \frac{\frac{928.9}{18}}{\frac{928.9}{18} + \frac{80.8}{60}} = 0.975$$

or total **n** always equal **1** unit

$$1 = 0.025 + X_{sol.} \rightarrow X_{sol.} = 1 - 0.025 = 0.975$$

Example: Calculate the Eq. wt. for the following:

1 - $KHC_2O_4 . H_2C_2O_4 . 2H_2O + 3KOH \rightarrow 2K_2C_2O_4 + 5H_2O$

As reductant reagent: $C_2O_4^{2-} - 2e \rightarrow 2CO_2$

Eq. wt. $= \frac{M.wt.}{4}$

As acid:

Eq. wt. $= \frac{M.wt.}{3}$

2 - $2K_2Cr_2O_7 + 2H_2O + 3S \rightarrow 3SO_2 + 4KOH + 2Cr_2O_3$

Eq. wt. $= \frac{M.wt.}{6}$

3 - $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3PO_4$

Eq. wt. $= \frac{M.wt.}{2}$

4 - $Fe_2O_3 + 6HCl \rightarrow 3H_2O + 2FeCl_3$

Eq. wt. $= \frac{M.wt.}{6}$

4 - Na_2CO_3 as salt:

Eq. wt. $= \frac{M.wt.}{2*1}$

2 = no. of Na^+ atom 1 = the valance of Na^+

5 - $KMnO_4$ as oxidant reagent:

$KMnO_4 + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

Eq. wt. $= \frac{M.wt.}{5}$

6 - $FeSO_4$ as reductant reagent:

$Fe^{2+} \rightarrow Fe^{3+}$

Eq. wt. $= \frac{M.wt.}{1}$

7 - $AgNO_3$ as precipitate:

Eq. wt. $= \frac{M.wt.}{1}$

8 - $[Co^{2+}(C_5H_5N)_4](SCN)_2$ as complexation reaction:

$$\text{Eq. wt.} = \frac{\text{At.wt.of Co}}{2}$$

9 - $Na_2MO_4 + 8H^+ \rightarrow Mo^{3+} + 4H_2O$

$$\text{Eq. wt.} = \frac{\text{M.wt.}}{3} \quad \text{oxidation}$$

10 - $[Ni^{2+}(CN)_4]^{2-}$

$$\text{Eq. wt.} = \frac{\text{At.wt.of N}}{2}$$

Home Work: Calculate the Eq. wt. for the following:

1- $\underline{FeSO_4} + 2NaOH \rightarrow Fe(OH)_2 + Na_2SO_4$

2- $FeSO_4 + \underline{BaCl_2} \rightarrow FeCl_2 + BaSO_4$

3- $\underline{FeCl_3} + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl$

4- $\underline{HBr} + NH_4OH \rightarrow NH_4Br + H_2O$

5- $H_2SO_4 + \underline{Ca(OH)_2} \rightarrow CaSO_4 + 2H_2O$

6- $Mg(OH)_2 + \underline{2HCl} \rightarrow MgCl_2 + 2H_2O$

7- $\underline{2Al(OH)_3} + 3H_2SO_4 \rightarrow Al(SO_4)_3 + 6H_2O$

8- $\underline{K_2Cr_2O_7} + 2BaCl_2 + 2H_2O \rightarrow 2BaCrO4 + 2KCl + 2HCl$

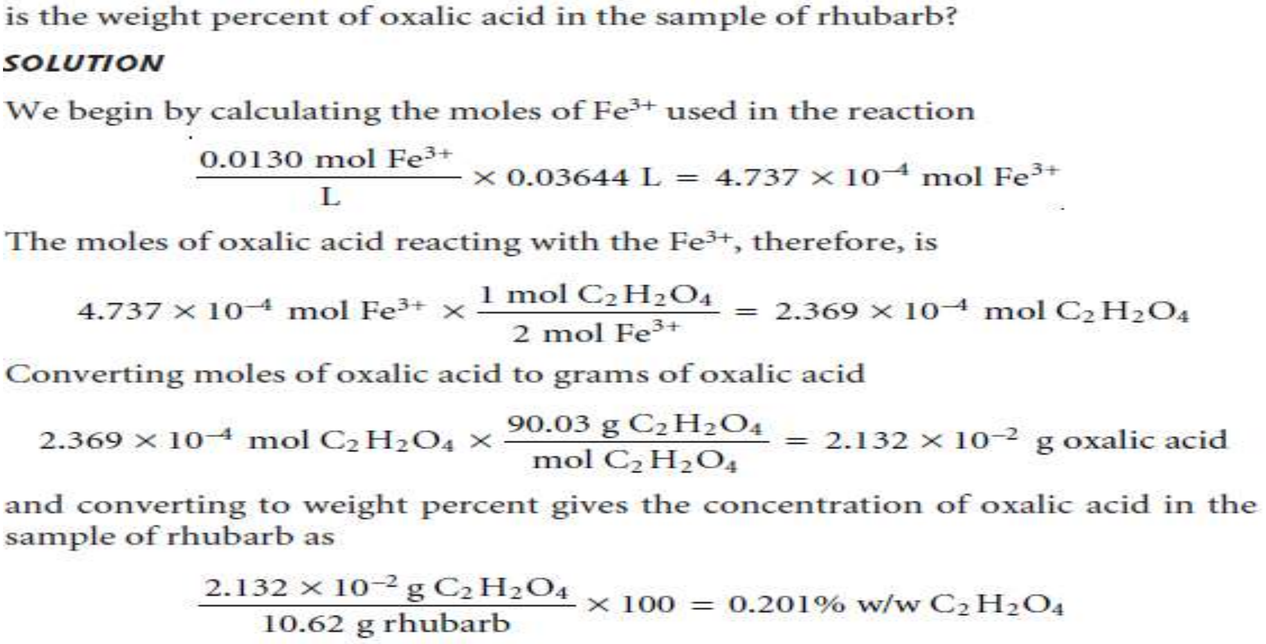
Stoichiometric Calculations:

A balanced chemical reaction indicates the quantitative relationships between the moles of reactants and products. These stoichiometries relationships provide the basis for many analytical calculations. Consider, for example, the problem of determining the amount of oxalic acid, $H_2C_2O_4$, in the sample. One method for this analysis uses the following reaction in which us oxidize oxalic acid to CO_2.

$$2Fe^{3+}(aq) + H_2C_2O_4(aq) + 2H_2O(l) + 2Fe^{2+}(aq) + 2CO_2(g) + 2H_3O^{+}(aq)$$

The balanced chemical reaction provides the stoichiometric relationship between the moles of Fe^{3+} used and the moles of oxalic acid in the sample being analyzed specifically, one mole of oxalic acid reacts with two moles of Fe^{3+}.

Example:



The amount of oxalic acid in a sample of rhubarb was determined by reacting with Fe^{3+} as outlined in reaction 2.2. In a typical analysis, the oxalic acid in 10.62 g of rhubarb was extracted with a suitable solvent. The complete oxidation of the oxalic acid to CO_2 required 36.44 mL of 0.0130 M Fe^{3+}. What is the weight percent of oxalic acid in the sample of rhubarb?

SOLUTION

We begin by calculating the moles of Fe^{3+} used in the reaction

$$\frac{0.0130 \text{ mol } Fe^{3+}}{L} \times 0.03644 \text{ L} = 4.737 \times 10^{-4} \text{ mol } Fe^{3+}$$

The moles of oxalic acid reacting with the Fe^{3+}, therefore, is

$$4.737 \times 10^{-4} \text{ mol } Fe^{3+} \times \frac{1 \text{ mol } C_2H_2O_4}{2 \text{ mol } Fe^{3+}} = 2.369 \times 10^{-4} \text{ mol } C_2H_2O_4$$

Converting moles of oxalic acid to grams of oxalic acid

$$2.369 \times 10^{-4} \text{ mol } C_2H_2O_4 \times \frac{90.03 \text{ g } C_2H_2O_4}{\text{mol } C_2H_2O_4} = 2.132 \times 10^{-2} \text{ g oxalic acid}$$

and converting to weight percent gives the concentration of oxalic acid in the sample of rhubarb as

$$\frac{2.132 \times 10^{-2} \text{ g } C_2H_2O_4}{10.62 \text{ g rhubarb}} \times 100 = 0.201\% \text{ w/w } C_2H_2O_4$$

Titration examples:

Exp: 1: A 50 ml of HCl required 29.71 ml of 0.01963 M Ba $(OH)_2$ to reach an end point bromocresolgreen indicator. Calculate the M of HCl.

$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$

mmole of HCl = mmole $Ba(OH)_2$

$50 \ast M = 2\,(29.71 \ast 0.01963)$

$$M = \frac{2 \ast 29.71 \ast 0.01963}{50} = 0.0233 \text{ M}$$

Exp: 2: Titration of 0.2121 g of pure $Na_2C_2O_4$ (134) required 43.31 ml of $KMnO_4$. What is the molarity of the $KMnO_4$ solution?

The chemical reaction is:

$2MnO_4^{1-} + C_2O_4^{2-} + 16H^{+} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

mmole of $C_2O_4^{2-} = \frac{5}{2}$ m mole of MnO_4^{-}

$(\frac{wt.(mg)}{F.\ wt.})\ C_2O_4^{2-} = \frac{5}{2}\ (V * M)_{MnO4^-}$

$\frac{0.2121}{134} = \frac{5}{2}\ (43.31 * M)$

$M = 1.46 * 10^{-5}$

Exp: 3: What mass of Ag_2CO_3 (275.7) will formed when 25 ml of 0.2 M $AgNO_3$ mixed with 50 ml of 0.08 M Na_2CO_3?

$2\ AgNO_3 + Na_2CO_3 \rightarrow Ag_2CO_3 + 2NaNO_3$

(25 ml $*$ 0.2 M) + (50 ml $*$ 0.08 M)

The mixing of these solutions will result in one possible outcome:

1- An excess $AgNO_3$

2- An excess Na_2CO_3

no. of mmole $AgNO_3$ = 25 $*$ 0.2 = 5 m mole = 5 $* 10^{-3}$ mole

no. of mmole Na_2CO_3 = 50 $*$ 0.08 = 4 m mole = 4 $* 10^{-3}$ mole

Each CO_3^- is react with 2 Ag^+

So: we need (4 $*$ 2) mmole of $AgNO_3$

Since: we have insufficient $AgNO_3$, so that the $AgNO_3$ will be limited regent.

$\frac{wt.Ag_2CO_3}{F.wt\ .Ag_2CO_3} = \frac{1}{2}\ (\frac{wt.\ Ag_2NO_3}{F.wt\ .Ag_2NO_3})$ no. of mole $AgNO_3$

wt. g = $\frac{1}{2} * 5 * 276 * 10^{-3}$ **Note:** 5 $* 10^{-3}$ is no. of $AgNO_3$ mole.

= 0.69 g Ag_2CO_3

Exp: 4: The organic matter in a 3.776 g sample of a mercuric ointment decomposed with HNO_3. After dilution, the Hg^{+2} is titrated with 21.30 ml of a 0.1144 M solution of NH_4SCN. Calculate the % Hg (200.59) in the ointment. The titration involves the formation of a stable neutral complex $Hg\ (SCN)_2$.

$Hg^{2+} + 2SCN^- \rightarrow Hg\ (SCN)_2$

mmole of SCN ≡ 2 m mole Hg^{2+}

$(V * M)_{SCN} = 2\ (\frac{mg}{At.wt})_{Hg2+}$

$21.3 * 0.1144 = \frac{mg}{200.59}$

$(mg)_{Hg2+} = \frac{21.3*0.1144*200.59}{2} = 244.39$ mg

$\% Hg = \frac{244.39}{3.776*1000} * 100 = 6.472\ \%$

Or

$(m.eq)_{Hg2+} \equiv m.eq.\ SCN^-$ (N = M) for SCN- n = 1

$(\frac{mg}{At.wt/n})_{Hg2+} = (V * M)_{SCN^-}$

$mg_{Hg2+} = 244.39$

$\% Hg^{2+} = \frac{244.39}{3.776} * 100 = 6.472$

Exp: 5: A 0.8040 g an iron one is dissolved in acid. The iron is then reduced Fe^{2+} and titrated with 47.22 ml of 0.02242 M $KMnO_4$ solution. Calculate the result of this analysis in term:

a- % Fe (55.847)

b- % Fe_3O_4 (231.54)

The reaction:

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

♦ a ♦ mmole of . Fe^{2+} = 5 mmole of MnO_4^-

$$\left(\frac{wt.mg}{F.wt}\right)_{Fe^{2+}} = 5\ (V * M)_{MnO4^-}$$

mg. Fe^{2+} = 5 * 47.22 * 0.03342 * 55.847

= 295.62 mg = 0.2956 g

$$\% Fe = \frac{wt.of.Fe}{wt.of\ sample} * 100 = \frac{0.2956}{0.8040} * 100 = 36.77\ \%$$

♦ b ♦ each MnO_4^- = 5 Fe^{2+}

There for:

$Fe_3O_4 = 3\ Fe^{2+} = \frac{3}{5}\ MnO_4^-$ multiply by 5

$5Fe_3O_4 = 15Fe^{2+} = 3MnO_4^-$

mmole of Fe_3O_4 = $\frac{5}{3}$ mmole MnO_4^-

$$\left(\frac{mg}{F.wt}\right)_{Fe3O4} = \frac{5}{3}\ (V * M)_{MnO4^-}$$

$$mg\ Fe_3O_4 = \frac{5}{3}\ (47.22 * 0.02242 * 231.54) = 408.54\ mg$$

$$\% Fe_3O_4 = \frac{408.54}{804} * 100 = 50.81\ \%$$

Exp: 6: a: What mass of $AgNO_3$ (169.9) is needed to convert 2.33 g of Na_2CO_3 (106) to Ag_2CO_3?

b: What mass of Ag_2CO_3 (275.7) will be formed ?

The reaction is:

$$2\ AgNO_{3\ aq} + Na_2CO_3 \rightarrow Ag_2CO_{3\ s} + 2NaNO_{3\ aq}$$

a: no. of mole $AgNO_3$ = 2 mole of Na_2CO_3

$$\left(\frac{wt.gram}{F.wt.}\right)_{AgNO3} = 2\left(\frac{wt.gram}{F.wt.}\right)_{AgNO3}$$

$$\frac{X}{164.6} = 2 * \frac{2.33}{106} \rightarrow X = \frac{2*2.33*169.6}{106} = 7.47\ g\ AgNO_3$$

b: mole Ag_2CO_3 = mole Na_2CO_3 = $\frac{1}{2}$ mole $AgNO_3$

$$\frac{g}{F.wt\ Ag_2CO_3} = \frac{g}{F.wt\ Na_2CO_3} = \frac{1}{2}\ \frac{g}{F.wt\ AgNO_3}$$

$$\frac{X}{169.6} = \frac{2.33}{106} = \frac{1}{2} * \frac{7.47}{169.6}$$

X = 6.06 g Ag_2CO_3

Exp: 7: What will be the molar analytical concentration of Na_2CO_3 in the solution produced, when 25 ml of 0.2 M $AgNO_3$ is mixed with 50 ml of 0.08 M Na_2CO_3?

mmole of reacted Na_2CO_3 = $\frac{1}{2}$ m mole $AgNO_3$

mmole of unreacted Na_2CO_3 = Total mmole Na_2CO_3 – mmole of reacted Na_2CO_3

mmole of unreacted Na_2CO_3 = Total mmole Na_2CO_3 – $\frac{1}{2}$ mmole $AgNO_3$

mmole of total Na_2CO_3 = 50 * 0.08 = 4 mmole

mmole $AgNO_3$ = 25 * 0.2 = 5 mmole

mmole of unreacted Na_2CO_3 = $4 - (\frac{1}{2} * 5)$

= 1.5 mmole = 1.5 * 10^{-3} mole

$$M = \frac{no.of\ mole}{V_{total}} = \frac{1.5 * 10^{-3}}{50+25} = 0.02\ Na_2CO_3$$

Exp: 8: What will be the molar analytical concentration of $AgNO_3$ in the solution produced, when 25 ml of 0.2 M AgCl mixed with 100 ml of 0.08 M $NaNO_3$?

mmole $NaNO_3$ = mmole AgCl = mmole $AgNO_3$

mmole $AgNO_3$ = 25 $*$ 0.2 = 0.5 mmole = 5 $*$ 10^{-4} mole.

$$M = \frac{5 * 10^{-4}}{100+25} = 4 * 10^{-7}\ M$$

Home Work:

1- Describe the preparation of 2 L of 0.108 of $BaCl_2$ from $BaCl_2 . 2H_2O$ (244.3 g/mol).

2- Describe the preparation of 500 ml of 0.074 M Cl^- solution from solid $BaCl_2 . 5H_2O$ (244.3) and Cl (35.5).

3- What is the molar concentration of HNO_3 (63.0 g/mol) in a solution that has a sp.g 1.42 and 70.5 %.

4- Describe the preparation of 100 ml of 6 M HCl from concentrated solution that has sp.g 1.18 g/ml and 37 % HCl (36.5 g/mole).

5- How many mole and mmole of Na_2CO_3 are found in 0.1 g?

6- How many mole and mmole of $CuSO_4$ are found in 250 ml solution contain 5 ppm?

CHEMICAL EQUILIBRIUM

The chemical composition of aqueous solution:

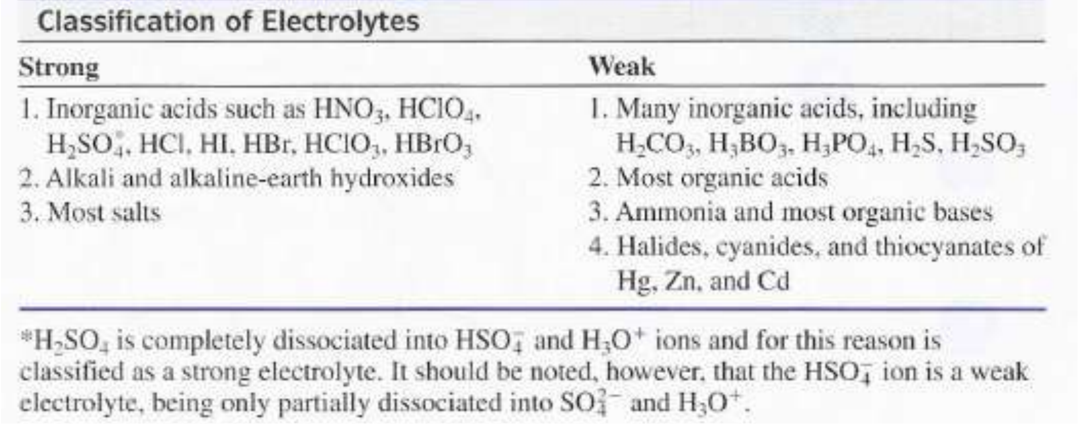
Water is the most plentiful solvent on earth, is easily purified and not toxic. It therefore finds widespread use as a medium for carrying out chemical analysis.

Classifying Solutions of Electrolytes

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.

Acids and Bases:

According to the Bronsted-Lowry theory, an acid is a proton donor and a base is a proton acceptor. For a molecule to behave as an acid, it must encounter a proton acceptor (or base). A molecule that can accept a proton behaves as a base if it encounters an acid.



Classification of Electrolytes

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

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

Conjugate Acids and Bases:

The product formed when an acid gives up a proton is a potential proton acceptor and is called the **conjugate base** of the parent acid. For example, when the species, acid gives up a proton, the species base, is formed, as shown by the reaction:

$$\text{Acid 1} \longrightarrow \text{base 1} + \text{proton}$$

Here, acid 1 and base 1 are a conjugate acid/base pair. Similarly, every base produces a conjugate acid as a result of accepting a proton. That is,

$$\text{Base 2} + \text{proton} \longrightarrow \text{acid 2}$$

When these two processes are combined, the result is an acid/base, or **neutralization reaction.**

$$\text{acid}_1 + \text{base}_2 \rightleftharpoons \text{base}_1 + \text{acid}_2$$

The extent to which this reaction proceeds depends on the relative tendencies of the two bases to accept a proton (or the two acids to donate a proton).

$$\underset{\text{base}_1}{NH_3} + \underset{\text{acid}_2}{H_2O} \rightleftharpoons \underset{\substack{\text{conjugate}\\ \text{acid}_1}}{NH_4^+} + \underset{\substack{\text{conjugate}\\ \text{base}_2}}{OH^-}$$

In this reaction, ammonia (base.) reacts with water, which is labeled acid, to give the conjugate acid, ammonium ion and hydroxide ion, which is the conjugate base of the acid water. In contrast, water acts as a proton acceptor, or base, in an aqueous solution of nitrous acid:

$$\underset{\text{base}_1}{H_2O} + \underset{\text{acid}_2}{HNO_2} \rightleftharpoons \underset{\substack{\text{conjugate}\\ \text{acid}_1}}{H_3O^+} + \underset{\substack{\text{conjugate}\\ \text{base}_2}}{NO_2^-}$$

Many solvents are proton donors or proton acceptors and can thus induce basic or acidic behavior in solutes dissolved in them.

Amphiprotic Species:

Species that possess both acidic and basic properties are amphiprotic. An example is dihydrogen phosphate ion:

$$\underset{\text{base}_1}{H_2PO_4^-} + \underset{\text{acid}_2}{H_3O^+} \rightleftharpoons \underset{\text{acid}_1}{H_3PO_4} + \underset{\text{base}_2}{H_2O}$$

Here, H_3P0_4 is the conjugate acid of the original base. In the presence of a proton acceptor, such as hydroxide ion, however, $H_2P0_4^-$ behaves as an acid and donates a proton to form the conjugate base:

$$\underset{\text{acid}_1}{H_2PO_4^-} + \underset{\text{base}_2}{OH^-} \rightleftharpoons \underset{\text{base}_1}{HPO_4^{2-}} + \underset{\text{acid}_2}{H_2O}$$

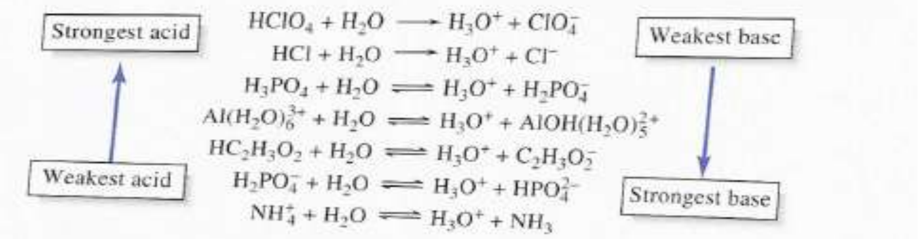
The simplest amino acids are an important class of amphiprotic compounds that contain both a weak acid and a weak base functional group. When dissolved in water, an amino acid such as glycine undergoes a kind of internal acid/base reaction to produce a **zwitterions species** that bears both a positive and a negative charge.

$$\underset{\text{glycine}}{NH_2CH_2COOH} \rightleftharpoons \underset{\text{zwitterion}}{NH_3^+CH_2COO^-}$$

Water is the classic example of an amphiprotic solvent.

Strengths of Acids and Bases:

The figure shows the dissociation reactions of a few common acids in water. The first two are **strong acids** because reaction with the solvent is sufficiently complete that no undissociated solute molecules are left in aqueous solution. The remainder is **weak acids,** which react in completely with water to give solutions containing significant quantities of both the parent acid and its conjugate base. Note that acids can be cationic, anionic, or electrically neutral. The same holds for bases.



$$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$$
$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$
$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + AlOH(H_2O)_5^{2+}$$
$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$$
$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

Chemical equilibrium:

The reactions used in analytical chemistry they proceed in a state of chemical equilibrium in which the ratio of concentrations of reactants and products is constant. Equilibrium- constant expressions are **algebraic** equations that describe the concentration relationships existing among reactants and products at equilibrium.

$$H_3AsO_4 + 3I^- + 2H^+ \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$$

$$H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 3I^- + 2H^+$$

Consider the chemical reaction:

$$wW + xX \rightleftharpoons yY + zZ$$

$$K = \frac{[Y]^y[Z]^z}{[W]^w[X]^x}$$

When Z is a pure solid or liquid or solvent the value of K will be:

$$K = \frac{[Y]^y}{[W]^w[X]^x}$$

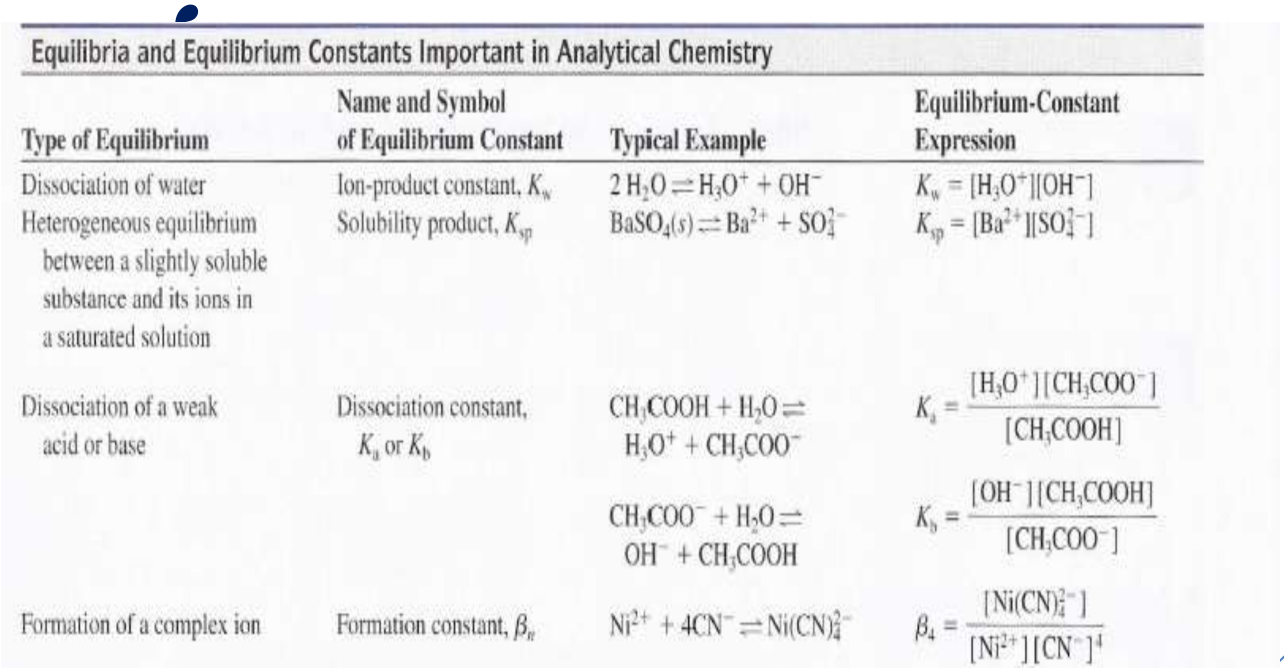
The small letter expresses the number of moles for the reactant and product.

Where the square-bracketed [] terms have the following meanings:

1. Molar concentration if the species is a dissolved solute.
2. Partial pressure in atmospheres if the species is a gas.

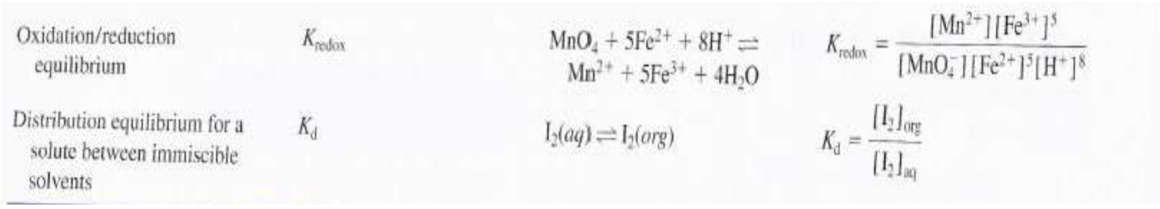
Types of Equilibrium Constants Encountered in Analytical Chemistry:

The table summarizes the types of chemical equilibria and equilibrium constants that are of importance in analytical chemistry:



Equilibria and Equilibrium Constants Important in Analytical Chemistry

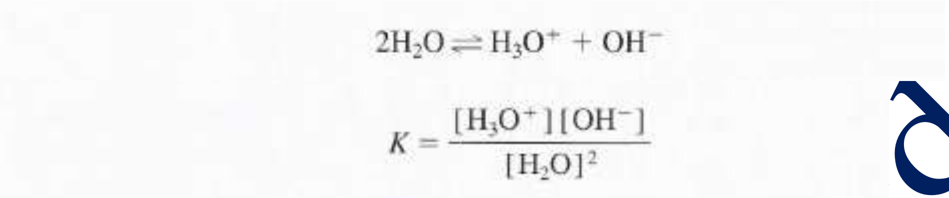
Type of Equilibrium	Name and Symbol of Equilibrium Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water	Ion-product constant, K_w	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	$K_w = [H_3O^+][OH^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, K_{sp}	$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$
		$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
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	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$

Applying the Ion-Product Constant for Water:

Aqueous solutions contain small concentrations of hydronium and hydroxide ions as a consequence of the dissociation reaction. An equilibrium constant for this reaction can be formulated as shown in equation below:

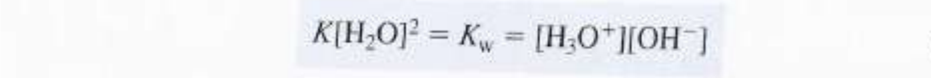


$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

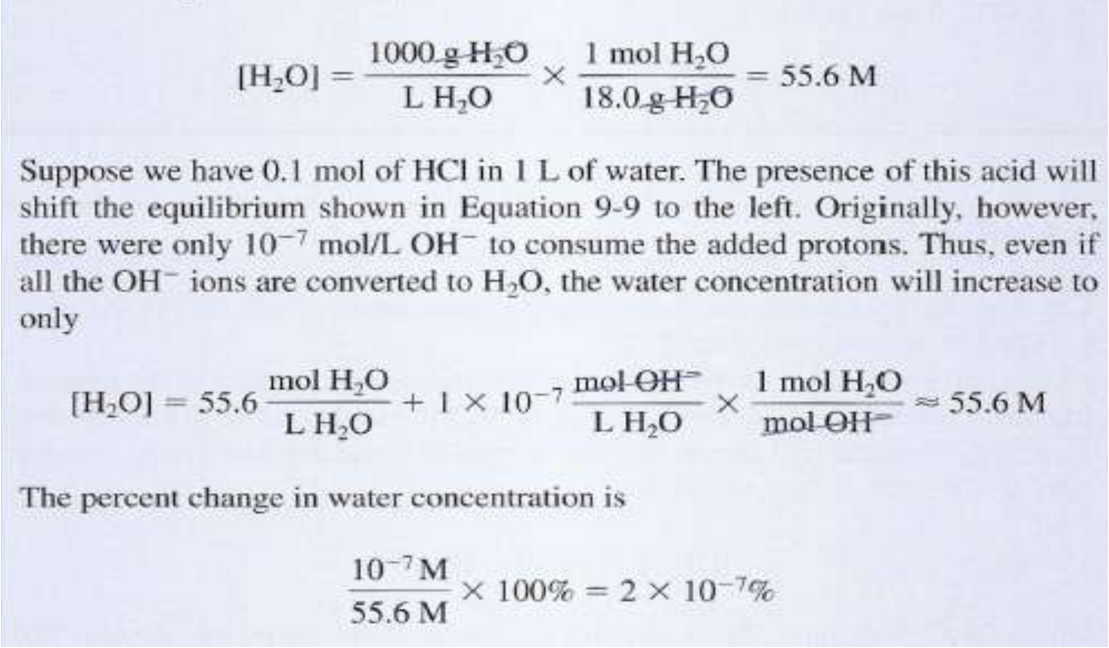
The concentration of water in dilute aqueous solutions is enormous, however, when compared with the concentration of **hydrogen** and **hydroxide** ions.

The ion-product constant (K_w) for water permits the ready calculation of the hydronium and hydroxide ion concentrations of aqueous solutions.



$$K[H_2O]^2 = K_w = [H_3O^+][OH^-]$$

Why water does not appear in equilibrium constant expression for aqueous solution?



In a dilute aqueous solution, the molar concentration of water is

$$[H_2O] = \frac{1000\,\cancel{g\,H_2O}}{L\,H_2O} \times \frac{1\text{ mol }H_2O}{18.0\,\cancel{g\,H_2O}} = 55.6\text{ M}$$

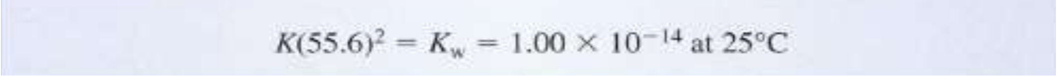
Suppose we have 0.1 mol of HCl in 1 L of water. The presence of this acid will shift the equilibrium shown in Equation 9-9 to the left. Originally, however, there were only 10^{-7} mol/L OH^- to consume the added protons. Thus, even if all the OH^- ions are converted to H_2O, the water concentration will increase to only

$$[H_2O] = 55.6\frac{\text{mol }H_2O}{L\,H_2O} + 1 \times 10^{-7}\frac{\cancel{\text{mol }OH^-}}{L\,H_2O} \times \frac{1\text{ mol }H_2O}{\cancel{\text{mol }OH^-}} \approx 55.6\text{ M}$$

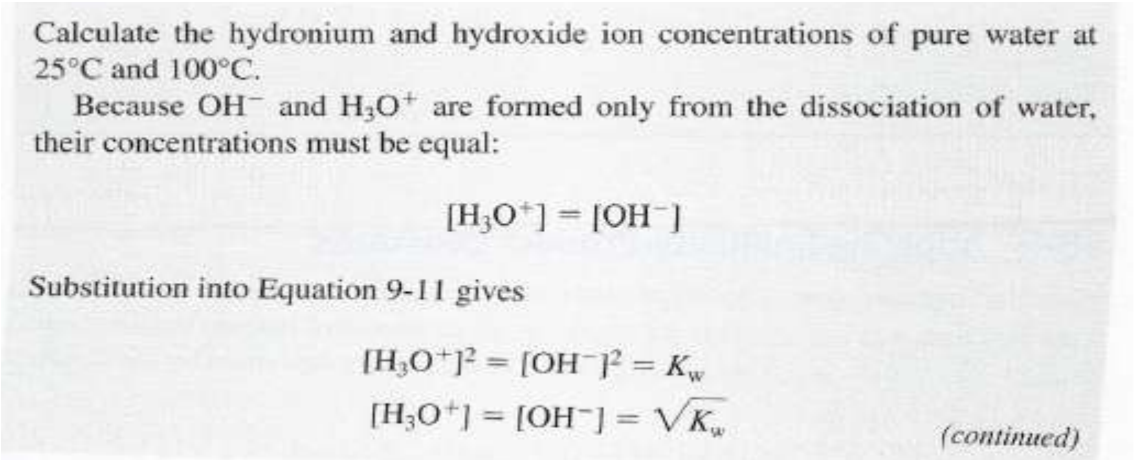
The percent change in water concentration is

$$\frac{10^{-7}\text{ M}}{55.6\text{ M}} \times 100\% = 2 \times 10^{-7}\%$$

This percent is negligible so the molar concentration of water is considered as 55.6.



$$K(55.6)^2 = K_w = 1.00 \times 10^{-14}\text{ at }25°C$$



Calculate the hydronium and hydroxide ion concentrations of pure water at 25°C and 100°C.

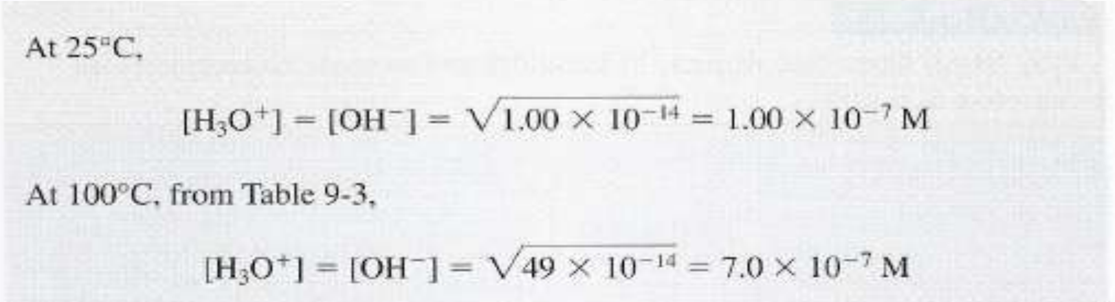
Because OH^- and H_3O^+ are formed only from the dissociation of water, their concentrations must be equal:

$$[H_3O^+] = [OH^-]$$

Substitution into Equation 9-11 gives

$$[H_3O^+]^2 = [OH^-]^2 = K_w$$
$$[H_3O^+] = [OH^-] = \sqrt{K_w}$$

(continued)

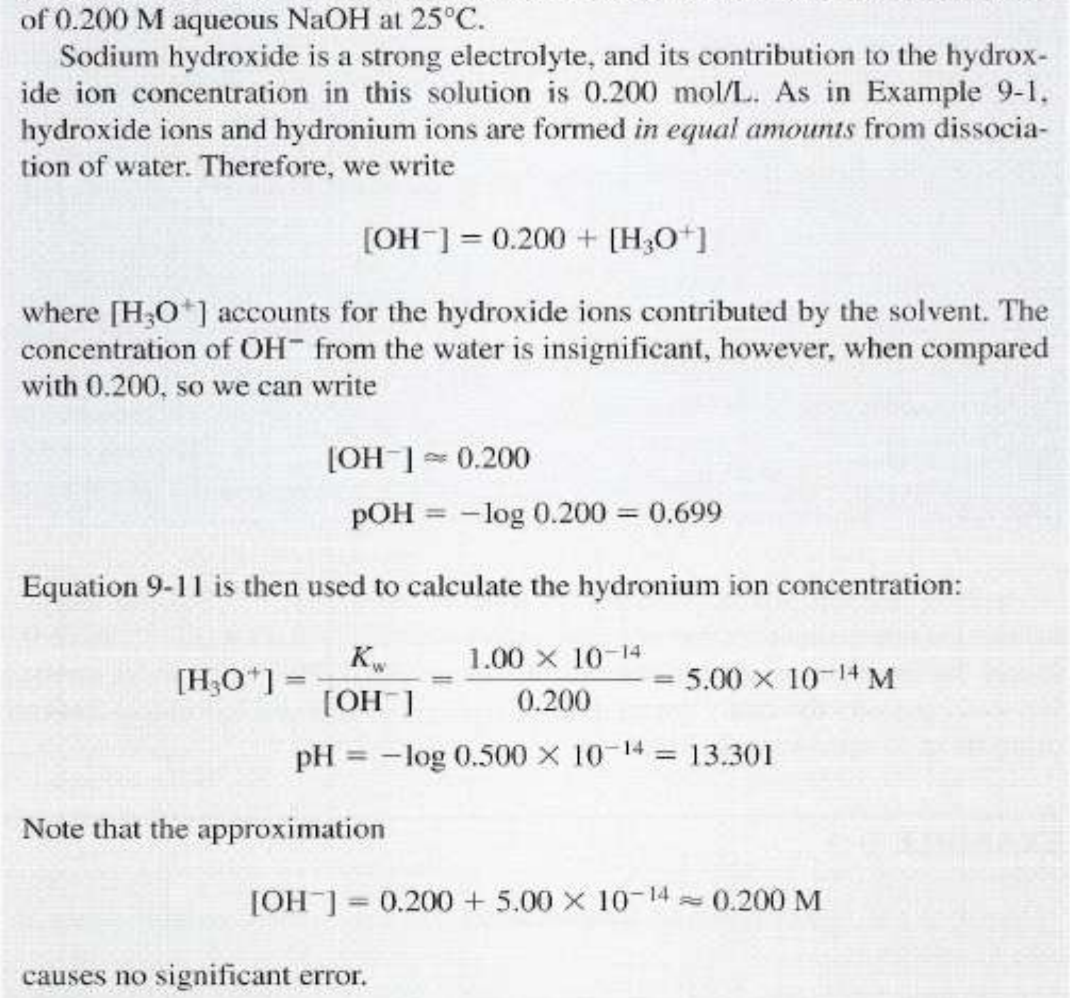


At 25°C,

$$[H_3O^+] = [OH^-] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\ M$$

At 100°C, from Table 9-3,

$$[H_3O^+] = [OH^-] = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7}\ M$$



Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of 0.200 M aqueous NaOH at 25°C.

Sodium hydroxide is a strong electrolyte, and its contribution to the hydroxide ion concentration in this solution is 0.200 mol/L. As in Example 9-1, hydroxide ions and hydronium ions are formed *in equal amounts* from dissociation of water. Therefore, we write

$$[OH^-] = 0.200 + [H_3O^+]$$

where $[H_3O^+]$ accounts for the hydroxide ions contributed by the solvent. The concentration of OH^- from the water is insignificant, however, when compared with 0.200, so we can write

$$[OH^-] \approx 0.200$$
$$pOH = -\log 0.200 = 0.699$$

Equation 9-11 is then used to calculate the hydronium ion concentration:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.200} = 5.00 \times 10^{-14}\ M$$
$$pH = -\log 0.500 \times 10^{-14} = 13.301$$

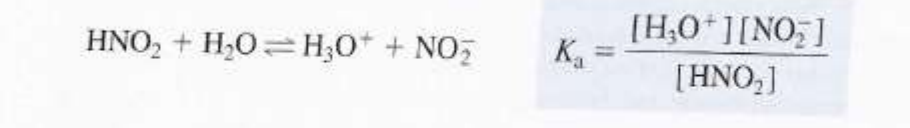
Note that the approximation

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

causes no significant error.

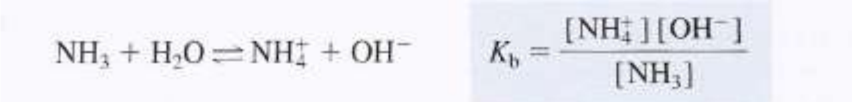
Applying Acid-Base Dissociation Constants:

When a weak acid or a weak base is dissolved in water, partial dissociation occurs. Thus, for nitrous acid, we can write where **K_a;** is the **acid dissociation constant** for nitrous acid.



