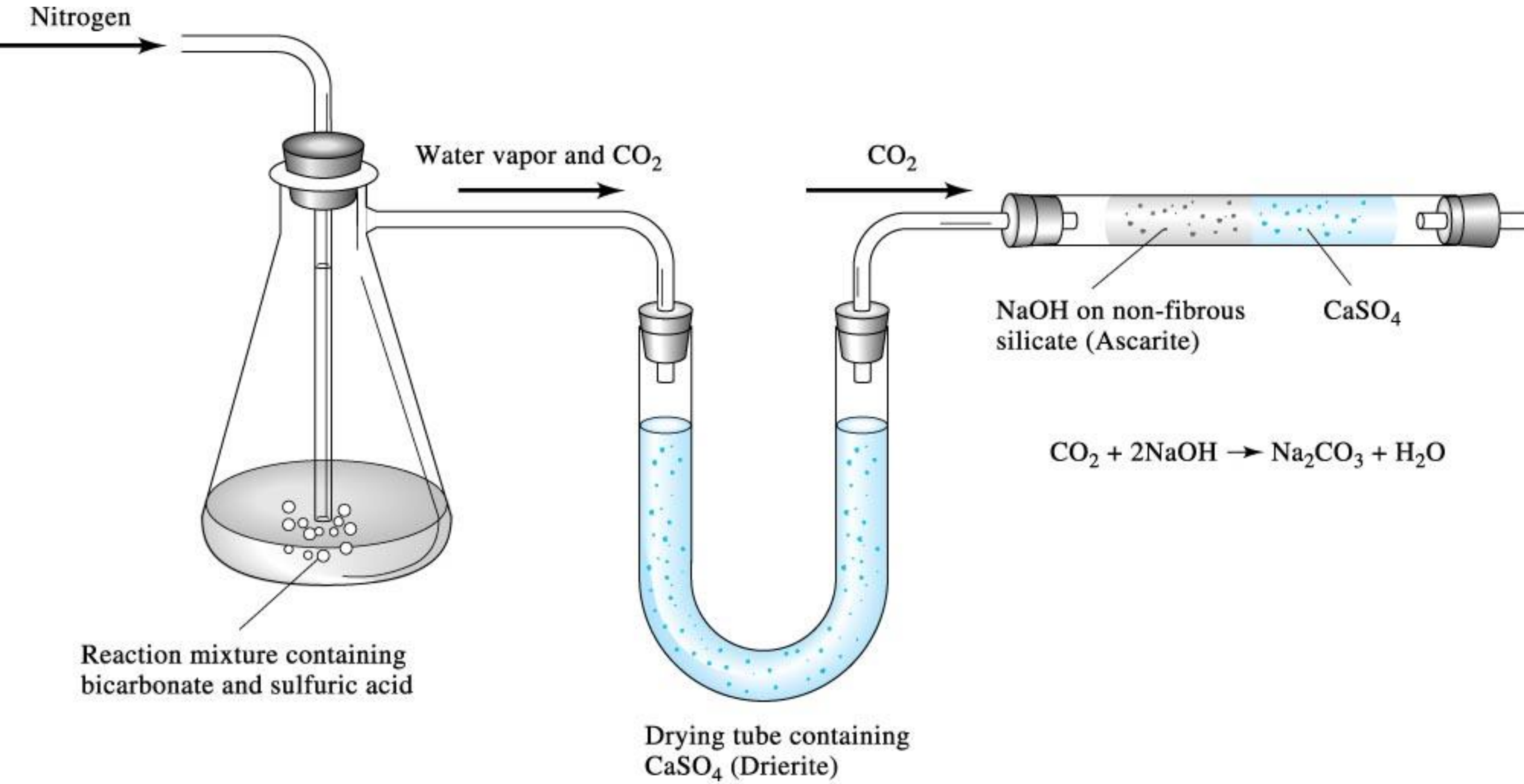
Chapter 12

Gravimetric Methods of Analysis

Gravimetric methods of analysis are based on the measurement of <u>mass</u>. There are two major types of gravimetric methods:

- **Precipitation methods:** in this method the analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, and converted to a product of known composition by suitable heat treatment, and the product is weighed.
- **Volatilization methods:** in this the analyte or its decomposition products are volatilized at a suitable temperature. The volatile product is then collected and weighed, or, alternatively, the mass of the product is determined indirectly from the loss in mass of the sample.