$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^- \qquad K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

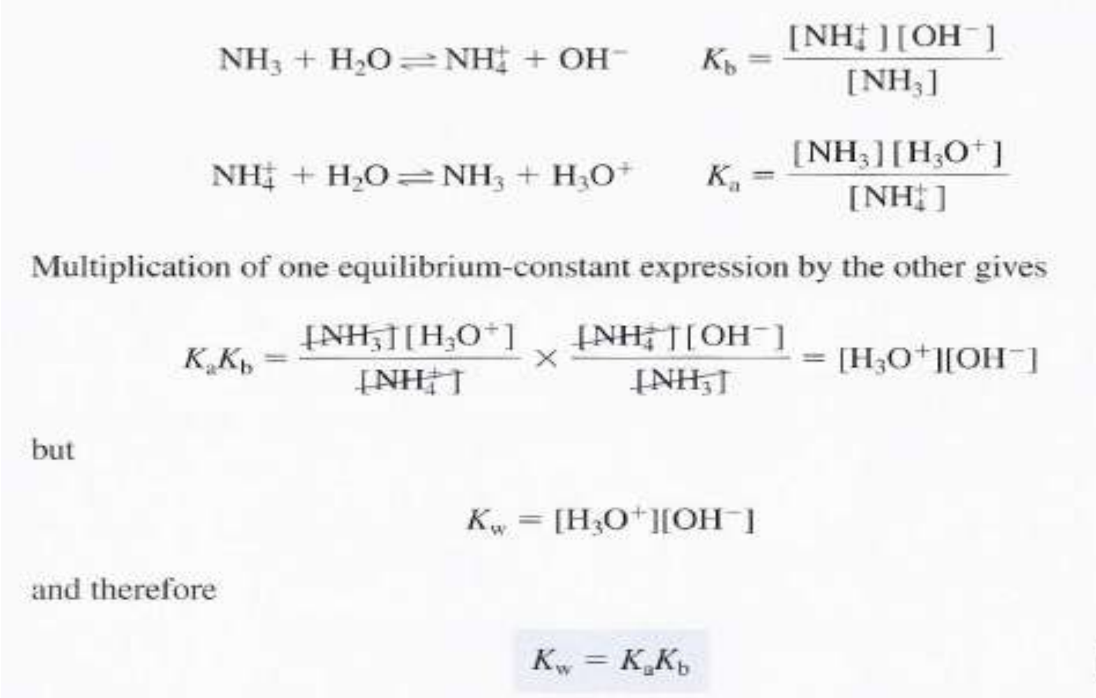
In an analogous way, the **base dissociation constant (K_b)** for ammonia is:



$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Dissociation Constants for Conjugate Acid/Base Pairs:

Consider the base dissociation-constant expression for ammonia and the acid dissociation-constant expression for its conjugate acid, ammonium ion:



$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Multiplication of one equilibrium-constant expression by the other gives

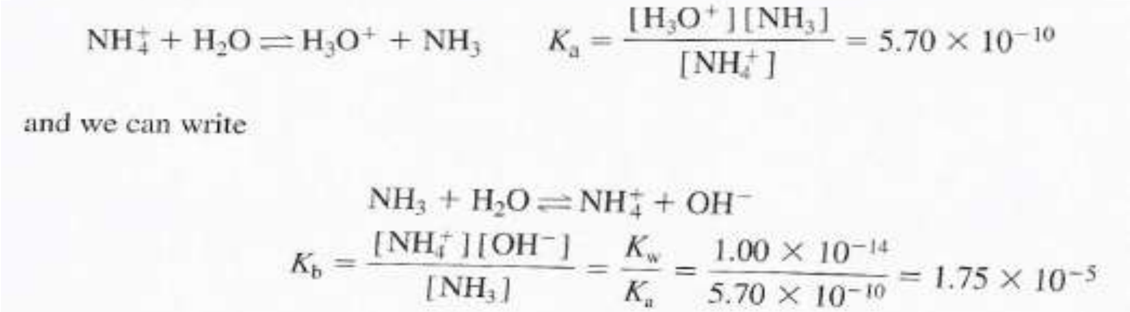
$$K_aK_b = \frac{\cancel{[NH_3]}[H_3O^+]}{\cancel{[NH_4^+]}} \times \frac{\cancel{[NH_4^+]}[OH^-]}{\cancel{[NH_3]}} = [H_3O^+][OH^-]$$

but

$$K_w = [H_3O^+][OH^-]$$

and therefore

$$K_w = K_aK_b$$

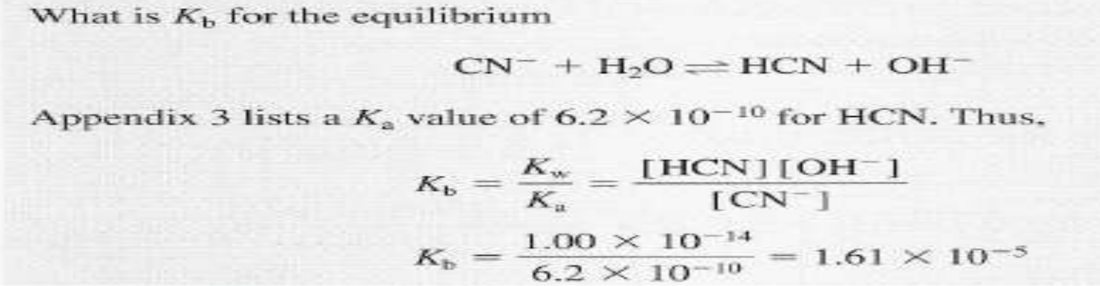


$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3 \qquad K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = 5.70 \times 10^{-10}$$

and we can write

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{5.70 \times 10^{-10}} = 1.75 \times 10^{-5}$$



What is K_b for the equilibrium

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

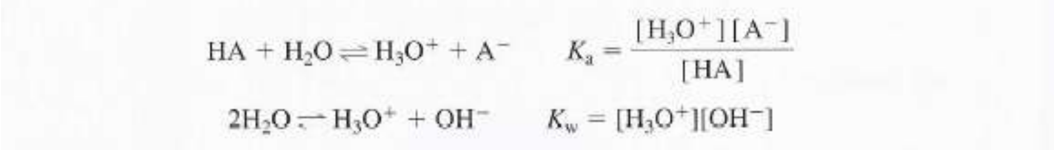
Appendix 3 lists a K_a value of 6.2×10^{-10} for HCN. Thus,

$$K_b = \frac{K_w}{K_a} = \frac{[HCN][OH^-]}{[CN^-]}$$

$$K_b = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

Hydronium Ion Concentration of Solutions of Weak Acids:

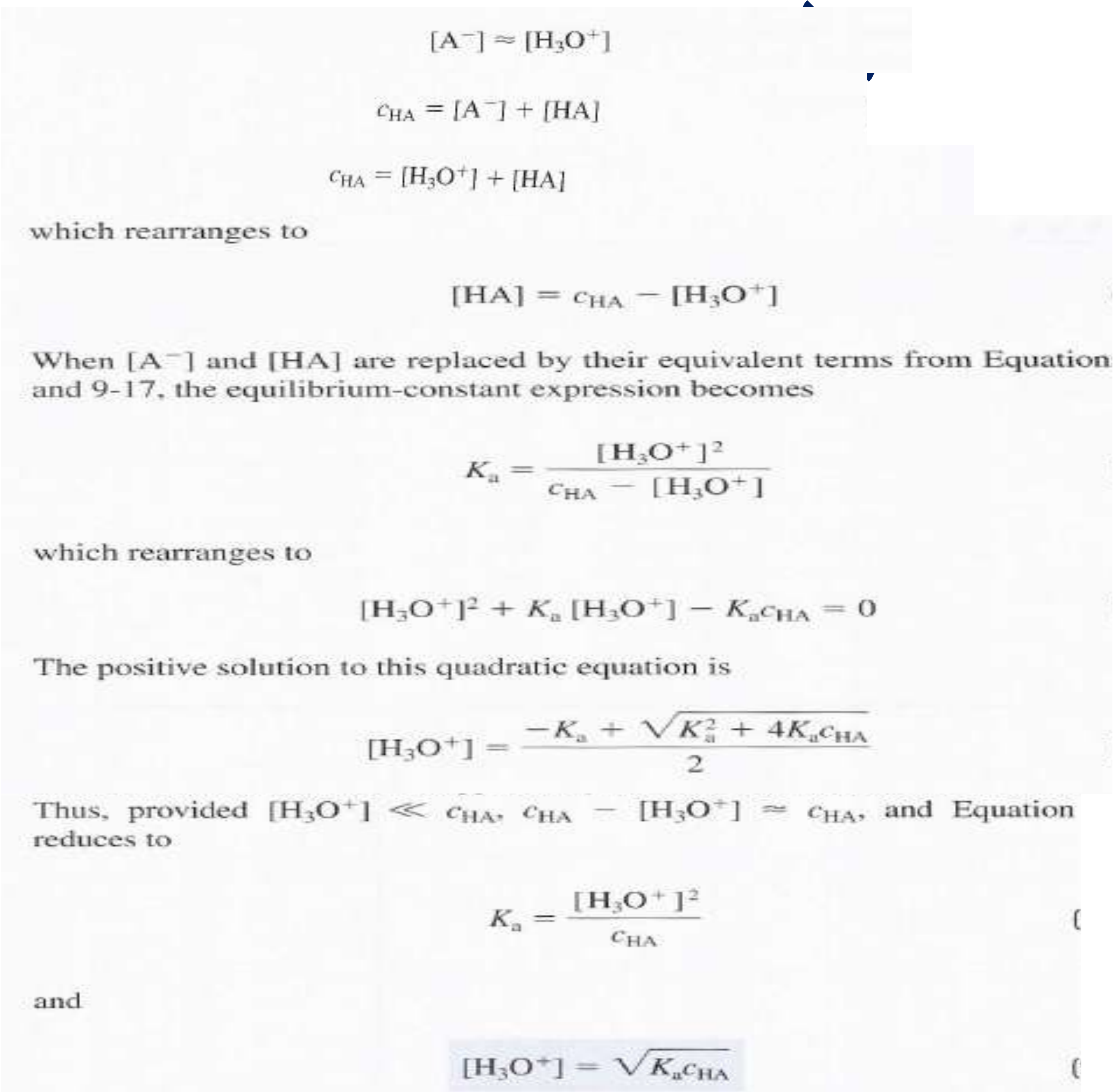
When the weak acid HA is dissolved in water, two equilibria are established that yield hydronium ions: Ordinarily, the hydronium ions produced from the first reaction suppress the dissociation of water. The contribution of hydronium ions from the second equilibrium is negligible.



$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_w = [H_3O^+][OH^-]$$

Furthermore, the sum of the molar concentrations of the weak acid and its conjugate base must equal the analytical concentration of the acid C_{HA} because the solution contains no other source of A^- so:



$$[A^-] \approx [H_3O^+]$$

$$c_{HA} = [A^-] + [HA]$$

$$c_{HA} = [H_3O^+] + [HA]$$

which rearranges to

$$[HA] = c_{HA} - [H_3O^+]$$

When $[A^-]$ and $[HA]$ are replaced by their equivalent terms from Equation and 9-17, the equilibrium-constant expression becomes

$$K_a = \frac{[H_3O^+]^2}{c_{HA} - [H_3O^+]}$$

which rearranges to

$$[H_3O^+]^2 + K_a[H_3O^+] - K_a c_{HA} = 0$$

The positive solution to this quadratic equation is

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a c_{HA}}}{2}$$

Thus, provided $[H_3O^+] \ll c_{HA}$, $c_{HA} - [H_3O^+] \approx c_{HA}$, and Equation reduces to

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

and

$$[H_3O^+] = \sqrt{K_a c_{HA}}$$

Where [HA] and C_{HA} are the molar and analytical concentration respectively.

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

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

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

Calculate the hydronium ion concentration in a solution that is 2.0×10^{-4} M in aniline hydrochloride, $C_6H_5NH_3Cl$.

In aqueous solution, dissociation of the salt to Cl^- and $C_6H_5NH_3^+$ is complete. The weak acid $C_6H_5NH_3^+$ dissociates as follows:

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+ \qquad K_a = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]}$$

If we look in Appendix 3, we find that the K_a for $C_6H_5NH_3^+$ is 2.51×10^{-5}. Proceeding as in Example 9-7, we have

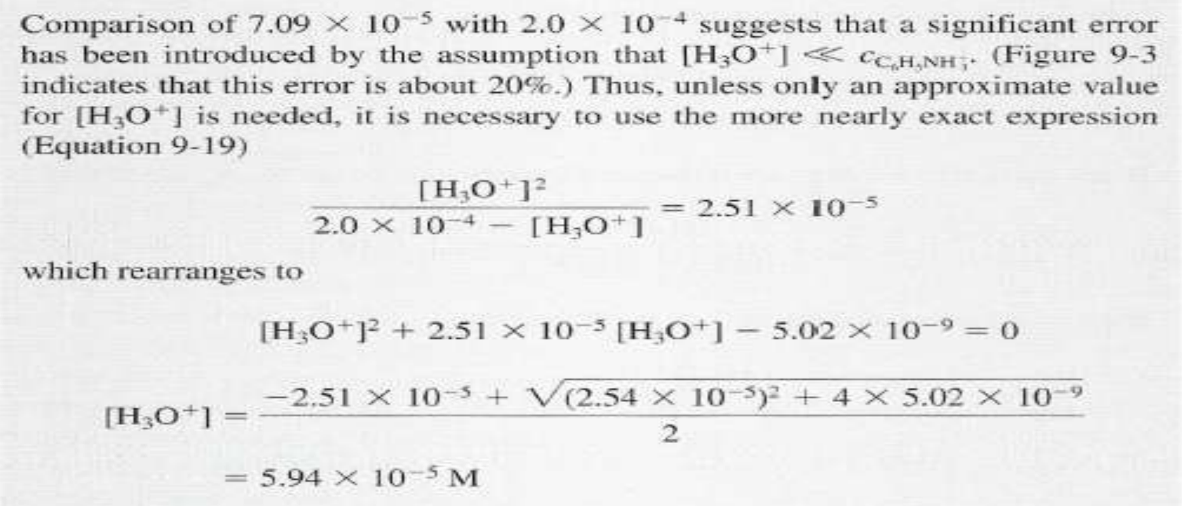
$$[H_3O^+] = [C_6H_5NH_2]$$

$$[C_6H_5NH_3^+] = 2.0 \times 10^{-4} - [H_3O^+]$$

Assume that $[H_3O^+] \ll 2.0 \times 10^{-4}$, and substitute the simplified value for $[C_6H_5NH_3^+]$ into the dissociation-constant expression to obtain (see Equation 9-21)

$$\frac{[H_3O^+]^2}{2.0 \times 10^{-4}} = 2.51 \times 10^{-5}$$

$$[H_3O^+] = \sqrt{5.02 \times 10^{-9}} = 7.09 \times 10^{-5}\,M$$



Comparison of 7.09×10^{-5} with 2.0×10^{-4} suggests that a significant error has been introduced by the assumption that $[H_3O^+] \ll c_{C_6H_5NH_3^+}$. (Figure 9-3 indicates that this error is about 20%.) Thus, unless only an approximate value for $[H_3O^+]$ is needed, it is necessary to use the more nearly exact expression (Equation 9-19)

$$\frac{[H_3O^+]^2}{2.0 \times 10^{-4} - [H_3O^+]} = 2.51 \times 10^{-5}$$

which rearranges to

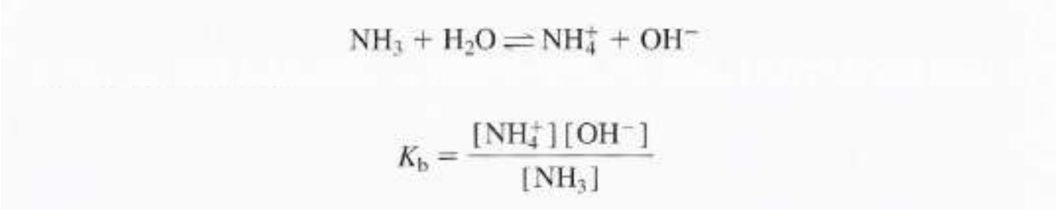
$$[H_3O^+]^2 + 2.51 \times 10^{-5}[H_3O^+] - 5.02 \times 10^{-9} = 0$$

$$[H_3O^+] = \frac{-2.51 \times 10^{-5} + \sqrt{(2.54 \times 10^{-5})^2 + 4 \times 5.02 \times 10^{-9}}}{2}$$

$$= 5.94 \times 10^{-5}\ M$$

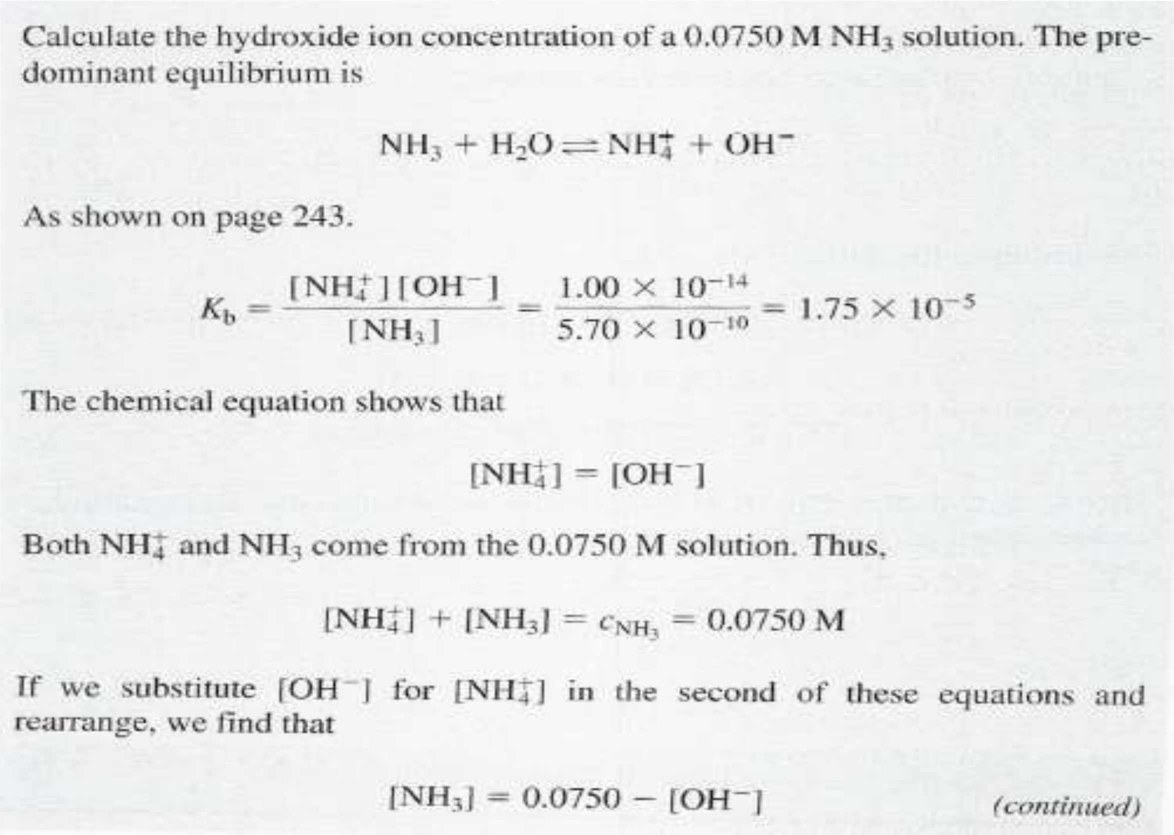
Hydronium Ion Concentration of Solutions of Weak Bases:

The techniques discussed in previous sections are readily adapted to the calculation of the hydroxide or hydronium ion concentration in solutions of weak bases.



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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$



Calculate the hydroxide ion concentration of a 0.0750 M NH_3 solution. The predominant equilibrium is

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

As shown on page 243.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{1.00 \times 10^{-14}}{5.70 \times 10^{-10}} = 1.75 \times 10^{-5}$$

The chemical equation shows that

$$[NH_4^+] = [OH^-]$$

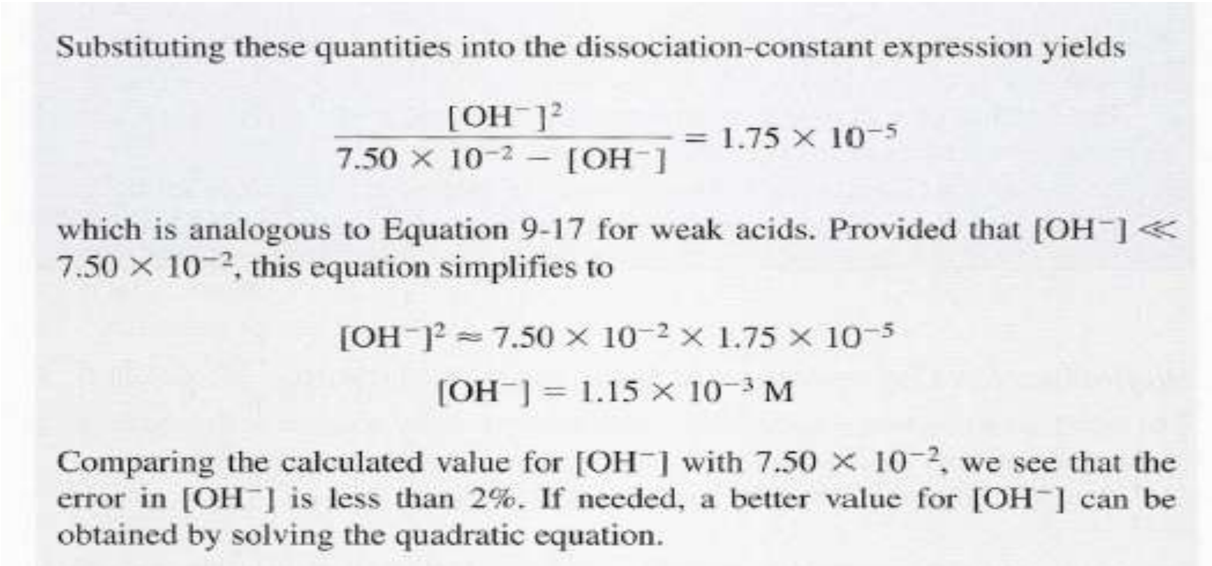
Both NH_4^+ and NH_3 come from the 0.0750 M solution. Thus,

$$[NH_4^+] + [NH_3] = c_{NH_3} = 0.0750\ M$$

If we substitute $[OH^-]$ for $[NH_4^+]$ in the second of these equations and rearrange, we find that

$$[NH_3] = 0.0750 - [OH^-]$$

(continued)



Substituting these quantities into the dissociation-constant expression yields

$$\frac{[OH^-]^2}{7.50 \times 10^{-2} - [OH^-]} = 1.75 \times 10^{-5}$$

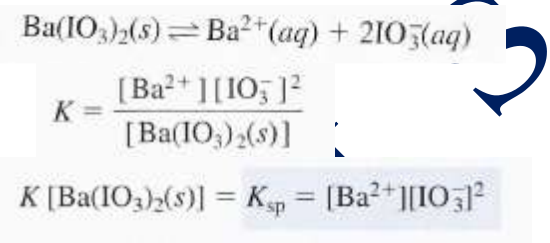
which is analogous to Equation 9-17 for weak acids. Provided that $[OH^-] \ll 7.50 \times 10^{-2}$, this equation simplifies to

$$[OH^-]^2 \approx 7.50 \times 10^{-2} \times 1.75 \times 10^{-5}$$
$$[OH^-] = 1.15 \times 10^{-3}\ M$$

Comparing the calculated value for $[OH^-]$ with 7.50×10^{-2}, we see that the error in $[OH^-]$ is less than 2%. If needed, a better value for $[OH^-]$ can be obtained by solving the quadratic equation.

Applying Solubility-Product Constants:

Most, but not all, sparingly soluble salts are essentially completely dissociated in saturated aqueous solution. For example, when an excess of barium iodate is equilibrated with water, the dissociation process is adequately described by the equation:

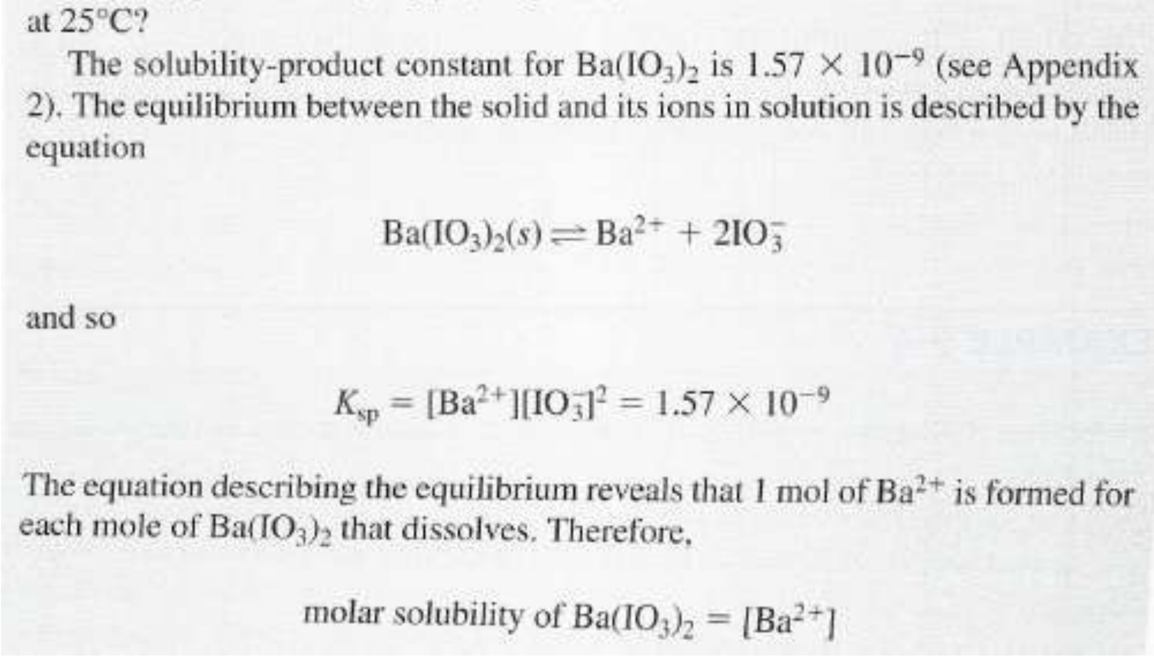


$$Ba(IO_3)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2IO_3^-(aq)$$

$$K = \frac{[Ba^{2+}][IO_3^-]^2}{[Ba(IO_3)_2(s)]}$$

$$K\,[Ba(IO_3)_2(s)] = K_{sp} = [Ba^{2+}][IO_3^-]^2$$

Where the new constant is called the **solubility-product constant or the solubility product.** The solubility-product expression permits the ready calculation of the solubility of a sparingly soluble substance that ionizes completely in water.



How many grams of $Ba(IO_3)_2$ (487 g/mol) can be dissolved in 500 mL of water at 25°C?

The solubility-product constant for $Ba(IO_3)_2$ is 1.57×10^{-9} (see Appendix 2). The equilibrium between the solid and its ions in solution is described by the equation

$$Ba(IO_3)_2(s) \rightleftharpoons Ba^{2+} + 2IO_3^-$$

and so

$$K_{sp} = [Ba^{2+}][IO_3^-]^2 = 1.57 \times 10^{-9}$$

The equation describing the equilibrium reveals that 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

$$[Ba^{2+}](2[Ba^{2+}])^2 = 4[Ba^{2+}]^3 = 1.57 \times 10^{-9}$$

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

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

$$\text{solubility} = 7.32 \times 10^{-4}\ M$$

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

$$\text{no. mmol } Ba(IO_3)_2 = 7.32 \times 10^{-4} \frac{\text{mmol } Ba(IO_3)_2}{\cancel{\text{mL}}} \times 500\ \cancel{\text{mL}}$$

The mass of $Ba(IO_3)_2$ in 500 mL is given by

$$\text{mass } Ba(IO_3)_2 = (7.32 \times 10^{-4} \times 500)\ \cancel{\text{mmol } Ba(IO_3)_2} \times 0.487 \frac{\text{g } Ba(IO_3)_2}{\cancel{\text{mmol } Ba(IO_3)_2}}$$

$$= 0.178\ g$$

The Effect of a Common Ion on the Solubility of a Precipitate:

The **common-ion** effect is a mass-action effect predicted from the **Le Châtelier's principle** and is demonstrated by the following examples.

Calculate the molar solubility of $Ba(IO_3)_2$ in a solution that is 0.0200 M in $Ba(NO_3)_2$.

The solubility is no longer equal to $[Ba^{2+}]$ because $Ba(NO_3)_2$ is also a source of barium ions. We know, however, that the solubility is related to $[IO_3^-]$:

$$\text{molar solubility of } Ba(IO_3)_2 = \frac{1}{2}[IO_3^-]$$

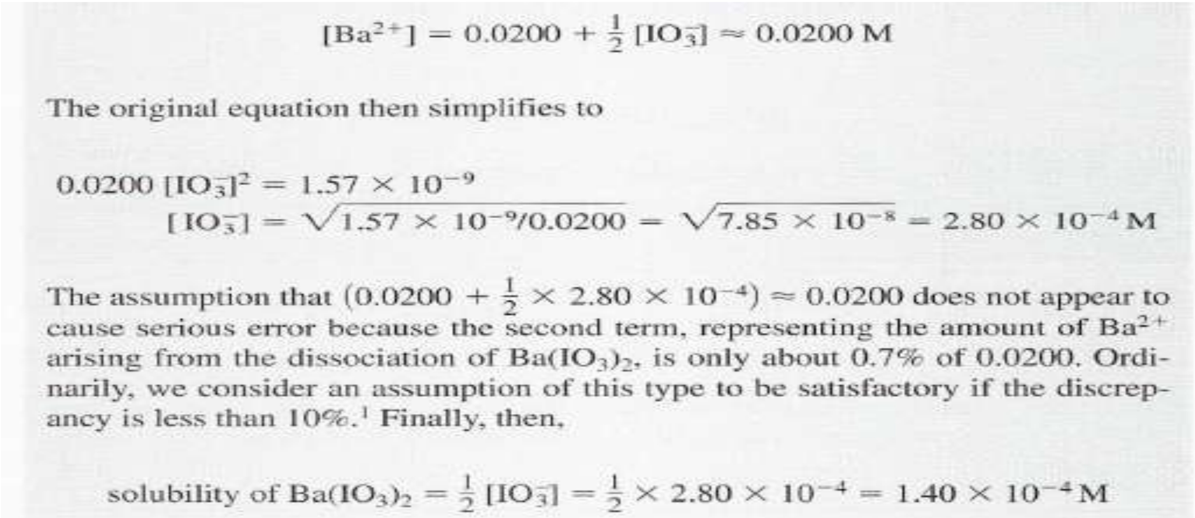
There are two sources of barium ions: $Ba(NO_3)_2$ and $Ba(IO_3)_2$. The contribution from the former is 0.0200 M, and that from the latter is equal to the molar solubility, or $\frac{1}{2}[IO_3^-]$. Thus,

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

Substitution of these quantities into the solubility-product expression yields

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

Since the exact solution for $[IO_3^-]$ requires solving a cubic equation, we seek an approximation that simplifies the algebra. The small numerical value of K_{sp} suggests that the solubility of $Ba(IO_3)_2$ is not large, and this is confirmed by the result obtained in Example 9-3. Moreover, barium ion from $Ba(NO_3)_2$ will further repress the limited solubility of $Ba(IO_3)_2$. Thus, it is reasonable to seek a provisional answer to the problem by assuming that 0.0200 is large with respect to $\frac{1}{2}[IO_3^-]$. That is, $\frac{1}{2}[IO_3^-] \ll 0.0200$, and



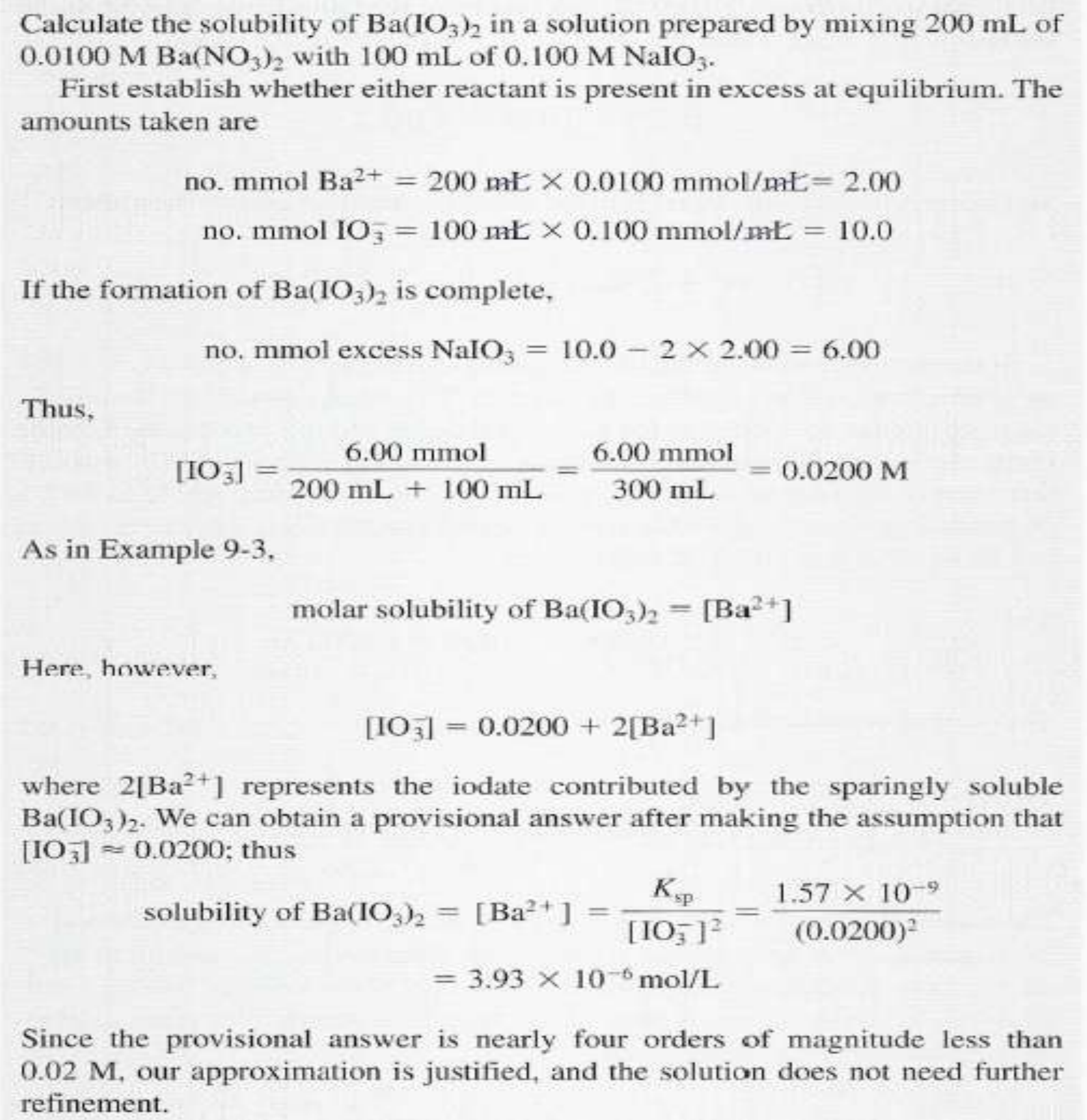
$$[Ba^{2+}] = 0.0200 + \tfrac{1}{2}[IO_3^-] \approx 0.0200\ M$$

The original equation then simplifies to

$$0.0200\,[IO_3^-]^2 = 1.57 \times 10^{-9}$$
$$[IO_3^-] = \sqrt{1.57 \times 10^{-9}/0.0200} = \sqrt{7.85 \times 10^{-8}} = 2.80 \times 10^{-4}\ M$$

The assumption that $(0.0200 + \frac{1}{2} \times 2.80 \times 10^{-4}) \approx 0.0200$ does not appear to cause serious error because the second term, representing the amount of Ba^{2+} arising from the dissociation of $Ba(IO_3)_2$, is only about 0.7% of 0.0200. Ordinarily, we consider an assumption of this type to be satisfactory if the discrepancy is less than 10%.[1] Finally, then,

$$\text{solubility of } Ba(IO_3)_2 = \tfrac{1}{2}[IO_3^-] = \tfrac{1}{2} \times 2.80 \times 10^{-4} = 1.40 \times 10^{-4}\ M$$



Calculate the solubility of $Ba(IO_3)_2$ in a solution prepared by mixing 200 mL of 0.0100 M $Ba(NO_3)_2$ with 100 mL of 0.100 M $NaIO_3$.

First establish whether either reactant is present in excess at equilibrium. The amounts taken are

$$\text{no. mmol } Ba^{2+} = 200\ \cancel{mL} \times 0.0100\ mmol/\cancel{mL} = 2.00$$
$$\text{no. mmol } IO_3^- = 100\ \cancel{mL} \times 0.100\ mmol/\cancel{mL} = 10.0$$

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

$$\text{no. mmol excess } NaIO_3 = 10.0 - 2 \times 2.00 = 6.00$$

Thus,

$$[IO_3^-] = \frac{6.00\ mmol}{200\ mL + 100\ mL} = \frac{6.00\ mmol}{300\ mL} = 0.0200\ M$$

As in Example 9-3,

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

Here, however,

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

where $2[Ba^{2+}]$ represents the iodate contributed by the sparingly soluble $Ba(IO_3)_2$. We can obtain a provisional answer after making the assumption that $[IO_3^-] \approx 0.0200$; thus

$$\text{solubility of } Ba(IO_3)_2 = [Ba^{2+}] = \frac{K_{sp}}{[IO_3^-]^2} = \frac{1.57 \times 10^{-9}}{(0.0200)^2}$$
$$= 3.93 \times 10^{-6}\ mol/L$$

Since the provisional answer is nearly four orders of magnitude less than 0.02 M, our approximation is justified, and the solution does not need further refinement.

Solving Equilibrium Problems for Complex Systems:

Example, when water is saturated with sparingly soluble barium sulfate, three equilibria develop:

$$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$$
$$SO_4^{2-} + H_3O^+ \rightleftharpoons HSO_4^- + H_2O$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

If hydronium ions are added to this system, the second equilibrium is shifted to the right by the common-ion effect. The resulting decrease in sulfate concentration causes the first equilibrium to shift to the right as well, which increases the solubility of the barium sulfate. The solubility of barium sulfate is also increased when acetate ions are added to an aqueous suspension of barium sulfate because acetate ions tend to form a soluble complex with barium ions, as shown by the reaction:

$$Ba^{2+} + OAc^- \rightleftharpoons BaOAc^+$$

Again, the common-ion effect causes both this equilibrium and the solubility equilibrium to shift to the right; an increase in solubility results.
The solution of a multiple-equilibrium problem requires us to develop as many independent equations as there are participants in the system being studied. For example, if we wish to compute the solubility of barium sulfate in a solution of acid, we need to be able to calculate the concentration of all the species present in the solution. There are five species.

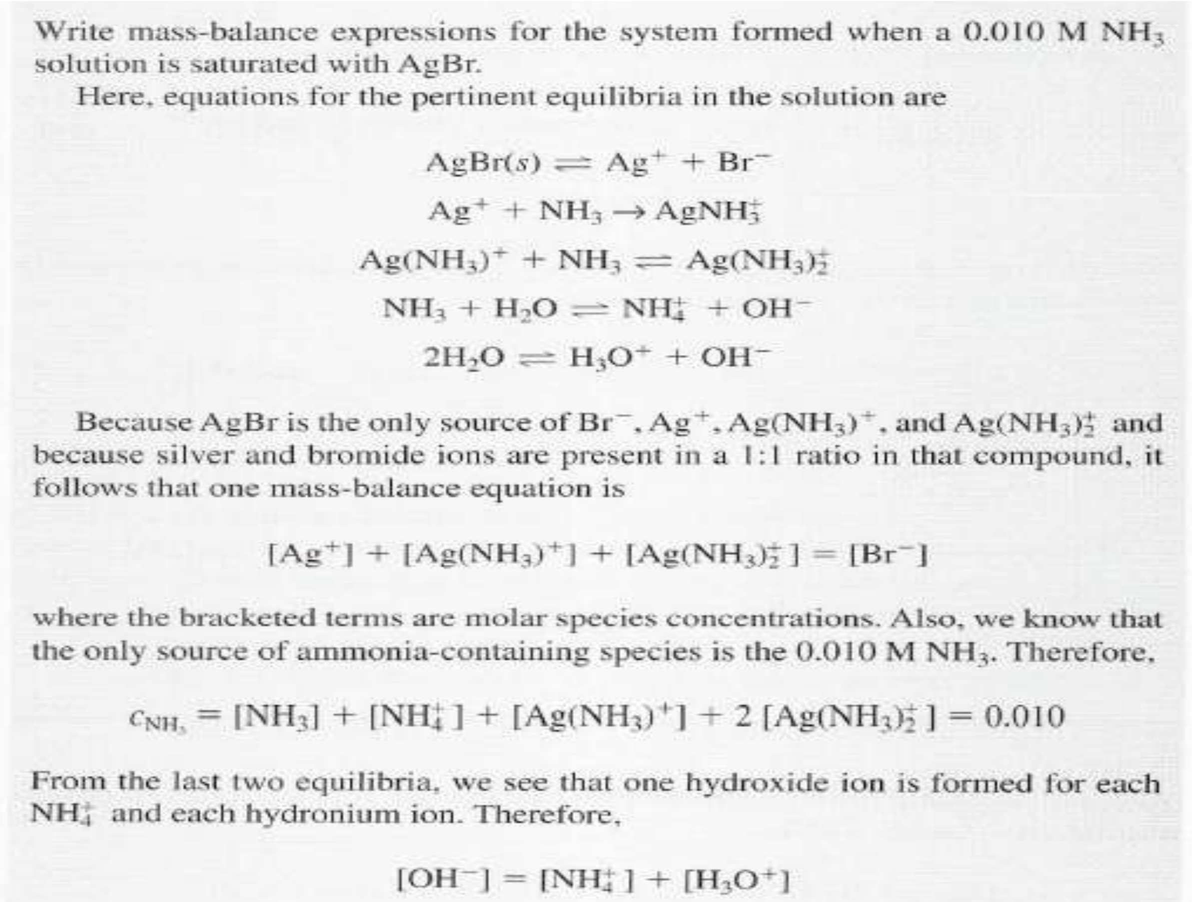
$$[Ba^{2+}],\ [SO_4^{2-}],\ [HSO_4^-],\ [H_3O^+],\text{ and }[OH^-].$$

To calculate the solubility of barium sulfate in this solution rigorously, it is then necessary to develop five independent algebraic equations that can be solved simultaneously to give the five concentrations.
Three types of algebraic equations are used in solving multiple-equilibrium problems: (1) equilibrium-constant expressions, (2) mass-balance equations, and (3) a single charge-balance equation.
Mass-balance equations relate the equilibrium concentrations of various species in a solution to one another and to the analytical concentrations of the various solutes. We can derive such equations from information about how the solution was prepared and from a knowledge of the kinds of equilibria that are present in the solution.
Example: Calculate the molar solubility of $BaSO_4$ a solution in which $[H_3O^+]$ is 2.5 M.
$K_{sp} = 1.1 \ast 10^{-10}$
$BaSO_4 \Leftrightarrow Ba^{2+} + SO_4^{2-}$
$H_2O + HSO_4^- \Leftrightarrow H_3O^+ + SO_4^{2-}$ $K_1 = 1.02 \ast 10^{-2}$
$S = Ba^{2+} = [SO_4^{2-}] + [HSO_4^-]$
$K_{sp} = [Ba^{2+}] = [SO_4^{2-}] = 1.1 \ast 10^{-10}$ ……………………………………(1)
$K_1 = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = 1.02 \ast 10^{-2}$ ……………………………………..(2)
Mass balance requires that
$[Ba^{2+}] = [SO_4^{2-}] + [HSO_4^-]$ ………………………………………………(3)
$[H_3O^+] = 2.5$ M ……………………………………………………………..(4)
Substituted 4 in 2
$K_1 = \frac{[2.5][SO_4^{2-}]}{[HSO_4^-]} = 1.02 \ast 10^{-2}$
$[HSO_4^-] = 245.1\ [SO_4^{2-}]$ ………………………………………………..(5)
Substituted 4 in 2

$[Ba^{2+}] = [SO_4{}^{2-}] + 245.1\,[SO_4{}^{2-}] = 246.1\,[SO_4{}^{2-}]$ ……………………(6)

Substituted 6 in 1

$[Ba^{2+}] = 246.1\,[SO_4{}^{2-}] = 1.1 * 10^{-10}$



Write mass-balance expressions for the system formed when a 0.010 M NH_3 solution is saturated with AgBr.

Here, equations for the pertinent equilibria in the solution are

$$AgBr(s) \rightleftharpoons Ag^+ + Br^-$$
$$Ag^+ + NH_3 \rightarrow AgNH_3^+$$
$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+$$
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Because AgBr is the only source of Br^-, Ag^+, $Ag(NH_3)^+$, and $Ag(NH_3)_2^+$ and because silver and bromide ions are present in a 1:1 ratio in that compound, it follows that one mass-balance equation is

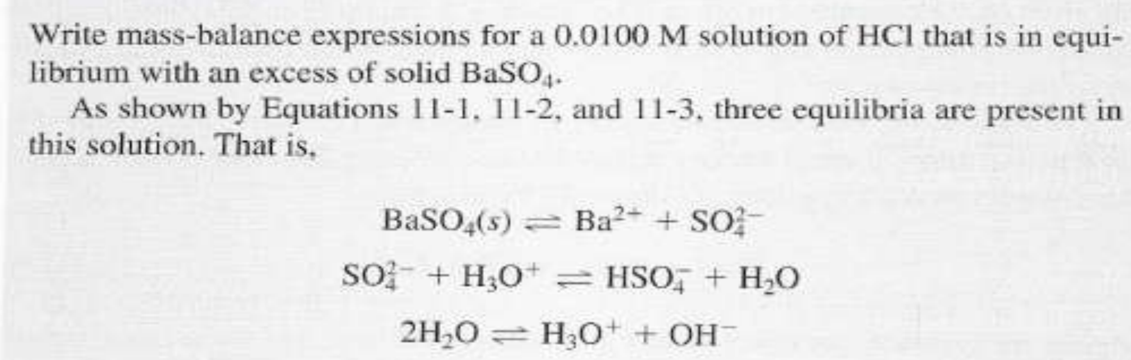
$$[Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] = [Br^-]$$

where the bracketed terms are molar species concentrations. Also, we know that the only source of ammonia-containing species is the 0.010 M NH_3. Therefore,

$$c_{NH_3} = [NH_3] + [NH_4^+] + [Ag(NH_3)^+] + 2\,[Ag(NH_3)_2^+] = 0.010$$

From the last two equilibria, we see that one hydroxide ion is formed for each NH_4^+ and each hydronium ion. Therefore,

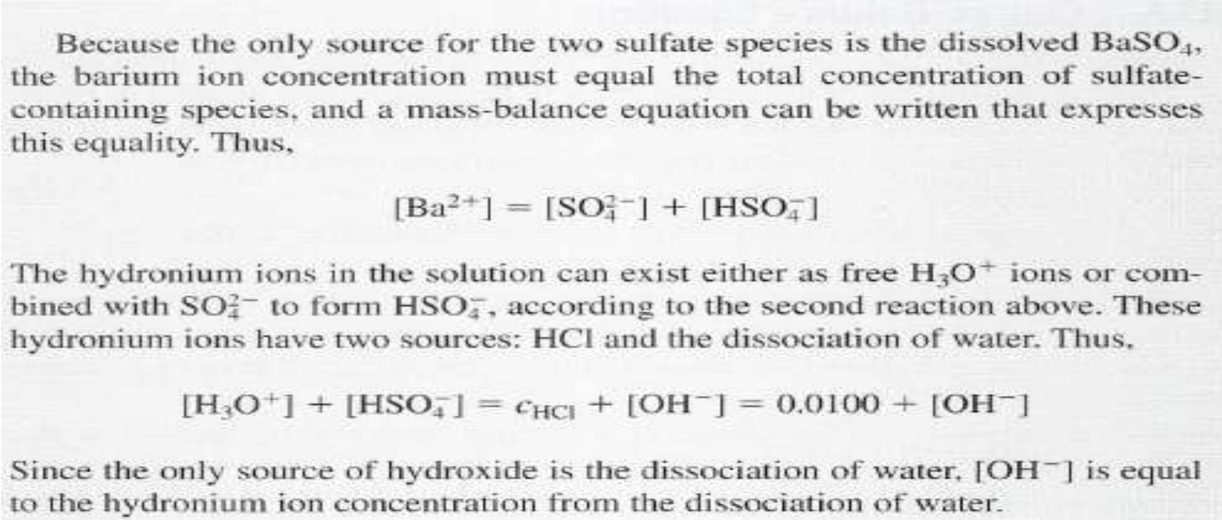
$$[OH^-] = [NH_4^+] + [H_3O^+]$$



Write mass-balance expressions for a 0.0100 M solution of HCl that is in equilibrium with an excess of solid $BaSO_4$.

As shown by Equations 11-1, 11-2, and 11-3, three equilibria are present in this solution. That is,

$$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$$
$$SO_4^{2-} + H_3O^+ \rightleftharpoons HSO_4^- + H_2O$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$



Because the only source for the two sulfate species is the dissolved $BaSO_4$, the barium ion concentration must equal the total concentration of sulfate-containing species, and a mass-balance equation can be written that expresses this equality. Thus,

$$[Ba^{2+}] = [SO_4^{2-}] + [HSO_4^-]$$

The hydronium ions in the solution can exist either as free H_3O^+ ions or combined with SO_4^{2-} to form HSO_4^-, according to the second reaction above. These hydronium ions have two sources: HCl and the dissociation of water. Thus,

$$[H_3O^+] + [HSO_4^-] = c_{HCl} + [OH^-] = 0.0100 + [OH^-]$$

Since the only source of hydroxide is the dissociation of water, $[OH^-]$ is equal to the hydronium ion concentration from the dissociation of water.

Charge-Balance Equation:

Electrolyte solutions are electrically neutral, even though they may contain millions of charged ions. Solutions are neutral because the molar concentration of positive charge in an electrolyte solution always equals the molar concentration of negative charge. That is, for any solution containing electrolytes, we may write:

no. mol/L positive charge = no. mol/L negative charge

Now, consider how we would write a charge-balance equation for a 0.100 M solution of sodium chloride. Positive charges in this solution are supplied by Na^+ and H_3O^+ (from the dissociation of water). Negative charges come from Cl^- and OH^-. The morality of positive and negative charges are:

mol/L positive charge = $[Na^+] + [H_3O^+] = 0.100 + 1 \text{ x } 10^{-7}$

mol/L negative charge = $[Cl^-] + [OH^-] = 0.100 + 1 \text{ x } 10^{-7}$

We write the charge-balance equation by equating the concentrations of positive and negative charges. That is,

$$[Na^+] + [H_3O^+] = [Cl^-] + [OH^-] = 0.100 + 1 \times 10^{-7}$$

Now consider a solution that has an analytical concentration of magnesium chloride of 0.100 M. Here, the molarities of positive and negative charge are given by:

mol/L positive charge = 2 $[Mg^{2+}] + [H_3O^+] = 2 \text{ X } 0.100 + 1 \text{ X } 10^{-7}$

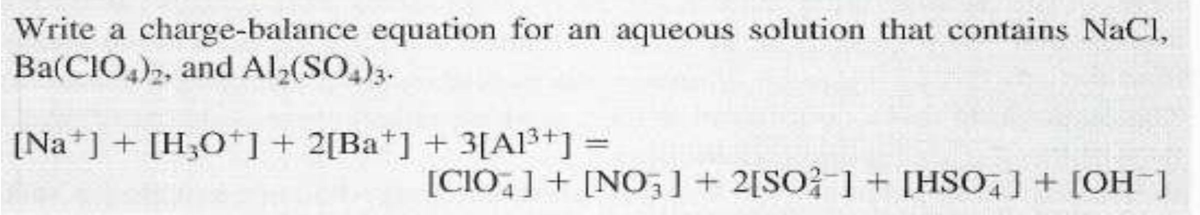
mol/L negative charge = $[Cl^-] + [OH^-] = 2 \text{ X } 0.100 + 1 \text{ X } 10^{-7}$

In the first equation, the molar concentration of magnesium ion is multiplied by two (2 x 0.100) because 1 mol of that ion contributes 2 mol of positive charge to the solution. In the second equation, the molar chloride ion concentration is twice that of the magnesium chloride concentration, or 2 x 0.100.

$$2[Mg^{2+}] + [H_3O^+] = [Cl^-] + [OH^-] = 0.200 + 1 \times 10^{-7}$$

For a neutral solution, $[H_3O^+]$ and $[OH^-]$ are very small and equal, so that we can ordinarily simplify the charge-balance equation to:

$2 [Mg^{2+}] = [Cl^-] = 0.200$ M



Write a charge-balance equation for an aqueous solution that contains NaCl, $Ba(ClO_4)_2$, and $Al_2(SO_4)_3$.

$$[Na^+] + [H_3O^+] + 2[Ba^+] + 3[Al^{3+}] = [ClO_4^-] + [NO_3^-] + 2[SO_4^{2-}] + [HSO_4^-] + [OH^-]$$

Steps for Solving Problems Involving Several Equilibria:

Step 1. Write a set of balanced chemical equations for all pertinent equilibria.

Step 2. State the quantity being sought in terms of equilibrium concentrations.

Step 3. Write equilibrium-constant expressions for all equilibria developed in Step 1, and find numerical values for the constants in tables of equilibrium constants.

Step 4. Write mass-balance expressions for the system.

Step 5. If possible, write a charge - balance expression of the system.

Step 6. Count the number of unknown concentrations in the equations developed in Steps 3, 4, and 5, and compare this number with the number of independent equations. Step 6 is critical because it shows whether an exact solution to the problem is possible.

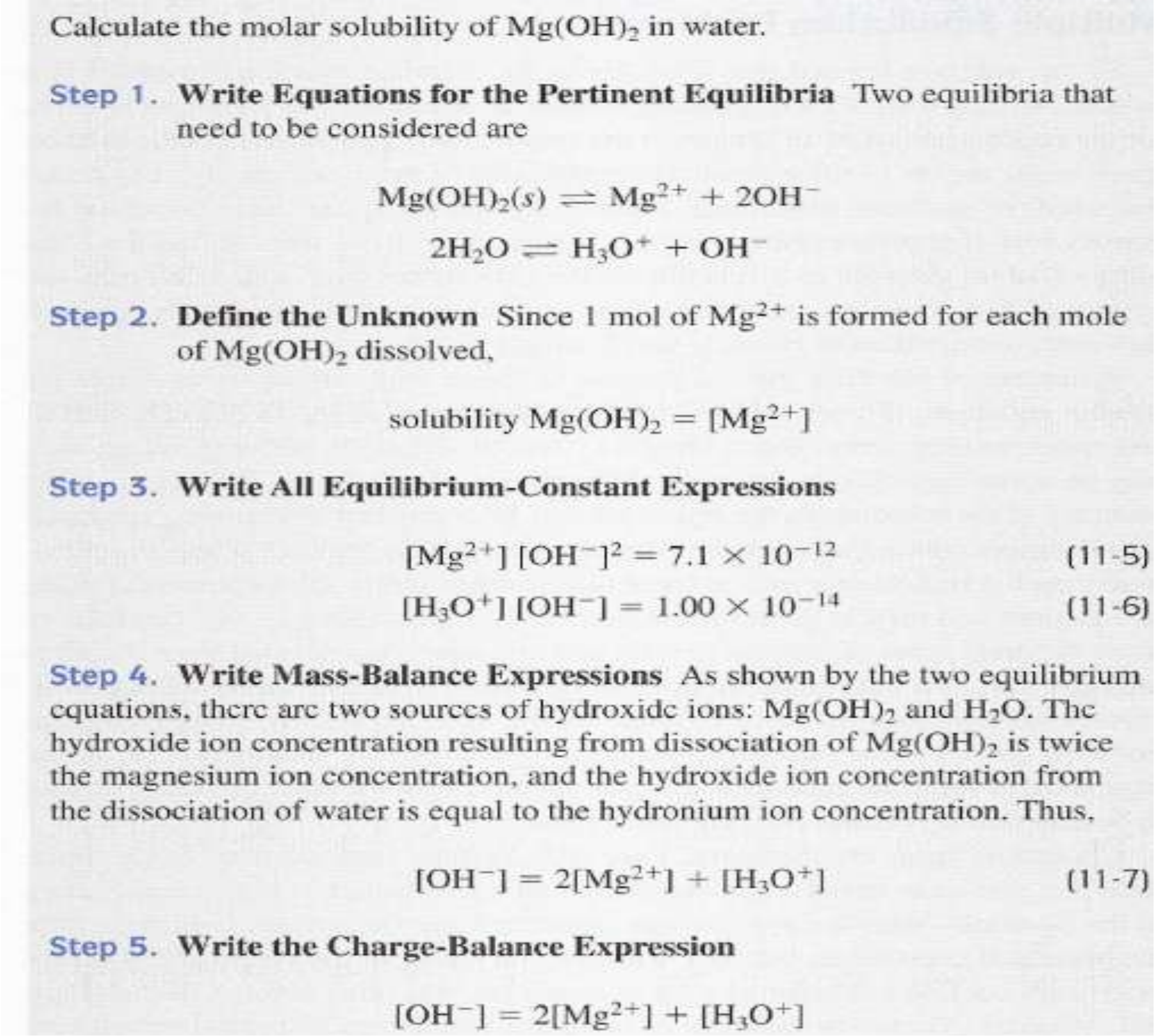
If the number of unknowns is identical to the number of equations, the problem has been reduced to one of *algebra* alone. That is, answers can be obtained with sufficient perseverance. On the other hand, if there are not enough equations even after approximations are made, the problem should be abandoned. If a sufficient number of equations have been developed, proceed to either step 7a or step 7b.

Step 7a. Make suitable approximations to reduce the number of unknowns equilibrium concentrations and thus the number of equations needed to provide an answer, as defined in step 2, precede to steps 8 and 9.

Step 7b. Solve the simultaneous equations exactly for the concentrations required by Step 2 by means of a computer program.

Step 8. Solve manually the simplified algebraic equations to give provisional concentrations for the species in the solution.

Step 9. Check the validity of the approximations.



Calculate the molar solubility of $Mg(OH)_2$ in water.

Step 1. **Write Equations for the Pertinent Equilibria** Two equilibria that need to be considered are

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

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

Step 2. **Define the Unknown** Since 1 mol of Mg^{2+} is formed for each mole of $Mg(OH)_2$ dissolved,

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

Step 3. **Write All Equilibrium-Constant Expressions**

$$[Mg^{2+}][OH^-]^2 = 7.1 \times 10^{-12} \qquad (11\text{-}5)$$

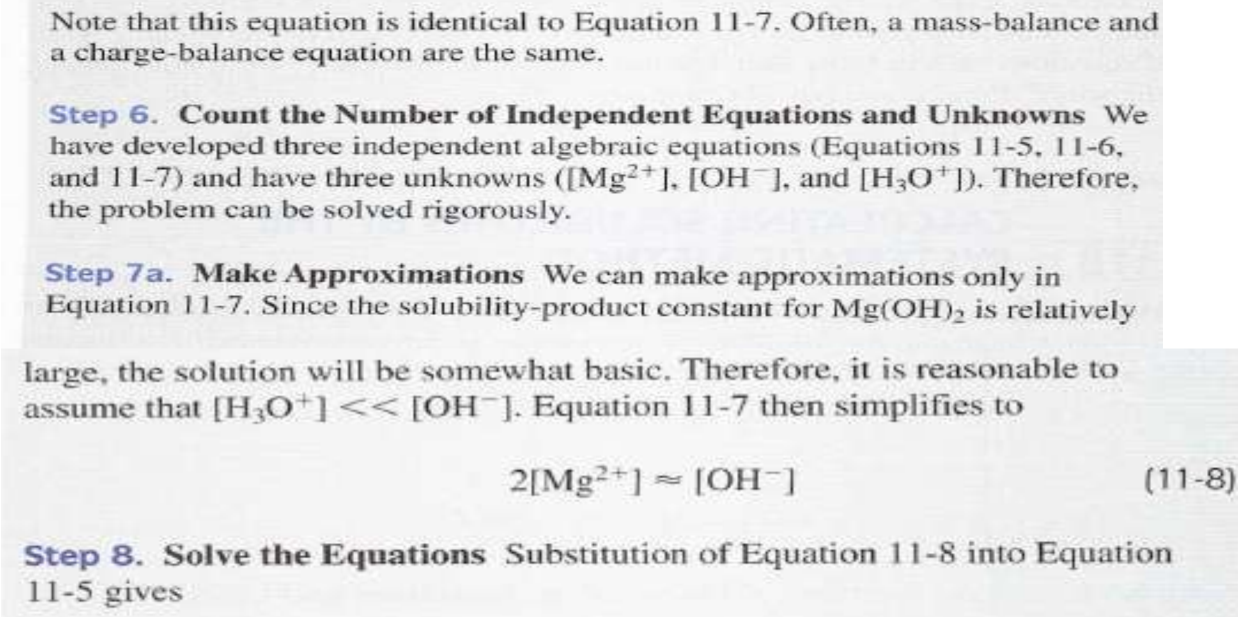
$$[H_3O^+][OH^-] = 1.00 \times 10^{-14} \qquad (11\text{-}6)$$

Step 4. **Write Mass-Balance Expressions** As shown by the two equilibrium equations, there are two sources of hydroxide ions: $Mg(OH)_2$ and H_2O. The hydroxide ion concentration resulting from dissociation of $Mg(OH)_2$ is twice the magnesium ion concentration, and the hydroxide ion concentration from the dissociation of water is equal to the hydronium ion concentration. Thus,

$$[OH^-] = 2[Mg^{2+}] + [H_3O^+] \qquad (11\text{-}7)$$

Step 5. **Write the Charge-Balance Expression**

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



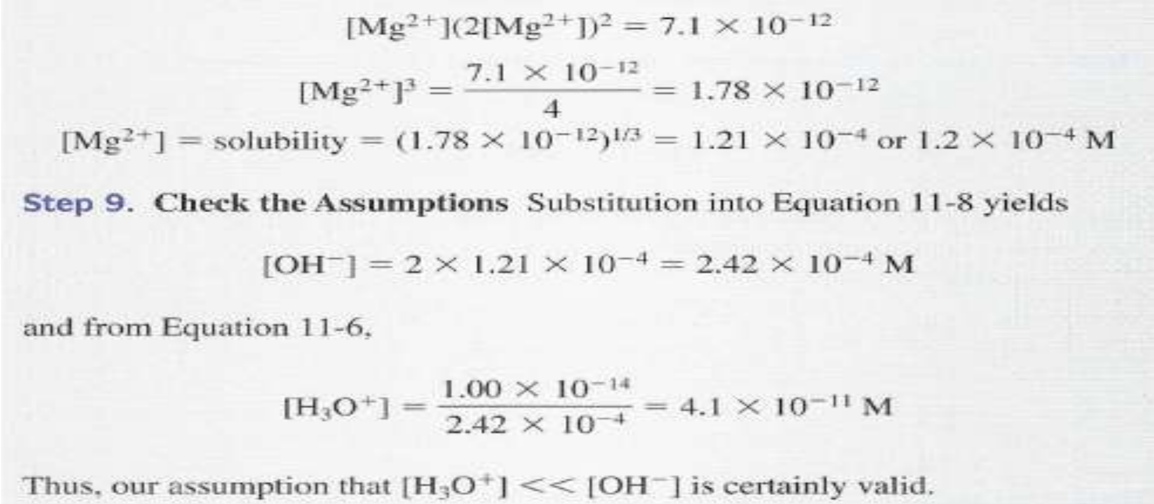
Note that this equation is identical to Equation 11-7. Often, a mass-balance and a charge-balance equation are the same.

Step 6. Count the Number of Independent Equations and Unknowns We have developed three independent algebraic equations (Equations 11-5, 11-6, and 11-7) and have three unknowns ($[Mg^{2+}]$, $[OH^-]$, and $[H_3O^+]$). Therefore, the problem can be solved rigorously.

Step 7a. Make Approximations We can make approximations only in Equation 11-7. Since the solubility-product constant for $Mg(OH)_2$ is relatively large, the solution will be somewhat basic. Therefore, it is reasonable to assume that $[H_3O^+] << [OH^-]$. Equation 11-7 then simplifies to

$$2[Mg^{2+}] \approx [OH^-] \tag{11-8}$$

Step 8. Solve the Equations Substitution of Equation 11-8 into Equation 11-5 gives



$$[Mg^{2+}](2[Mg^{2+}])^2 = 7.1 \times 10^{-12}$$

$$[Mg^{2+}]^3 = \frac{7.1 \times 10^{-12}}{4} = 1.78 \times 10^{-12}$$

$$[Mg^{2+}] = \text{solubility} = (1.78 \times 10^{-12})^{1/3} = 1.21 \times 10^{-4} \text{ or } 1.2 \times 10^{-4}\text{ M}$$

Step 9. Check the Assumptions Substitution into Equation 11-8 yields

$$[OH^-] = 2 \times 1.21 \times 10^{-4} = 2.42 \times 10^{-4}\text{ M}$$

and from Equation 11-6,

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{2.42 \times 10^{-4}} = 4.1 \times 10^{-11}\text{ M}$$

Thus, our assumption that $[H_3O^+] << [OH^-]$ is certainly valid.

Example: Write mass – balance expression for a solution that is :

♦ 0.2 M of H_3AsO_4

$0.2 = [H_3AsO_4] + [H_3AsO^-{}_4] + [H_3AsO^{2-}{}_4] + [AsO^{3-}{}_4]$

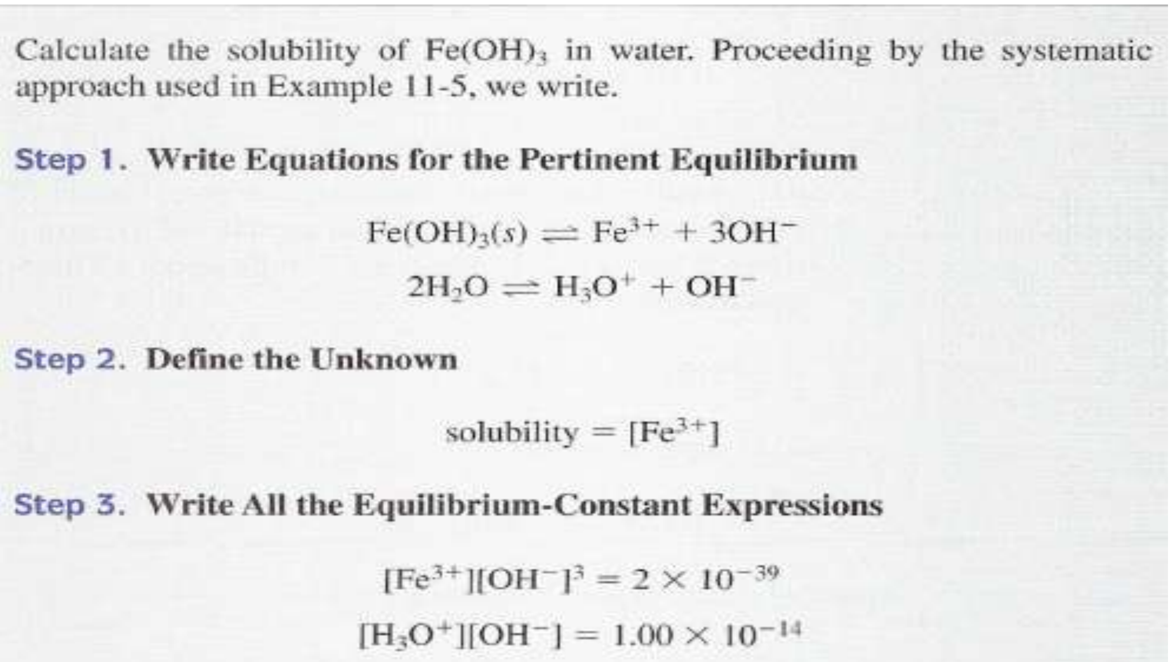
♦ 0.05 M of HClO and 0.1 of NaClO

$0.05 + 0.1 = [ClO^-] + [HClO]$

0.1 M of NaOH saturated with Zn $(OH)_4$

$Zn(OH)_4 + 2OH^- \Leftrightarrow Zn(OH)_4{}^{2-}$

$0.1 = [Na^+] = [OH^-] + 2[Zn(OH)_4{}^{2-}]$



Calculate the solubility of $Fe(OH)_3$ in water. Proceeding by the systematic approach used in Example 11-5, we write.

Step 1. Write Equations for the Pertinent Equilibrium

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

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

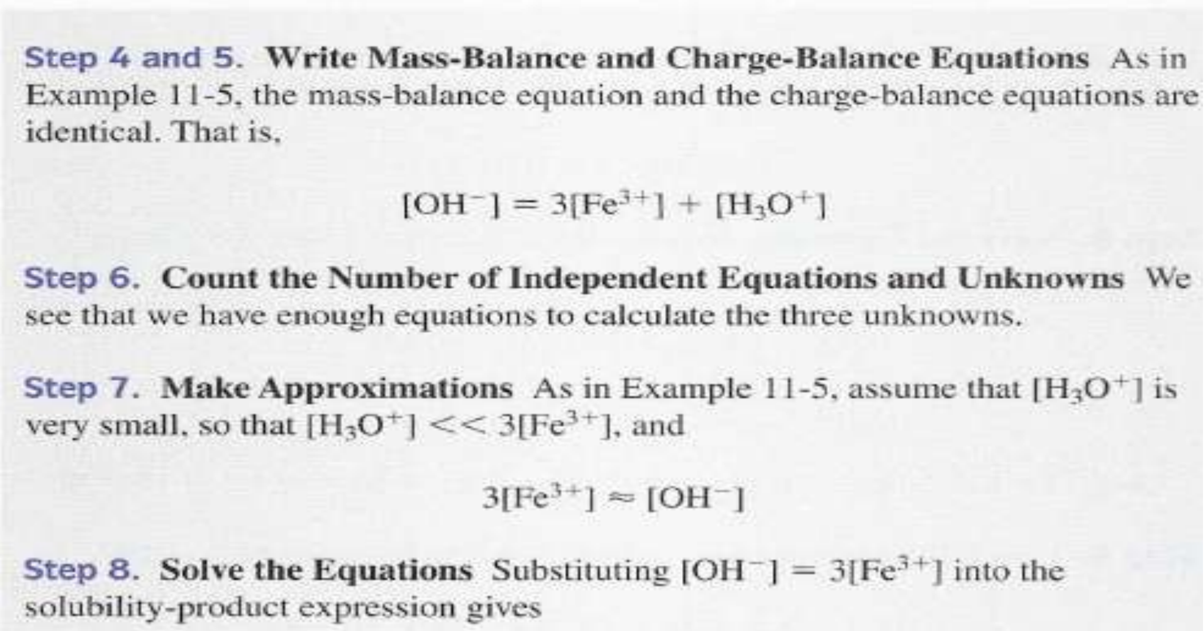
Step 2. Define the Unknown

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

Step 3. Write All the Equilibrium-Constant Expressions

$$[Fe^{3+}][OH^-]^3 = 2 \times 10^{-39}$$

$$[H_3O^+][OH^-] = 1.00 \times 10^{-14}$$



Step 4 and 5. Write Mass-Balance and Charge-Balance Equations As in Example 11-5, the mass-balance equation and the charge-balance equations are identical. That is,

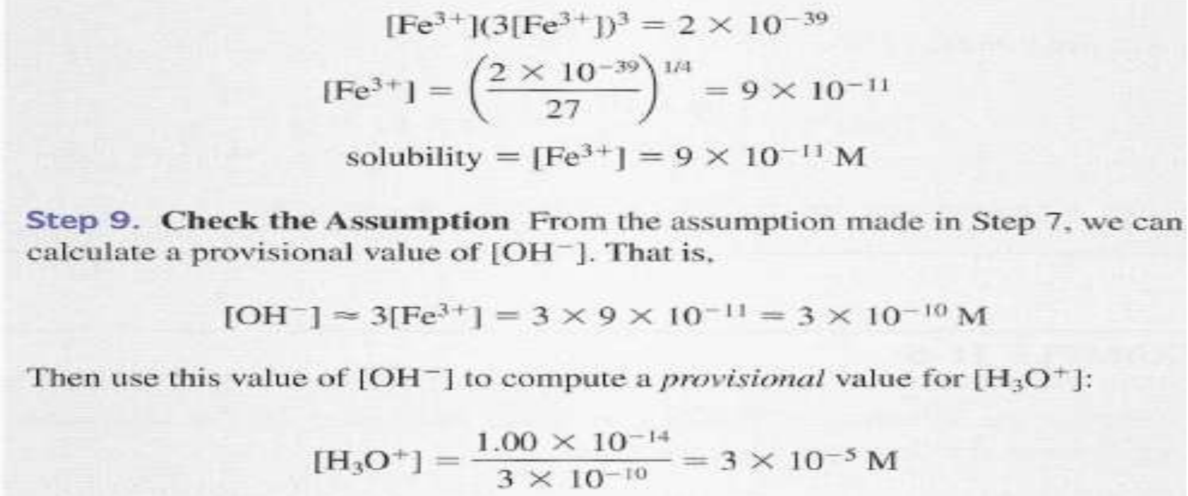
$$[OH^-] = 3[Fe^{3+}] + [H_3O^+]$$

Step 6. Count the Number of Independent Equations and Unknowns We see that we have enough equations to calculate the three unknowns.

Step 7. Make Approximations As in Example 11-5, assume that $[H_3O^+]$ is very small, so that $[H_3O^+] << 3[Fe^{3+}]$, and

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

Step 8. Solve the Equations Substituting $[OH^-] = 3[Fe^{3+}]$ into the solubility-product expression gives



$$[Fe^{3+}](3[Fe^{3+}])^3 = 2 \times 10^{-39}$$

$$[Fe^{3+}] = \left(\frac{2 \times 10^{-39}}{27}\right)^{1/4} = 9 \times 10^{-11}$$

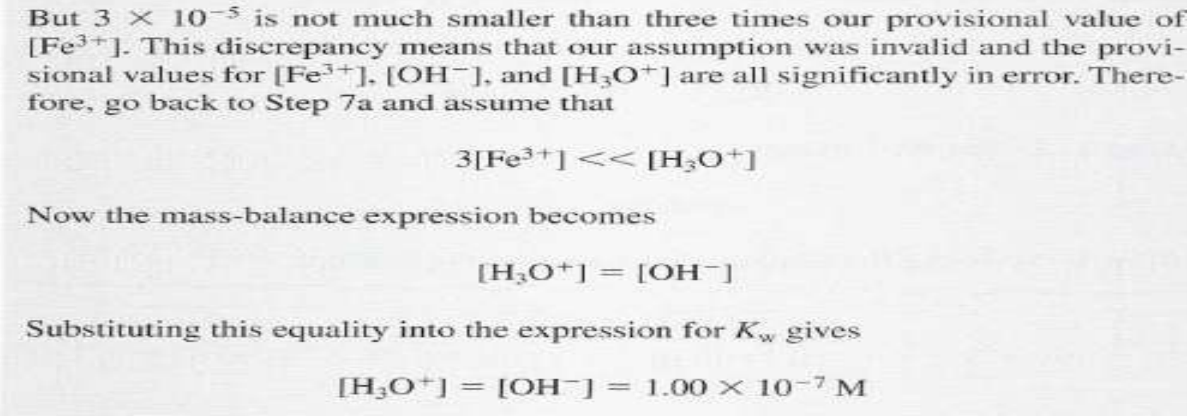
$$\text{solubility} = [Fe^{3+}] = 9 \times 10^{-11}\ M$$

Step 9. Check the Assumption From the assumption made in Step 7, we can calculate a provisional value of $[OH^-]$. That is,

$$[OH^-] \approx 3[Fe^{3+}] = 3 \times 9 \times 10^{-11} = 3 \times 10^{-10}\ M$$

Then use this value of $[OH^-]$ to compute a *provisional* value for $[H_3O^+]$:

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{3 \times 10^{-10}} = 3 \times 10^{-5}\ M$$



But 3×10^{-5} is not much smaller than three times our provisional value of $[Fe^{3+}]$. This discrepancy means that our assumption was invalid and the provisional values for $[Fe^{3+}]$, $[OH^-]$, and $[H_3O^+]$ are all significantly in error. Therefore, go back to Step 7a and assume that

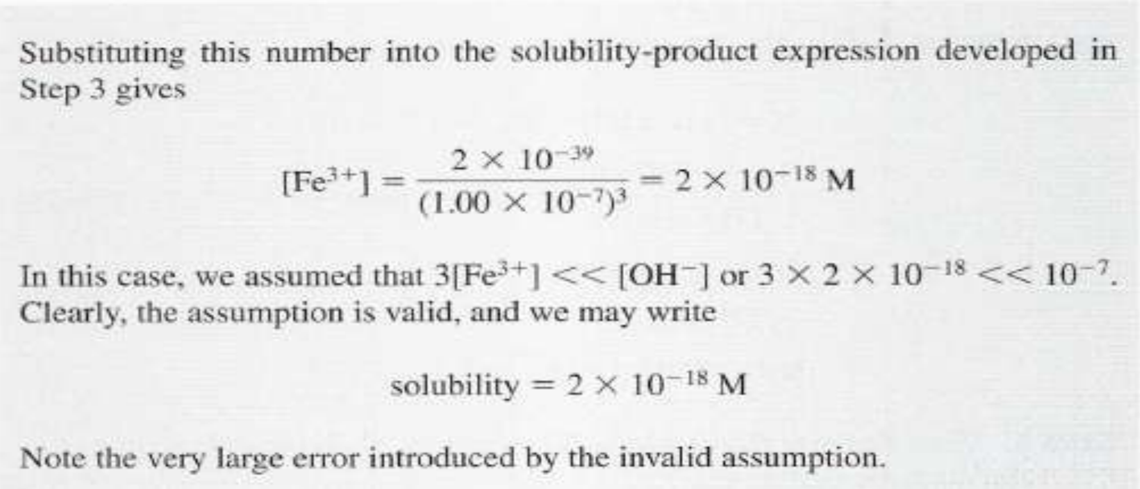
$$3[Fe^{3+}] << [H_3O^+]$$

Now the mass-balance expression becomes

$$[H_3O^+] = [OH^-]$$

Substituting this equality into the expression for K_w gives

$$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}\ M$$



Substituting this number into the solubility-product expression developed in Step 3 gives

$$[Fe^{3+}] = \frac{2 \times 10^{-39}}{(1.00 \times 10^{-7})^3} = 2 \times 10^{-18}\ M$$

In this case, we assumed that $3[Fe^{3+}] << [OH^-]$ or $3 \times 2 \times 10^{-18} << 10^{-7}$. Clearly, the assumption is valid, and we may write

$$\text{solubility} = 2 \times 10^{-18}\ M$$

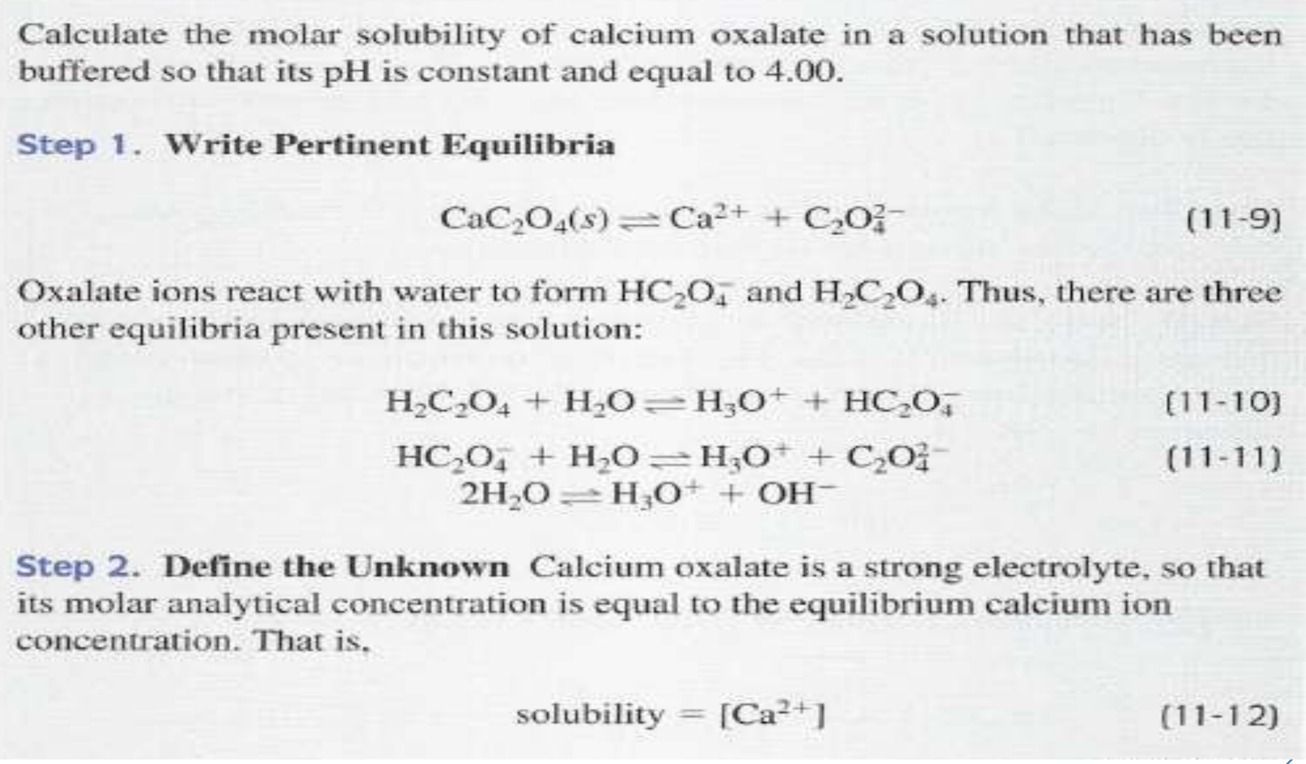
Note the very large error introduced by the invalid assumption.

The Effect of pH on Solubility:

The solubility of precipitates containing an anion with basic properties, a cation with acidic properties, or both will depend on the pH.

Solubility Calculations when the pH is Constant:

Analytical precipitations are usually performed in buffered solutions in which the pH is fixed at some predetermined and known value.



Calculate the molar solubility of calcium oxalate in a solution that has been buffered so that its pH is constant and equal to 4.00.

Step 1. Write Pertinent Equilibria

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+} + C_2O_4^{2-} \qquad (11\text{-}9)$$

Oxalate ions react with water to form $HC_2O_4^-$ and $H_2C_2O_4$. Thus, there are three other equilibria present in this solution:

$$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^- \qquad (11\text{-}10)$$

$$HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-} \qquad (11\text{-}11)$$

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

Step 2. Define the Unknown Calcium oxalate is a strong electrolyte, so that its molar analytical concentration is equal to the equilibrium calcium ion concentration. That is,

$$\text{solubility} = [Ca^{2+}] \qquad (11\text{-}12)$$

Step 3. Write All the Equilibrium-Constant Expressions

$$[Ca^{2+}][C_2O_4^{2-}] = K_{sp} = 1.7 \times 10^{-9} \qquad (11\text{-}13)$$

$$\frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} = K_1 = 5.60 \times 10^{-2} \qquad (11\text{-}14)$$

$$\frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = K_2 = 5.42 \times 10^{-5} \qquad (11\text{-}15)$$

$$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

Step 4. Mass-Balance Expressions Because CaC_2O_4 is the only source of Ca^{2+} and the three oxalate species.

$$[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4] = \text{solubility} \qquad (11\text{-}16)$$

Moreover, the problem states that the pH is 4.00. Thus,

$$[H_3O^+] = 1.00 \times 10^{-4} \text{ and } [OH^-] = K_w/[H_3O^+] = 1.00 \times 10^{-10}$$

Step 5. Write Charge-Balance Expression A buffer is required to maintain the pH at 4.00. The buffer most likely consists of some weak acid HA and its conjugate base, A^-. The nature of the three species and their concentrations have not been specified, however, so we do not have enough information to write a charge-balance equation.

Step 6. Count the Number of Independent Equations and Unknowns We have four unknowns ($[Ca^{2+}]$, $[C_2O_4^{2-}]$, $[HC_2O_4^-]$, and $[H_2C_2O_4]$) as well as four independent algebraic relationships (Equations 11-13, 11-14, 11-15, and 11-16). Therefore, an exact solution can be obtained, and the problem becomes one of algebra.

Step 7a. Make Approximations An exact solution is so readily obtained in this case that we will not bother with approximations.

Step 8. Solve the Equations A convenient way to solve the problem is to substitute Equations 11-14 and 11-15 into 11-16 in such a way as to develop a relationship between $[Ca^{2+}]$, $[C_2O_4^{2-}]$, and $[H_3O^+]$. Thus, we rearrange Equation 11-15 to give

$$[HC_2O_4^-] = \frac{[H_3O^+][C_2O_4^{2-}]}{K_2}$$

Substituting numerical values for $[H_3O^+]$ and K_2 gives

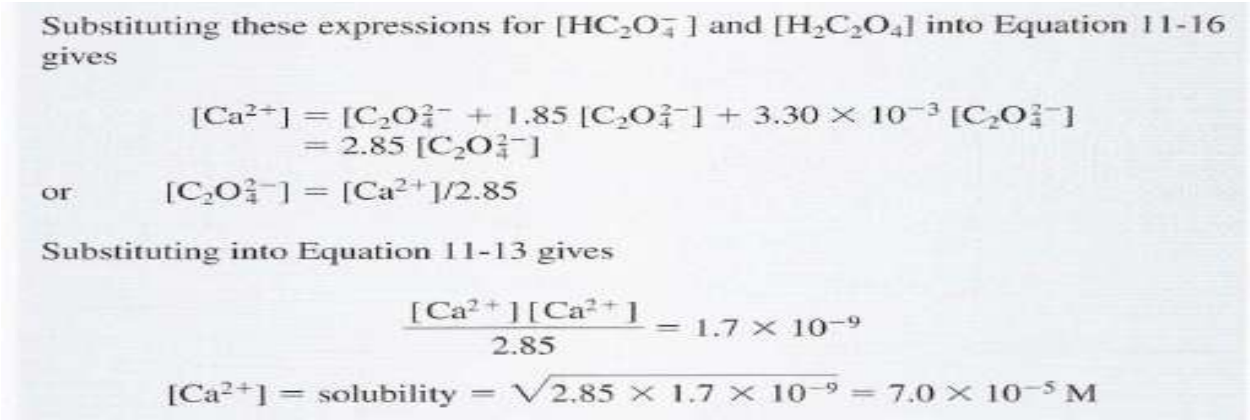
$$[HC_2O_4^-] = \frac{1.00 \times 10^{-4}[C_2O_4^{2-}]}{5.42 \times 10^{-5}} = 1.85\,[C_2O_4^{2-}]$$

Substituting this relationship into Equation 11-14 and rearranging gives

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

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

$$[H_2C_2O_4] = \frac{1.85 \times 10^{-4}[C_2O_4^{2-}]}{5.60 \times 10^{-2}} = 3.30 \times 10^{-3}\,[C_2O_4^{2-}]$$



Substituting these expressions for $[HC_2O_4^-]$ and $[H_2C_2O_4]$ into Equation 11-16 gives

$$[Ca^{2+}] = [C_2O_4^{2-}] + 1.85\,[C_2O_4^{2-}] + 3.30 \times 10^{-3}\,[C_2O_4^{2-}]$$
$$= 2.85\,[C_2O_4^{2-}]$$

or $$[C_2O_4^{2-}] = [Ca^{2+}]/2.85$$

Substituting into Equation 11-13 gives

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

$$[Ca^{2+}] = \text{solubility} = \sqrt{2.85 \times 1.7 \times 10^{-9}} = 7.0 \times 10^{-5}\text{ M}$$

Example: Calculate the molar solubility of $Ag_2C_2O_4$ in solution that has a fixed H_3O^+ concentration of $1 * 10^{-9}$ M $K_{sp} = 3.5 * 10^{-11}$, $K_1 = 5.6 * 10^{-2}$, $K_2 = 5.42 * 10^{-5}$.

Solution:

Step 1: $Ag_2C_2O_4 \Leftrightarrow 2Ag^+ + C_2O_4^{2-}$

$H_2C_2O_4 + H_2O \Leftrightarrow H_3O^+ + HC_2O_4^-$

$HC_2O_4^- + H_2O \Leftrightarrow H_3O^+ + C_2O_4^{2-}$

Step 2: S = solubility = $[Ag^+] / 2$

Step 3: $[Ag^+]^2\,[C_2O_4^{2-}] = K_{sp} = 3.5 * 10^{-11}$ ……………………………… (1)

$\frac{[H_3O^+][HC_2O4^-]}{[H_2C_2O_4]} = K_1 = 5.6 * 10^{-2}$ ……………………………… (2)

$= \frac{[H_3O^+][C_2O4^{-2}]}{[HC_2O4^-]} = K_2 = 5.42 * 10^{-5}$ ……………………………….. (3)

Step 4: $[Ag^+] = 2\,([C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4])$ …………………….. (4)

$= [H_3O^+] = 1 * 10^{-9}$ ……………………………………………….. (5)

Step 5: no charge balance equation (why)

Step 6: we have four unknowns: $[Ag^+]$, $[C_2O_4^{2-}]$, $[HC_2O_4^-]$ and $[H_2C_2O_4]$

Step 7: No approximations needed

Step 8: substituting 5 into 3 and rearranging

$[HC_2O_4^-] = \frac{1.0 * 10^{-9}\,[C_2O4^{-2}]}{5.42 * 10^{-5}} = 0.01845\,[C_2O_4^{2-}]$ ……………………….. (6)

Substituting this relationship (6 and 5) into 2 and rearranging

$[H_2C_2O_4] = \frac{1.0 * 10^{-9} * 0.01845\,[C_2O4^{-2}]}{5.60 * 10^{-5}} = 3.29 * 10^{-7}\,[C_2O_4^{2-}]$ ………… (7)

Substituting (6 and 7) in (4)

$[Ag^+] = 2\,[C_2O_4^{2-}]\ 2 * (0.01845\,[C_2O_4^{2-}]) + 2 * (3.29 * 10^{-7}\,[C_2O_4^{2-}])$

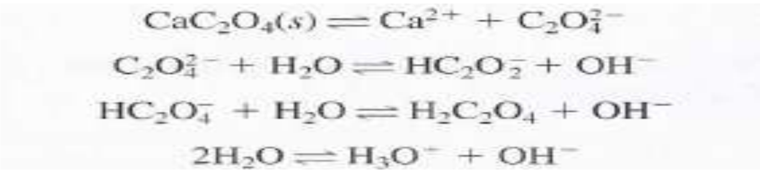
$[Ag^+] = 2.037\,[C_2O_4^{2-}]$

Substituting 8 in 1

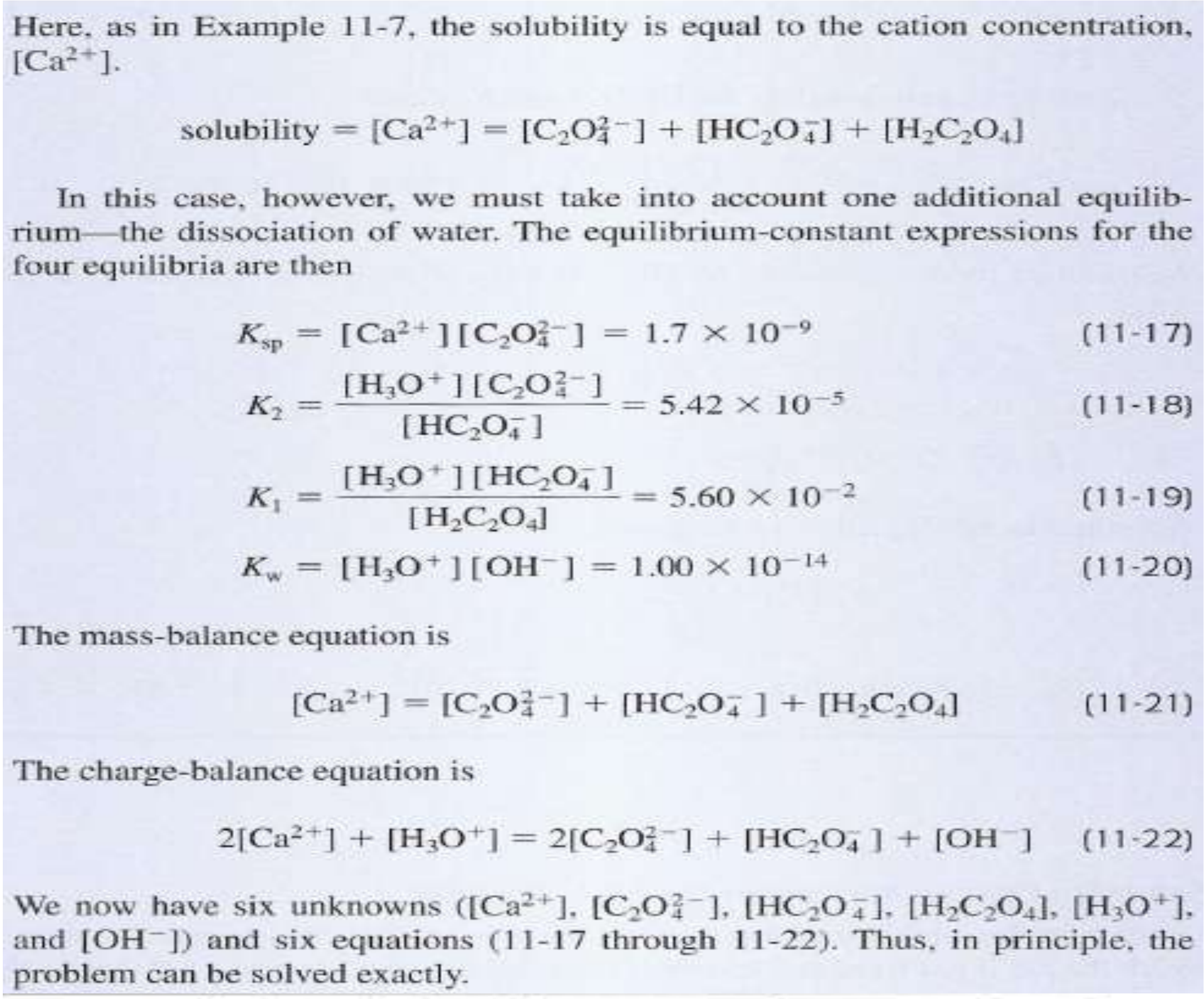
$S = 2.1 * 10^{-4}$

Solubility calculations when the pH is variable:

To determine the solubility of CaC_2O_4 in pure water, we must take into account the change in OH^- and H_3O^+ that accompanies the solution process. In this example, there are four equilibria to consider.



$$CaC_2O_4(s) \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$$
$$C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^- + OH^-$$
$$HC_2O_4^- + H_2O \rightleftharpoons H_2C_2O_4 + OH^-$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$



Here, as in Example 11-7, the solubility is equal to the cation concentration, $[Ca^{2+}]$.