$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

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PROPERTIES OF PRECIPITATES AND PRECIPITATING REAGENTS

A gravimetric precipitating agent should react specifically, and selectively with the analyte.

The ideal precipitating reagent would react with the analyte to give a product that is

1. Readily filtered and washed free of contaminants
2. Of sufficiently low solubility so that no significant loss of the solid occurs during filtration and washing
3. Unreactive with constituents of the atmosphere
4. Of known composition after it is dried or, if necessary, ignited

Particle Size and Filterability of Precipitates

Precipitates made up of large particles are generally desirable in gravimetric work because large particles are easy to filter and wash free of impurities. In addition, such precipitates are usually purer than are precipitates made up of fine particles.

What Factors Determine Particle Size?

The particle size of solids formed by precipitation varies enormously.

- ☐ At one extreme are **colloidal suspension**, whose tiny particles are invisible to the naked eye (10^{-7} to 10^{-4} cm in diameter). Colloidal particles show no tendency to settle from solution, nor are they easily filtered.
- ☐ At the other extreme are particles with dimensions on the order of tenths of millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a **crystalline suspension**. The particles of a crystalline suspension tend to settle spontaneously and are readily filtered.

- The particle size of a precipitate is influenced by experimental variables as precipitate solubility, temperature, reactant concentrations, and the rate at which reactants are mixed.
- The particle size is related to a single property of the system called its **relative supersaturation**, where

$$\text{relative supersaturation} = (Q - S) / S$$

In this equation, Q is the concentration of the solute at any instant and S is its equilibrium solubility.

- ➢ when $(Q - S)/ S$ is large, the precipitate tends to be colloidal.
- ➢ when $(Q - S)/ S$ is small, a crystalline solid is more likely

How do Precipitates Form (*Mechanism*)?

Precipitates form in two ways, by **nucleation** and by **particle growth**. The particle size of a freshly formed precipitate is determined by which way is faster.

In ***nucleation***, a few ions, atoms, or molecules (perhaps as few as four or five) come together to form a stable solid. Often, these nuclei form on the surface of suspended solid contaminants, such as dust particles.

Further precipitation then involves a competition between additional nucleation and growth on existing nuclei (***particle growth***).

If nucleation predominates, a precipitate containing a *large number of small particles results*;

If growth predominates, a *smaller number of larger particles is produced*.

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Controlling Particle Size

Experimental variables that minimize supersaturation and thus lead to **crystalline** precipitates include:

- elevated temperatures to increase the solubility of the precipitate (S in Equation),
- dilute solutions (to minimize Q), and
- slow addition of the precipitating agent with good stirring.
- The last two measures also minimize the concentration of the solute (Q) at any given instant.

- Larger particles can also be obtained by pH control, provided the solubility of the precipitate depends on pH.
  - See example in p**317**