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

In this case, however, we must take into account one additional equilibrium—the dissociation of water. The equilibrium-constant expressions for the four equilibria are then

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.7 \times 10^{-9} \qquad (11\text{-}17)$$

$$K_2 = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = 5.42 \times 10^{-5} \qquad (11\text{-}18)$$

$$K_1 = \frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} = 5.60 \times 10^{-2} \qquad (11\text{-}19)$$

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \qquad (11\text{-}20)$$

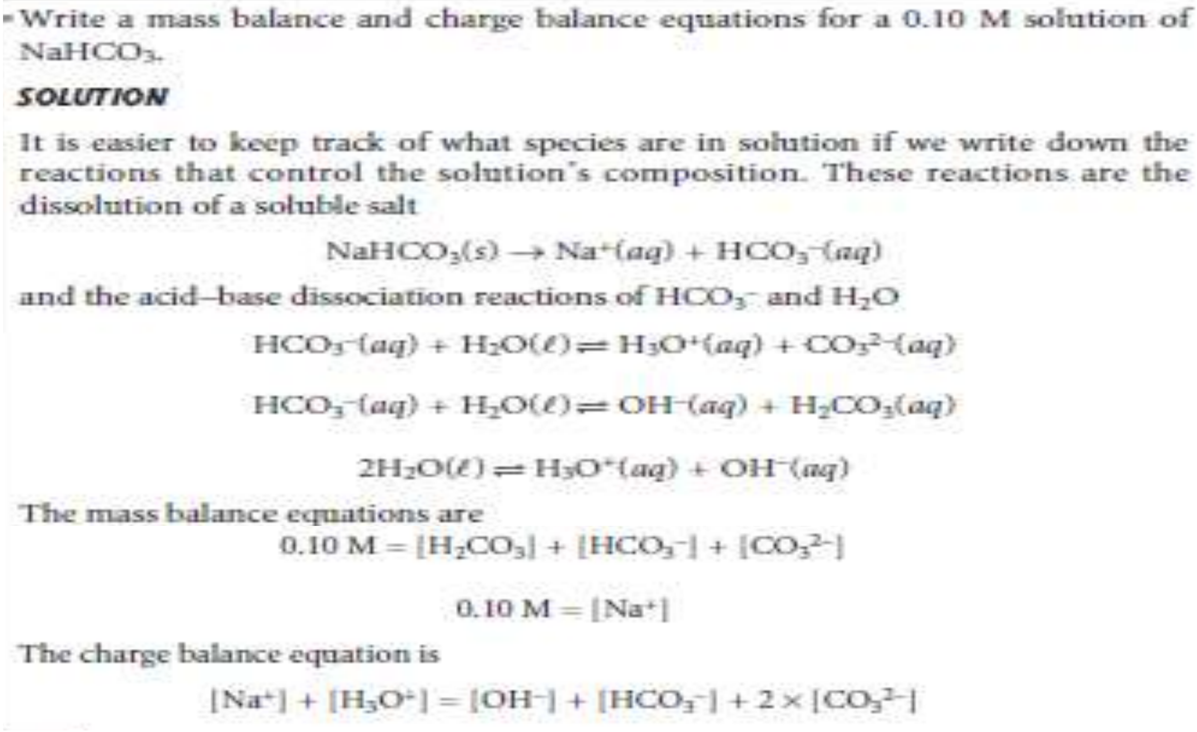
The mass-balance equation is

$$[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4] \qquad (11\text{-}21)$$

The charge-balance equation is

$$2[Ca^{2+}] + [H_3O^+] = 2[C_2O_4^{2-}] + [HC_2O_4^-] + [OH^-] \qquad (11\text{-}22)$$

We now have six unknowns ($[Ca^{2+}]$, $[C_2O_4^{2-}]$, $[HC_2O_4^-]$, $[H_2C_2O_4]$, $[H_3O^+]$, and $[OH^-]$) and six equations (11-17 through 11-22). Thus, in principle, the problem can be solved exactly.



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

SOLUTION

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

$$NaHCO_3(s) \rightarrow Na^+(aq) + HCO_3^-(aq)$$

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

$$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

$$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons OH^-(aq) + H_2CO_3(aq)$$

$$2H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The mass balance equations are

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

$$0.10\text{ M} = [Na^+]$$

The charge balance equation is

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

Calculate the solubility of $Pb(IO_3)_2$ in 1.0×10^{-4} M $Pb(NO_3)_2$.

SOLUTION

Letting x equal the change in the concentration of Pb^{2+}, the equilibrium concentrations are

$$[Pb^{2+}] = 1.0 \times 10^{-4} + x \qquad [IO_3^-] = 2x$$

and

$$(1.0 \times 10^{-4} + x)(2x)^2 = 2.5 \times 10^{-13}$$

We start by assuming that

$$[Pb^{2+}] = 1.0 \times 10^{-4} + x \approx 1.0 \times 10^{-4}\ \text{M}$$

and solve for x, obtaining a value of 2.50×10^{-5}. Substituting back gives the calculated concentration of Pb^{2+} at equilibrium as

$$[Pb^{2+}] = 1.0 \times 10^{-4} + 2.50 \times 10^{-5} = 1.25 \times 10^{-4}\ \text{M}$$

a value that differs by 25% from our approximation that the equilibrium concentration is 1.0×10^{-4} M. This error seems unreasonably large. Rather than shouting in frustration, we make a new assumption. Our first assumption that the concentration of Pb^{2+} is 1.0×10^{-4} M was too small. The calculated concentration of 1.25×10^{-4} M, therefore, is probably a little too large. Let us assume that

$$[Pb^{2+}] = 1.0 \times 10^{-4} + x \approx 1.2 \times 10^{-4}\ \text{M}$$

Substituting into the solubility product equation and solving for x gives us

$$x = 2.28 \times 10^{-5}$$

or a concentration of Pb^{2+} at equilibrium of

$$[Pb^{2+}] = 1.0 \times 10^{-4} + (2.28 \times 10^{-5}) = 1.23 \times 10^{-4}\ \text{M}$$

which differs from our assumed concentration of 1.2×10^{-4} M by 2.5%. This seems to be a reasonable error since the original concentration of Pb^{2+} is given to only two significant figures. Our final solution, to two significant figures, is

$$[Pb^{2+}] = 1.2 \times 10^{-4}\ \text{M} \qquad [IO_3^-] = 4.6 \times 10^{-5}\ \text{M}$$

and the solubility of $Pb(IO_3)_2$ is 2.3×10^{-5} mol/L. This iterative approach to solving an equation is known as the method of successive approximations.

Write the equation of mass balance for a 0.100 M solution of acetic acid.

Solution

The equilibria are

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

We know that the analytical concentration of acetic acid is equal to the sum of the equilibrium concentrations of all its species:

$$C_{\text{HOAc}} = [\text{HOAc}] + [\text{OAc}^-] = 0.100\ M$$

A second mass balance expression may be written for the equilibrium concentration of H^+, which is derived from both HOAc and H_2O. We obtain one H^+ for each OAc^- and one for each OH^-:

$$[H^+] = [OAc^-] + [OH^-]$$

Write a charge balance equation for a saturated solution of CdS.

Solution

The equilibria are

$$CdS \rightleftharpoons Cd^{2+} + S^{2-}$$
$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$$
$$HS^- + H_2O \rightleftharpoons H_2S + OH^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Again, the charge concentration for the singly charged species (H^+, OH^-, HS^-) will be equal to the concentrations of the species. But for Cd^{2+} and S^{2-}, the charge concentration will be twice their concentrations. We must again equate the positive and negative charge concentrations.

$$2[Cd^{2+}] + [H^+] = 2[S^{2-}] + [HS^-] + [OH^-]$$

Write a charge balance equation for Example 6.7.

Solution

$$[Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] + [NH_4^+] + [H^+] = [Cl^-] + [OH^-]$$

Since all are singly charged species, the charge concentrations are equal to the molar concentrations.

Titration curves in titrimetric methods:

As noted an end point is an observable physical change that occurs near the equivalence point of a titration. The two most widely used end points involve:

(1) Changes in **color** due to the reagent, the analyte, or an indicator.

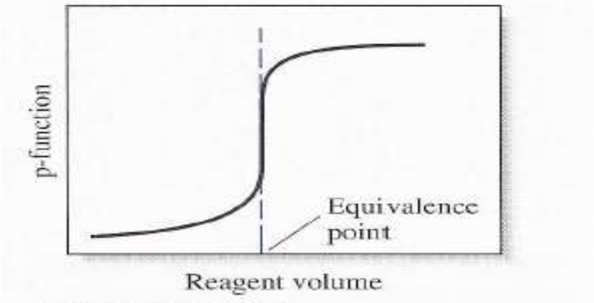
(2) A change in **potential** of an electrode that responds to the concentration of the reagent or the analyte.

Types of Titration Curves:

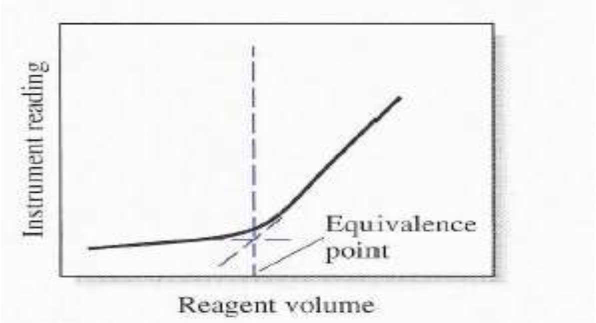
Two general types of titration curves (and thus two general types of end point) are encountered in titrimetric methods. In the first type, called a **sigmoidal curve**.

A sigmoidal curve, in which the **p-function** of analyte (or sometimes the reagent) is plotted as a function of reagent volume. In the second type of curve, called **a linear**

segment curve, in this type of curve, the vertical axis represents an instrument reading that is directly proportional to the concentration of the analyte or the reagent.



(a) Sigmoidal curve



(b) Linear-segment curve

Concentration Changes during Titrations:

The equivalence point in a titration is characterized by major changes in the relative concentrations of reagent and analyte. The table illustrates this phenomenon. The data in the second column of the table show the changes in the hydronium ion concentration as a 50 ml of aliquot of a 0.1 M solution HCl titrated with a 0.1 M solution of NaOH. The neutralization reaction is described by the equation:

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

Vol. of NaOH 0.1 M	$[H_3O^+]$ M	pH	pOH
0	1x 10^{-1}	1	13
40.91	1x 10^{-2}	2	12
49.01	1x 10^{-3}	3	11
49.90	1x 10^{-4}	4	10
49.99	1x 10^{-5}	5	9
49.999	1x 10^{-6}	6	8
50.0	1x 10^{-7}	7	7
50.001	1x 10^{-8}	8	6
50.01	1x 10^{-9}	9	5
50.1	1x 10^{-10}	10	4
51.01	1x 10^{-11}	11	3
61.11	1x 10^{-12}	12	2

Principles of Neutralization Titrations:

The standard solutions used in neutralization titrations are strong acids or strong bases because these substances react more completely with an analyte than do their weaker counterparts, and they therefore provide sharper end points.

Acid/Base Indicators:

An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form. For example, the behavior of an acid-type indicator, **Hln**, is described by the equilibrium:

$$\underset{\text{acid color}}{HIn} + H_2O \rightleftharpoons \underset{\text{base color}}{In^-} + H_3O^+$$

Here, internal structural changes accompany dissociation and cause the color change. The equilibrium for a base-type indicator, In, is:

$$\underset{\text{base color}}{\mathrm{In}} + \mathrm{H_2O} \rightleftharpoons \underset{\text{acid color}}{\mathrm{InH^+}} + \mathrm{OH^-}$$

The equilibrium-constant expression for the dissociation of an acid-type indicator takes the form:

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \qquad [\mathrm{H_3O^+}] = K_a\frac{[\mathrm{HIn}]}{[\mathrm{In^-}]}$$

The human eye is not very sensitive to color differences in a solution containing a mixture of **HIn** and **In**$^-$, particularly when the ratio **[Hln] / [ln$^-$]** is greater than about 10 or smaller than about 0.1.

As a result, we can write that the average indicator, Hln, exhibits its pure acid color when

$$\frac{[\mathrm{HIn}]}{[\mathrm{In^-}]} \geq \frac{10}{1} \quad \text{and its base color when} \quad \frac{[\mathrm{HIn}]}{[\mathrm{In^-}]} \leq \frac{1}{10}$$

If the two concentration ratios are substituted into the equation, the range of hydronium ion concentrations needed to change the indicator color can be evaluated. So, for the full acid color:

$$[\mathrm{H_3O^+}] = 10K_a$$

With a little more algebra, we can derive a similar relationship for a basic-type indicator.

$$[\mathrm{H_3O^+}] = 0.1\,K_a$$

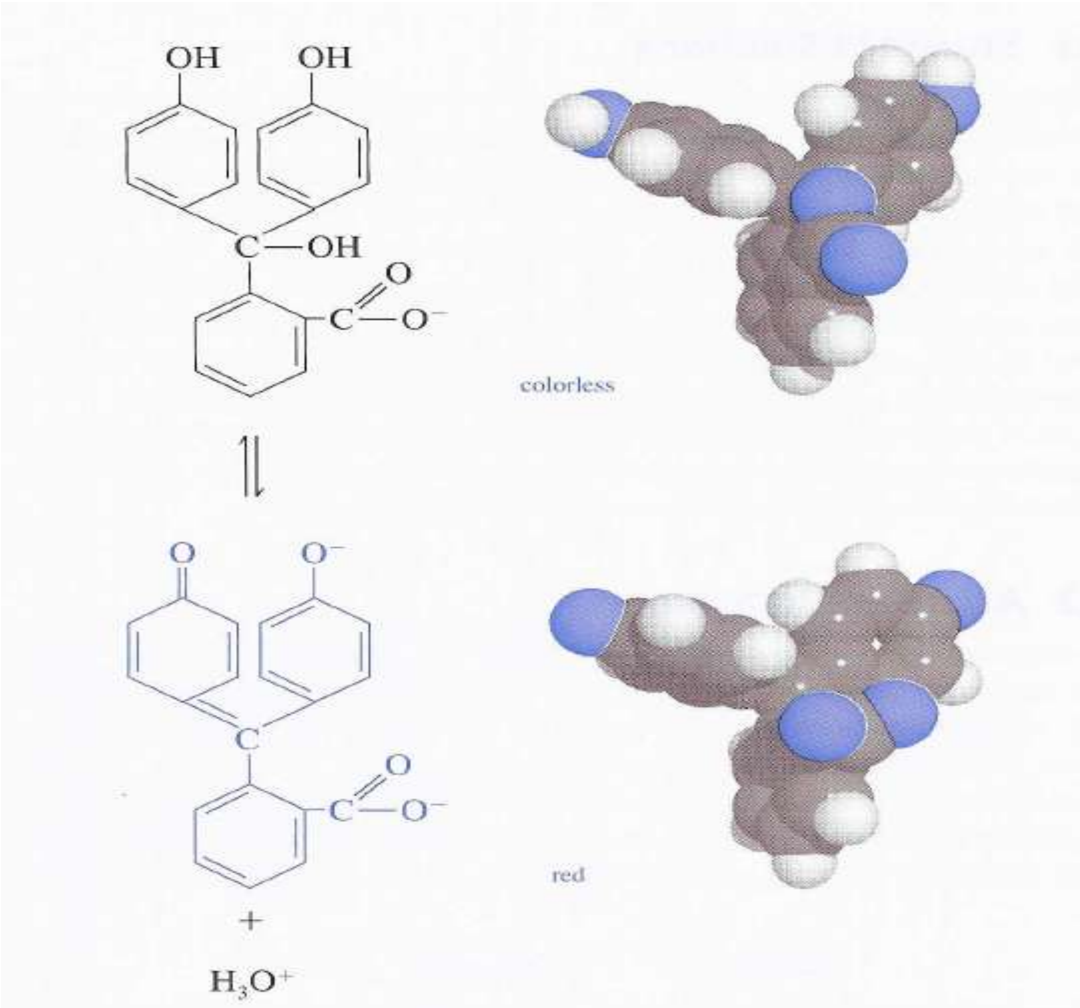
To obtain the indicator pH range, we take the negative logarithms of the two expressions:

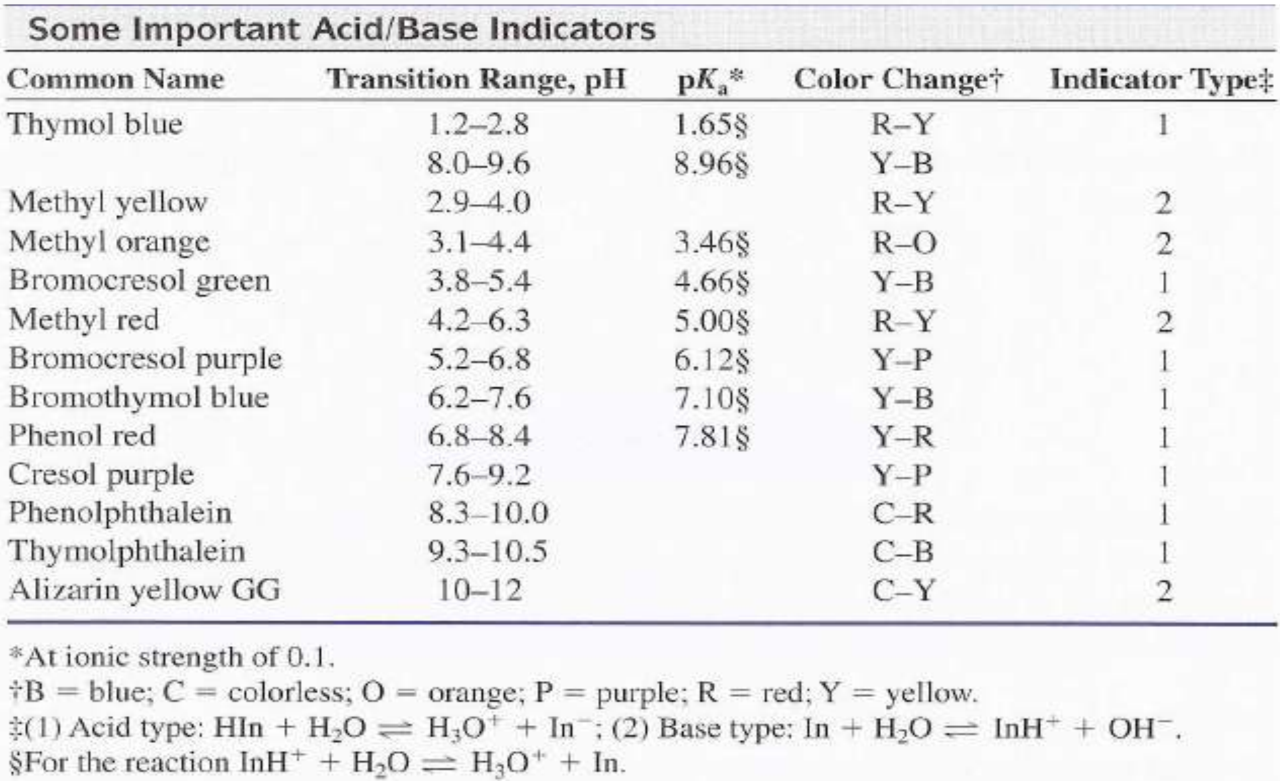
$$\mathrm{pH(acid\ color)} = -\log\,(10K_a) = \mathrm{p}K_a + 1$$

$$\mathrm{pH(basic\ color)} = -\log\,(0.1K_a) = \mathrm{p}K_a - 1$$

$$\text{indicator pH range} = \mathrm{p}K_a \pm 1$$

This expression shows that an indicator with an acid dissociation constant of 1x 10^{-5} (pKa = 5) typically shows a complete color change when the pH of the solution in which it is dissolved changes from 4 to 6.





Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK_a*	Color Change†	Indicator Type‡
Thymol blue	1.2–2.8	1.65§	R–Y	1
	8.0–9.6	8.96§	Y–B	
Methyl yellow	2.9–4.0		R–Y	2
Methyl orange	3.1–4.4	3.46§	R–O	2
Bromocresol green	3.8–5.4	4.66§	Y–B	1
Methyl red	4.2–6.3	5.00§	R–Y	2
Bromocresol purple	5.2–6.8	6.12§	Y–P	1
Bromothymol blue	6.2–7.6	7.10§	Y–B	1
Phenol red	6.8–8.4	7.81§	Y–R	1
Cresol purple	7.6–9.2		Y–P	1
Phenolphthalein	8.3–10.0		C–R	1
Thymolphthalein	9.3–10.5		C–B	1
Alizarin yellow GG	10–12		C–Y	2

*At ionic strength of 0.1.

†B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

‡(1) Acid type: $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$; (2) Base type: $In + H_2O \rightleftharpoons InH^+ + OH^-$.

§For the reaction $InH^+ + H_2O \rightleftharpoons H_3O^+ + In$.

طريقة حل المسائل الرياضية لتسحيحات الحامض / قاعدة وحساب الدالة الحامضية و اشتقاق منحني المعايرة

* - تسحيح حامض قوي مع قاعدة قوية او العكس

1 - Strong acid with strong Base or strong base with strong acid:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

1 - **قبل الأضافة initial point**

يحسب تركيز H^+ من خلال الخطوة التالية :

بما أن الحامض من الحوامض القوية والتي تتأين بشكل كامل لذلك فأن تركيز H^+ هو نفسه تركيز الحامض القوي المعطى في السؤال وذلك قبل الأضافة .

$\equiv pH = -Log\,[H^+]$ $[H^+] = C_{HA}$ تركيز الحامض الأصلي

ومنه نحسب الدالة الحامضية .

ملاحظة : في تسحيح قاعدة قوية مع حامض قوي نحسب $[OH^-]$ من تركيز القاعدة الأصلي قبل الأضافة

$\equiv pOH = -Log\,[OH^-]$ $[OH^-] = C_A^-$ تركيز القاعدة الأصلي

ومنه نحسب الدالة pOH ثم نحسب pH بعد ذلك .

2 - **بعد الأضافة قبل نقطة التكافؤ after addition before equivalent point**

نحسب تركيز $[H^+]$ للحامض عند كل أضافة

$$[H^+] = \frac{[M*V]_{org.\,acid} - [M*V]_{add.\,base}}{V_{total}}$$

ملاحظة : org هو original ومعناه الأصلي و .add تعني المضاف.

ثم نحسب الدالة الحامضية .

في حالة القاعدة القوية نحسب $[OH^-]$

$$[OH^-] = \frac{[M*V]_{org.\,base} - [M*V]_{add.\,acid}}{V_{total}}$$

ومنه نحسب الدالة pOH ثم نحسب pH بعد ذلك .

3 - **عند نقطة التكافؤ at equivalent point**

$$[H^+] = [OH^-] = \sqrt{1 * 10^{-14}}$$

$$pH = pOH = 7$$

4 - **بعد نقطة التكافؤ after equivalent point**

يتم أولا حساب تركيز $[OH^-]$

$$[OH^-] = \frac{[M*V]_{add.base} - [M*V]_{org.acid}}{V_{total}}$$

فنحسب pOH ثم نحسب pH

ملاحظة : في حالة تسحيح قاعدة قوية مع حامض قوي نحسب $[H^+]$ أولا ثم pH

$$[H^+] = \frac{[M*V]_{add.acid} - [M*V]_{org.base}}{V_{total}}$$

(**ملاحظة :** تحسب قيم pH لكل أضافة قبل نقطة التكافؤ وكذلك كل أضافة بعد نقطة التكافؤ) .

*** - تسحيح حامض ضعيف مع قاعدة قوية titration of weak acid with strong base**

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$[A^-] \equiv [CH_3COO^-]$$

1 - قبل الأضافة

يتم حساب تركيز $[H^+]$ من خلال قيمة ثابت التفكك وتركيز الحامض الأصلي

$[H^+] = \sqrt{K_a[HA]}$ ثم نحسب pH

أو نحسب pH مباشرة

$$pH = \frac{1}{2} pK_a - \frac{1}{2} Log [HA]$$

بعد الأضافة

يتم حساب تركيز $[H^+]$ من خلال حساب كمية (تركيز) الحامض المتبقية وتركيز الملح المتكون

$$pH = pK_a + Log \frac{[salt]}{[acid]} \qquad (1)$$

- يتم حساب [salt] من خلال عدد مولات (ملي مول) القاعدة المضافة

$$(M * V)_{add\ base} = no.\ of\ mole\ salt$$

ثم تقسم عدد مولات الملح على الحجم الكلي نحصل على تركيز [salt]

- يتم حساب [acid] من خلال المعادلة أدناه :

Remained acid = original acid – add base

R. mmole acid = $(\text{mmol. acid})_{\text{org. acid}} - (\text{mmol . base})_{\text{add. base}}$

$$[\text{Acid}] = \frac{\text{R.m mol .acid}}{V_{\text{total}}}$$

في هذه الحالة نستطيع حساب الدالة الحامضية بطريقتين:

الأولى : هو تطبيق مباشر للمعادلة (1)

$$pH = pK_a + \text{Log}\frac{[\text{ salt }]}{[\text{ acid }]}$$

الثانية : تطبيق معادلة ثابت التفكك كما في الأمثلة في المحاضرات.

وبنفس الطريقة يتم حساب pH لكل الأضافات قبل نقطة التكافؤ .

2 ـ عند نقطة التكافؤ : يتم حساب الدالة الحامضية من القانون ادناه.

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\text{Log C}$$

حيث أن C هو تركيز الملح و هو يساوي تركيز أيون الخلات عند نقطة التكافؤ (A^-)

$$[A^-] = [CH_3COO^-] = \frac{V_{eq.} * M}{V_{total}}$$

V_{eq} : حجم التكافؤ

3 ـ بعد نقطة التكافؤ : نحسب تركيز $[OH^-]$

$$[OH^-] = \frac{[\,M*V\,]_{\text{add . base}} - [\,M*V\,]_{\text{org . acid}}}{V_{\text{total}}}$$

ومنه نحسب pOH ثم نحسب pH

(**ملاحظة :** في النقطة الثالثة 3 بالأمكان حساب pH بتطبيق معادلة ثابت التفكك كما في الأمثلة في المحاضرات)

*** ـ تسحيح قاعدة ضعيفة مع حامض قوي**

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

$$NH_4OH \rightleftharpoons NH_4^{\ +} + OH^-$$

$$K_b = \frac{[NH_4^{+}][OH^-]}{[NH_4OH]} \qquad [NH_4^{+}] = [\text{Salt}]$$

1 ـ قبل الأضافة

يتم حساب [OH^-] من تركيز القاعدة الأصلي

$$[OH^-] = [NH_4^+] \qquad [OH^-] = \sqrt{K_b[Base]}$$

حيث يمكن حساب pOH ثم pH

[Base] هو تركيز القاعدة الأصلي الذي يعطى في السؤال.

او حساب pOH من المعادلة ادناه.

$$pOH = \frac{1}{2}pK_b - \frac{1}{2}\text{Log}\,[Base]$$

2 - بعد الاضافة قبل نقطة التكافؤ

يتم حساب [pOH] من القانون التالي

$$pOH = pK_b + \text{Log}\,\frac{[salt]}{[acid]}$$

- [Salt] يمكن حسابه من خلال عدد مولات (ملي مول) الحامض المضاف

$$(M*V)_{add.\ acid} = mmole\ [salt]$$

ومن ثم يقسم على الحجم الكلي نحصل على تركيز [salt]

- حساب [Base] بنفس طريقة حساب [acid] في المعايرة السابقة ولكن تعكس الحالة

$$R.\ mmol.\ Base = \frac{[M*V]_{org.\ base} - [M*V]_{add.\ acid}}{V_{total}}$$

ويتم حساب pOH بعد تعويض قيم [salt] و [Base]

وبنفس الطريقة يتم حساب pOH و pH لكل الأضافات الأولى .

3 - عند نقطة التكافؤ : تحسب الدالة الحامضية كما يلي

$$pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\text{Log}\,C$$

حيث C هو تركيز الملح وهو يساوي تركيز أيونات كلوريد الأمونيوم أو جذر الأمونيوم عند نقطة التكافؤ $[NH_4^+]$

وهي يساوي عدد ملي مولات الحامض المضاف مقسوما على الحجم الكلي .

$$[NH_4Cl] = [NH_4^+] = \frac{[M*V_{eq}]_{acid\ .add}}{V_{total}}$$

V_{eq} : حجم التكافؤ للحامض المضاف

4 - بعد نقطة التكافؤ

نحسب $[H^+]$

$$[H^+] = \frac{[\,M*V\,]_{add\ .acid} - [\,M*V\,]_{org\ .base}}{V_{total}}$$

ومنه نحسب pH

***- تسحيح حامض ضعيف مع قاعدة ضعيف**

1 - قبل الأضافة

$$pH = \frac{1}{2}\,pK_a - \frac{1}{2}\,Log\,[acid]$$

2 - بعد الأضافة

$$pH = pK_a + Log\,\frac{[\,salt\,]}{[\,acid\,]}$$

3 - نقطة التكافؤ

$$pH = \frac{1}{2}\,pK_w + \frac{1}{2}\,pK_a - \frac{1}{2}\,PK_b$$

4 - عند نقطة التكافؤ

$$pH = \frac{1}{2}\,pK_w - \frac{1}{2}\,pK_b - Log\,\frac{[\,salt\,]}{[\,base\,]}$$

***- معايرة قاعدة ضعيفة مع حامض ضعيف**

1 - قبل الأضافة

$$pOH = \frac{1}{2}\,pK_b - \frac{1}{2}\,Log\,[Base]$$

2 - بعد الأضافة

$$pOH = pK_b + Log\,\frac{[\,salt\,]}{[\,acid\,]}$$

3 - نقطة التكافؤ

$$pOH = \frac{1}{2}\,pK_w + \frac{1}{2}\,pK_a - \frac{1}{2}\,pK_b$$

4 - بعد نقطة التكافؤ

$$pOH = \frac{1}{2}\,PK_w - \frac{1}{2}\,pK_a - Log\frac{[\,salt\,]}{[\,acid\,]}$$

تميه الاملاح الضعيفة

1 - أملاح الأحماض الضعيفة

$$NaA \longrightarrow Na^+ + A$$

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

الملح يتأين كليا في الماء

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \text{Log } C$$

حيث أن C هو تركيز الملح

$$[A^-] \cong [C] \cong [NaA]$$

2 - أملاح القواعد الضعيفة

$$BX \longrightarrow B^+ + X^-$$

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

$$[B^+] \cong [C] \cong [BX]$$

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \text{Log } C$$

3 - أملاح ذات شقين ضعيفين

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

المحاليل المنظمة

1 - محلول منظم من حامض ضعيف و أحد أملاحه

$$pH = pK_a + \text{Log}\frac{[\,salt\,]}{[\,acid\,]}$$

2 - محلول منظم من قاعدة ضعيفة و أحد أملاحها

$$pH = pK_w - pK_b - \text{Log}\frac{[\,salt\,]}{[\,base\,]}$$

$$pOH = pK_b + \text{Log}\frac{[\,salt\,]}{[\,base\,]}$$

Titration of strong acids with strong base:

The hydronium ions in an aqueous solution of a strong acid have two sources:

1- The reaction of the acid with water
2- The dissociation of water itself.

In all but the most dilute solutions, however, the contribution from the strong acid far exceeds that of the solvent. So, for a solution of HCI with a concentration greater than about 10^{-6} M we can write:

$$[H_3O^+] = c_{HCl} + [OH^-] \approx c_{HCl}$$

An analogous relationship applies for a solution of a strong base, such as sodium hydroxide. That is:

$$[OH^-] = c_{NaOH} + [H_3O^+] \approx c_{NaOH}$$

Three types of calculations must be done to construct:

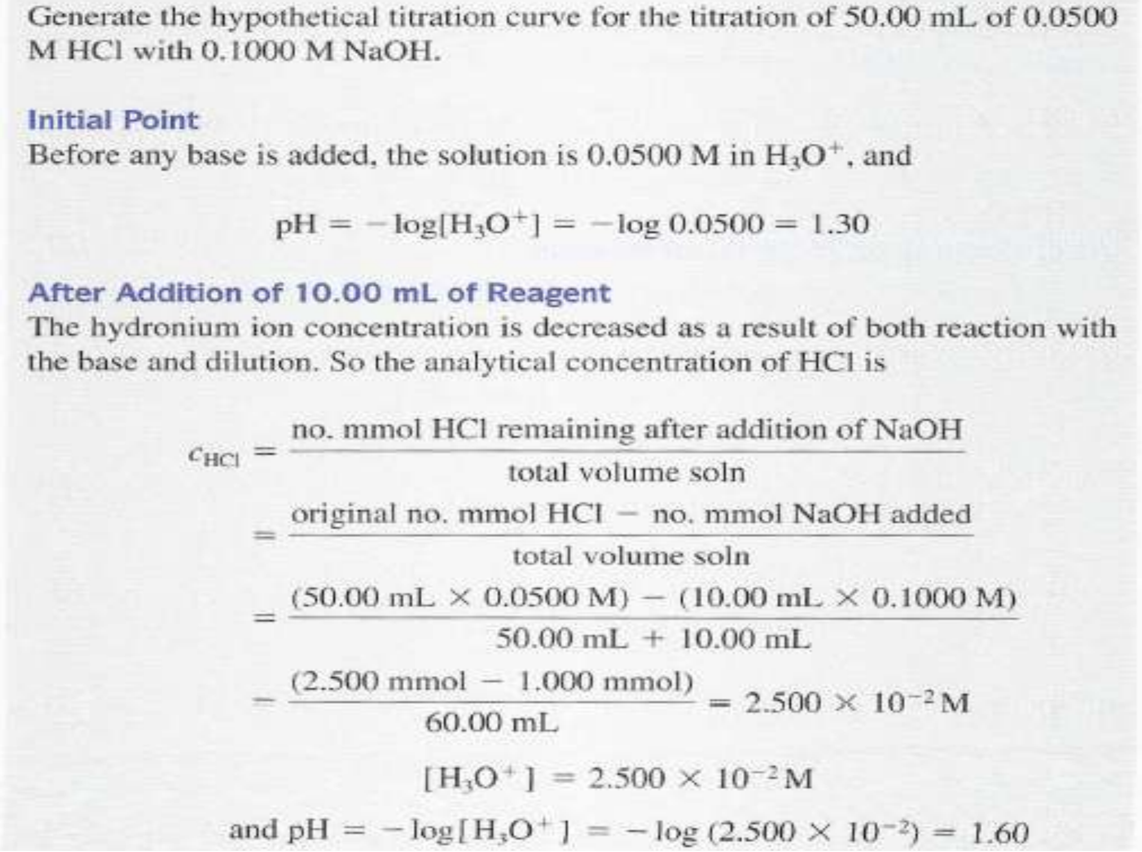
1 – before addition.
2 – after addition and before equivalence point.
3 – at equivalence point.
4 – after addition and after equivalence point.

$$K_w = [H_3O^+][OH^-]$$

$$-\log K_w = -\log[H_3O^+][OH^-] = -\log[H_3O^+] - \log[OH^-]$$

$$pK_w = pH + pOH$$

$$-\log 10^{-14} = pH + pOH = 14.00$$



Generate the hypothetical titration curve for the titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH.

Initial Point

Before any base is added, the solution is 0.0500 M in H_3O^+, and

$$pH = -\log[H_3O^+] = -\log 0.0500 = 1.30$$

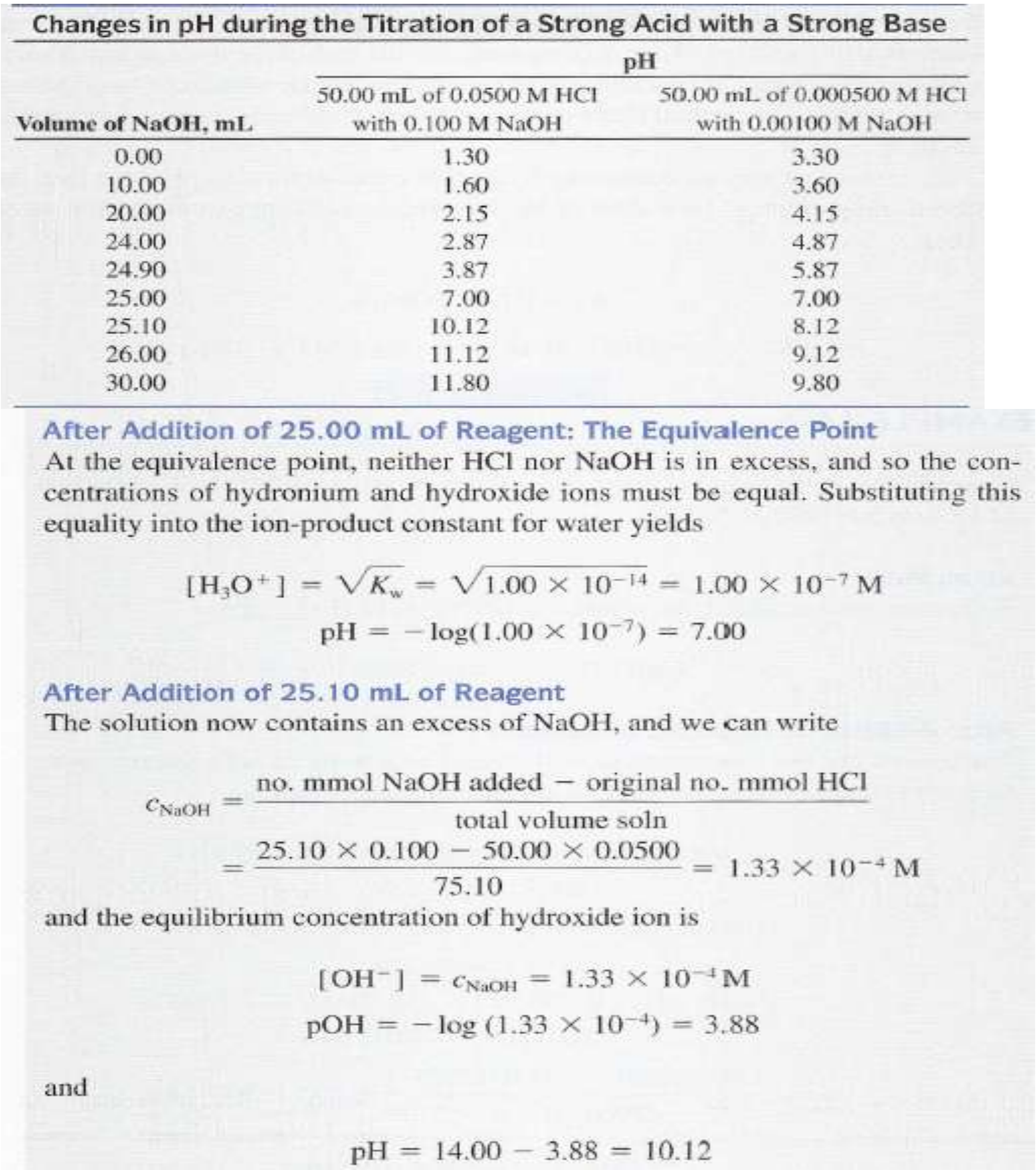
After Addition of 10.00 mL of Reagent

The hydronium ion concentration is decreased as a result of both reaction with the base and dilution. So the analytical concentration of HCl is

$$\begin{aligned} c_{HCl} &= \frac{\text{no. mmol HCl remaining after addition of NaOH}}{\text{total volume soln}} \\ &= \frac{\text{original no. mmol HCl} - \text{no. mmol NaOH added}}{\text{total volume soln}} \\ &= \frac{(50.00\text{ mL} \times 0.0500\text{ M}) - (10.00\text{ mL} \times 0.1000\text{ M})}{50.00\text{ mL} + 10.00\text{ mL}} \\ &= \frac{(2.500\text{ mmol} - 1.000\text{ mmol})}{60.00\text{ mL}} = 2.500 \times 10^{-2}\text{ M} \end{aligned}$$

$$[H_3O^+] = 2.500 \times 10^{-2}\text{ M}$$

$$\text{and pH} = -\log[H_3O^+] = -\log(2.500 \times 10^{-2}) = 1.60$$



Changes in pH during the Titration of a Strong Acid with a Strong Base

Volume of NaOH, mL	pH 50.00 mL of 0.0500 M HCl with 0.100 M NaOH	 50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80

After Addition of 25.00 mL of Reagent: The Equivalence Point

At the equivalence point, neither HCl nor NaOH is in excess, and so the concentrations of hydronium and hydroxide ions must be equal. Substituting this equality into the ion-product constant for water yields

$$[H_3O^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\text{ M}$$

$$\text{pH} = -\log(1.00 \times 10^{-7}) = 7.00$$

After Addition of 25.10 mL of Reagent

The solution now contains an excess of NaOH, and we can write

$$c_{\text{NaOH}} = \frac{\text{no. mmol NaOH added} - \text{original no. mmol HCl}}{\text{total volume soln}}$$

$$= \frac{25.10 \times 0.100 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4}\text{ M}$$

and the equilibrium concentration of hydroxide ion is

$$[OH^-] = c_{\text{NaOH}} = 1.33 \times 10^{-4}\text{ M}$$

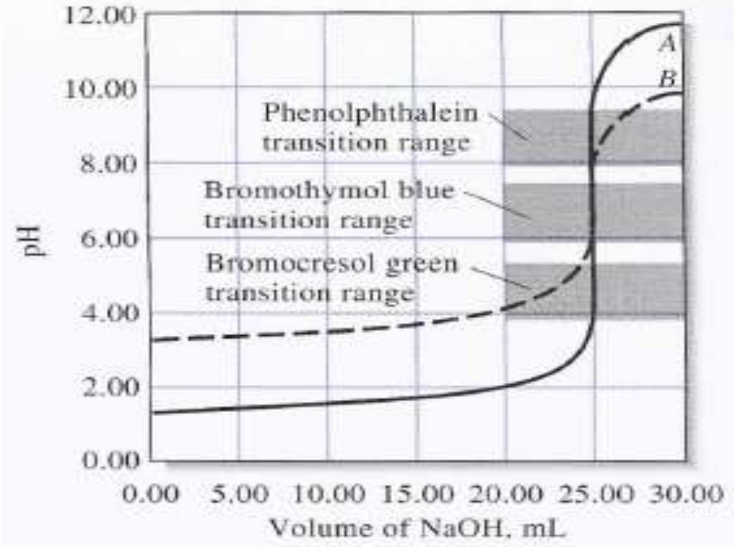
$$\text{pOH} = -\log(1.33 \times 10^{-4}) = 3.88$$

and

$$\text{pH} = 14.00 - 3.88 = 10.12$$

Choosing an Indicator:

Figure shows that the selection of an indicator is not critical when the reagent concentration is approximately 0.1 M. Note, however, that bromocresol green is unsuited for a titration involving the 0.001 M reagent because the color change occurs over a 5-mL range well before the equivalence point. The use of phenolphthalein is subject to similar objections. Of the three indicators, then, only bromothymol blue provides a satisfactory end point with a minimal systematic error in the titration of the more dilute solution.