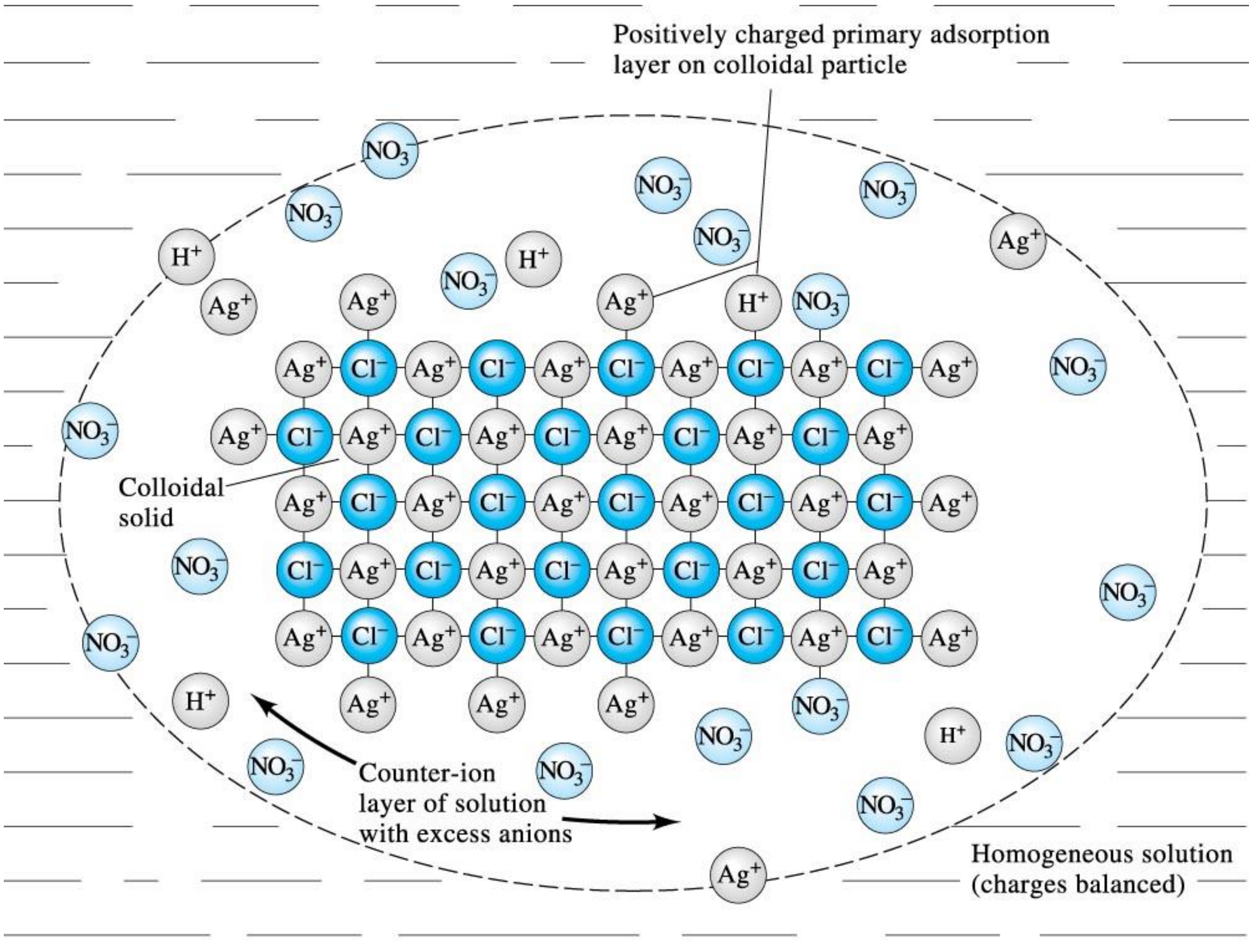
Colloidal Precipitates

Individual colloidal particles are so *small* that they are not retained by ordinary filters.

Coagulation of Colloids the individual particles of most colloids to give a filterable, amorphous mass that will settle out of solution.

Coagulation can be hastened (يُسْرِع) by *heating*, *stirring*, and *adding an electrolyte* to the medium.

Colloidal suspensions are stable because all the particles present are either positively or negatively charged. This charge results from cations or anions that are bound to the surface of the particles. *The process by which ions are retained on the surface of a solid is known as* **adsorption**. We can readily demonstrate that colloidal particles are charged by observing their migration when placed in an electrical field.


Positively charged primary adsorption layer on colloidal particle
Colloidal solid
Counter-ion layer of solution with excess anions
Homogeneous solution (charges balanced)
Ag^+
Cl^-
NO_3^-
H^+

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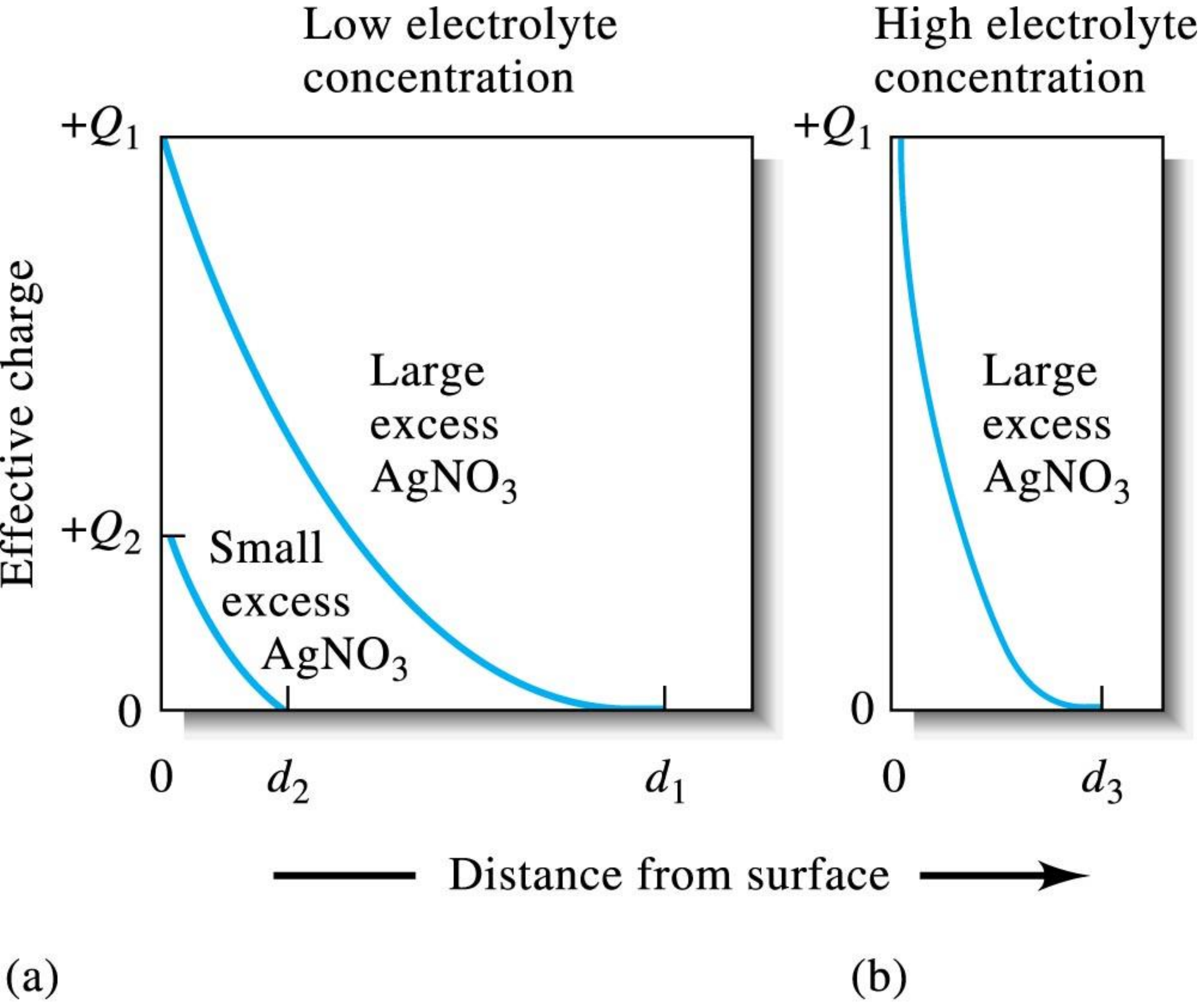