Titrating of Strong Base with Strong Acid:

Titration curves for strong bases are derived in an analogous way to those for strong acids. Short of the equivalence point, the solution is highly basic, the hydroxide ion concentration being numerically related to the analytical molarity of the base. The solution is neutral at the equivalence point and becomes acidic in the region beyond the equivalence point; then the hydronium ion concentration is equal to the analytical concentration of the excess strong acid.

Calculate the pH during the titration of 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl after the addition of the following volumes of reagent: (a) 24.50 mL, (b) 25.00 mL, (c) 25.50 mL.

(a) At 24.50 mL added, $[H_3O^+]$ is very small and cannot be computed from stoichiometric considerations but can be obtained from $[OH^-]$

$$[OH^-] = c_{NaOH} = \frac{\text{original no. mmol NaOH} - \text{no. mmol HCl added}}{\text{total volume of solution}}$$

$$= \frac{50.00 \times 0.0500 - 24.50 \times 0.100}{50.00 + 24.50} = 6.71 \times 10^{-4}\ \text{M}$$

$$[H_3O^+] = K_w/(6.71 \times 10^{-4}) = 1.00 \times 10^{-14}/(6.71 \times 10^{-4})$$

$$= 1.49 \times 10^{-11}\ \text{M}$$

$$\text{pH} = -\log(1.49 \times 10^{-11}) = 10.83$$

(b) This is the equivalence point where $[H_3O^+] = [OH^-]$

$$[H_3O^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\ \text{M}$$

$$\text{pH} = -\log(1.00 \times 10^{-7}) = 7.00$$

(c) At 25.50 mL added,

$$[H_3O^+] = c_{HCl} = \frac{(25.50 \times 0.100 - 50.00 \times 0.0500}{75.50}$$

$$= 6.62 \times 10^{-4}\ \text{M}$$

$$\text{pH} = -\log(6.62 \times 10^{-4}) = 3.18$$

Titration curves for weak acids:

Four distinctly different types of calculations are needed to derive a titration curve for a weak acid (or a weak base):

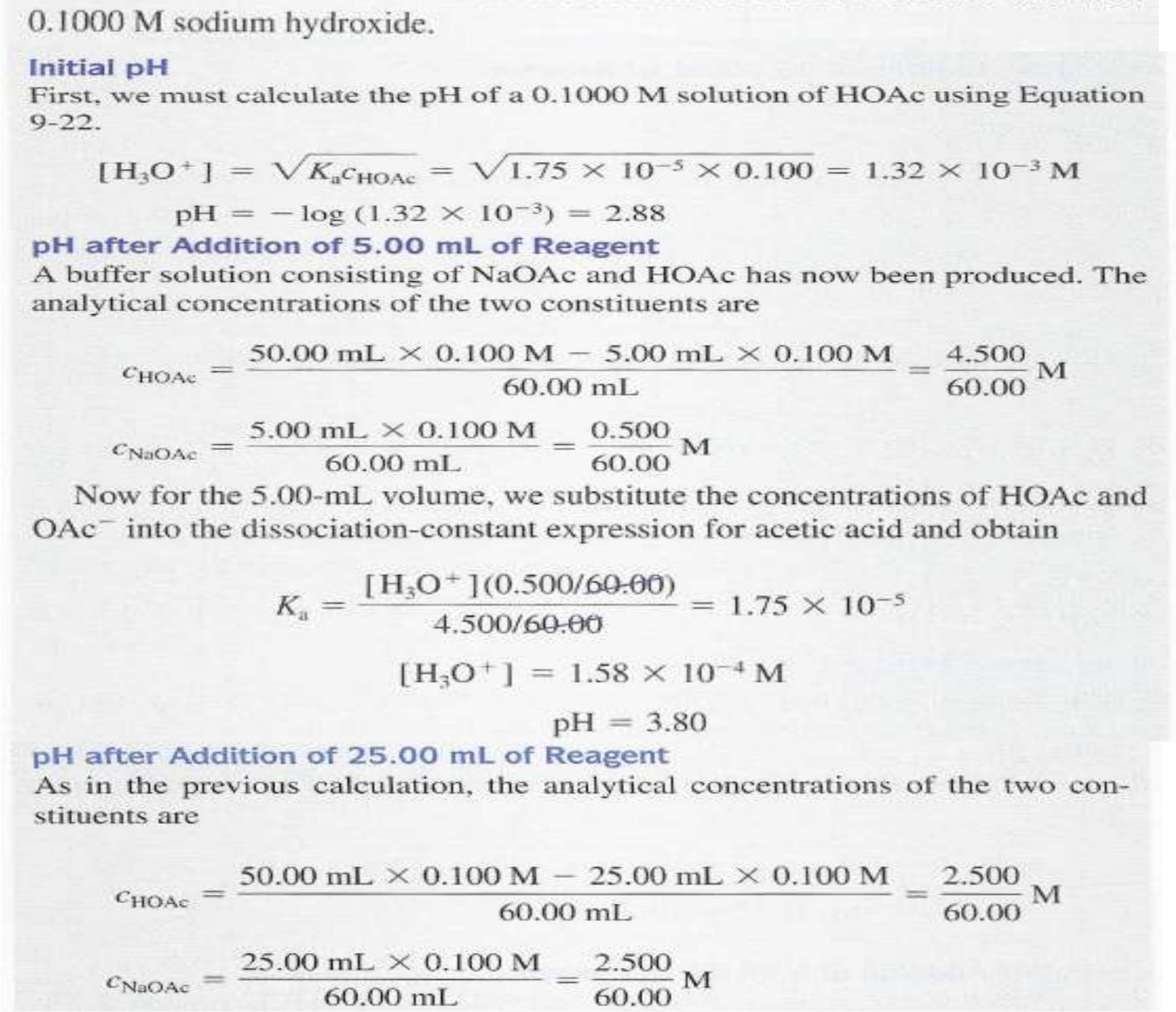
1. At the beginning, the solution contains only a weak acid or a weak base, and the pH is calculated from the concentration of that solute and its dissociation constant.

2. after various increments of titrant have been added (in quantities up to, but not including, an equivalent amount), the solution consists of a series of buffers.

The pH of each buffer can be calculated from the analytical concentrations of the conjugate base or acid and the residual concentrations of the weak acid or base.

3. At the equivalence point, the solution contains only the conjugate of the weak acid or base being titrated (that is, a salt), and the pH is calculated from the concentration of this product.

4. Beyond the equivalence point, the excess of strong acid or base titrant represses the acidic or basic character of the reaction product to such an extent that the pH is governed largely by the concentration of the excess titrant.



Generate a curve for the titration of 50.00 mL of 0.1000 M acetic acid with 0.1000 M sodium hydroxide.

Initial pH

First, we must calculate the pH of a 0.1000 M solution of HOAc using Equation 9-22.

$$[H_3O^+] = \sqrt{K_a c_{HOAc}} = \sqrt{1.75 \times 10^{-5} \times 0.100} = 1.32 \times 10^{-3}\ M$$

$$pH = -\log(1.32 \times 10^{-3}) = 2.88$$

pH after Addition of 5.00 mL of Reagent

A buffer solution consisting of NaOAc and HOAc has now been produced. The analytical concentrations of the two constituents are

$$c_{HOAc} = \frac{50.00\ mL \times 0.100\ M - 5.00\ mL \times 0.100\ M}{60.00\ mL} = \frac{4.500}{60.00}\ M$$

$$c_{NaOAc} = \frac{5.00\ mL \times 0.100\ M}{60.00\ mL} = \frac{0.500}{60.00}\ M$$

Now for the 5.00-mL volume, we substitute the concentrations of HOAc and OAc⁻ into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[H_3O^+](0.500/\cancel{60.00})}{4.500/\cancel{60.00}} = 1.75 \times 10^{-5}$$

$$[H_3O^+] = 1.58 \times 10^{-4}\ M$$

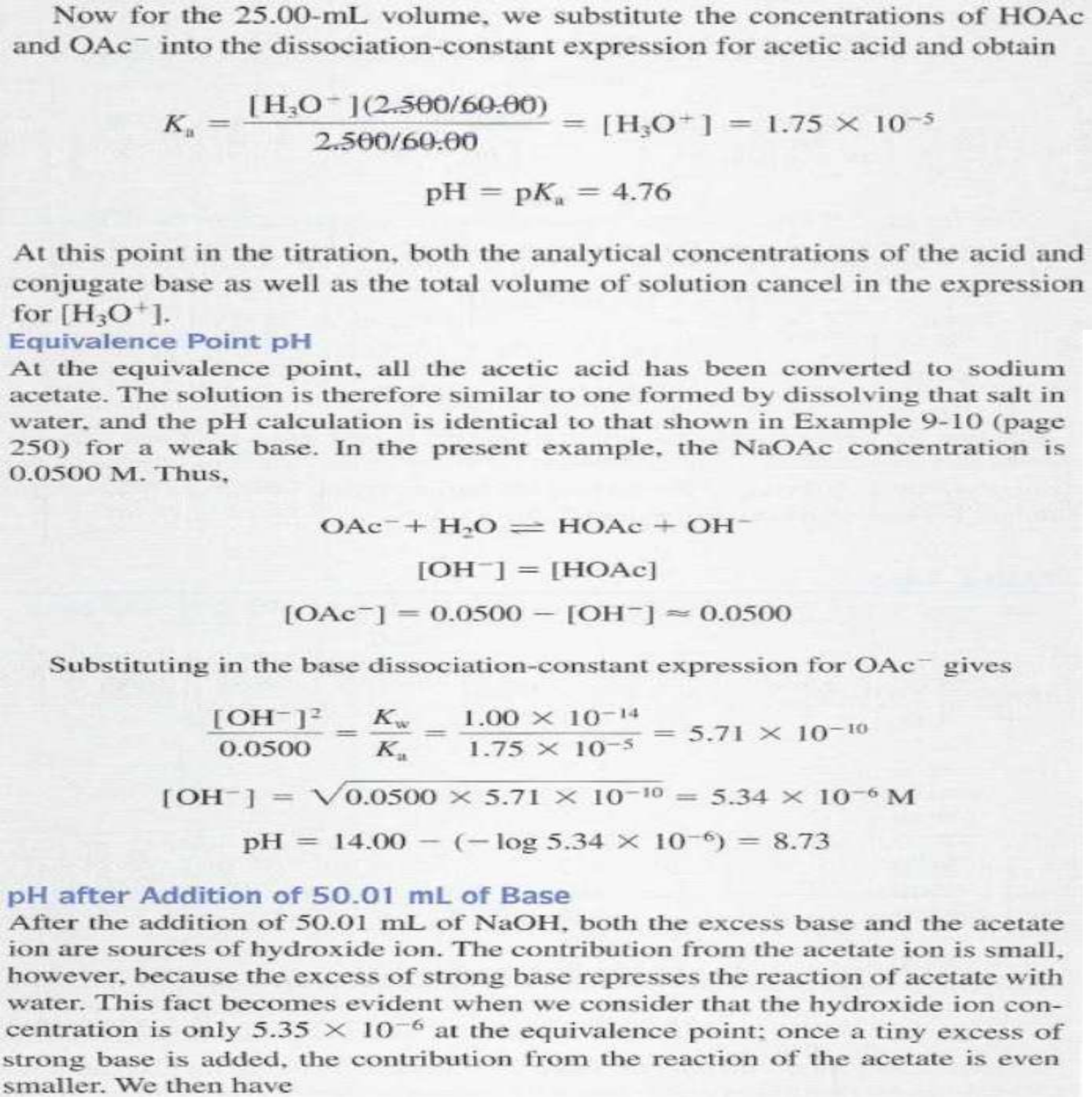
$$pH = 3.80$$

pH after Addition of 25.00 mL of Reagent

As in the previous calculation, the analytical concentrations of the two constituents are

$$c_{HOAc} = \frac{50.00\ mL \times 0.100\ M - 25.00\ mL \times 0.100\ M}{60.00\ mL} = \frac{2.500}{60.00}\ M$$

$$c_{NaOAc} = \frac{25.00\ mL \times 0.100\ M}{60.00\ mL} = \frac{2.500}{60.00}\ M$$



Now for the 25.00-mL volume, we substitute the concentrations of HOAc and OAc⁻ into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[H_3O^+](\cancel{2.500/60.00})}{\cancel{2.500/60.00}} = [H_3O^+] = 1.75 \times 10^{-5}$$

$$pH = pK_a = 4.76$$

At this point in the titration, both the analytical concentrations of the acid and conjugate base as well as the total volume of solution cancel in the expression for $[H_3O^+]$.

Equivalence Point pH

At the equivalence point, all the acetic acid has been converted to sodium acetate. The solution is therefore similar to one formed by dissolving that salt in water, and the pH calculation is identical to that shown in Example 9-10 (page 250) for a weak base. In the present example, the NaOAc concentration is 0.0500 M. Thus,

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$$

$$[OH^-] = [HOAc]$$

$$[OAc^-] = 0.0500 - [OH^-] \approx 0.0500$$

Substituting in the base dissociation-constant expression for OAc⁻ gives

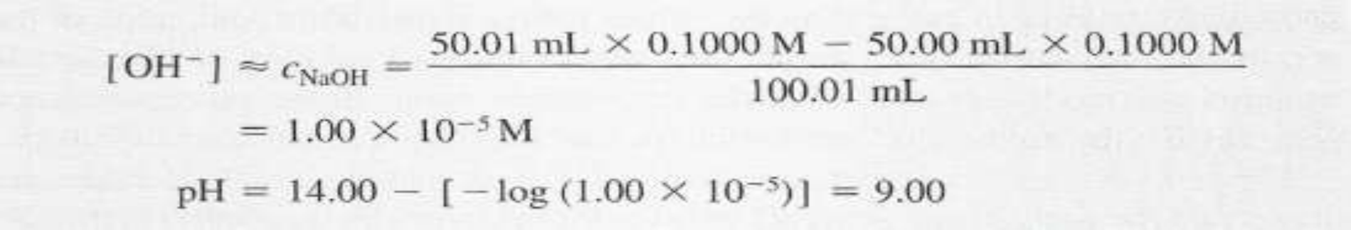
$$\frac{[OH^-]^2}{0.0500} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

$$[OH^-] = \sqrt{0.0500 \times 5.71 \times 10^{-10}} = 5.34 \times 10^{-6}\ M$$

$$pH = 14.00 - (-\log 5.34 \times 10^{-6}) = 8.73$$

pH after Addition of 50.01 mL of Base

After the addition of 50.01 mL of NaOH, both the excess base and the acetate ion are sources of hydroxide ion. The contribution from the acetate ion is small, however, because the excess of strong base represses the reaction of acetate with water. This fact becomes evident when we consider that the hydroxide ion concentration is only 5.35×10^{-6} at the equivalence point; once a tiny excess of strong base is added, the contribution from the reaction of the acetate is even smaller. We then have



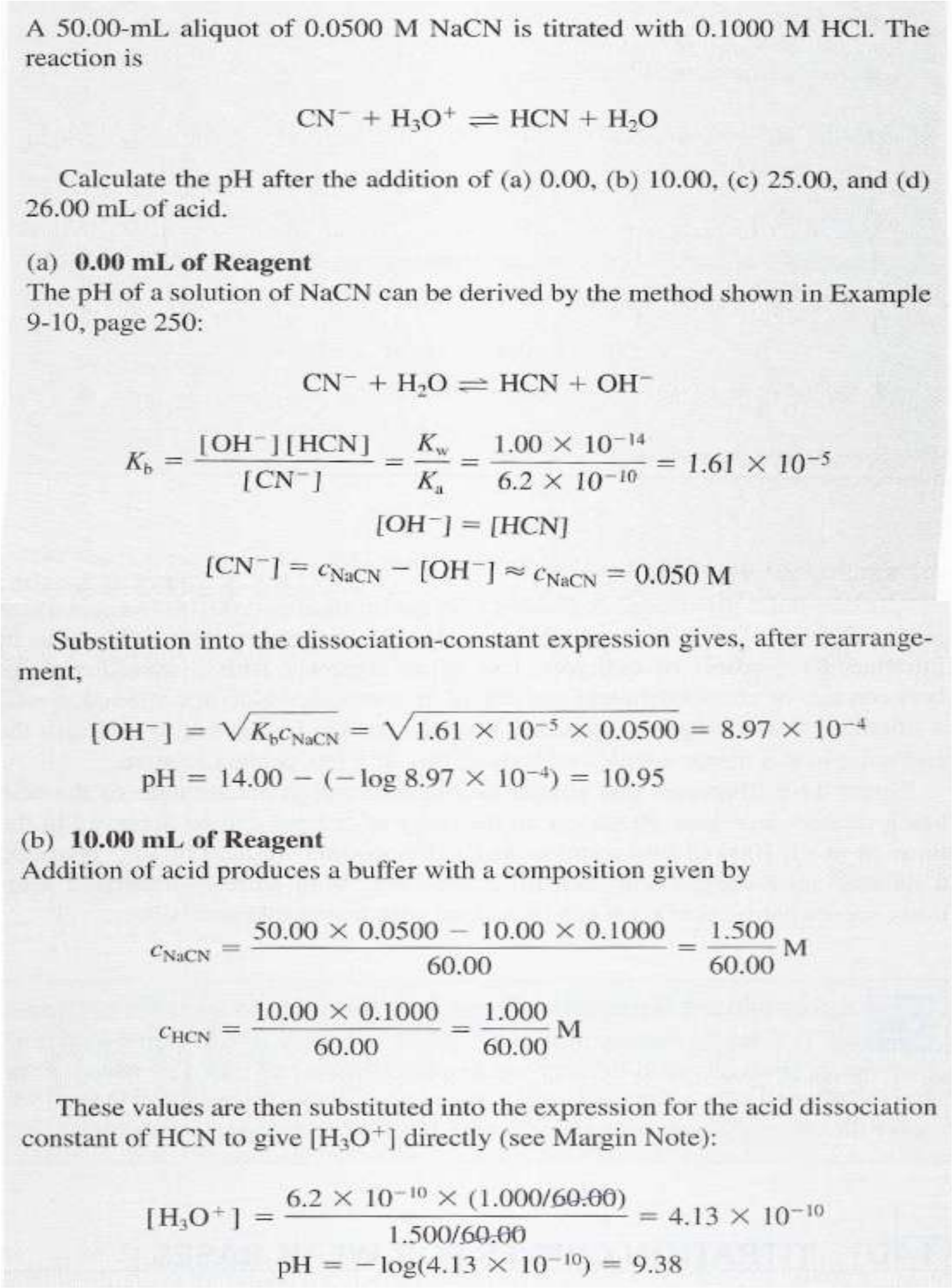
$$[OH^-] \approx c_{NaOH} = \frac{50.01\ mL \times 0.1000\ M - 50.00\ mL \times 0.1000\ M}{100.01\ mL}$$

$$= 1.00 \times 10^{-5}\ M$$

$$pH = 14.00 - [-\log(1.00 \times 10^{-5})] = 9.00$$

Titration curves for weak bases:

The calculations needed to draw the titration curve for a weak base are analogous to those for a weak acid.



A 50.00-mL aliquot of 0.0500 M NaCN is titrated with 0.1000 M HCl. The reaction is

$$CN^- + H_3O^+ \rightleftharpoons HCN + H_2O$$

Calculate the pH after the addition of (a) 0.00, (b) 10.00, (c) 25.00, and (d) 26.00 mL of acid.

(a) **0.00 mL of Reagent**

The pH of a solution of NaCN can be derived by the method shown in Example 9-10, page 250:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

$$[OH^-] = [HCN]$$

$$[CN^-] = c_{NaCN} - [OH^-] \approx c_{NaCN} = 0.050\ M$$

Substitution into the dissociation-constant expression gives, after rearrangement,

$$[OH^-] = \sqrt{K_b c_{NaCN}} = \sqrt{1.61 \times 10^{-5} \times 0.0500} = 8.97 \times 10^{-4}$$

$$pH = 14.00 - (-\log 8.97 \times 10^{-4}) = 10.95$$

(b) **10.00 mL of Reagent**

Addition of acid produces a buffer with a composition given by

$$c_{NaCN} = \frac{50.00 \times 0.0500 - 10.00 \times 0.1000}{60.00} = \frac{1.500}{60.00}\ M$$

$$c_{HCN} = \frac{10.00 \times 0.1000}{60.00} = \frac{1.000}{60.00}\ M$$

These values are then substituted into the expression for the acid dissociation constant of HCN to give $[H_3O^+]$ directly (see Margin Note):

$$[H_3O^+] = \frac{6.2 \times 10^{-10} \times (1.000/60.00)}{1.500/60.00} = 4.13 \times 10^{-10}$$

$$pH = -\log(4.13 \times 10^{-10}) = 9.38$$

(c) **25.00 mL of Reagent**

This volume corresponds to the equivalence point, where the principal solute species is the weak acid HCN. Thus,

$$c_{HCN} = \frac{25.00 \times 0.1000}{75.00} = 0.03333\ M$$

$$[H_3O^+] = \sqrt{K_a c_{HA}}$$

$$[H_3O^+] = \sqrt{K_a c_{HCN}} = \sqrt{6.2 \times 10^{-10} \times 0.03333} = 4.45 \times 10^{-6}\,M$$

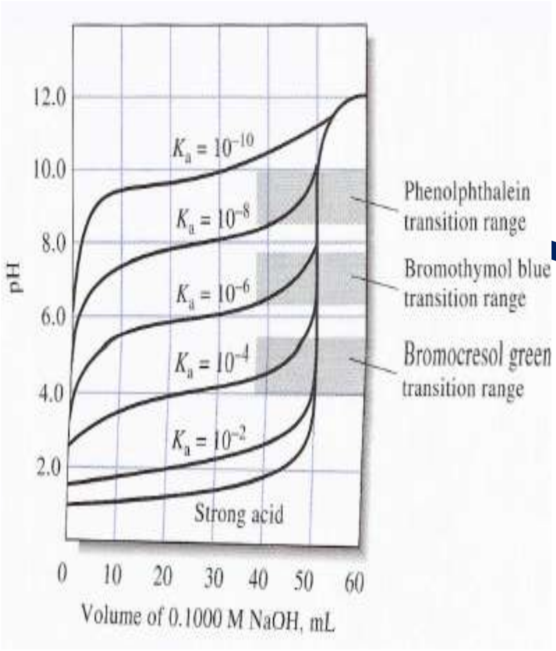
$$pH = -\log(4.45 \times 10^{-6}) = 5.34$$

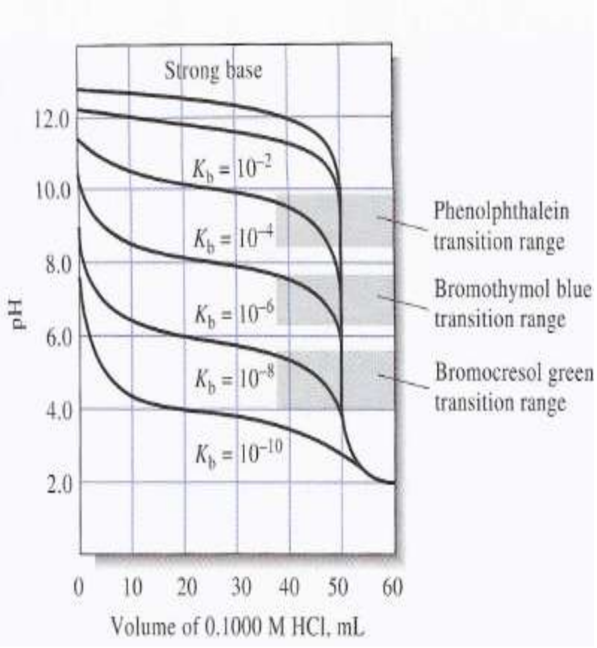
(d) **26.00 mL of Reagent**

The excess of strong acid now present represses the dissociation of the HCN to the point where its contribution to the pH is negligible. Thus,

$$[H_3O^+] = c_{HCl} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{76.00} = 1.32 \times 10^{-3}\,M$$

$$pH = -\log(1.32 \times 10^{-3}) = 2.88$$





Buffer solutions:

By definition, **a buffer solution resists** changes in pH with dilution or with addition of acids or bases. Generally, buffer solutions are prepared from a conjugate acid/base pair, such as acetic acid/sodium acetate or ammonium chloride/ammonia.

Calculation of the pH of Buffer Solutions:

A solution containing a weak acid, HA, and its conjugate base, A-, may be acidic, neutral, or basic, depending on the position of two competitive equilibria:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad K_b = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a}$$

If the first equilibrium lies farther to the right than the second, the solution is acidic. If the second equilibrium is more favorable, the solution is basic. These two equilibrium-constant expressions show that the relative concentrations of the hydronium and hydroxide ions depend not only on the magnitudes of K_a and K_b but also on the ratio between the concentrations of the acid and its conjugate base.

To find the pH of a solution containing both an acid, HA, and its conjugate base, NaA, we need to express the equilibrium concentrations of HA and NaA in terms of their analytical concentrations, C_{HA} and C_{NaA}. An examination of the two equilibria reveals that the first reaction decreases the concentration of HA by an amount equal to $[H_3O^+]$, whereas the second increases the HA concentration by an amount equal to$[OH^-]$ Thus, the species concentration of HA is related to its analytical concentration by the equation:

$$[HA] = c_{HA} - [H_3O^+] + [OH^-]$$

Similarly, the first equilibrium will increase the concentration of A^- by an amount equal to $[H_3O^+]$, and the second will decrease this concentration by the amount $[OH^-]$. Thus:

$$[A^-] = c_{NaA} + [H_3O^+] - [OH^-]$$

Because of the inverse relationship between $[H_3O^+]$ and $[OH^-]$, it is *always* possible to eliminate one or the other from equations. Moreover, the *difference* in concentration between these two species is usually so small relative to the molar concentrations of acid and conjugate base that equations simplify to:

$$[HA] \approx c_{HA}$$

$$[A^-] \approx c_{NaA}$$

$$[H_3O^+] = K_a \frac{c_{HA}}{c_{NaA}}$$

Properties of Buffer Solutions:

In this section, we illustrate the resistance of buffers to changes of pH brought about by dilution or addition of strong acids or bases.

The Henderson-Hasselbalch Equation

$$-\log [H_3O^+] = -\log K_a + \log \frac{c_{NaA}}{c_{HA}} \qquad pH = pK_a + \log \frac{c_{NaA}}{c_{HA}}$$

What is the pH of a solution that is 0.400 M in formic acid and 1.00 M in sodium formate?

The pH of this solution will be affected by the K_w of formic acid and the K_b of formate ion.

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^- \qquad K_a = 1.80 \times 10^{-4}$$

$$HCOO^- + H_2O \rightleftharpoons HCOOH + OH^- \qquad K_b = \frac{K_w}{K_a} = 5.56 \times 10^{-11}$$

Since the K_a for formic acid is orders of magnitude larger than the K_b for formate, the solution will be acidic and K_a will determine the H_3O^+ concentration. We can thus write

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = 1.80 \times 10^{-4}$$

$$[HCOO^-] \approx c_{HCOO^-} = 1.00\ M$$

$$[HCOOH] \approx c_{HCOOH} = 0.400\ M$$

Substitution into Equation 9-29 gives, with rearrangement,

$$[H_3O^+] = 1.80 \times 10^{-4} \times \frac{0.400}{1.00} = 7.20 \times 10^{-5}\ M$$

Note that the assumption that $[H_3O^+] \ll c_{HCOOH}$ and that $[H_3O^+] \ll c_{HCOO^-}$ is valid. Thus,

$$pH = -\log(7.20 \times 10^{-5}) = 4.14$$

Calculate the pH of a solution that is 0.200 M in NH_3 and 0.300 M in NH_4Cl. In Appendix 3, we find that the acid dissociation constant K_a for NH_4^+ is 5.70×10^{-10}.

The equilibria we must consider are

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_a = 5.70 \times 10^{-10}$$

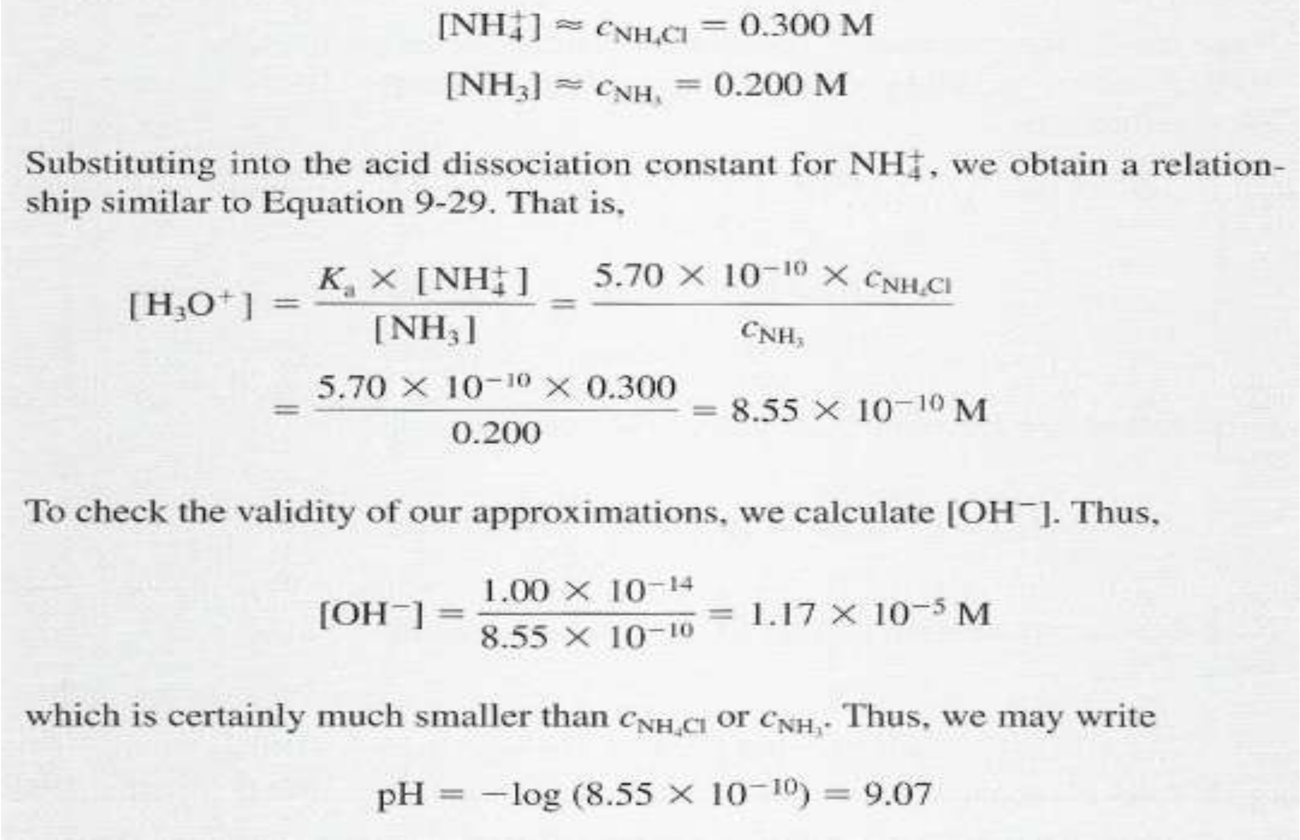
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{5.70 \times 10^{-10}} = 1.75 \times 10^{-5}$$

$$[NH_4^+] = c_{NH_4Cl} + [OH^-] - [H_3O^+] \approx c_{NH_4Cl} + [OH^-]$$

$$[NH_3] = c_{NH_3} + [H_3O^+] - [OH^-] \approx c_{NH_3} - [OH^-]$$

Because K_b is several orders of magnitude larger than K_a, we have assumed that the solution is basic and that $[OH^-]$ is much larger than $[H_3O^+]$. Thus, we have neglected the concentration of H_3O^+ in these approximations.

Also assume that $[OH^-]$ is much smaller than c_{NH_4Cl} and c_{NH_3} so that



$$[NH_4^+] \approx c_{NH_4Cl} = 0.300\ M$$

$$[NH_3] \approx c_{NH_3} = 0.200\ M$$

Substituting into the acid dissociation constant for NH_4^+, we obtain a relationship similar to Equation 9-29. That is,

$$[H_3O^+] = \frac{K_a \times [NH_4^+]}{[NH_3]} = \frac{5.70 \times 10^{-10} \times c_{NH_4Cl}}{c_{NH_3}}$$

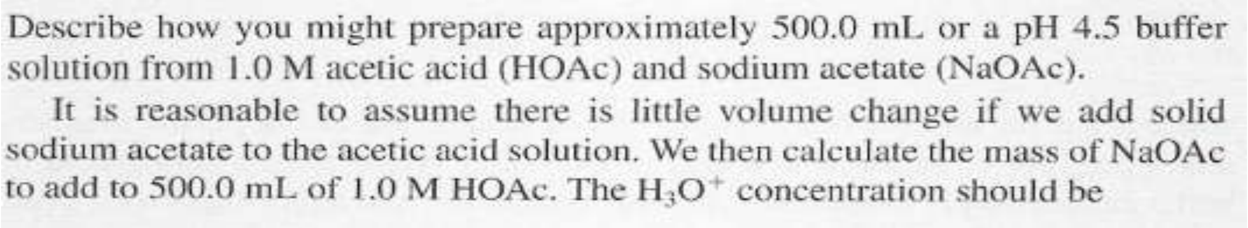
$$= \frac{5.70 \times 10^{-10} \times 0.300}{0.200} = 8.55 \times 10^{-10}\ M$$

To check the validity of our approximations, we calculate $[OH^-]$. Thus,

$$[OH^-] = \frac{1.00 \times 10^{-14}}{8.55 \times 10^{-10}} = 1.17 \times 10^{-5}\ M$$

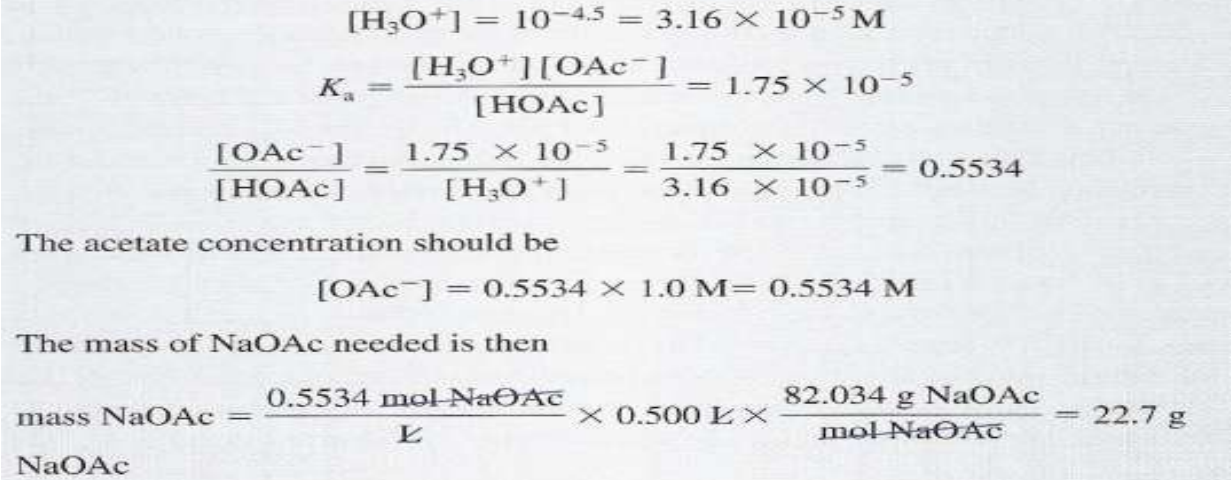
which is certainly much smaller than c_{NH_4Cl} or c_{NH_3}. Thus, we may write

$$pH = -\log(8.55 \times 10^{-10}) = 9.07$$



Describe how you might prepare approximately 500.0 mL or a pH 4.5 buffer solution from 1.0 M acetic acid (HOAc) and sodium acetate (NaOAc).

It is reasonable to assume there is little volume change if we add solid sodium acetate to the acetic acid solution. We then calculate the mass of NaOAc to add to 500.0 mL of 1.0 M HOAc. The H_3O^+ concentration should be



$$[H_3O^+] = 10^{-4.5} = 3.16 \times 10^{-5}\ M$$

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.75 \times 10^{-5}$$

$$\frac{[OAc^-]}{[HOAc]} = \frac{1.75 \times 10^{-5}}{[H_3O^+]} = \frac{1.75 \times 10^{-5}}{3.16 \times 10^{-5}} = 0.5534$$

The acetate concentration should be

$$[OAc^-] = 0.5534 \times 1.0\ M = 0.5534\ M$$

The mass of NaOAc needed is then

$$\text{mass NaOAc} = \frac{0.5534\ \cancel{\text{mol NaOAc}}}{\cancel{L}} \times 0.500\ \cancel{L} \times \frac{82.034\ \text{g NaOAc}}{\cancel{\text{mol NaOAc}}} = 22.7\ \text{g}$$

NaOAc

Example: Calculate the pH of a solution prepared by mixing 2.0 ml of a strong acid solution of pH 3.0 and 3.0 ml of a strong base of pH 10.0

$[H^+] = 1.0*10^{-3}$ M

mmole H^+ = M*V

mmole $H^+ = 2*1.0*10^{-3} = 2*10^{-3}$ mmole

For the strong base

pOH = 14-10= 4.0

$[OH^-] = 1.0 * 10^{-4}$ M

mmole OH^- = M*V = $1.0*10^{-4}*3 = 3*10^{-4}$ m mole

So we have an excess of acid

mmole. $H^+ = 2.0 * 10^{-3} – 3.0 * 10\text{-}^4 = 1.7 * 10^{-3}$ mmole

$[H^+] = \frac{1.7*10-3}{5\ ml} = 3.4*10^{-4}$ M

pH = - Log $[3.4*10^{-4}]$ M

= 4 - 0.53 = 3.47

Example: calculate the pH and pOH of a $1.0* 10^{-7}$ solution HCl?

$HCl \longrightarrow H^+ + CL^-$

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

$(H^+)(OH^-) = 1.0*10^{-14}$

$[H^+]_{H2O} = [OH^-]_{H2O} = X$

$[H^+]_{total} = C_{HCL} + [H^+]_{H2O}$

$[H^+]_{H2O}[OH^-]_{H2O} = 1.0 *10\text{-}^{14}$

$[H^+]_{total} = [H^+]_{HCl} + [H^+]_{H20}$

$(1.0 * 10^{-7} + X)(X) = 1.0* 10^{-14}$

$X^2 + (1.0 * 10^{-7} X) – (1.0 * 10\text{-}^{14}) = 0$

$$X = \frac{-B \mp \sqrt{B^2-4\ AC}}{2A}$$

$$X= \frac{-(1.0*10^-7) \mp \sqrt{(1.010^-7*)^2-4\ (\ 1.0*10^{-14})}}{2}$$

$X = 6.2 * 10^{-8}$ from water

$[H^+]_{total} = 1.0 * 10^{-7} + 6.2 * 10^{-8}$

$= 1.62 * 10^{-7}$

pH = - log $1.62 * 10^{-7}$

= 7 – 0.21 = 6.79

pOH = 14- 6.79 = 7.21

Example: calculate the pH of 0.1 M solution CH_3COONa.

$K_a = 1.72 * 10^{-5}$

$NaOAC \longrightarrow Na^+ + OAC^-$

$OAC^- + H_2O \longleftrightarrow HOAC + OH^-$

$$K_a = \frac{[HOAC\ ][\ OH^-]}{[\ OAC^-]}$$

$[OH^-] = [OAC^-] = X$

$$K_a = \frac{Kw}{Ka} = \frac{1*10^{-14}}{1.75*10^{-5}}$$

$X= OH = 7\text{-}6*10^{-6}$

$$[H^+] = \frac{1*10^{-14}}{7.6*10^{-6}} = 1.3 * 10^{-9}\ M$$

pH = - Log $1.3 *10\text{-}^9$ = 8.89

pOH = 14 – 8 .89 = 5 .11

$[OH^-] = \sqrt{Kb\ CA}$

This example for salt of weak acid.

Example: calculate the pH 0f 0.25 M solution of ammonium chloride NH_4Cl.

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$

$NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$

$NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+$

$$K_a = \frac{Kw}{Ka} = \frac{[NH4OH][H^+]}{[NH4^+]} = \frac{X^2}{0.25} = \frac{1*10^{-14}}{1.75*10^{-5}}$$

$X = [H^+] = 1.2 \times 10^{-5}$ M

pH = - Log $1.2 * 10^{-5}$ = 4.92

This example for salt of weak bases

$$[H^+] = \sqrt{Ka\ CBH^+}$$

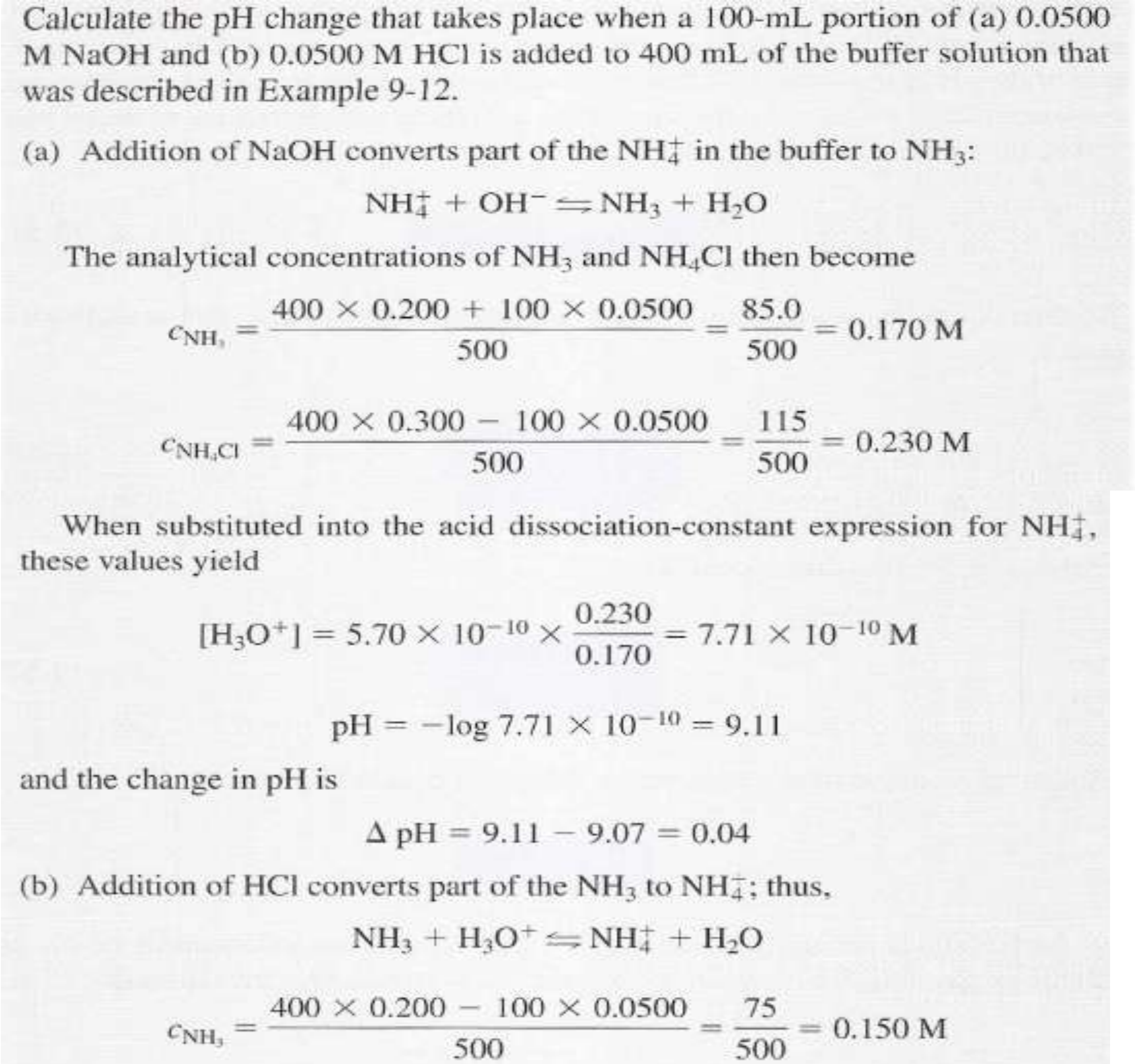
Factors affected the pH of buffer solution:

1- The Effect of Dilution:

The pH of a buffer solution remains essentially independent of dilution until the concentrations of the species it contains are decreased to the point where the approximations used to develop equations become invalid.