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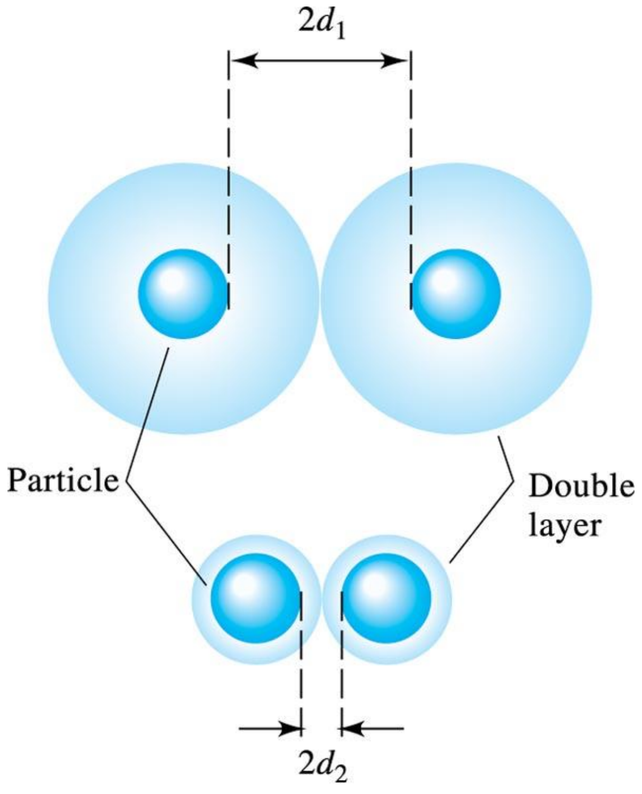

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- Effect of $AgNO_3$ and electrolyte concentration on the thickness of the double layer surrounding a colloidal AgCl particle in a solution containing excess$AgNO_3$.
- The effective charge (Q) can be thought of as a measure of the repulsive force that the particle exerts on like particles in the solution.

Peptization of Colloids

Peptization refers to the process by which a coagulated colloid *reverts* to its original dispersed state.

When a coagulated colloid is washed, some of the electrolyte responsible for its coagulation is leached from the internal liquid in contact with the solid particles. Removal of this electrolyte has the effect of increasing the volume of the counter-ion layer. The repulsive forces responsible for the original colloidal state are then reestablished, and particles detach themselves from the coagulated mass. The washings become cloudy as the freshly dispersed particles pass through the filter.

- *Practical Treatment* of *Colloidal Precipitates*

Colloids are best precipitated from hot, stirred solutions containing sufficient electrolyte to ensure coagulation. The filterability of a coagulated colloid frequently improves if it is allowed to stand for an hour or more in contact with the hot solution from which it was formed. During this process, which is known as **digestion,** weakly bound water appears to be lost from the precipitate; the result is a denser mass that is easier to filter.

Crystalline Precipitates

- Crystalline precipitates are generally more easily filtered and purified than coagulated colloids. In addition, the size of individual crystalline particles, and thus their filterability, can be controlled to a degree.
- The particle size of crystalline solids can often be improved significantly by minimizing Q, maximizing S, or both in Equation. Minimization of Q is generally accomplished by using *dilute solution and adding the precipitating from hot solution or by adjusting the pH of the precipitation medium.*
- Digestion of crystalline precipitates (without stirring) for some time after formation frequently yields a purer, more filterable product. The improvement in filterability results from the *dissolution* and *recrystallization*.

Coprecipitation

Coprecipitation is the phenomenon in which soluble compounds are removed from solution during precipitate formation.

There are four types of coprecipitation:

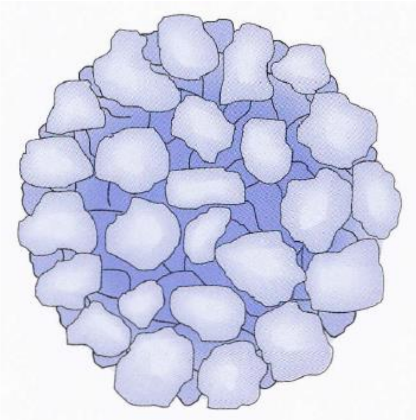
i) surface adsorption
ii) mixed-crystal formation
iii) occlusion
iv) mechanical entrapment

- Surface adsorption and mixed crystal formation are equilibrium processes, whereas
- occlusion and mechanical entrapment arise from the kinetics of crystal growth.

Surface Adsorption

Adsorption is a common source of coprecipitation that is likely to cause significant *contamination* of precipitates with large specific surface areas, that is coagulated colloids.

Coagulation of a colloid does not significantly decrease the amount of adsorption because the coagulated solid still contains large internal surface areas that remain exposed to the solvent. The coprecipitated contaminant on the coagulated colloid consists of the lattice ion originally adsorbed on the surface before coagulation and the counter ion of opposite charge held in the film of solution immediately adjacent to the particle. The net effect of surface adsorption is therefore the carrying down of an otherwise soluble compound as a surface contaminant.



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Minimizing Adsorbed Impurities on Colloids

The purity of many coagulated colloids is improved by **digestion**. During this process, water is expelled from the solid to give a denser mass that has a smaller specific surface area for adsorption.

Washing a coagulate colloid with a solution containing a volatile electrolyte may also be helpful because any nonvolatile electrolyte added earlier to cause coagulation is displace by the volatile species. Washing generally does not remove much of the primarily adsorbed ions because the attraction between these ions and the surface of the solid is too strong. Exchange occurs, however between existing counter ions and ions in the wash liquid.

Reprecipitation

- A drastic but effective way to minimize the effects of adsorption is reprecipitation, or double precipitation.
- Here, the filtered solid is redissolved and reprecipitated. The first precipitate ordinarily carries down only a fraction of the contaminant present in the original solvent. Thus, the solution containing the redissolved precipitate has a significantly lower contaminant concentration than the original, and even less adsorption occurs during the second precipitation.
- Reprecipitation adds substantially to the time required for an analysis.

Mixed-Crystal Formation

- In mixed-crystal formation, one of the ions in the crystal lattice of a solid is replaced by an ion of another element. For this exchange to occur, it is necessary that the two ions have the same charge and that their sizes differ by no more than about 5%. Furthermore, the two salts must belong to the same crystal class. For example, $MgKPO_4$, in $MgNH_4PO_4$, $SrSO_4$ in $BaSO_4$, and MnS in CdS.
- The extent of mixed-crystal contamination increases as the ratio of contaminant to analyte concentration increases. Mixed-crystal formation is troublesome because little can be done about it. Separation of the interfering ion may have to be carried out before the final precipitation step. Alternatively, a different precipitating reagent may be used.

Occlusion and Mechanical Entrapment

- When a crystal is growing rapidly during precipitate formation, foreign ions in the counter-ion layer may become trapped, or occluded, within the growing crystal.
- Mechanical entrapment occurs when crystals lie close together during growth. Here, several crystals grow together and in so doing trap a portion of the solution in a tiny pocket.
- Both occlusion and mechanical entrapment are at a minimum when the rate of precipitate formation is low, that is, under conditions of low supersaturation. Digestion is often remarkably helpful in reducing these types of copreipitation. The rapid solution and reprecipitation that goes on at the elevated temperature of digestion opens up the pockets and allows the impurities to escape into the solution.

Precipitation from Homogeneous Solution

Precipitation from homogeneous solution is a technique in which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction.

Local reagent excesses do not occur because the precipitating agent appears gradually and homogeneously throughout the solution and reacts immediately with the analyte. As a result, the relative supersaturation is kept low during the entire precipitation. In general, homogeneously formed precipitates, both colloidal and crystalline, are better suited for analysis than a solid formed by direct addition of a precipitating reagent.