2 - The effect of added acids and bases:

Example illustrates a second property of buffer solutions, their resistance to pH change after addition of small amounts of strong acids or bases.



Calculate the pH change that takes place when a 100-mL portion of (a) 0.0500 M NaOH and (b) 0.0500 M HCl is added to 400 mL of the buffer solution that was described in Example 9-12.

(a) Addition of NaOH converts part of the NH_4^+ in the buffer to NH_3:

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

The analytical concentrations of NH_3 and NH_4Cl then become

$$c_{NH_3} = \frac{400 \times 0.200 + 100 \times 0.0500}{500} = \frac{85.0}{500} = 0.170\ M$$

$$c_{NH_4Cl} = \frac{400 \times 0.300 - 100 \times 0.0500}{500} = \frac{115}{500} = 0.230\ M$$

When substituted into the acid dissociation-constant expression for NH_4^+, these values yield

$$[H_3O^+] = 5.70 \times 10^{-10} \times \frac{0.230}{0.170} = 7.71 \times 10^{-10}\ M$$

$$pH = -\log 7.71 \times 10^{-10} = 9.11$$

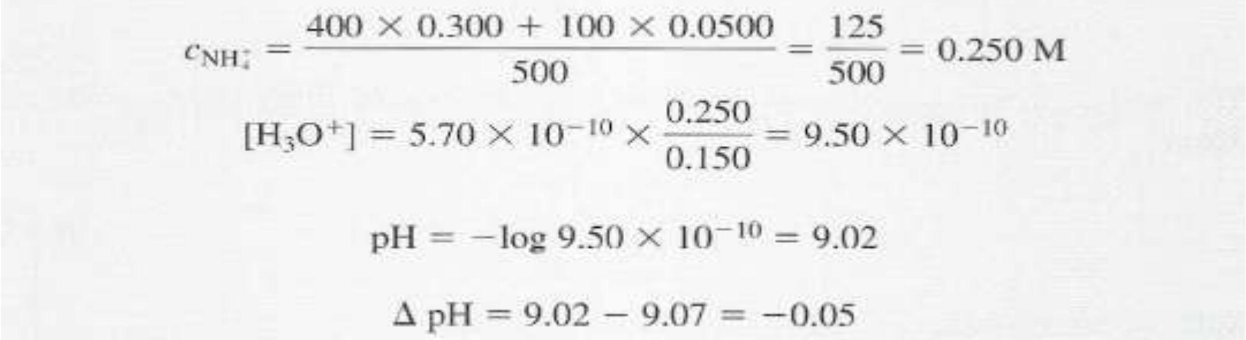
and the change in pH is

$$\Delta\ pH = 9.11 - 9.07 = 0.04$$

(b) Addition of HCl converts part of the NH_3 to NH_4^+; thus,

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

$$c_{NH_3} = \frac{400 \times 0.200 - 100 \times 0.0500}{500} = \frac{75}{500} = 0.150\ M$$



$$c_{NH_4^+} = \frac{400 \times 0.300 + 100 \times 0.0500}{500} = \frac{125}{500} = 0.250 \text{ M}$$

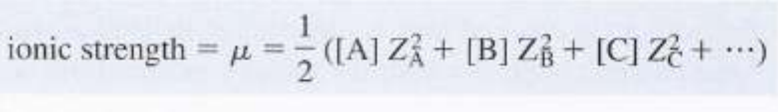
$$[H_3O^+] = 5.70 \times 10^{-10} \times \frac{0.250}{0.150} = 9.50 \times 10^{-10}$$

$$\text{pH} = -\log 9.50 \times 10^{-10} = 9.02$$

$$\Delta \text{ pH} = 9.02 - 9.07 = -0.05$$

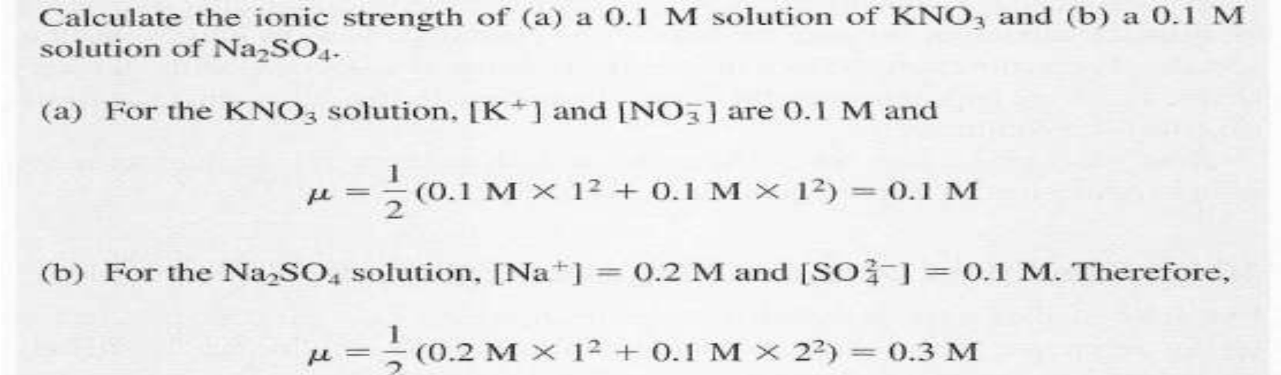
3 – The effect of ionic strength:

The effect of added electrolyte on equilibria is independent of the chemical nature of the electrolyte but depends on a property of the solution called the ionic strength. This quantity is defined as:



$$\text{ionic strength} = \mu = \frac{1}{2}([A] Z_A^2 + [B] Z_B^2 + [C] Z_C^2 + \cdots)$$

Where [A], [B], [C], represent the species molar concentrations of ions A, B, C, ... and Z_A, Z_B, Z_C, are their charges.



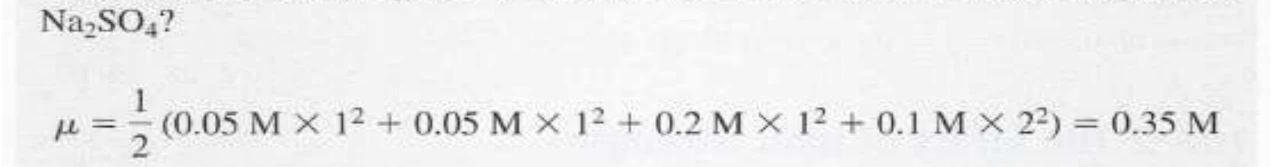
Calculate the ionic strength of (a) a 0.1 M solution of KNO_3 and (b) a 0.1 M solution of Na_2SO_4.

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

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

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

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



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

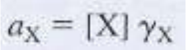
$$\mu = \frac{1}{2}(0.05 \text{ M} \times 1^2 + 0.05 \text{ M} \times 1^2 + 0.2 \text{ M} \times 1^2 + 0.1 \text{ M} \times 2^2) = 0.35 \text{ M}$$

4 – The salt effect:

This result from the electrostatic attractive and repulsive forces that exist between the ions of an electrolyte and the ions involved in equilibrium. These forces cause each ion from the dissociated reactant to be surrounded by a sheath of solution that contains a slight excess of electrolyte ions of opposite charge.

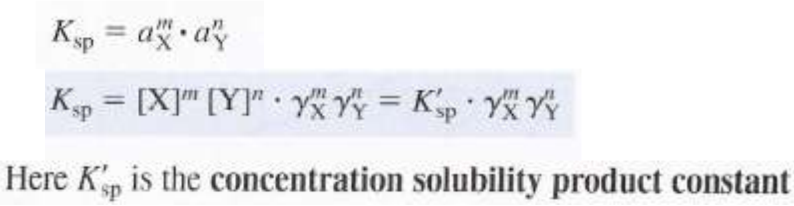
Activity coefficients:

Chemists use a term called activity, *a*, to account for the effects of electrolytes on chemical equilibria, The activity, or effective concentration, of species X depends on the ionic strength of the medium and is defined by:



$$a_X = [X] \gamma_X$$

Where a_x is the activity of the species X, [X] is its molar concentration, and γ_x is **activity coefficient.** The activity coefficient and thus the activity of X vary in ionic strength. The thermodynamic solubility product expression is defined by the equation:



$$K_{sp} = a_X^m \cdot a_Y^n$$

$$K_{sp} = [X]^m [Y]^n \cdot \gamma_X^m \gamma_Y^n = K'_{sp} \cdot \gamma_X^m \gamma_Y^n$$

Here K'_{sp} is the **concentration solubility product constant**

Activity coefficients have the following properties:

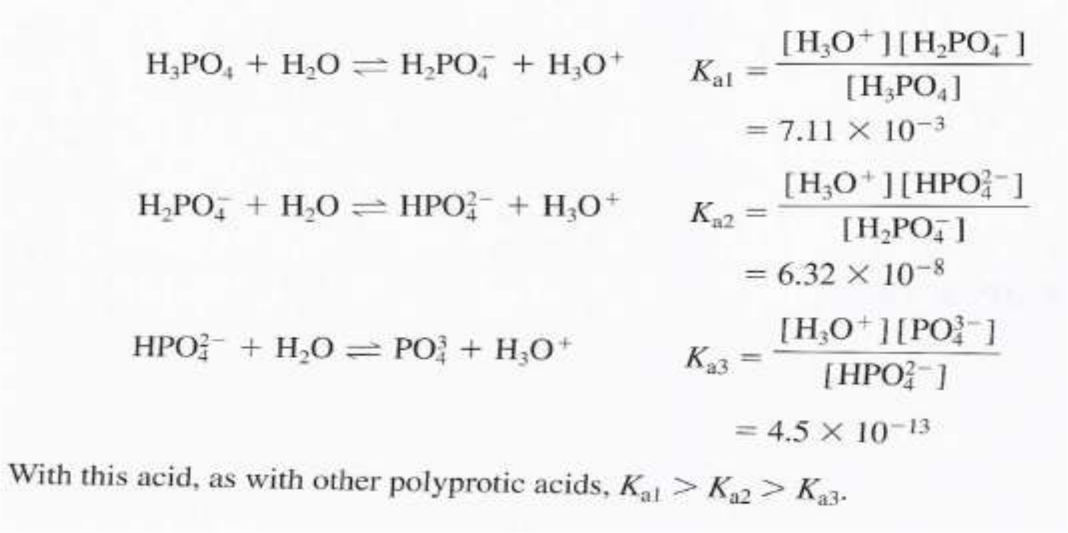
1. The activity coefficient of a species is a measure of the effectiveness with which that species influences equilibrium. In very dilute solutions, in which the ionic strength is minimal, this effectively becomes constant, and the activity coefficient is unity.
2. In solutions that are not too concentrated, the activity coefficient for a given species are independent of the nature of the electrolyte and dependent only on the ionic strength.
3. For a given ionic strength, the activity coefficient of an ion departs further from unity as the charge carried by the species increases.
4. The activity coefficient of an uncharged molecule is approximately unity, regardless of ionic strength.
5. At any given ionic strength, the activity coefficients of ions of the same charge are approximately equal.
6. The activity coefficient of a given ion describes its effective behavior in all equilibria in which it participates.

Poly functional acids and bases:

Several species have two or more acidic or basic functional groups. Generally, the two groups differ in strength and, as a consequence; exhibit two or more end points in a neutralization titration.

The Phosphoric Acid System:

Phosphoric acid is a typical polyfunctional acid. In aqueous solution, it undergoes the following three dissociation reactions:



$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \qquad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.32 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3} + H_3O^+ \qquad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.5 \times 10^{-13}$$

With this acid, as with other polyprotic acids, $K_{a1} > K_{a2} > K_{a3}$.

When we add two adjacent stepwise equilibria, we multiply the two equilibria constants to obtain the equilibrium constant for the resulting overall reaction. Thus, for the first two dissociation equilibria for H_3PO_4, we write:

$$K_{a1}K_{a2} = \frac{[H_3O^+]^2[HPO_4^{2-}]}{[H_3PO_4]}$$
$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} = 4.49 \times 10^{-10}$$

Similarly, for the reaction

$$H_3PO_4 \rightleftharpoons 3H_3O^+ + PO_4^{3-}$$

we may write

$$K_{a1}K_{a2}K_{a3} = \frac{[H_3O^+]^3[PO_4^{3-}]}{H_3PO_4}$$
$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} \times 4.5 \times 10^{-13} = 2.0 \times 10^{-22}$$

The pH of blood is 7.40. What is the ratio of $[HPO_4^{2-}]/[H_2PO_4^-]$ in the blood (assume 25°C)?

$$pH = pK_a + \log\frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

$$pK_{a2} = 7.12$$

$$pH = 7.12 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$7.40 = 7.12 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{1.9}{1}$$

For a given total **analytical concentration** of phosphoric acid, write

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

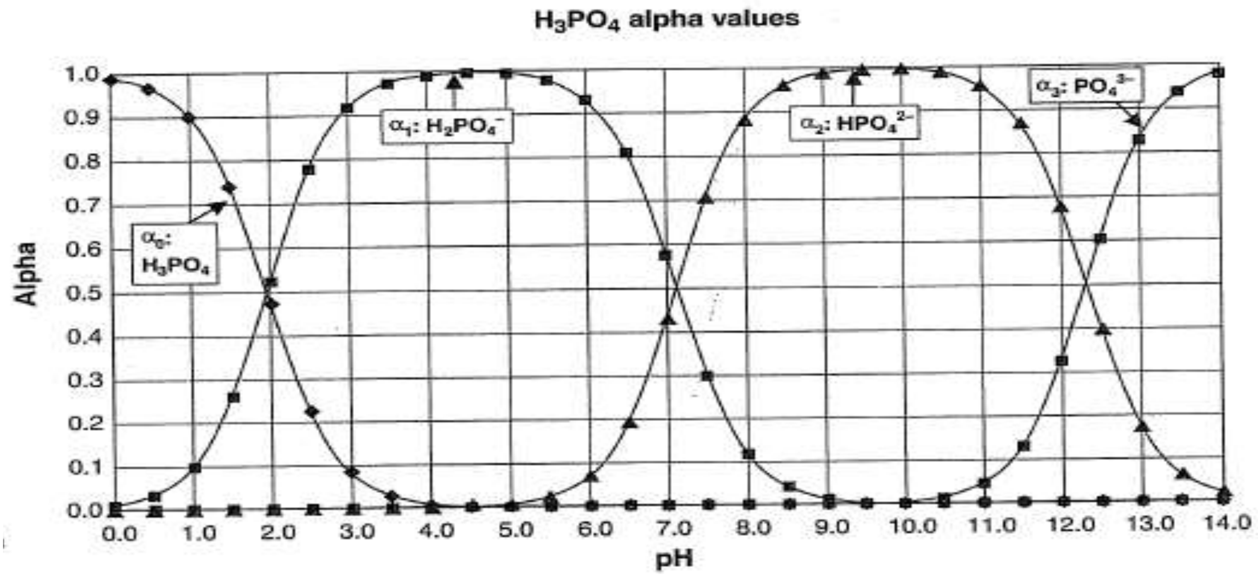
$$\alpha_0 = \frac{[H_3PO_4]}{C_{H_3PO_4}} \qquad \alpha_1 = \frac{[H_2PO_4^-]}{C_{H_3PO_4}} \qquad \alpha_2 = \frac{[HPO_4^{2-}]}{C_{H_3PO_4}}$$

$$\alpha_3 = \frac{[PO_4^{3-}]}{C_{H_3PO_4}} \qquad \alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 = 1$$

$$\alpha_1 = \frac{K_{a1}[H^+]^2}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

$$\alpha_2 = \frac{K_{a1}K_{a2}[H^+]}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

$$\alpha_3 = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$



$$[PO_4^{3-}] = \frac{K_{a3}[HPO_4^{2-}]}{[H^+]}$$

$$[HPO_4^{2-}] = \frac{K_{a2}[H_2PO_4^-]}{[H^+]}$$

$$[H_2PO_4^-] = \frac{K_{a1}[H_3PO_4]}{[H^+]} \qquad [HPO_4^{2-}] = \frac{K_{a1}K_{a2}[H_3PO_4]}{[H^+]^2} \qquad [PO_4^{3-}] = \frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{[H^+]^3}$$

$$C_{H_3PO_4} = \frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{[H^+]^3} + \frac{K_{a1}K_{a2}[H_3PO_4]}{[H^+]^2} + \frac{K_{a1}[H_3PO_4]}{[H^+]} + [H_3PO_4]$$

$$\alpha_0 = \frac{1}{(K_{a1}K_{a2}K_{a3}/[H^+]^3) + (K_{a1}K_{a2}/[H^+]^2) + (K_{a1}/[H^+]) + 1}$$

which can be rearranged to

$$\boxed{\alpha_0 = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}}$$

Calculate the equilibrium concentration of the different species in a 0.10 *M* phosphoric acid solution at pH 3.00 ($[H^+] = 1.0 \times 10^{-3}$ *M*).

Solution

Substituting into Equation 7.72,

$$\alpha_0 = \frac{(1.0 \times 10^{-3})^3}{(1.0 \times 10^{-3})^3 + (1.1 \times 10^{-2})(1.0 \times 10^{-3})^2 + (1.1 \times 10^{-2})(7.5 \times 10^{-8})(1.0 \times 10^{-3}) + (1.1 \times 10^{-2})(7.5 \times 10^{-8})(4.8 \times 10^{-13})}$$

$$= \frac{1.0 \times 10^{-9}}{1.2 \times 10^{-8}} = 8.3 \times 10^{-2}$$

$$[H_3PO_4] = C_{H_3PO_4}\,\alpha_0 = 0.10 \times 8.3 \times 10^{-2} = 8.3 \times 10^{-3}\ M$$

Similarly,

$$\alpha_1 = 0.92$$
$$[H_2PO_4^-] = C_{H_3PO_4}\,\alpha_1 = 0.10 \times 0.92 = 9.2 \times 10^{-2}\ M$$
$$\alpha_2 = 6.9 \times 10^{-5}$$
$$[HPO_4^{2-}] = C_{H_3PO_4}\,\alpha_2 = 0.10 \times 6.9 \times 10^{-5} = 6.9 \times 10^{-6}\ M$$
$$\alpha_3 = 3.3 \times 10^{-14}$$
$$[PO_4^{3-}] = C_{H_3PO_4}\,\alpha_3 = 0.10 \times 3.3 \times 10^{-14} = 3.3 \times 10^{-15}\ M$$

We see that at pH 3, the majority (91%) of the phosphoric acid exists as $H_2PO_4^-$ and 8.3% exists as H_3PO_4. Only 3.3×10^{-12}% exists as PO_4^{3-}!

Example: Calculate the conc. of all phosphate species for 0.05 H_3PO_4 , whose pH has been adjusted pH = 1.5.

Solution:

at pH = 1.5 $[H_3O^+] = 10^{-1.5} = 3.16 * 10^{-3}$

Since this pH left C_1 on the figure, we use k_1 to determine $[H_2PO_4^-]$, knowing that $[H_3PO_4]$ will be the major species.

$$K_1 = 7.1 * 10^{-3} = \frac{[H_3O^+]\,[H_2PO_4^-]}{[H_3PO_4]} = \frac{3.16 * 10^{-3}\ \ [H_2PO_4^-]}{[H_3PO_4]}$$

$[H_2PO_4^-] = \frac{7.1 * 10^{-3}}{3.16 * 10^{-3}} [H_3PO_4] = 0.225\ [H_3PO_4]$

$C_{H3A} = 0.05 \cong [H_3PO_4] + [H_2PO_4^-]$

$0.05 = [H_3PO_4] + 0.225\ [H_3PO_4]$

$[H_3PO_4] = \frac{0.05}{1.225} = 0.041\ M$

$[H_2PO_4^-] = 0.225\ [H_3PO_4] \longrightarrow 0.009\ M$

HPO_4^{2-} and PO_4^{3-} can be calculated by using K_2 and K_3

$K_2 = 6.3 * 10^{-8} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$

$= [HPO_4^{2-}] = \frac{6.3 * 10^{-8} * 0.009}{3.16 * 10^{-3}} = 1.8 * 10^{-8}\ M$

$K_3 = 4.2 * 10^{-13} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$

$PO_4^{3-} = \frac{4.2 * 10^{-13} * 1.8 * 10^{-8}}{3.16 * 10^{-3}} = 2.4 * 10^{-19}\ M$

Example: Calculate the concentration of all phosphate species in a 0.03 M H_3PO_4 solution at pH = 8.

Solution:

$$\alpha_{H3PO4} = \frac{[10^{-8}]^3}{[(10^{-8})^3 + 7.1 * 10^{-3}\ (10^{-8})^2 + 7.1 * 10^{-3} * 6.3 * 10^{-8} * 10^{-8} + 7.1 * 10^{-3} * 6.3 * 10^{-8} * 4.2 * 10^{-13}]}$$

For the follow equation:

$$\alpha_{H3PO4} = \frac{[H3O^+]^3}{[(H_3O^+)^3 + K_1\ (H_3O^+)^2 + K_1K_2(H_3O^+) + K_1K_2K_3]}$$ **represented as D**

Not that $[H_3O^+] = [H^+]$ all ways:

$\alpha_{H3PO4} = 1.93 * 10^{-7}$

$\alpha_{H3PO4} * C_{H3PO4} = [H_3PO_4]$

$1.93 * 10^{-7} * 0.03 = 5.8 * 10^{-9} \longrightarrow [H_3PO_4]$

$\alpha_{H2PO4^-} = \frac{K_1\ (H_3O^+)^2}{D} = \frac{7.1 * 10^{-3}\ (10^{-8})^2}{5.18 * 10^{-18}} = 0.137$

$[H_2PO_4^-] = \alpha_{H2PO4^-}\ x\ C_{H3PO4} = 0.137 * 0.03 = 4.1 * 10^{-3}\ M$

$\alpha_{HPO4^{2-}} = \frac{7.13 * 10^{-3} * 6.3 * 10^{0}}{5.18 * 10^{-18}} = 0.863$

$[HPO_4^{2-}] = \alpha_{HPO4^{2-}}\ x\ C_{H3PO4} = 0.863 * 0.03 = 2.59 * 10^{-2}\ M$

$\alpha_{PO4^{3-}} = \frac{7.13 * 10^{-3} * 6.3 * 10^{-8} * 4.2 * 10^{-13}}{5.18 * 10^{-18}} = 3.62 * 10^{-5}$

$[PO_4^{3-}] = \alpha_{PO4^{3-}}\ x\ C_{H3PO4} = 3.62 * 10^{-5} * 0.03 = 1.1 * 10^{-6}\ M$

Polyprotic acids (poly functional acid):

Q1/ calculate the pH of a 0.1 M H_3PO_4 solution. $K_a = 1.1\ x\ 10^{-2}$

$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$

$$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_2PO_4^-]}$$

$[H_3O^+] = [H_2PO_4^-]$ $[H_3PO_4] = C_{H3PO4}$

$$K_{a1} = \frac{[H_3O+]^2}{C_{H3PO4} - [H_3O^+]} = [H_3O^+]^2 + [H_3O^+]K_{a1} - C_{H3PO4}$$

$$[H_3O^+] = \frac{-(1.1\times10^{-2})\pm\sqrt{(1.1\times10^{-2})^2-4(-1.1\times10^{-3})}}{2}$$

$$= 0.028\ M = [H^+]$$

$pH = -\ Log\ [H^+] = -\ Log\ \sqrt{}0.1673 = 0.944$

Q2/calculate the pH of 0.1 M Na_3PO_4. Ka_3 =4.8 x10^{-13}

$K_b = K_w / K_a = 1.0*10^{-14} / 4.8\ x10^{-13} = 0.02$

$$PO_4^{-3} + H_2O \rightleftarrows HPO_4^{-2} + OH^-$$

$K_b = [OH^-]\ x\ [HPO_4^{-2}] / [PO_4^{-3}]$ ………………… (1)

$[OH^-] = [HPO_4^{-2}]$ and $[PO_4^{-3}] = C_{Na3PO4} - [OH^-]$

Substituted in equation (1):

$[OH^-]^2 + k_b\ [OH^-] - k_b\ C_{Na3PO4} = 0$

$$[OH^-] = \frac{-0.02 \pm\sqrt{(0.02)^2-4(-0.02\ X\ 0.1)}}{2}$$

$$= 0.036\ M$$

$pOH = -\ Log\ 0.036 = 1.44 \Longrightarrow pH = 12.56$

Typical applications of neutralization titrations:

Neutralization titrations are used to determine the inorganic, organic, and biological species that possess inherent acidic or basic properties. Two major types of end points find widespread use in neutralization titrations. The first is a visual end point based on indicators. The second is a potentiometric end point, in which the potential of a glass/calomel electrode system is determined by a voltage-measuring device.

Elemental Analysis:

Generally, the elements susceptible to this type of analysis are nonmetallic and include carbon, nitrogen, chlorine, bromine, and fluorine, as well as a few other less common species. Pretreatment converts the element to an inorganic acid or base that is then titrated. A few examples follow.

Nitrogen:

Thus, analytical methods for the determination of nitrogen, particularly in organic substrates. The most common method for determining organic nitrogen is the **Kjeldahl method.**

1 – In the Kjeldahl method, the sample is decomposed in hot, concentrated sulfuric acid to convert the bound nitrogen to ammonium ion.

2 – The resulting solution is then cooled, diluted, and made basic.

3 – The liberated ammonia is distilled, collected in an acidic solution, and determined by a neutralization titration.

Amine and amide nitrogen are quantitatively converted to ammonium ion.

Nitro, azo, and azoxy groups are likely to yield the element or its various oxides, all of which are lost from the hot acidic medium. This loss can be avoided by pretreating the sample with a reducing agent to form products that behave as amide or amine nitrogen.

Certain aromatic heterocyclic compounds, such as pyridine and its derivatives, are particularly resistant to complete decomposition by sulfuric acid.

Numerous modifications of the original procedure have been proposed.

1 – In the most widely used modification, a neutral salt, such as potassium sulfate, is added to increase the boiling point of the sulfuric acid solution and thus the temperature at which the decomposition occurs.

2 – In another modification, a solution of hydrogen peroxide is added to the mixture after the digestion has decomposed most of the organic matrix.

Sulfur:

Sulfur in organic and biological materials are conveniently determined by burning the sample in a stream of oxygen. The sulfur dioxide (as well as the sulfur trioxide) formed during the oxidation is collected by distillation into a dilute solution of hydrogen peroxide:

$$SO_2(g) + H_2O_2 \rightarrow H_2SO_4$$

The sulfuric acid is then titrated with standard base.

The Determination of Inorganic Nitrogen Substances:

Ammonium Salts:

Ammonium salts are conveniently determined by conversion to ammonia with strong base followed by distillation. The ammonia is collected and titrated as in the Kjeldahl method.

Nitrates and Nitrites:

These ions are first reduced to ammonium ion by **Devarda's alloy** (50% Cu, 45% AI, 5% Zn). Granules of the alloy are introduced into a strongly alkaline solution of the sample in a Kjeldahl flask. The ammonia is distilled after reaction is complete. **Arnd's alloy** (60% Cu, 40% Mg) has also been used as the reducing agent.

The Determination of Organic Functional Groups:

Brief descriptions of methods for the more common groups follow:

Carboxylic and Sulfonic Acid Groups:

Most carboxylic acids have dissociation constants that range between 10^{-4} and 10^{-6}, and thus these compounds are readily titrated. An indicator that changes color in a basic range, such as phenolphthalein, is required.

The carboxylic acids which are not sufficiently soluble in water, the acid can be dissolved in ethanol and titrated with aqueous base.

Alternatively, the acid can be dissolved in an excess of standard base followed by back-titration with standard acid.

Sulfonic acids are generally strong acids and readily dissolve in water; their titration with a base is therefore straightforward.

Neutralization titrations are often employed to determine the equivalent weight of purified organic acids. Equivalent weights serve as an aid in the qualitative identification of organic acids.

Amine Groups:

Aliphatic amines generally have base dissociation constants on the order of 10^{-5} and can thus be titrated directly with a solution of a strong acid (saturated cyclic amines such as **bipyeridine** can also be titrated) .

Many amines that are too weak to be titrated as bases in water are readily titrated in non aqueous solvents, such as anhydrous acetic acid, which enhance their basicity. (aromatic amines, cyclic amines with aromatic character).

Ester Croups:

Esters are commonly determined by **saponification** with a measured quantity of standard base:

$$R_1COOR_2 + OH^- \rightarrow R_1COO^- + HOR_2$$

The excess base is then titrated with standard acid.

Hydroxyl Croups:

Hydroxyl groups in organic compounds can be determined by esterification with various carboxylic acid anhydrides in pyridine or chlorides; the two most common reagents are acetic anhydride and phthalic anhydride. With acetic anhydride, the reaction is:

$$(CH_3CO)_2O + ROH \rightarrow CH_3COOR + CH_3COOH$$

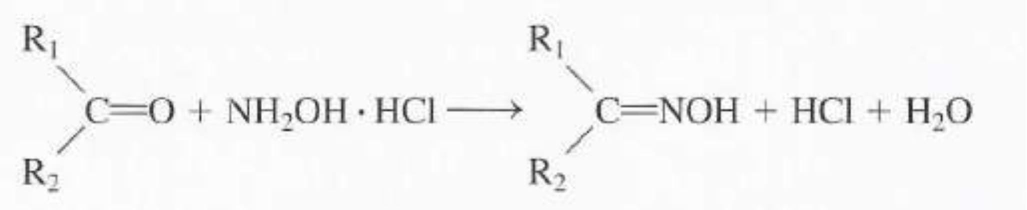
After heating, water is added to hydrolyze the unreacted anhydride:

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

The acetic acid is then titrated with a standard solution of alcoholic sodium or potassium hydroxide.

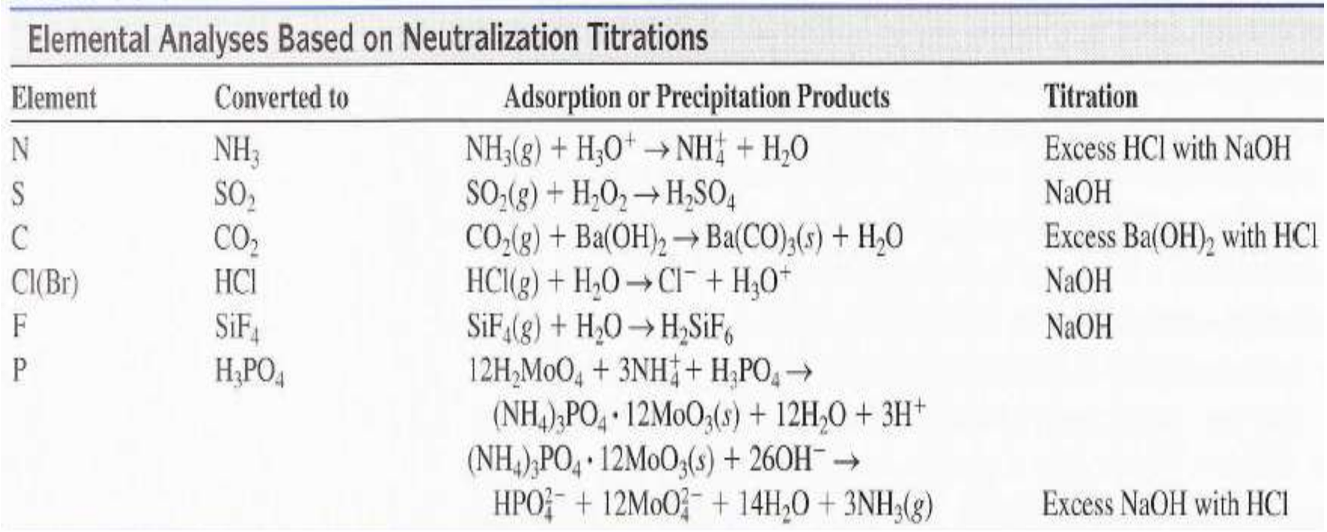
Carbonyl Croups:

Many aldehydes and ketones can be determined with a solution of hydroxylamine hydrochloride. The reaction, which produces an Oxime, is:



$$R_1R_2C{=}O + NH_2OH \cdot HCl \longrightarrow R_1R_2C{=}NOH + HCl + H_2O$$

Where R_2 may be an atom of hydrogen. The liberated hydrochloric acid is titrated with base.



Elemental Analyses Based on Neutralization Titrations

Element	Converted to	Adsorption or Precipitation Products	Titration
N	NH_3	$NH_3(g) + H_3O^+ \rightarrow NH_4^+ + H_2O$	Excess HCl with NaOH
S	SO_2	$SO_2(g) + H_2O_2 \rightarrow H_2SO_4$	NaOH
C	CO_2	$CO_2(g) + Ba(OH)_2 \rightarrow Ba(CO)_3(s) + H_2O$	Excess $Ba(OH)_2$ with HCl
Cl(Br)	HCl	$HCl(g) + H_2O \rightarrow Cl^- + H_3O^+$	NaOH
F	SiF_4	$SiF_4(g) + H_2O \rightarrow H_2SiF_6$	NaOH
P	H_3PO_4	$12H_2MoO_4 + 3NH_4^+ + H_3PO_4 \rightarrow$ $(NH_4)_3PO_4 \cdot 12MoO_3(s) + 12H_2O + 3H^+$ $(NH_4)_3PO_4 \cdot 12MoO_3(s) + 26OH^- \rightarrow$ $HPO_4^{2-} + 12MoO_4^{2-} + 14H_2O + 3NH_3(g)$	Excess NaOH with HCl

Precipitation titrimetry:

Precipitation titrimetry, which is based on the reactions that yield ionic compounds of limited solubility, is one of the oldest analytical techniques.

By far the most widely used and most important precipitating reagent is silver nitrate, which is used for the determination of the halides, the halide-like anions (SCN^-, CN^-, CNO^-), mercaptans, fatty acids, and several divalent and trivalent inorganic anions. Titrimetric methods based on silver nitrate are sometimes called **argentometric methods.**

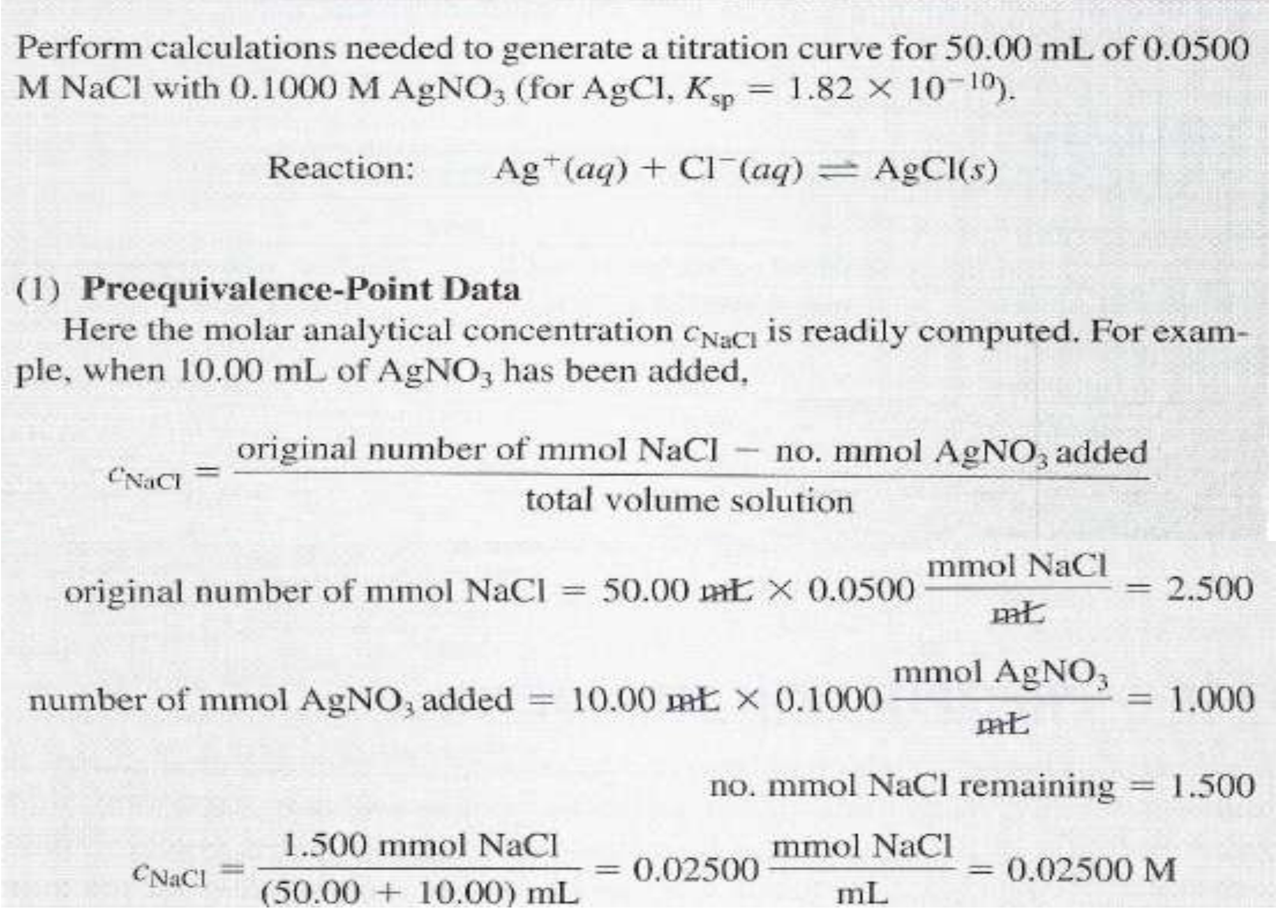
Precipitation Titration Curves Involving Silver Ion:

The most common method of determining the halide ion concentration of aqueous solutions is titration with a standard solution of silver nitrate. The reaction product is solid silver halide. A titration curve for this method usually consists of a plot of pAg versus the volume of silver nitrate added.

To construct titration curves, four types of calculations are required, each of which corresponds to a distinct stage in the reaction:

1 – before addition.
2 – after addition and before equivalence point.
3 – at equivalence point.
4 – after addition and after equivalence point.

Example demonstrates how pAg is determined for each of these stages.



Perform calculations needed to generate a titration curve for 50.00 mL of 0.0500 M NaCl with 0.1000 M $AgNO_3$ (for AgCl, $K_{sp} = 1.82 \times 10^{-10}$).

Reaction: $$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

(1) **Preequivalence-Point Data**

Here the molar analytical concentration c_{NaCl} is readily computed. For example, when 10.00 mL of $AgNO_3$ has been added,

$$c_{NaCl} = \frac{\text{original number of mmol NaCl} - \text{no. mmol } AgNO_3 \text{ added}}{\text{total volume solution}}$$

$$\text{original number of mmol NaCl} = 50.00\ \cancel{\text{mL}} \times 0.0500\ \frac{\text{mmol NaCl}}{\cancel{\text{mL}}} = 2.500$$

$$\text{number of mmol } AgNO_3 \text{ added} = 10.00\ \cancel{\text{mL}} \times 0.1000\ \frac{\text{mmol } AgNO_3}{\cancel{\text{mL}}} = 1.000$$

$$\text{no. mmol NaCl remaining} = 1.500$$

$$c_{NaCl} = \frac{1.500 \text{ mmol NaCl}}{(50.00 + 10.00)\text{ mL}} = 0.02500\ \frac{\text{mmol NaCl}}{\text{mL}} = 0.02500\text{ M}$$

$$[Cl^-] = 0.02500\ M$$

$$[Ag^+] = K_{sp}/[Cl^-] = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9}\ M$$

$$pAg = -\log(7.28 \times 10^{-9}) = 8.14$$

Additional points defining the curve in the preequivalence-point region are obtained in the same way. Results of calculations of this kind are shown in the second column of Table 13-2.

(2) Equivalence Point pAg

Here,

$$[Ag^+] = [Cl^-] \quad \text{and} \quad [Ag^+][Cl^-] = 1.82 \times 10^{-10} = [Ag^+]^2$$

$$[Ag^+] = 1.349 \times 10^{-5}\ M \quad \text{and} \quad pAg = -\log(1.349 \times 10^{-5}) = 4.87$$

(3) Postequivalence-Point Data

At 26.00 mL $AgNO_3$ added, Ag^+ is in excess, so

$$[Ag^+] = c_{AgNO_3} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{50.00 - 26.00} = 1.316 \times 10^{-3}\ M$$

$$pAg = -\log(1.316 \times 10^{-3}) = 2.88$$

Changes in pAg in the Titration of Cl^- With Standard $AgNO_3$

	pAg	
Volume of $AgNO_3$	50.00 mL of 0.0500 M NaCl with 0.1000 M $AgNO_3$	50.00 mL of 0.00500 M NaCl with 0.01000 M $AgNO_3$
10.00	8.14	7.14
20.00	7.59	6.59
24.00	6.87	5.87
25.00	4.87	4.87
26.00	2.88	3.88
30.00	2.20	3.20
40.00	1.78	2.78

Indicators for Argentometric Titrations:

Chromate Ion; the Mohr Method:

Sodium chromate can serve as an indicator for the argentometric determination of chloride, bromide, and cyanide ions by reacting with silver ion to form a brick-red silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region. The silver ion concentration at chemical equivalence in the titration of chloride with silver ions is given by:

$$[Ag^+] = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}\ M$$

◀ Mohr method for chloride.

Titration reaction $$Ag^+ + Cl^- \rightleftharpoons \underset{\text{white}}{AgCl(s)}$$

The chromate ion concentration required to initiate formation of silver chromate under this condition can be computed from the solubility constant for silver chromate:

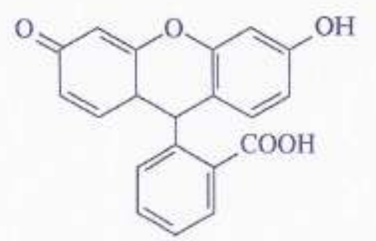
$$[CrO_4^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{1.2\times10^{-12}}{(1.35\times10^{-5})^2} = 6.6\times10^{-3}\ M$$

Indicator reaction

$$2\,Ag^+ + CrO_4^{2-} \rightleftharpoons \underset{red}{Ag_2CrO_4(s)}$$

Adsorption Indicators: The Fajans Method

An **adsorption indicator** is an organic compound that tends to be adsorbed onto the surface of the solid in a precipitation titration. Ideally, the adsorption (or desorption) occurs near the equivalence point and results not only in a color change but also in a transfer of color from the solution to the solid (or the reverse). Fluorescein is a typical adsorption indicator that is useful for the titration of chloride ion with silver nitrate. In aqueous solution, fluorescein partially dissociates into hydronium ions and negatively charged fluoresceinate ions that are yellow-green. The fluoresceinate ion forms an intensely red silver salt. Whenever this dye is used as an indicator, however, its concentration is never large enough to precipitate as silver fluoresceinate.



fluorescein

Iron (III) Ion; the Volhard Method:

In the Volhard method, silver ions are titrated with a standard solution of thiocyanate ion:

$$\underset{excess}{Ag^+} + Cl^- \rightleftharpoons \underset{white}{AgCl(s)} \qquad SCN^- + Ag^+ \rightleftharpoons \underset{white}{AgSCN(s)}$$

Iron (III) serves as the indicator. The solution turns red with the first slight excess of thiocyanate ion:

$$Fe^{3+} + SCN^- \rightleftharpoons \underset{red}{FeSCN^{2+}} \qquad K_f = 1.05\times10^3 = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$$

The titration must be carried out in acidic solution to prevent precipitation of iron (III) as the hydrated oxide.

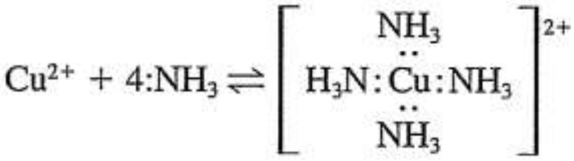
The indicator concentration is not critical in the Volhard titration.

The most important application of the Volhard method is the indirect determination of halide ions. A measured excess of standard silver nitrate solution is added to the sample, and the excess silver is determined by back-titration with a standard thiocyanate solution. The strong acidic environment required for the Volhard procedure represents a distinct advantage over other titrimetric methods of halide analysis because such ions as carbonate, oxalate, and arsenate (which form slightly soluble silver salts in neutral media but not in acidic media) do not interfere.