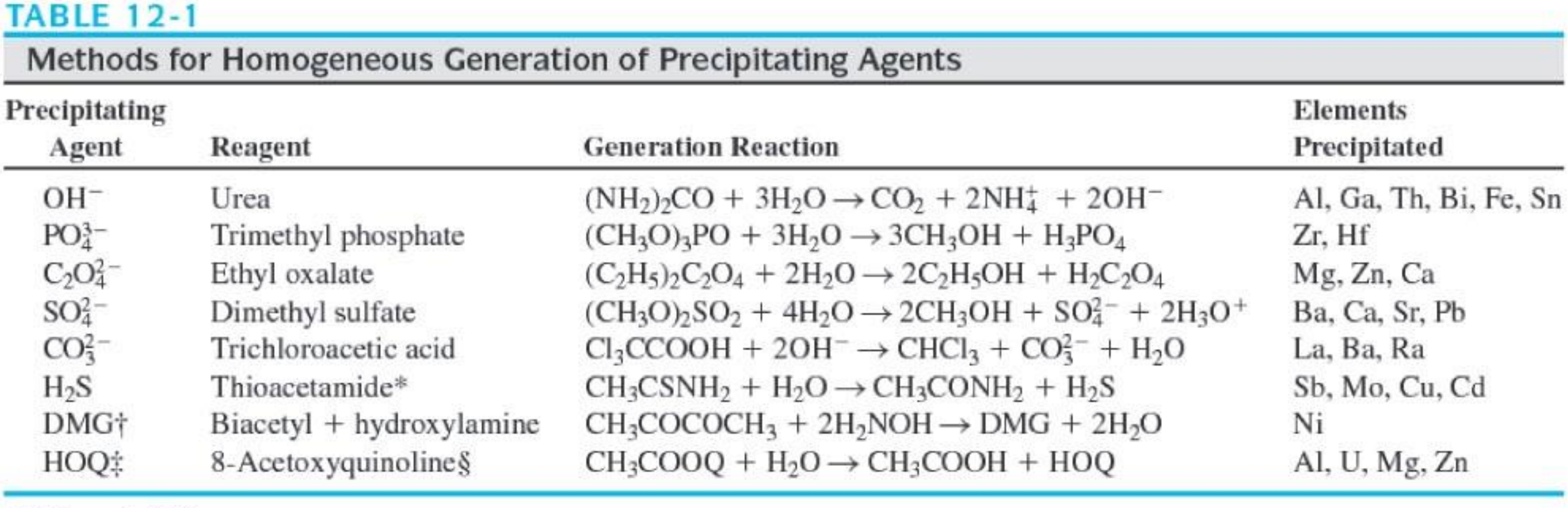
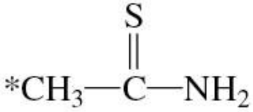


TABLE 12-1

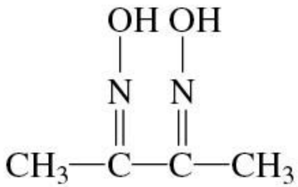
Methods for Homogeneous Generation of Precipitating Agents

Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH^-	Urea	$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
PO_4^{3-}	Trimethyl phosphate	$(CH_3O)_3PO + 3H_2O \rightarrow 3CH_3OH + H_3PO_4$	Zr, Hf
$C_2O_4^{2-}$	Ethyl oxalate	$(C_2H_5)_2C_2O_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2C_2O_4$	Mg, Zn, Ca
SO_4^{2-}	Dimethyl sulfate	$(CH_3O)_2SO_2 + 4H_2O \rightarrow 2CH_3OH + SO_4^{2-} + 2H_3O^+$	Ba, Ca, Sr, Pb
CO_3^{2-}	Trichloroacetic acid	$Cl_3CCOOH + 2OH^- \rightarrow CHCl_3 + CO_3^{2-} + H_2O$	La, Ba, Ra
H_2S	Thioacetamide*	$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$	Sb, Mo, Cu, Cd
DMG†	Biacetyl + hydroxylamine	$CH_3COCOCH_3 + 2H_2NOH \rightarrow DMG + 2H_2O$	Ni
HOQ‡	8-Acetoxyquinoline§	$CH_3COOQ + H_2O \rightarrow CH_3COOH + HOQ$	Al, U, Mg, Zn



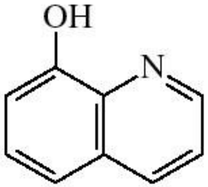
$$*CH_3-\overset{\overset{\displaystyle S}{\|}}{C}-NH_2$$

†DMG = Dimethylglyoxime =



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{\overset{N}{\underset{}{\overset{\|}{C}}}}-\overset{\overset{\displaystyle OH}{|}}{\overset{N}{\underset{}{\overset{\|}{C}}}}-CH_3$$

‡HOQ = 8-Hydroxyquinoline =



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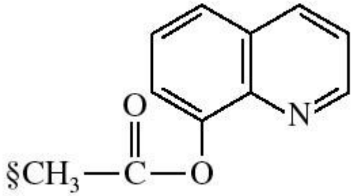