Complexes and Formation Constants:

Complexes play an important role in many chemical and biochemical processes.

Many cations will form complexes in solution with a variety of substances that have a pair of unshared electrons (e.g., on N, O, S atoms in the molecule) capable of satisfying the coordination number of the metal, [The metal ion is a Lewis acid (electron pair acceptor), and the complexer is a Lewis base (electron pair donor).] The number of molecules of the complexing agent, called the ligand, will depend on the coordination number of h e metal and on the number of complexing groups on the ligand molecule. Ammonia is a simple complexing agent with one pair of unshared electrons that will complex copper ion:



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

Ammonia will also complex with silver ion to form a colorless complex. Two ammonia molecules complex with each silver ion in a stepwise fashion and we can write an equilibrium constant for each step, called the formation constant K_f.

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

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

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ \quad K_f = K_{f1} \cdot K_{f2} = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 2.5 \times 10^7$$

For the formation of a simple 1:1 complex, for example, M + L = ML, the formation constant is simply K_f = [M] [L] / [ML].

The formation constant is also called the stability constant K_s, K_{stable} .

The equilibrium constants are simply the reciprocals of the formation constants, and they are called instability constants K_i, or dissociation constants K_d

You can use either constant calculation, as long as you use it with the proper reaction and the correct expression.

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

The donor species, or **ligand,** must have at least one pair of unshared electrons available for bond formation. Water, ammonia, and halide ions are common inorganic ligands. In fact, most metal ions in aqueous solution actually exist as aqua complexes. Copper (II) in aqueous solution, for example, is readily complexed by water molecules to form species such as Cu $(H_2O)_4^{2+}$. We often simplify such complexes in chemical equations by writing the metal ion as if it were uncomplexed Cu^{2+}.

Complexation Equilibria:

Complexation reactions involve a metal ion M reacting with a ligand L to form a complex ML, as shown in Equation:

$$M + L \rightleftharpoons ML$$

Complexation reactions occur in a stepwise fashion; the reaction in equation is often followed by additional reactions:

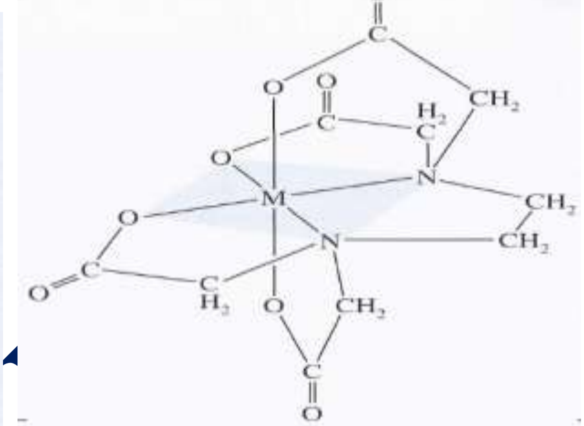
$$\begin{aligned} ML + L &\rightleftharpoons ML_2 \\ ML_2 + L &\rightleftharpoons ML_3 \\ \vdots \quad & \quad \vdots \\ ML_{n-1} + L &\rightleftharpoons ML_n \end{aligned}$$

The equilibrium constants for complex formation reactions are generally written as formation constants. Thus, each of the Reactions is associated with a stepwise formation constant, K_1 through K_4. For example, K_1 = [ML] /[M] [L], K_2 = [ML_2] / [ML] [L], and so on.

These have overall formation constants designated by the symbol β_n Thus, shown below.

For a given species like ML, we can calculate an alpha value, which is the fraction of the total metal concentration existing in that form.

$$\begin{aligned} M + L &\rightleftharpoons ML & \beta_1 &= \frac{[ML]}{[M][L]} = K_1 \\ M + 2L &\rightleftharpoons ML_2 & \beta_2 &= \frac{[ML_2]}{[M][L]^2} = K_1K_2 \\ M + 3L &\rightleftharpoons ML_3 & \beta_3 &= \frac{[ML_3]}{[M][L]^3} = K_1K_2K_3 \\ \vdots \quad & \quad \vdots \\ M + nL &\rightleftharpoons ML_n & \beta_n &= \frac{[ML_n]}{[M][L]^n} = K_1K_2 \cdots K_n \end{aligned}$$



Thus, α_M is the fraction of the total metal present at equilibrium as the free metal, α_{ML} is the fraction present as ML, and so on. As derived in Feature, the alpha values are given by

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

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

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

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

Q3/A divalent metal M^{2+} reacts with a ligand L to from 1:1 complex

$M^{+2} + L \longleftrightarrow ML^{+2}$ $\qquad K_f = [ML^{+2}] / [M^{+2}][L] = 1.0x\ 1^8$

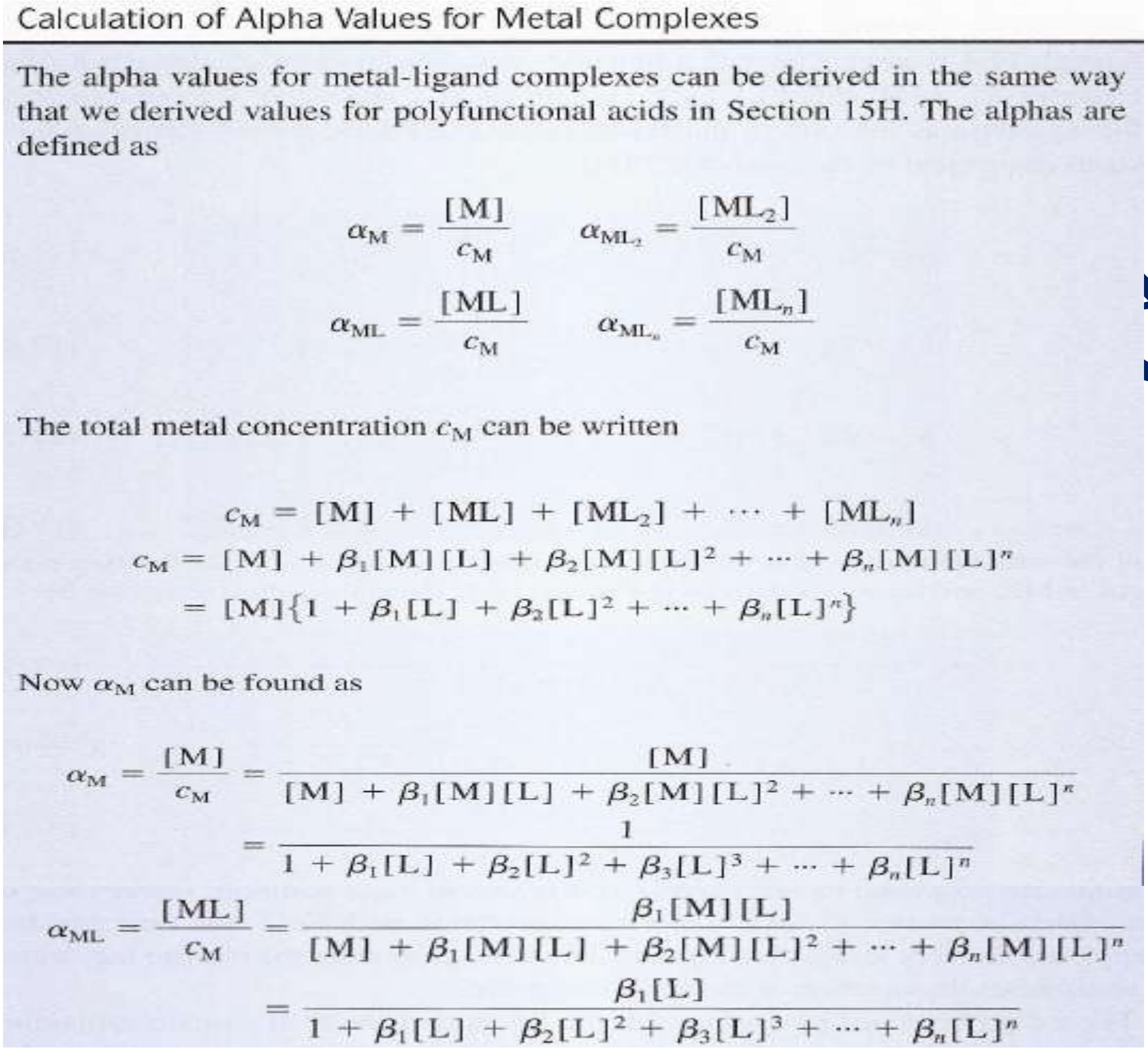
Calculate the conc. of M^{2+} in a solution prepared by mixing equal volume of 0.2 M (M^{2+}) and 0.2 M L

$K_f = [ML^{+2}] / [M^{+2}][L] = 1.0x\ 1^8 = 0.1 / (X)(X)$

$(X^2) = 0.1 / 1.0\text{x } 1^8$

$(X) = [M^{+2}] = \sqrt{0.1} / 1.0\text{x } 1^8$

$= 3.2 \text{ x } 10^{-5}$



Calculation of Alpha Values for Metal Complexes

The alpha values for metal-ligand complexes can be derived in the same way that we derived values for polyfunctional acids in Section 15H. The alphas are defined as

$$\alpha_M = \frac{[M]}{c_M} \qquad \alpha_{ML_2} = \frac{[ML_2]}{c_M}$$

$$\alpha_{ML} = \frac{[ML]}{c_M} \qquad \alpha_{ML_n} = \frac{[ML_n]}{c_M}$$

The total metal concentration c_M can be written

$$c_M = [M] + [ML] + [ML_2] + \cdots + [ML_n]$$

$$c_M = [M] + \beta_1[M][L] + \beta_2[M][L]^2 + \cdots + \beta_n[M][L]^n$$

$$= [M]\{1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n\}$$

Now α_M can be found as

$$\alpha_M = \frac{[M]}{c_M} = \frac{[M]}{[M] + \beta_1[M][L] + \beta_2[M][L]^2 + \cdots + \beta_n[M][L]^n}$$

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

$$\alpha_{ML} = \frac{[ML]}{c_M} = \frac{\beta_1[M][L]}{[M] + \beta_1[M][L] + \beta_2[M][L]^2 + \cdots + \beta_n[M][L]^n}$$

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

Complexometric titrations:

Titrimetric methods based on complex formation, sometimes called **complexometric methods,** have been used for more than a century.

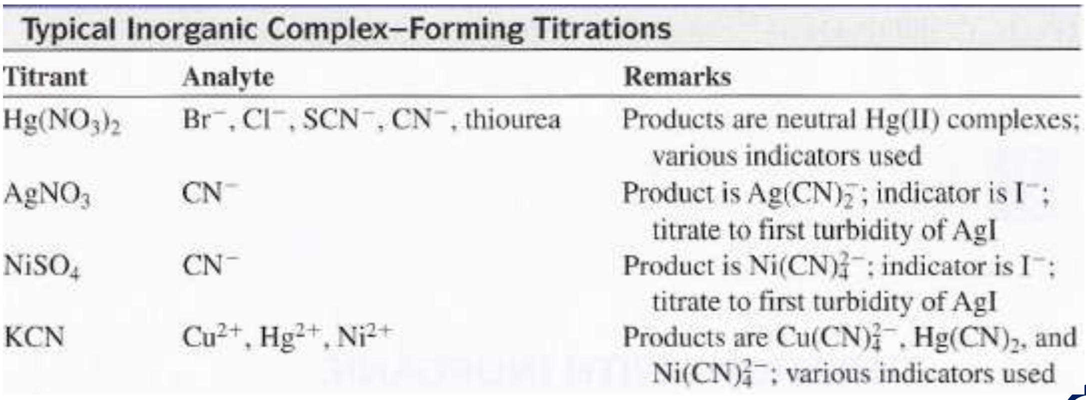
A chelate is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five - or six-member heterocyclic ring.

A ligand that has a single donor group, such as ammonia, is called **unidentate** (single -toothed), whereas one such as glycine, which has two groups available for covalent bonding, is called **bidentate.** Tridentate, tetradentate, pentadentate, and hexadentate chelating agents are also known.

Here, a metal ion reacts with a suitable ligand to form a complex, and the equivalence point is determined by an indicator or an appropriate instrumental method.

The progress of a complexometric titration is generally illustrated by a titration curve, which is usually a plot of pM = - log [M] as a function of the volume of titrant added. Most often, in complexometric titrations the ligand is the titrant and the metal ion the analyte, although occasionally the reverse is true.

The most widely used complexometric titration employing a unidentate ligand is the titration of cyanide with silver nitrate, a method introduced by Liebig in the 1850s. This method involves the formation of the soluble Ag $(CN)_2$. Other common inorganic complexing agents and their applications are listed in Table.



Typical Inorganic Complex–Forming Titrations

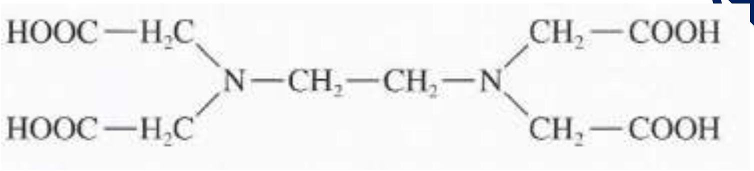
Titrant	Analyte	Remarks
$Hg(NO_3)_2$	Br^-, Cl^-, SCN^-, CN^-, thiourea	Products are neutral Hg(II) complexes; various indicators used
$AgNO_3$	CN^-	Product is $Ag(CN)_2^-$; indicator is I^-; titrate to first turbidity of AgI
$NiSO_4$	CN^-	Product is $Ni(CN)_4^{2-}$; indicator is I^-; titrate to first turbidity of AgI
KCN	Cu^{2+}, Hg^{2+}, Ni^{2+}	Products are $Cu(CN)_4^{2-}$, $Hg(CN)_2$, and $Ni(CN)_4^{2-}$; various indicators used

Amonocarboxylic acid titration:

Tertiary amines that also contain carboxylic acid groups form remarkably stable chelates with many metal ions.

Ethylenediaminetetraacetic Acid (EDTA):

Ethylenediaminetetraacetic acid-also called (ethylenedinitrilo) tetraacetic acid which is commonly shortened to EDTA, is the most widely used complexometric titrant. EDTA has the structural formula:



The EDTA molecule has six potential sites for bonding a metal ion: the four carboxyl groups and the two amino groups, each of the latter with an unshared pair of electrons. Thus, EDTA is a hexadentate ligand.

Complexes of EDTA and Metal Ions:

EDTA is a remarkable reagent not only because it forms chelates with all cations except alkali metals but also because most of these chelates are sufficiently stable for titrations. Solutions of EDTA are particularly valuable as titrants because the reagent combines with metal ions in a 1:1 ratio regardless of the charge on the cation. For example, the silver and aluminum complexes are formed by the reactions:

$$Ag^+ + Y^{4-} \rightleftharpoons AgY^{3-}$$

$$Al^{3+} + Y^{4-} \rightleftharpoons AlY^-$$

Formation Constants for EDTA Complexes

Cation	K_{MY}*	log K_{MY}	Cation	K_{MY}	log K_{MY}
Ag^+	2.1×10^7	7.32	Cu^{2+}	6.3×10^{18}	18.80
Mg^{2+}	4.9×10^8	8.69	Zn^{2+}	3.2×10^{16}	16.50
Ca^{2+}	5.0×10^{10}	10.70	Cd^{2+}	2.9×10^{16}	16.46
Sr^{2+}	4.3×10^8	8.63	Hg^{2+}	6.3×10^{21}	21.80
Ba^{2+}	5.8×10^7	7.76	Pb^{2+}	1.1×10^{18}	18.04
Mn^{2+}	6.2×10^{13}	13.79	Al^{3+}	1.3×10^{16}	16.13
Fe^{2+}	2.1×10^{14}	14.33	Fe^{3+}	1.3×10^{25}	25.1
Co^{2+}	2.0×10^{16}	16.31	V^{3+}	7.9×10^{25}	25.9
Ni^{2+}	4.2×10^{18}	18.62	Th^{4+}	1.6×10^{23}	23.2

Table above lists formation constants K_{MY} for common EDTA complexes. Note that the constant refers to the equilibrium involving the fully unprotonated species Y^{4-} with the metal ion:

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+} \qquad K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}][Y^{4-}]}$$

Equilibrium Calculations Involving EDTA:

A titration curve for the reaction of a cation M^{n+} with EDTA consists of a plot of pM versus reagent volume.

Fortunately, EDTA titrations are always performed in solutions that are buffered to a known pH to avoid interference by other cations or to ensure satisfactory indicator behavior. Calculating $[M^{n+}]$ in a buffered solution containing EDTA is a relatively straightforward procedure provided that the pH is known. **In** this computation, use is made of the alpha value for H_4Y. that α_4 for H_4Y can be defined as:

$$\alpha_4 = \frac{[Y^{4-}]}{c_T}$$

where C_T is the total molar concentration of uncomplexed EDTA:

$$c_T = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y]$$

Conditional Formation Constants:

To obtain the conditional formation constant for the equilibrium, we substitute $\alpha_4 C_T$from for $[Y^{4-}]$ in the formation constant expression:

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+} \qquad K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\alpha_4 c_T}$$

Combining the two constants α_4 and K_{MY} yields the conditional formation constant K'_{MY}

$$K'_{MY} = \alpha_4 K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]c_T}$$

where K'_{MY} is a constant *only at the pH for which α_4 is applicable.*

Conditional constants are readily computed and provide a simple means by which the equilibrium concentration of the metal ion and the complex can be calculated at the equivalence point and where there is an excess of reactant. Note that replacement of $[Y^{4-}]$ with C_T in the equilibrium-constant expression greatly simplifies calculations because C_T is easily determined from the reaction stoichiometry, whereas is $[Y^{4-}]$ not.

Computing α_4 Values for EDTA Solutions:

Thus, α_4 for EDTA is where K_1, K_2, K_3, and K_4 are the four dissociation constants for H_4Y and D is the denominator of Equation:

$$\alpha_0 = [H^+]^4/D \qquad \alpha_2 = K_1K_2[H^+]^2/D$$
$$\alpha_1 = K_1[H^+]^3/D \qquad \alpha_3 = K_1K_2K_3[H^+]/D$$

$$\alpha_4 = \frac{K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4} \qquad \alpha_4 = \frac{K_1K_2K_3K_4}{D}$$

The example illustrates how Y^{4-} is calculated for a solution of known pH.

Calculate the molar Y^{4-} concentration in a 0.0200 M EDTA solution buffered to a pH of 10.00.

At pH 10.00, α_4 is 0.35 (see Figure 17-4). Thus,

$$[Y^{4-}] = \alpha_4 c_T = 0.35 \times 0.0200 = 7.00 \times 10^{-3}\ M$$

Calculate the fraction of EDTA that exists as Y^{4-} at pH 10, and from this calculate pCa in 100 mL of solution of 0.100 *M* Ca^{2+} at pH 10 after adding 100 mL of 0.100 *M* EDTA.

Solution

From Equation 9.12,

$$\frac{1}{\alpha_4} = 1 + \frac{1.0 \times 10^{-10}}{5.5 \times 10^{-11}} + \frac{(1.0 \times 10^{-10})^2}{(6.9 \times 10^{-7})(5.5 \times 10^{-11})}$$
$$+ \frac{(1.0 \times 10^{-10})^3}{(2.2 \times 10^{-3})(6.9 \times 10^{-7})(5.5 \times 10^{-11})}$$
$$+ \frac{(1.0 \times 10^{-10})^4}{(1.0 \times 10^{-2})(2.2 \times 10^{-3})(6.9 \times 10^{-7})(5.5 \times 10^{-11})}$$
$$= 1 + 1.82 + 2.6 \times 10^{-4} + 1.2 \times 10^{-11} + 1.2 \times 10^{-19} = 2.82$$
$$\alpha_4 = 0.35$$

Stoichiometric amounts of Ca^{2+} and EDTA are added to produce an equivalent amount of CaY^{2-}, less the amount dissociated:

$$\text{mmol } Ca^{2+} = 0.100\ M \times 100\ \text{mL} = 10.0\ \text{mmol}$$
$$\text{mmol EDTA} = 0.100\ M \times 100\ \text{mL} = 10.0\ \text{mmol}$$

We have formed 10.0 mmol CaY^{2-} in 200 mL, or 0.0500 *M*:

$$\begin{array}{lll} Ca^{2+} + & \text{EDTA} \rightleftharpoons & CaY^{2-} \\ x & x & 0.0500\ M - x \\ & & \approx 0.0500\ M \text{ (since } K_f \text{ is large)} \end{array}$$

where x represents the total equilibrium EDTA concentration in all forms, C_{H_4Y}. $[Y^{4-}]$, needed to apply Equation 9.10, is equal to $\alpha_4 C_{H_4Y}$. Hence, we can write Equation 9.10 as:

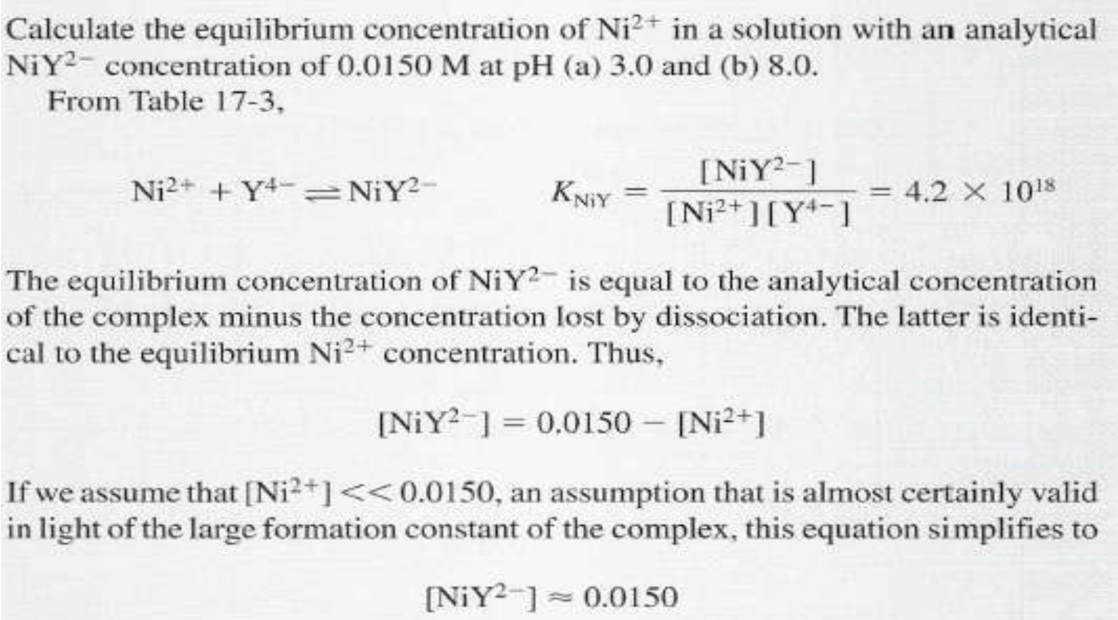
$$K_f = \frac{[CaY^{2-}]}{[Ca^{2+}]\alpha_4[C_{H_4Y}]}$$

From Appendix C, $K_f = 5.0 \times 10^{10}$. Hence,

$$5.0 \times 10^{10} = \frac{0.0500}{(x)(0.35)(x)}$$
$$x = 1.7 \times 10^{-6}\ M$$
$$\text{pCa} = 5.77$$

Calculation of the Cation Concentration in EDTA Solutions:

In an EDTA titration, we are interested in finding the cation concentration as a function of f the amount if titrant (EDTA) added. Prior to the equivalence point, the canon is in excess, and its concentration can be found from the reaction stoichiometry. At the equivalence point and in the postequivalence-point region, however, the conditional formation constant of the complex must be used to calculate the cation concentration. Example below demonstrates how the cation concentration can be calculated in a solution of an EDTA complex. Example illustrates this calculation when excess EDTA is present.



Calculate the equilibrium concentration of Ni^{2+} in a solution with an analytical NiY^{2-} concentration of 0.0150 M at pH (a) 3.0 and (b) 8.0.

From Table 17-3,

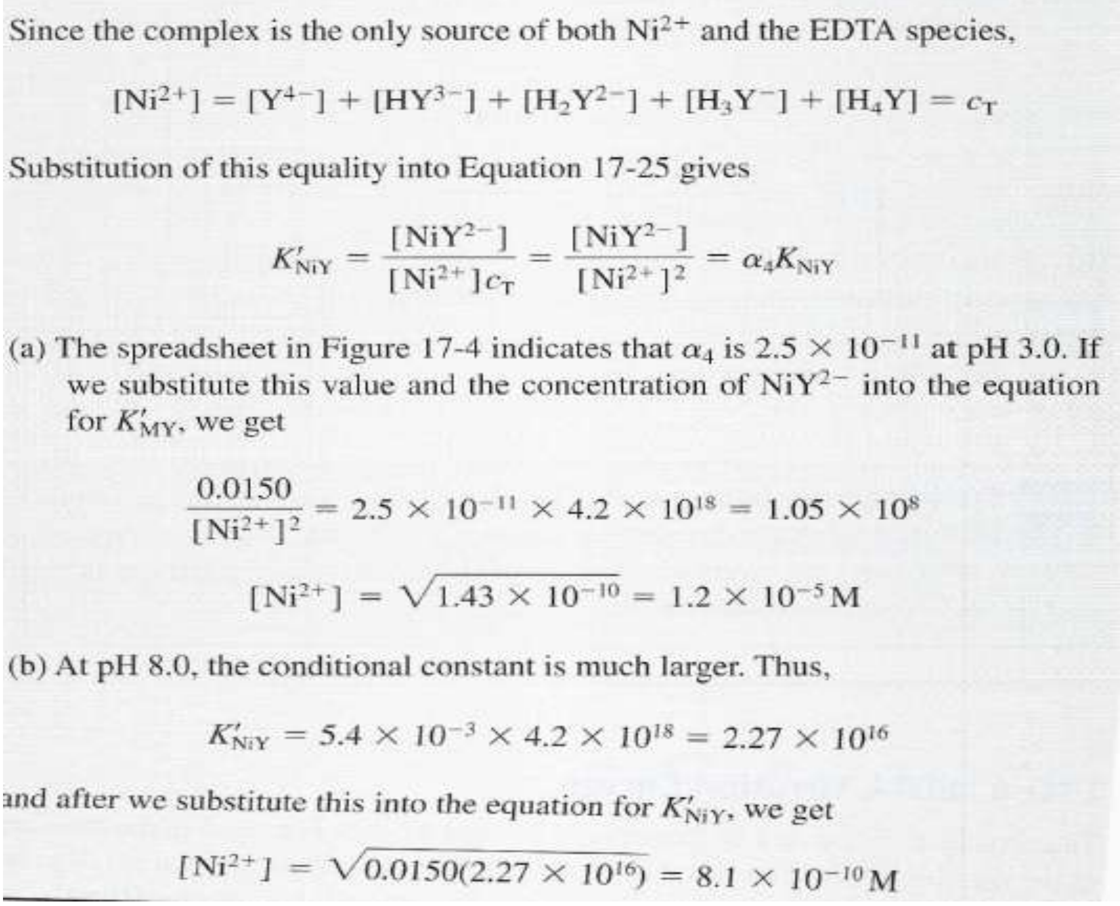
$$Ni^{2+} + Y^{4-} \rightleftharpoons NiY^{2-} \qquad K_{NiY} = \frac{[NiY^{2-}]}{[Ni^{2+}][Y^{4-}]} = 4.2 \times 10^{18}$$

The equilibrium concentration of NiY^{2-} is equal to the analytical concentration of the complex minus the concentration lost by dissociation. The latter is identical to the equilibrium Ni^{2+} concentration. Thus,

$$[NiY^{2-}] = 0.0150 - [Ni^{2+}]$$

If we assume that $[Ni^{2+}] << 0.0150$, an assumption that is almost certainly valid in light of the large formation constant of the complex, this equation simplifies to

$$[NiY^{2-}] \approx 0.0150$$



Since the complex is the only source of both Ni^{2+} and the EDTA species,

$$[Ni^{2+}] = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y] = c_T$$

Substitution of this equality into Equation 17-25 gives

$$K'_{NiY} = \frac{[NiY^{2-}]}{[Ni^{2+}]c_T} = \frac{[NiY^{2-}]}{[Ni^{2+}]^2} = \alpha_4 K_{NiY}$$

(a) The spreadsheet in Figure 17-4 indicates that α_4 is 2.5×10^{-11} at pH 3.0. If we substitute this value and the concentration of NiY^{2-} into the equation for K'_{MY}, we get

$$\frac{0.0150}{[Ni^{2+}]^2} = 2.5 \times 10^{-11} \times 4.2 \times 10^{18} = 1.05 \times 10^{8}$$

$$[Ni^{2+}] = \sqrt{1.43 \times 10^{-10}} = 1.2 \times 10^{-5} M$$

(b) At pH 8.0, the conditional constant is much larger. Thus,

$$K'_{NiY} = 5.4 \times 10^{-3} \times 4.2 \times 10^{18} = 2.27 \times 10^{16}$$

and after we substitute this into the equation for K'_{NiY}, we get

$$[Ni^{2+}] = \sqrt{0.0150/(2.27 \times 10^{16})} = 8.1 \times 10^{-10} M$$

EDTA Titration Curves:

Use a spreadsheet to construct the titration curve of pCa versus volume of EDTA for 50.0 mL of 0.00500 M Ca^{2+} being titrated with 0.0100 M EDTA in a solution buffered to a constant pH of 10.0.

Initial Entries

The spreadsheet is shown in Figure 17-5. The initial volume of Ca^{2+} is entered into cell B3, and the initial Ca^{2+} concentration is entered into E2. The EDTA concentration is entered into cell E3. The volumes for which pCa values are to be calculated are entered into cells A5 through A19.

Calculating the Conditional Constant

The conditional formation constant for the calcium/EDTA complex at pH 10 is obtained from the formation constant of the complex (see Table 17-3) and the α_4 value for EDTA at pH 10 (see Figure 17-4). Thus, if we substitute into Equation 17-25, we get

$$K'_{CaY} = \frac{[CaY^{2-}]}{[CaY^{2+}]c_T} = \alpha_4 K_{CaY}$$
$$= 0.35 \times 5.0 \times 10^{10} = 1.75 \times 10^{10}$$

This value is entered into cell B2.

Preequivalence-Point Values for pCa

The initial $[Ca^{2+}]$ at 0.00 mL titrant is just the value in cell E2. Hence, `=E2` is entered into cell B5. The initial pCa is calculated from the initial $[Ca^{2+}]$ by taking the negative logarithm, as shown in the documentation for cell E5 (cell A26). This formula is copied into cells E6 through E19. For the other entries prior to the equivalence point, the equilibrium concentration of Ca^{2+} is equal to the untitrated excess of the cation plus any dissociation of the complex, the latter being equal numerically to c_T. Usually, c_T is small relative to the analytical concentration of the uncomplexed calcium ion. Thus, for example, after 5.00 mL of EDTA has been added,

$$[Ca^{2+}] = \frac{50.0 \text{ mL} \times 0.00500 \text{ M} - 5.00 \text{ mL} \times 0.0100 \text{ M}}{(50 + 5.00) \text{ mL}} + c_T$$
$$\approx \frac{50.0 \text{ mL} \times 0.00500 \text{ M} - 5.00 \text{ mL} \times 0.0100 \text{ M}}{55.00 \text{ mL}}$$

We thus enter into cell B6 the formula shown in the documentation section of the spreadsheet (cell A21). The reader should verify that the spreadsheet formula is equivalent to the expression for $[Ca^{2+}]$ just given. The volume of titrant (A6) is the only value that changes in this preequivalence-point region. Hence, other preequivalence-point values of pCa are calculated by copying the formula in cell B6 into cells B7 through B10.

Equivalence-Point pCa

At the equivalence point (25.00 mL of EDTA), we follow the method shown in Example 17-2 and first compute the analytical concentration of CaY^{2-}:

$$c_{CaY^{2-}} = \frac{(50.0 \times 0.00500)\ \text{mmol}}{(50.0 + 25.0)\ \text{mL}}$$

The only source of Ca^{2+} ions is the dissociation of the complex. It also follows that the Ca^{2+} concentration must be equal to the sum of the concentrations of the uncomplexed EDTA, c_T. Thus,

$$[Ca^{2+}] = c_T \qquad \text{and} \qquad [CaY^{2-}] = c_{CaY^{2-}} - [Ca^{2+}] \approx c_{CaY^{2-}}$$

The formula for $[CaY^{2-}]$ is thus entered into cell C11, as shown in the documentation in cell A24. The reader should again be able to verify this formula. To obtain $[Ca^{2+}]$, we substitute into the expression for K'_{CaY},

$$K'_{CaY} = \frac{[CaY^{2-}]}{[Ca^{2+}]c_T} \approx \frac{c_{CaY^{2-}}}{[Ca^{2+}]^2}$$

$$[Ca^{2+}] = \sqrt{\frac{c_{CaY^{2-}}}{K'_{CaY}}}$$

We thus enter into cell B11 the formula corresponding to this expression, as shown in cell A22.

Postequivalence-Point pCa

Beyond the equivalence point, analytical concentrations of CaY^{2-} and EDTA are obtained directly from the stoichiometric data. Since there is now excess EDTA, a calculation similar to that in Example 17-3 is performed. Thus, after the addition of 26.0 mL of EDTA, we can write

$$c_{CaY^{2-}} = \frac{(50.0 \times 0.00500)\ \text{mmol}}{(50.0 + 26.0)\ \text{mL}}$$

$$c_{EDTA} = \frac{(26.0 \times 0.0100)\ \text{mL} - (50.0 \times 0.00500)\ \text{mL}}{76.0\ \text{mL}}$$

As an approximation,

$$[CaY^{2-}] = c_{CaY^{2-}} - [Ca^{2+}] \approx c_{CaY^{2-}} = \frac{(50.0 \times 0.00500)\ \text{mmol}}{(50.0 + 26.0)\ \text{mL}}$$

Since this expression is the same as that previously entered into cell C11, we copy that equation into cell C12. We also note that $[CaY^{2-}]$ will be given by this same expression (with the volume varied) throughout the remainder of the titration. Hence, the formula in cell C12 is copied into cells C13 through C19. Also, we approximate

$$c_T = c_{EDTA} + [Ca^{2+}] \approx c_{EDTA} = \frac{(26.0 \times 0.0100)\ \text{mL} - (50.0 \times 0.00500)\ \text{mL}}{76.0\ \text{mL}}$$

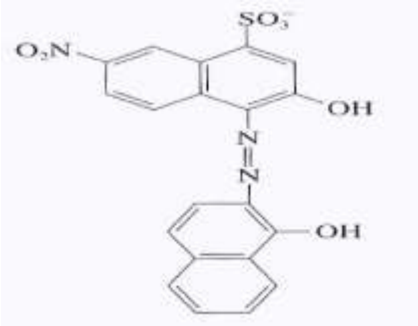
We enter this formula into cell D12 as shown in the documentation (cell A25) and copy it into cells D13 through D16.

To calculate $[Ca^{2+}]$, we then substitute into the conditional formation-

Indicators for EDTA Titrations:

In general, these indicators are organic dyes that form colored chelates with metal ions in a pM range that is characteristic of the particular cation and dye. The complexes are often intensely colored and are discernible to the eye at concentrations in the range of 10^{-6} to 10^{-7} M.

Eriochrome Black T is a typical metal ion indicator that is used in the titration of several common cations. The structural formula of Eriochrome Black T is shown in Figure. Its behavior as a weak acid is described by the equations:



$$H_2O + \underset{\text{red}}{H_2In^-} \rightleftharpoons \underset{\text{blue}}{HIn^{2-}} + H_3O^+ \qquad K_1 = 5 \times 10^{-7}$$

$$H_2O + \underset{\text{blue}}{HIn^{2-}} \rightleftharpoons \underset{\text{orange}}{In^{3-}} + H_3O^+ \qquad K_2 = 2.8 \times 10^{-12}$$

Titration Methods Employing EDTA:

Direct Titration:

Many of the metals in the periodic table can be determined by titration with standard EDTA solutions. Some methods are based on indicators that respond to the analyte itself, while others are based on an added metal ion.

Potentiometric Methods Potential measurements can be used for end point detection in the EDTA titration of those metal ions for which specific ion electrodes are available.

Spectrophotometric Methods Measurement of UV/VIS absorption can also be used to determine the end points of titrations. In these cases, an instrument responds to the color change in the titration rather than relying on a visual determination of the end point.

Back-titration Methods:

Back-titration is useful for the determination of cations that form stable EDTA complexes and for which a satisfactory indicator is not available. A measured excess of standard EDTA solution is added to the analyte solution. After the reaction is judged complete, the excess EDTA is back-titrated with a standard magnesium or zinc ion solution to an Eriochrome Black T.

Displacement Methods:

In displacement titrations, an unmeasured excess of a solution containing the magnesium or zinc complex of EDTA is introduced into the analyte solution. If the analyte forms a more stable complex than that of magnesium or zinc, the following displacement reaction occurs:

$$MgY^{2-} + M^{2+} \rightarrow MY^{2-} + Mg^{2+}$$

where M^{2+} represents the analyte cation. The liberated Mg^{2+} or, in some cases Zn^{2+}, is then titrated with a standard EDTA solution.

The Determination of Water Hardness:

The determination of hardness is a useful analytical test that provides a measure of the quality of water for household and industrial uses. The test is important to industry because hard water, on being heated, precipitates calcium carbonate, which clogs boilers and pipes.

Water hardness is ordinarily determined by an EDTA titration after the sample has been buffered to pH 10. Magnesium, which forms the least stable EDTA complex of all of the common multivalent cations in typical water samples, is not titrated until enough reagent has been added to complex all of the other cations in the sample. Therefore, a magnesium ion indicator, such as Calmagite or Eriochrome

Black T can serve as indicator in water hardness titrations. Often, a small concentration of the magnesium-EDTA chelate is incorporated into the buffer or the titrant to ensure sufficient magnesium ions for satisfactory indicator action.

Oxidation – reduction reactions:

In an **oxidation/reduction reaction,** electrons are transferred from one reactant to another. An example is the oxidation of iron (II) ions by cerium (IV) ions. The reaction is described by the equation:

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

A substance that has a strong affinity for electrons, such as Ce^{4+}, is called an **oxidizing agent,** or an **oxidant. A reducing agent, or reductant,** is a species, such as Fe^{2+}, that easily donates electrons to another species.

We can split any oxidation/reduction equation into two half-reactions that show which species gains electrons and which loses them. For example, Equation is the sum of the two half-reactions:

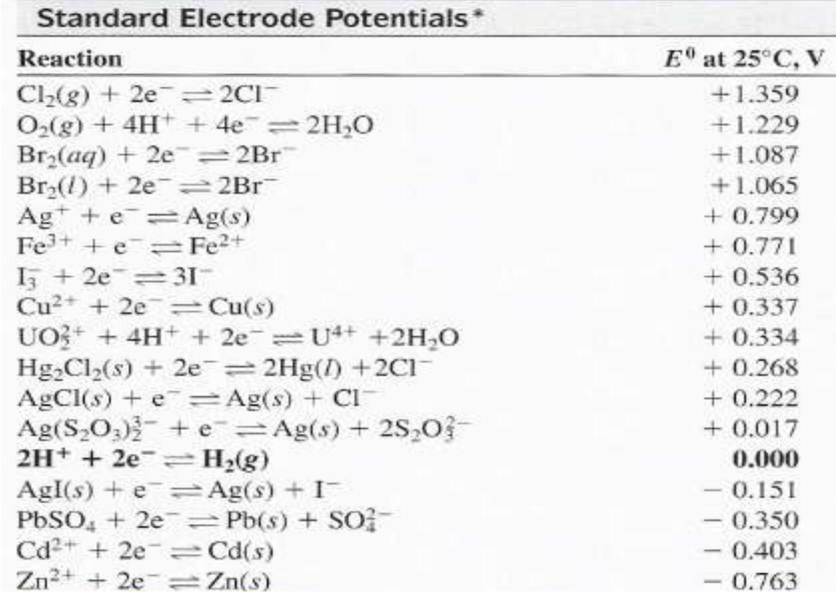
$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad \text{(reduction of } Ce^{4+}\text{)} \qquad Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \qquad \text{(oxidation of } Fe^{2+}\text{)}$$

Thus, for the oxidation of Fe^{2+} by MnO^-_4, the half-reactions are:

$$MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O \qquad 5Fe^{2+} \rightleftharpoons 5Fe^{3+} + 5e^-$$

An electrode potential is defined as the potential of a cell in which the electrode in question is the right-hand electrode and the standard hydrogen electrode is the left hand electrode.

The standard electrode potential, *E_O*, of a half-reaction is defined as its electrode potential when the activities of the reactants and products are all unity.



Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+ 0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+ 0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+ 0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+ 0.337
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+ 0.334
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+ 0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+ 0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+ 0.017
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	**0.000**
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	− 0.151
$PbSO_4 + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	− 0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	− 0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	− 0.763

The potential of a cell is the difference between two half-cell or single-electrode potentials, one associated with the half-reaction at the right-hand electrode (E_{right}), the other associated with the half-reaction at the left-hand electrode (E_{1eft}). According to the IUPAC sign convention we may write the cell potential E_{cell} as

$$E_{cell} = E_{right} - E_{left}$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d \cdots}{[A]^a[B]^b \cdots}$$

E^0 = the *standard electrode potential*, which is characteristic for each half-reaction
R = the ideal gas constant, 8.314 J K^{-1} mol^{-1}
T = temperature, K
n = number of moles of electrons that appears in the half-reaction for the electrode process as written
F = the faraday = 96,485 C (coulombs) per mole of electrons
ln = natural logarithm = 2.303 log

$$E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c[D]^d \cdots}{[A]^a[B]^b \cdots}$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^0 = +0.771 \text{ V}$$

does not change if we choose to write the reaction as

$$5Fe^{3+} + 5e^- \rightleftharpoons 5Fe^{2+} \qquad E^0 = +0.771 \text{ V}$$

Note, however, that the Nernst equation must be consistent with the half-reaction as written. For the first case, it will be

$$E = 0.771 - \frac{0.0592}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

and for the second

$$E = 0.771 - \frac{0.0592}{5} \log \frac{[Fe^{2+}]^5}{[Fe^{3+}]^5} = 0.771 - \frac{0.0592}{5} \log \left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)^5$$

$$= 0.771 - \frac{\cancel{5} \times 0.0592}{\cancel{5}} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Calculate the thermodynamic potential of the following cell:

$$Cu|Cu^{2+}(0.0200 \text{ M})||Ag^+(0.0200 \text{ M})|Ag$$

Note that the two half-reactions and standard potentials are:

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad E^0 = 0.799 \text{ V}$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s) \qquad E^0 = 0.337 \text{ V}$$

The electrode potentials are:

$$E_{Ag^+/Ag} = 0.799 - 0.0592 \log \frac{1}{0.0200} = 0.6984 \text{ V}$$

$$E_{Cu^{2+}/Cu} = 0.337 - \frac{0.0592}{2} \log \frac{1}{0.0200} = 0.2867 \text{ V}$$

We see from the cell diagram that the silver electrode is the right-hand electrode and the copper electrode is the left-hand electrode. Therefore, application of
Equation gives:

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{Ag}^+/\text{Ag}} - E_{\text{Cu}^{2+}/\text{Cu}} = 0.6984 - 0.2867 = +0.412\ \text{V}$$

Constructing of redox titration curves:

Electrode Potentials during Redox Titrations:

Consider the redox titration of iron (II) with a standard solution of cerium (IV). This reaction is widely used for the determination of iron in various kinds of samples. The titration reaction is:

$$\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$$

Consequently, the electrode potentials for the two half reactions are always identical; that is:

$$E_{\text{Ce}^{4+}/\text{Ce}^{3+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{system}}$$

Where we have termed E_{system} as the **potential of the system.** If a redox indicator has been added to this solution, the ratio of the concentrations of its oxidized and reduced forms must adjust so that the electrode potential for the indicator, E_{In}, is also equal to the system potential; thus, we may write:

$$E_{\text{In}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{system}}$$

We can calculate the electrode potential of a system from standard potential data. Thus, for the reaction under consideration, the titration mixture is treated as if it were part of the hypothetical cell:

$$\text{SHE} \| \text{Ce}^{4+}, \text{Ce}^{3+}, \text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$$

Where SHE symbolizes the standard hydrogen electrode. The potential of the platinum electrode with respect to the standard hydrogen electrode is determined by the tendencies of iron (III) and cerium (IV) to accept electrons-that is, by the tendencies of the following half-reactions to occur:

$$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$$

$$\text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+}$$

At the equivalence point in the titration of iron (II) with cerium (IV), the potential of the system is given by both:

$$E_{\text{eq}} = E^0_{\text{Ce}^{4+}/\text{Ce}^{3+}} - \frac{0.0592}{1}\log\frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \qquad E_{\text{eq}} = E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} - \frac{0.0592}{1}\log\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \qquad \begin{array}{l}[\text{Fe}^{3+}] = [\text{Ce}^{3+}] \\ [\text{Fe}^{2+}] = [\text{Ce}^{4+}]\end{array}$$

$$2E_{\text{eq}} = E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} + E^0_{\text{Ce}^{4+}/\text{Ce}^{3+}} - \frac{0.0592}{1}\log\frac{\cancel{[\text{Ce}^{3+}]}\cancel{[\text{Ce}^{4+}]}}{\cancel{[\text{Ce}^{4+}}\cancel{[\text{Ce}^{3+}]}} = E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} + E^0_{\text{Ce}^{4+}/\text{Ce}^{3+}}$$

$$E_{\text{eq}} = \frac{E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} + E^0_{\text{Ce}^{4+}/\text{Ce}^{3+}}}{2}$$

The Titration Curve:

Consider the titration of 50.00 ml of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0M in H_2SO_4 at all times. Formal potential data for both half-cell processes are available in Appendix 4 and are used for these calculations. That is:

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^{0'} = 1.44\ V\ (1\ M\ H_2SO_4)$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^{0'} = 0.68\ V\ (1\ M\ H_2SO_4)$$

Initial Potential:

In any case, we do not have enough information to calculate an initial potential.

Potential after the Addition of 5.00 mL of Cerium (IV):

When oxidant is added, Ce^{3+} and Fe^{3+} are formed, and the solution contains appreciable and easily calculated concentrations of three of the participants; that of the fourth, Ce^{4+}, is vanishingly small. Therefore, it is more convenient to use the concentrations of the two iron species to calculate the electrode potential of the system. The equilibrium concentration of Fe (III) is equal to its analytical concentration less the equilibrium concentration of the unreacted Ce (IV):

$$[Fe^{3+}] = \frac{5.00 \times 0.1000}{50.00 + 5.00} - [Ce^{4+}] = \frac{0.500}{55.00} - [Ce^{4+}]$$

Similarly, the Fe^{2+} concentration is given by its molarity plus the equilibrium concentration of unreacted $[Ce^{4+}]$:

$$[Fe^{2+}] = \frac{50.00 \times 0.0500 - 5.00 \times 0.1000}{55.00} + [Ce^{4+}] = \frac{2.00}{55.00} + [Ce^{4+}]$$

Thus, the foregoing two equations can be simplified to:

$$[Fe^{3+}] = \frac{0.500}{55.00} \quad \text{and} \quad [Fe^{2+}] = \frac{2.00}{55.00}$$

Substitution for $[Fe^{2+}]$ and $[Fe^{3+}]$ in the Nernst equation gives:

$$E_{system} = +0.68 - \frac{0.0592}{1} \log \frac{2.00/\cancel{55.00}}{0.20/\cancel{55.00}} = 0.64\ V$$

Equivalence-Point Potential:

Substitution of the two formal potentials into Equation yields

$$E_{eq} = \frac{E^{0'}_{Ce^{4+}/Ce^{3+}} + E^{0'}_{Fe^{3+}/Fe^{2+}}}{2} = \frac{1.44 + 0.68}{2} = 1.06\ V$$

Potential after the Addition of 25.10 mL of Cerium (IV):

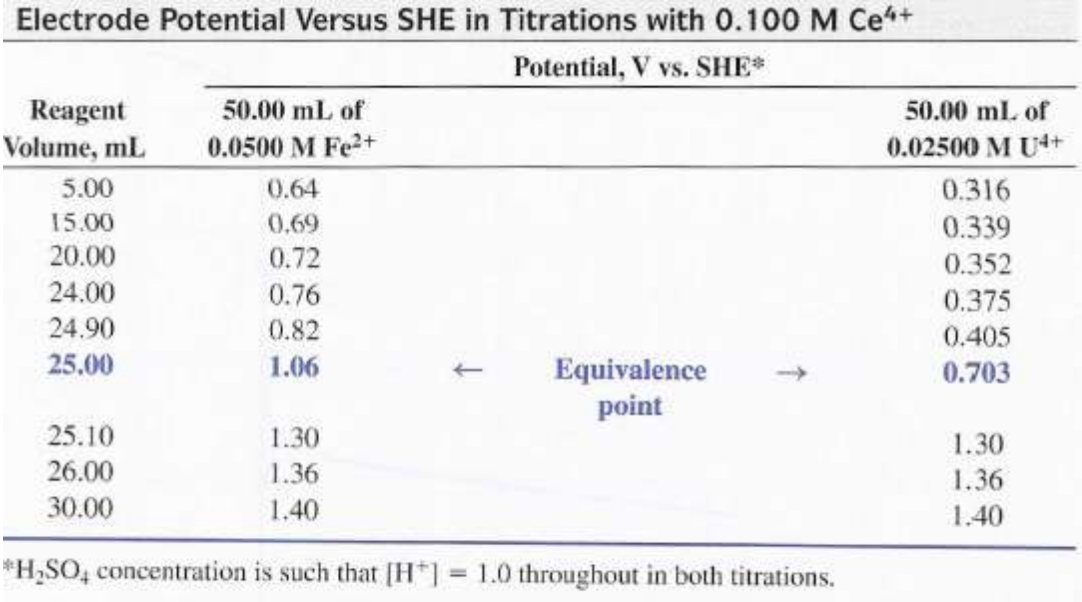
The molar concentrations of Ce (III), Ce (IV), and Fe (III) are easily computed at this point, but that for Fe (II) is not. Therefore, E_{system} computations based on the cerium half-reaction are more convenient. The concentrations of the two cerium ion species are:

$$[Ce^{3+}] = \frac{25.00 \times 0.1000}{75.10} - [Fe^{2+}] \approx \frac{2.500}{75.10}$$

$$[Ce^{4+}] = \frac{25.10 \times 0.1000 - 50.00 \times 0.0500}{75.10} + [Fe^{2+}] \approx \frac{0.010}{75.10}$$

Here, the iron (II) concentration is negligible with respect to the analytical concentrations of the two cerium species. Substitution into the Nernst equation for the cerium couple gives:

$$E = +1.44 - \frac{0.0592}{1}\log\frac{[Ce^{3+}]}{[Ce^{4+}]} = +1.44 - \frac{0.0592}{1}\log\frac{2.500/75.10}{0.010/75.10}$$
$$= +1.30\ V$$



Electrode Potential Versus SHE in Titrations with 0.100 M Ce^{4+}

	Potential, V vs. SHE*		
Reagent Volume, mL	50.00 mL of 0.0500 M Fe^{2+}		50.00 mL of 0.02500 M U^{4+}
5.00	0.64		0.316
15.00	0.69		0.339
20.00	0.72		0.352
24.00	0.76		0.375
24.90	0.82		0.405
25.00	1.06	← Equivalence point →	0.703
25.10	1.30		1.30
26.00	1.36		1.36
30.00	1.40		1.40

*H_2SO_4 concentration is such that $[H^+]$ = 1.0 throughout in both titrations.

Oxidation – reduction indicators:

Two types of chemical indicators are used to obtain end points for oxidation/reduction titrations: general redox indicators and specific indicators.

General Redox Indicators:

General oxidation/reduction indicators are substances that change color on being oxidized or reduced. In contrast to specific indicators, the color changes of true redox indicators are largely independent of the chemical nature of the analyte and titrant and depend instead on the changes in the electrode potential of the system that occur as the titration progresses.

The half-reaction responsible for color change in a typical general oxidation / reduction indicator can be written as:

$$In_{ox} + ne^- \rightleftharpoons In_{red}$$

If the indicator reaction is reversible, we can write:

$$E = E^0_{In_{ox}/In_{red}} - \frac{0.0592}{n}\log\frac{[In_{red}]}{[In_{ox}]}$$

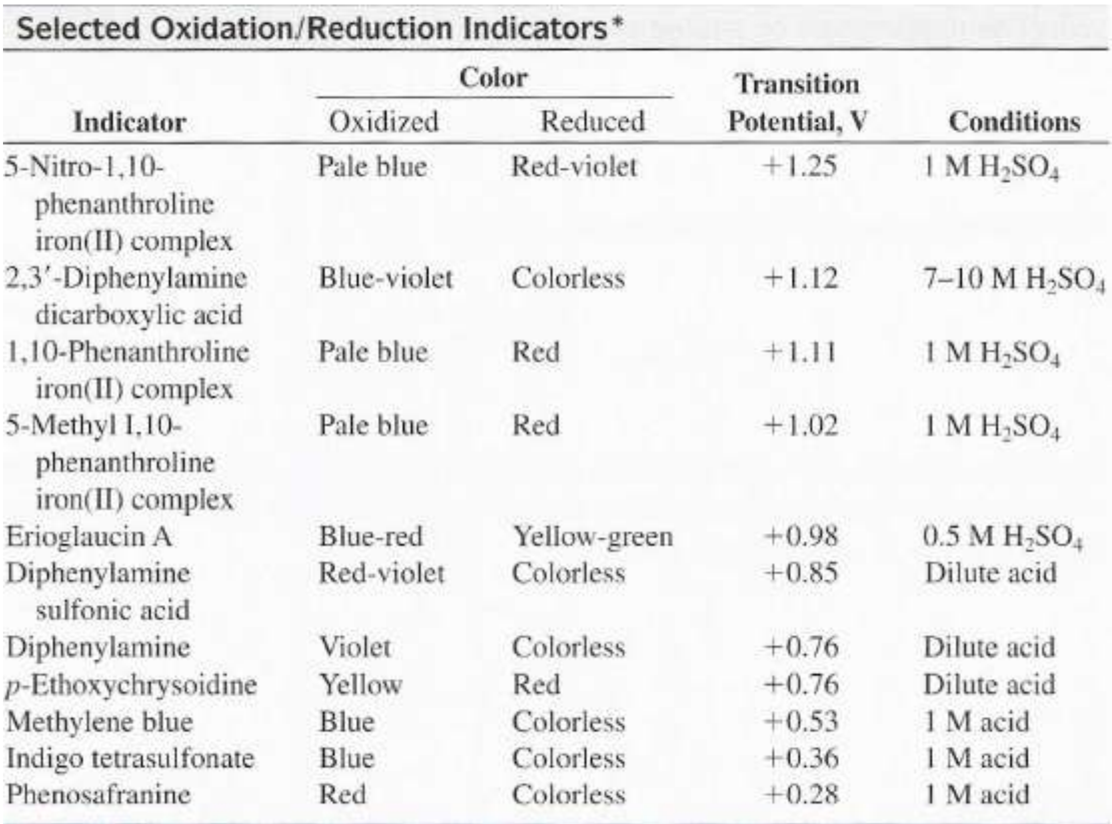
Typically, a change from the color of the oxidized form of the indicator to the color of the reduced form requires a change of about 100 in the ratio of reactant concentrations, that is, a color change is seen when:

$$\frac{[In_{red}]}{[In_{ox}]} \le \frac{1}{10} \quad \text{changes to} \quad \frac{[In_{red}]}{[In_{ox}]} \ge 10$$

The potential change required to produce the full color change of a typical general indicator can be found by substituting these two values into Equation, which gives:

$$E = E^0_{In} \pm \frac{0.0592}{n}$$

For many indicators, *n* = 2, and a change of 0.059 V is thus sufficient.



Selected Oxidation/Reduction Indicators*

Indicator	Color Oxidized	 Reduced	Transition Potential, V	Conditions
5-Nitro-1,10-phenanthroline iron(II) complex	Pale blue	Red-violet	+1.25	1 M H_2SO_4
2,3′-Diphenylamine dicarboxylic acid	Blue-violet	Colorless	+1.12	7–10 M H_2SO_4
1,10-Phenanthroline iron(II) complex	Pale blue	Red	+1.11	1 M H_2SO_4
5-Methyl 1,10-phenanthroline iron(II) complex	Pale blue	Red	+1.02	1 M H_2SO_4
Erioglaucin A	Blue-red	Yellow-green	+0.98	0.5 M H_2SO_4
Diphenylamine sulfonic acid	Red-violet	Colorless	+0.85	Dilute acid
Diphenylamine	Violet	Colorless	+0.76	Dilute acid
p-Ethoxychrysoidine	Yellow	Red	+0.76	Dilute acid
Methylene blue	Blue	Colorless	+0.53	1 M acid
Indigo tetrasulfonate	Blue	Colorless	+0.36	1 M acid
Phenosafranine	Red	Colorless	+0.28	1 M acid

Specific Indicators:

Perhaps the best-known specific indicator is **starch**, which forms a dark blue complex with triiodide ion. This complex signals the end point in titrations in which iodine is either produced or consumed. Another specific indicator is **potassium thiocyanate**, which may be used, for example, in the titration of iron (III) with solutions of titanium (III) sulfate, the end point involves the disappearance of the red color of the iron (III)/thiocyanate complex as a result of the marked decrease in the iron (III) concentration at the equivalence point.

Applications of Oxidation/Reduction Titrations:

Auxiliary oxidizing and reducing reagents:

Auxiliary Reducing Reagents:

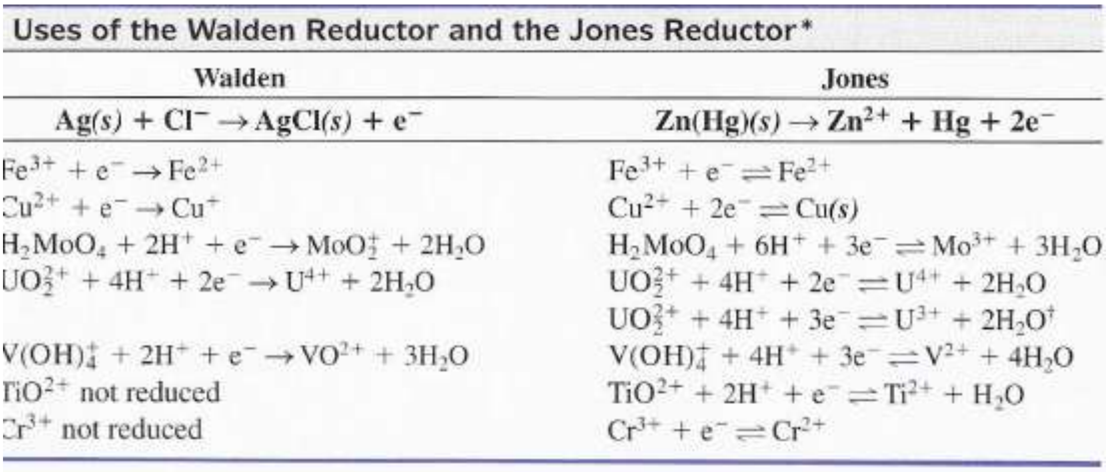
1 – **Jones reductor** has a diameter of about 2 cm and holds a 40- to 50-cm column of amalgamated zinc. Amalgamation is accomplished by allowing zinc granules to stand briefly in a solution of mercury (II) chloride, where the following reaction occurs:

$$2Zn(s) + Hg^{2+} \rightarrow Zn^{2+} + Zn(Hg)(s)$$

Zinc amalgam is nearly as effective for reductions as the pure metal and has the important virtue of inhibiting the reduction of hydrogen ions by zinc. This side reaction needlessly uses up the reducing agent and also contaminates the sample solution with a large amount of zinc (II) ions. Solutions that are quite acidic can be passed through a Jones reductor without significant hydrogen formation.

2 – Walden reductor, in which granular metallic silver held in a narrow glass column is the reductant. Silver is not a good reducing agent unless chloride or some other ion that forms a silver salt of low solubility is present. For this reason, prereductions with a Walden reductor are generally carried out from hydrochloric acid solutions of the analyte. The coating of silver chloride produced on the metal is removed periodically by dipping a zinc rod into the solution that covers the packing.

The table suggests that the **Walden reductor** is somewhat more selective in its action than is the **Jones reductor**.



Uses of the Walden Reductor and the Jones Reductor*

Walden	Jones
$Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$	$Zn(Hg)(s) \rightarrow Zn^{2+} + Hg + 2e^-$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
$Cu^{2+} + e^- \rightarrow Cu^+$	$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$
$H_2MoO_4 + 2H^+ + e^- \rightarrow MoO_2^+ + 2H_2O$	$H_2MoO_4 + 6H^+ + 3e^- \rightleftharpoons Mo^{3+} + 3H_2O$
$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$	$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$
	$UO_2^{2+} + 4H^+ + 3e^- \rightleftharpoons U^{3+} + 2H_2O^\dagger$
$V(OH)_4^+ + 2H^+ + e^- \rightarrow VO^{2+} + 3H_2O$	$V(OH)_4^+ + 4H^+ + 3e^- \rightleftharpoons V^{2+} + 4H_2O$
TiO^{2+} not reduced	$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{2+} + H_2O$
Cr^{3+} not reduced	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$

Auxiliary Oxidizing Reagents:

Sodium Bismuthate:

Sodium bismuthate is a powerful oxidizing agent capable, for example, of converting manganese (II) quantitatively to permanganate ion. This bismuth salt is a sparingly soluble solid with a formula that is usually written as $NaBiO_3$, although its exact composition is somewhat uncertain.

$$NaBiO_3(s) + 4H^+ + 2e^- \rightleftharpoons BiO^+ + Na^+ + 2H_2O$$

Ammonium Peroxydisulfate:

Ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, is also a powerful oxidizing agent. In acidic solution, it converts chromium (III) to dichromate, cerium (III) to cerium (IV), and manganese (II) to permanganate. The half-reaction is:

$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$$

The oxidations are catalyzed by traces of silver ion. The excess reagent is easily decomposed by a brief period of boiling:

$$2S_2O_8^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + O_2(g) + 4H^+$$

Sodium Peroxide and Hydrogen Peroxide:

Peroxide is a convenient oxidizing agent either as the solid sodium salt or as a dilute solution of the acid. The half-reaction for hydrogen peroxide in acidic solution is:

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^0 = 1.78\ V$$

After oxidation is complete, the solution is freed of excess reagent by boiling:

$$2H_2O_2 \rightarrow 2H_2O + O_2(g)$$

Applying standard reducing agents:

The two most common reductants:

Iron (III):

This procedure has been applied to the determination of organic peroxides; hydroxylamine; chromium (V1); cerium (1V); molybdenum (V1); nitrate, chlorate, and perchlorate ions; and numerous other oxidants (see, for example.

Thiosulfate ion:

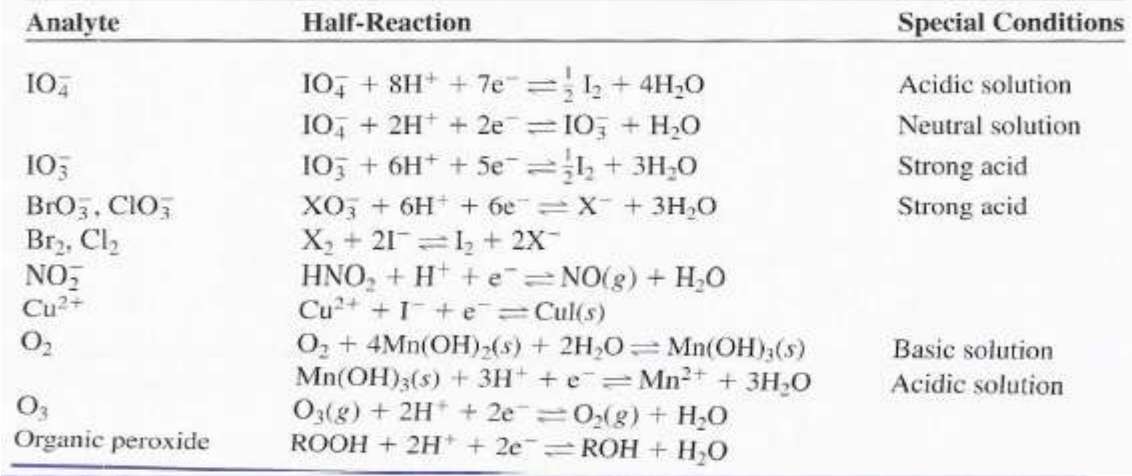
Thiosulfate ion is a moderately strong reducing agent that has been widely used to determine oxidizing agents by an indirect procedure that involves iodine as an intermediate. With iodine, thiosulfate ion is oxidized quantitatively to tetrathionate ion according to the half-reaction:

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$$

An example of this procedure is the determination of sodium hypochlorite in bleaches. The reactions are:

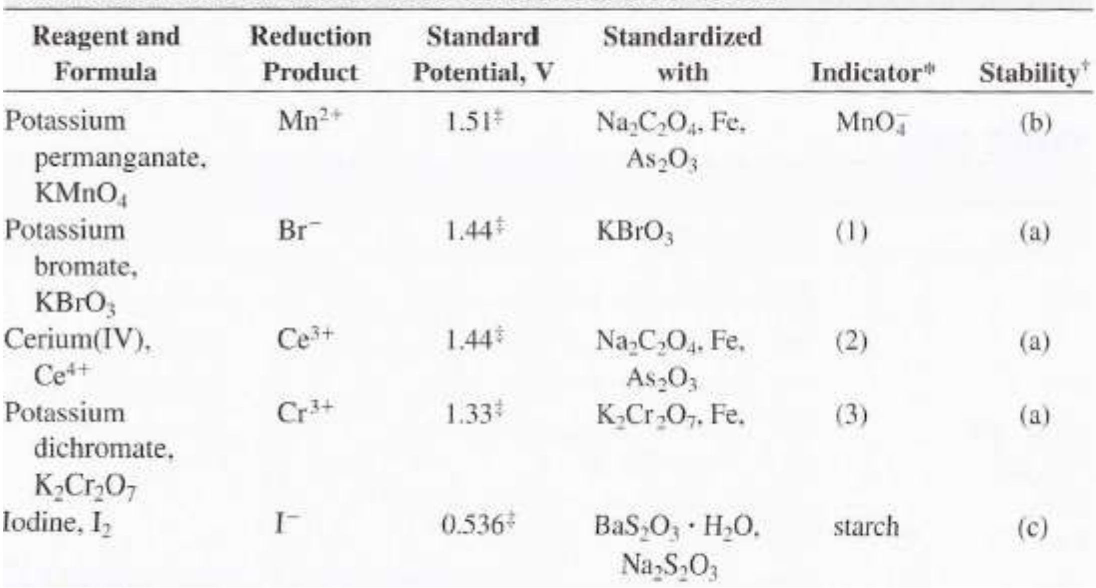
$$OCl^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O \qquad \text{(unmeasured excess KI)}$$

$$I_2 + S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \qquad (20\text{-}1)$$



Some Applications of Sodium Thiosulfate as a Reductant

Analyte	Half-Reaction	Special Conditions
IO_4^-	$IO_4^- + 8H^+ + 7e^- \rightleftharpoons \frac{1}{2} I_2 + 4H_2O$	Acidic solution
	$IO_4^- + 2H^+ + 2e^- \rightleftharpoons IO_3^- + H_2O$	Neutral solution
IO_3^-	$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2} I_2 + 3H_2O$	Strong acid
BrO_3^-, ClO_3^-	$XO_3^- + 6H^+ + 6e^- \rightleftharpoons X^- + 3H_2O$	Strong acid
Br_2, Cl_2	$X_2 + 2I^- \rightleftharpoons I_2 + 2X^-$	
NO_2^-	$HNO_2 + H^+ + e^- \rightleftharpoons NO(g) + H_2O$	
Cu^{2+}	$Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s)$	
O_2	$O_2 + 4Mn(OH)_2(s) + 2H_2O \rightleftharpoons Mn(OH)_3(s)$	Basic solution
	$Mn(OH)_3(s) + 3H^+ + e^- \rightleftharpoons Mn^{2+} + 3H_2O$	Acidic solution
O_3	$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$	
Organic peroxide	$ROOH + 2H^+ + 2e^- \rightleftharpoons ROH + H_2O$	



Some Common Oxidants Used as Standard Solutions

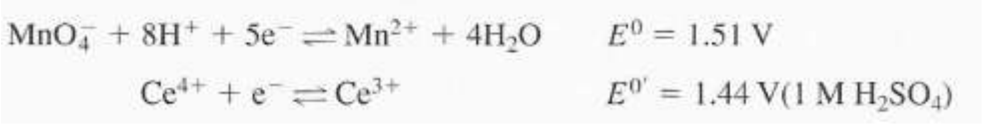
Reagent and Formula	Reduction Product	Standard Potential, V	Standardized with	Indicator*	Stability†
Potassium permanganate, $KMnO_4$	Mn^{2+}	1.51‡	$Na_2C_2O_4$, Fe, As_2O_3	MnO_4^-	(b)
Potassium bromate, $KBrO_3$	Br^-	1.44‡	$KBrO_3$	(1)	(a)
Cerium(IV), Ce^{4+}	Ce^{3+}	1.44‡	$Na_2C_2O_4$, Fe, As_2O_3	(2)	(a)
Potassium dichromate, $K_2Cr_2O_7$	Cr^{3+}	1.33‡	$K_2Cr_2O_7$, Fe	(3)	(a)
Iodine, I_2	I^-	0.536‡	$BaS_2O_3 \cdot H_2O$, $Na_2S_2O_3$	starch	(c)

Applying standard oxidizing agents:

Table summarizes the properties of five of the most widely used volumetric oxidizing reagents. Note that the standard potentials for these reagents vary from 0.5 to 1.5 V. The choice among them depends on the strength of the analyte as a reducing agent, the rate of reaction between oxidant and analyte, the stability of the standard oxidant solutions, the cost, and the availability of a satisfactory indicator.

The Strong Oxidants-Potassium Permanganate and Cerium (IV):

Solutions of permanganate ion and cerium (IV) ion are strong oxidizing reagents whose applications closely parallel one another. Half-reactions for the two are:

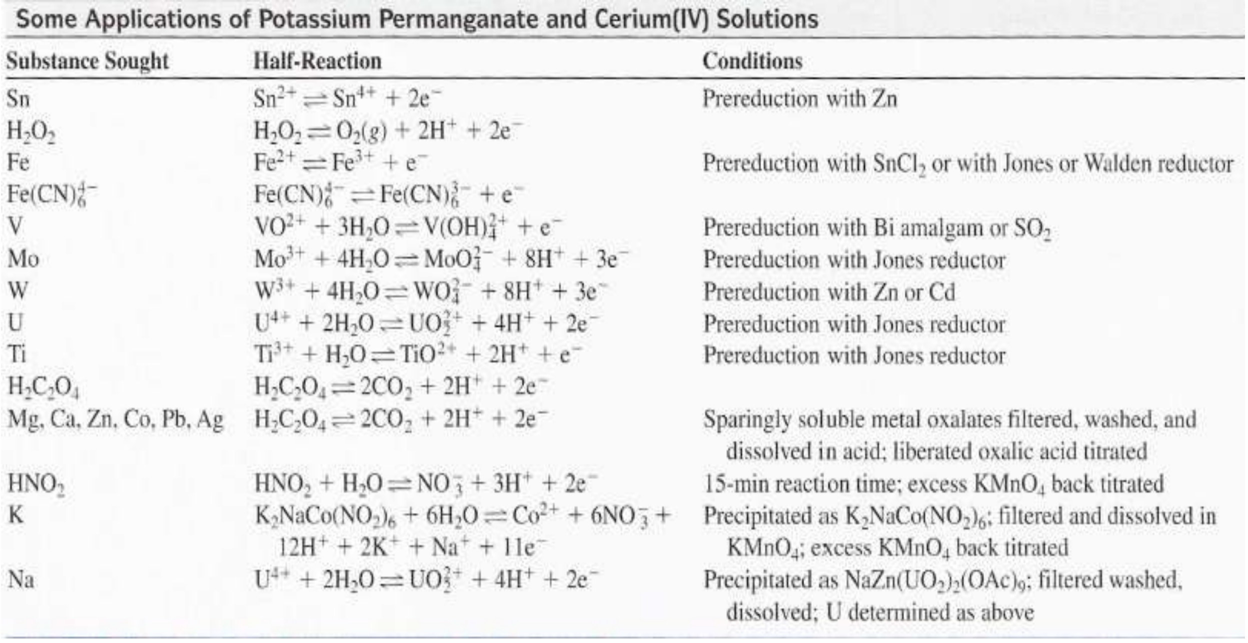


$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^0 = 1.51\ V$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^{0'} = 1.44\ V(1\ M\ H_2SO_4)$$

The formal potential shown for the reduction of cerium (IV) is for solutions that are 1 M in sulfuric acid. In 1 M perchloric acid and 1 M nitric acid, the potentials are 1.70 V and 1.61 V, respectively. Solutions of cerium (IV) in the latter two acids are not very stable and thus find limited application.

The half-reaction shown for permanganate ion occurs only in solutions that are 0.1 M or greater in strong acid. In less acidic media, the product may be Mn (III), Mn (IV), or Mn (VI), depending on conditions. There are many applications of permanganate and cerium (IV) solutions in the volumetric determination of inorganic species. Both reagents have also been applied to the determination of organic compounds with oxidizable functional groups.



Some Applications of Potassium Permanganate and Cerium(IV) Solutions

Substance Sought	Half-Reaction	Conditions
Sn	$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$	Prereduction with Zn
H_2O_2	$H_2O_2 \rightleftharpoons O_2(g) + 2H^+ + 2e^-$	
Fe	$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$	Prereduction with $SnCl_2$ or with Jones or Walden reductor
$Fe(CN)_6^{4-}$	$Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + e^-$	
V	$VO^{2+} + 3H_2O \rightleftharpoons V(OH)_4^{2+} + e^-$	Prereduction with Bi amalgam or SO_2
Mo	$Mo^{3+} + 4H_2O \rightleftharpoons MoO_4^{2-} + 8H^+ + 3e^-$	Prereduction with Jones reductor
W	$W^{3+} + 4H_2O \rightleftharpoons WO_4^{2-} + 8H^+ + 3e^-$	Prereduction with Zn or Cd
U	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$	Prereduction with Jones reductor
Ti	$Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^-$	Prereduction with Jones reductor
$H_2C_2O_4$	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	
Mg, Ca, Zn, Co, Pb, Ag	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Sparingly soluble metal oxalates filtered, washed, and dissolved in acid; liberated oxalic acid titrated
HNO_2	$HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-$	15-min reaction time; excess $KMnO_4$ back titrated
K	$K_2NaCo(NO_2)_6 + 6H_2O \rightleftharpoons Co^{2+} + 6NO_3^- + 12H^+ + 2K^+ + Na^+ + 11e^-$	Precipitated as $K_2NaCo(NO_2)_6$; filtered and dissolved in $KMnO_4$; excess $KMnO_4$ back titrated
Na	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$	Precipitated as $NaZn(UO_2)_3(OAc)_9$; filtered washed, dissolved; U determined as above

Comparing the Two Reagents:

1 – Solutions of cerium (IV) in sulfuric acid, however, are stable indefinitely, whereas permanganate solutions decompose slowly and thus require occasional restandardization.

2 – Furthermore, cerium (IV) solutions in sulfuric acid do not oxidize chloride ion and can be used to titrate hydrochloric acid solutions of analytes; in contrast, permanganate ion cannot be used with hydrochloric acid solutions unless special precautions are taken to prevent the slow oxidation of chloride ion that leads to overconsumption of the standard reagent.

3 – A further advantage of cerium (IV) is that a primary-standard grade salt of the reagent is available, thus making possible the direct preparation of standard solutions.

4 – The permanganate solutions, are more widely used.

5 – The color of permanganate solutions, which is intense enough to serve as an indicator in titrations.

6 – The permanganate solutions is their modest cost.

7- Another disadvantage of cerium (IV) solutions is their tendency to form precipitates of basic salts in solutions that are less than 0.1 M in strong acid.

Standardizing Permanganate and Ce (IV) Solutions:

Sodium oxalate is a widely used primary standard. In acidic solutions, the oxalate ion is converted to the undissociated acid. Thus, its reaction with permanganate can be described by:

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2(g) + 8H_2O$$

Sodium oxalate is also widely used to standardize Ce (IV) solutions. The reaction between Ce^{4+} and $H_2C_20_4$ is:

$$2Ce^{4+} + H_2C_2O_4 \rightarrow 2Ce^{3+} + 2CO_2(g) + 2H^+$$

Cerium (IV) standardizations against sodium oxalate are usually performed at 50°C in a hydrochloric acid solution containing iodine monochloride as a catalyst.

Potassium Dichromate:

In its analytical applications, dichromate ion is reduced to green chromium (III) ion:

$$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \rightleftharpoons 2\,Cr^{3+} + 7H_2O \qquad E^0 = 1.33\ V$$

Dichromate titrations are generally carried out in solutions that are about I M in hydrochloric or sulfuric acid. In these media, the formal potential for the half reaction is 1.0 to 1.1 V. Potassium dichromate solutions are indefinitely stable, can be boiled without decomposition, and do not react with hydrochloric acid. Moreover, primary standard reagent is available commercially and at a modest cost. The disadvantages of potassium dichromate compared with cerium (IV) and permanganate ion are its lower electrode potential and the slowness of its reaction with certain reducing agents.

Applying Potassium Dichromate Solutions:

The principal use of dichromate is the volumetric titration of iron (II) based on the reaction:

$$Cr_2O_7^{2-} + 6\,Fe^{2+} + 14\,H^+ \rightarrow 2Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$$

Often, this titration is performed in the presence of moderate concentrations of hydrochloric acid. The reaction of dichromate with iron (II) has been widely used for the indirect determination of a variety of oxidizing agents. In these applications, a measured excess of an iron (II) solution is added to an acidic solution of the analyte. The excess iron (II) is then back-titrated with standard potassium dichromate. This method has been applied to the determination of nitrate, chlorate, permanganate, and dichromate ions as well as organic peroxides and several other oxidizing agents.

Iodine:

Iodine is a weak oxidizing agent used primarily for the determination of strong reductants. The most accurate description of the half-reaction for iodine in these applications is:

$$I_3^- + 2e^- \rightleftharpoons 3I^- \qquad E^0 = 0.536\ V$$

where I^{3-} is the triiodide ion.

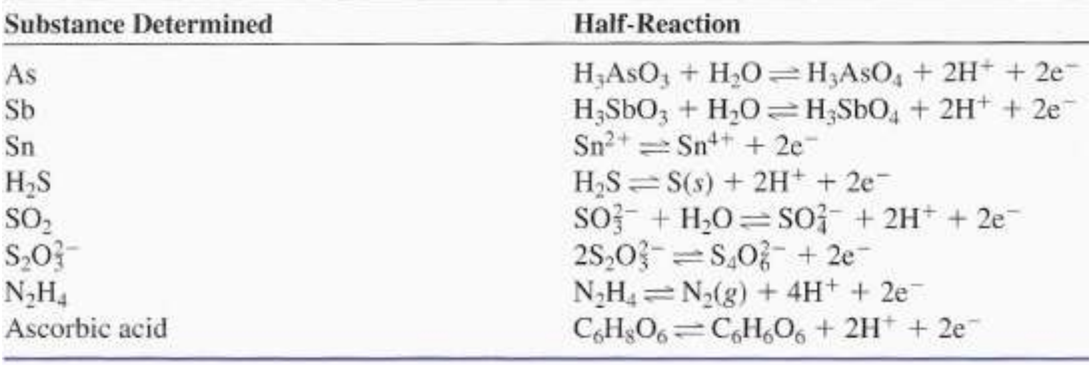
Standard iodine solutions have relatively limited application compared with the other oxidants we have described because of their significantly smaller electrode potential. Occasionally, however, this low potential is advantageous because it imparts a degree of selectivity that makes possible the determination of strong reducing agents in the presence of weak ones. An important advantage of iodine is the availability of a sensitive and reversible indicator for the titrations. Iodine solutions lack stability, however, and must be restandardized regularly.

Standardizing and Applying Iodine Solutions:

Iodine solutions can be standardized against anhydrous sodium thiosulfate or barium thiosulfate monohydrate, both of which are available commercially. The reaction between iodine and sodium thiosulfate:

$$I_2 + S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Often, solutions of iodine are standardized against solutions of sodium thiosulfate that have in turn been standardized against potassium iodate or potassium dichromate. Table summarizes methods that use iodine as an oxidizing agent.



Some Applications of Iodine Solutions

Substance Determined	Half-Reaction
As	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e^-$
Sb	$H_3SbO_3 + H_2O \rightleftharpoons H_3SbO_4 + 2H^+ + 2e^-$
Sn	$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$
H_2S	$H_2S \rightleftharpoons S(s) + 2H^+ + 2e^-$
SO_2	$SO_3^{2-} + H_2O \rightleftharpoons SO_4^{2-} + 2H^+ + 2e^-$
$S_2O_3^{2-}$	$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$
N_2H_4	$N_2H_4 \rightleftharpoons N_2(g) + 4H^+ + 2e^-$
Ascorbic acid	$C_6H_8O_6 \rightleftharpoons C_6H_6O_6 + 2H^+ + 2e^-$

Potassium Bromate as a Source of Bromine:

Primary-standard potassium bromate is available from commercial sources and can be used directly to prepare standard solutions that are stable indefinitely. Instead, the reagent is a convenient and widely used stable source of brornine. In this application, an unmeasured excess of potassium bromide is added to an acidic solution of the analyte.

$$\underset{\text{standard solution}}{BrO_3^-} + \underset{\text{excess}}{5Br^-} + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The primary use of standard potassium bromate is the determination of organic compounds that react with bromine. After acidification, the mixture is allowed to stand in a glass-stoppered vessel until the bromine/analyte reaction is judged complete. To determine the excess bromine, an excess of potassium iodide is introduced so that the following reaction occurs:

$$2I^- + Br_2 \rightarrow I_2 + 2Br^-$$

The liberated iodine is then titrated with standard sodium thiosulfate.

العوامل المؤكسدة (تسحيحات الأكسدة والاختزال)

أولا : برمنكنات البوتاسيوم potassium permanganate

1. عامل مؤكسد قوي $(KMnO_4)$
2. تفاعل نصف الخلية $MnO^-_4 + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ E=1.51V
3. تفاعل نصف الخلية يحصل في المحاليل الحامضية القوية (اكبر من 0.1M)
4. في المحاليل الحامضية الضعيفة والمتوسطة يكون ناتج الاختزال وحسب ظروف المحلول: $(Mn^{3+}$ or Mn^{4+} or $Mn^{5+})$
5. يستخدم في تقدير المواد اللاعضوية.
6. يستخدم في تقدير المواد العضوية ذات المجاميع القابلة للأكسدة.
7.

ثانيا : السيريوم الرباعي التكافؤ Cerium Cr^{4+}

1. عامل مؤكسد قوي
2. تفاعل نصف الخلية $Ce^{4+} + e^- \longrightarrow Ce^{3+}$ E=1.44V
3. تفاعل نصف الخلية اعلاه يحصل في $1\ M H_2SO_4$
4. في المحاليل 1 مولاري حامض البيركلوريك الجهد يكون 1.7 V
5. في محلول 1 مولاري حامض النتريك الجهد يكون 1.61V
6. محاليل السيريوم في حامض النتريك والبيركلوريك غير مستقرة بشكل عالي لذلك تطبيقاتها قليلة.
7. يستخدم في تقدير المواد اللاعضوية والمواد العضوية المادية على مجاميع قابلة للاكسدة.

ملاحظة مهمة (الفروقات بين السيريوم والبرمنكنات)

1. محلول السيريوم في حامض الكبريتيك مستقر بينما محلول البرمنكنات في حامض الكبريتيك غير مستقر يتفكك ببطيء لذلك يحتاج إلى اعادة تقيس (معايرة) دائما.
2. محلول السيريوم في حامض الكبريتيك لايوكسد الكلور ،لذلك يستخدم لمعايرة (المواد المحللة في محيط حامض HCl) بينما محلول البرمنكنات لا يمكن استخدامه لمعايرة المواد في محيط حامض HCl ما لم يتم اجراء بعض الاجراءات لان البرمنكنات توكسد الكلور ببطيء.
3. المادة القياسية الاولية للسيريوم متوفرة ولهذا تستطيع تحضير محلول قياسي مباشرة لايون السيريوم. بينما لا يمكن الحصول على مادة قياسية اولية للبرمنكنات لذلك تحتاج إلى معايرة المحلول المحضر للبرمنكنات مع مادة قياسية اولية اخرى هي (اوكزالات الصوديوم).
4. استخدامات برمنكنات البوتاسيوم اوسع واكثر والسبب يعود إلى اللون الواضح جدا للبرمنكنات حيث انها تعمل كدليل لعملية التسحيح فيما السيريوم لونه باهت يحتاج إلى دليل.
5. كلفة محلول برمنكنات البوتاسيوم واطئة قياسا لمحلول السيريوم.
6. محاليل السيريوم تميل إلى تكوين رواسب لاملاح قاعدية في المحاليل ذات الحامضية اقل من 0.1M بينما البرمنكنات لا تترك رواسب.

ثالثا : دايكرومات البوتاسيوم Potassium Dichromate $K_2Cr_2O_7$

1. عامل مؤكسد متوسط القوة اقل قوة من السيريوم والبرمنكنات (الدايكرومات اقل جهد قطب وابطيء في التفاعل).
2. يختزل في التطبيق ايون الدايكرومات إلى ايون الكروم الثلاثي ذي اللون الاخضر.
3. تفاعل نصف الخلية $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

E=1.33 V

4. التفاعل اعلاه يجري في محيط حامض (حامض الكبريتيك او حامض الهيدروكلوريك) بتركيز 1M
5. محلول الدايكرومات مستقر وممكن ان يتم تسخينه وبدون تفكيك.
6. لا يتفاعل مع حامض الهيدروكلوريك.
7. ممكن ان نحصل على مادة قياسية اولية بسهولة وبكلفة متوسطة.
8. تستخدم لتقدير المواد باستخدام التسحيح الرجعي (تفاعل الدايكرومات مع الحديد الثلاثي).
9. تستخدم لتقدير النترات البيروكلورات والبرمنكنات والبروكسيدات العضوية.

رابعا : الايودين Iodine I_2

1. عامل مؤكسد ضعيف اضعف من العوامل المؤكسدة السابقة.
2. نصف التفاعل $I_3^- + 2e^- \longrightarrow 3I^-$ E = 0.336 V
3. تطبيقاته قليلة لان جهد القطب صغير.
4. ولكن يمكن استخدامه لتقدير العوامل المختزلة القوية بوجود عامل مختزل ضعيف.
5. الايودين عامل مؤكسد يعمل كدليل ذاتي وله حساسية عالية.
6. محلوله ذو استقرارية قليلة لذلك يحتاج إلى معايرة دائما. يستخدم الثايوسلفيت للمعايرة.
7.

خامسا : برومات البوتاسيوم (كمصدر للبرومين) Potassium Bromate $KBrO_3$

1. عامل مؤكسد ضعيف.
2. تستخدم برومات البوتاسيوم كمصدر للبرومين Br_2 الذي يعمل كعامل مؤكسد

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

3. المادة القياسية الاولية برومات البوتاسيوم متوفرة بشكل كبير.
4. محلول برومات البوتاسيوم مستقر.
5. استخدام برومات البوتاسيوم كمادة مؤكسدة مباشرة قليل ولكن تستخدم لتحرير الايودين كما مر سابقا.
6. تستخدم لتقدير المركبات العضوية التي تتفاعل مع البرومين ، حيث يتم اضافة زيادة ثم يسحح البرومين الزائد المتكون مع I^- (يوديد البوتاسيوم).

(التطبيق المهم لتسحيحات الأكسدة والاختزال)

قياس الماء بطريقة كارل رفشر Karl – Fischer

1. نستخدم لتقدير الماء في كثير من النماذج الصلبة والعضوية السائلة.
2. تعتمد على عملية الاكسدة والاختزال الخاصة للماء.
3. يتم اكسدة ثاني اوكسيد الكبريت بواسطة الايودين في محيط ليس حامضي او قاعدة وانما يستخدم مادة (aprotic solvent).

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

4. في التفاعل اعلاه يتم استهلاك مولين في الماء لكل مول واحد من I_2.
5. من خلال معرفة كمية اليودين تستطيع معرفة كمية الماء.
6. يتأثر التحليل اعلاه بوجود الحوامض والقواعد في محيط التحليل.

Applications:

Karl Fischer reagent has been applied to the determination of water in numerous types of samples. There are several variations of the basic technique, depending on the solubility of the material, the state in which the water is retained, and the physical state of the sample. If the sample can be dissolved completely in methanol, a direct and rapid titration is usually feasible. This method has been applied to the determination of water in many organic acids, alcohols, esters, ethers, anhydrides, and halides. The hydrated salts of most organic acids, as well as the hydrates of a number of inorganic salts that are soluble in methanol, can also be determined by direct titration.

Direct titration of samples that are only partially dissolved in the reagent usually leads to incomplete recovery of the water. Satisfactory results with this type of sample are often obtained, however, by the addition of excess reagent and back titration with a standard solution of water in methanol after a suitable reaction time. An effective alternative is to extract the water from the sample by refluxing with anhydrous methanol or other organic solvents. The resulting solution is then titrated directly with the Karl Fischer solution.