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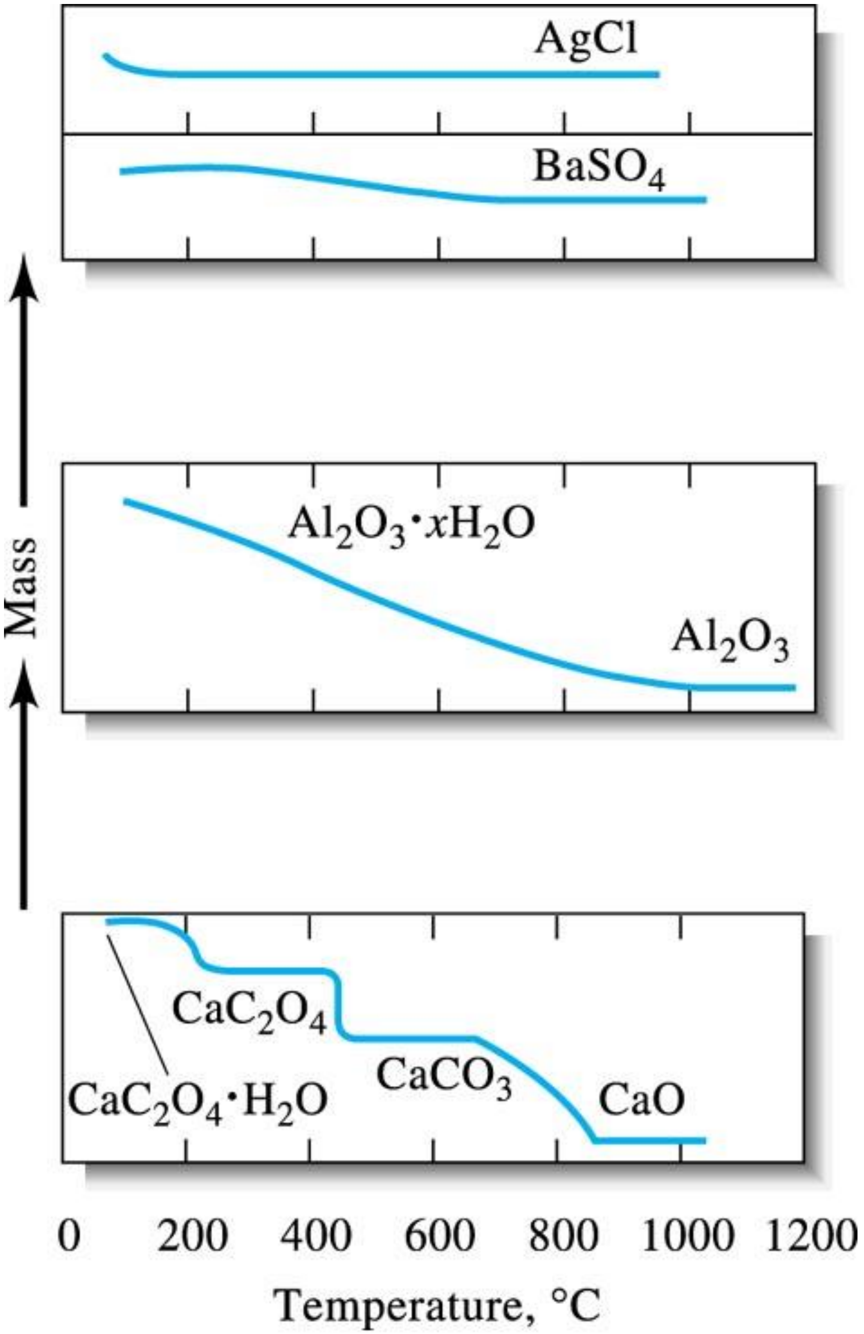
DRYING AND IGNITION OF PRECIPITATES

- After filtration, a gravimetric precipitate is heated until its mass becomes constant. Heating removes the solvent and any volatile species carried down with the precipitate. Some precipitates are also ignited to decompose the solid and form a compound of known composition. This new compound is often called the weighing form.
- The temperature required to produce a suitable weighing form varies from precipitate to precipitate.


AgCl
BaSO4
Al2O3·xH2O
Al2O3
CaC2O4
CaCO3
CaC2O4·H2O
CaO
Mass
0
200
400
600
800
1000
1200
Temperature, °C

Catalyst

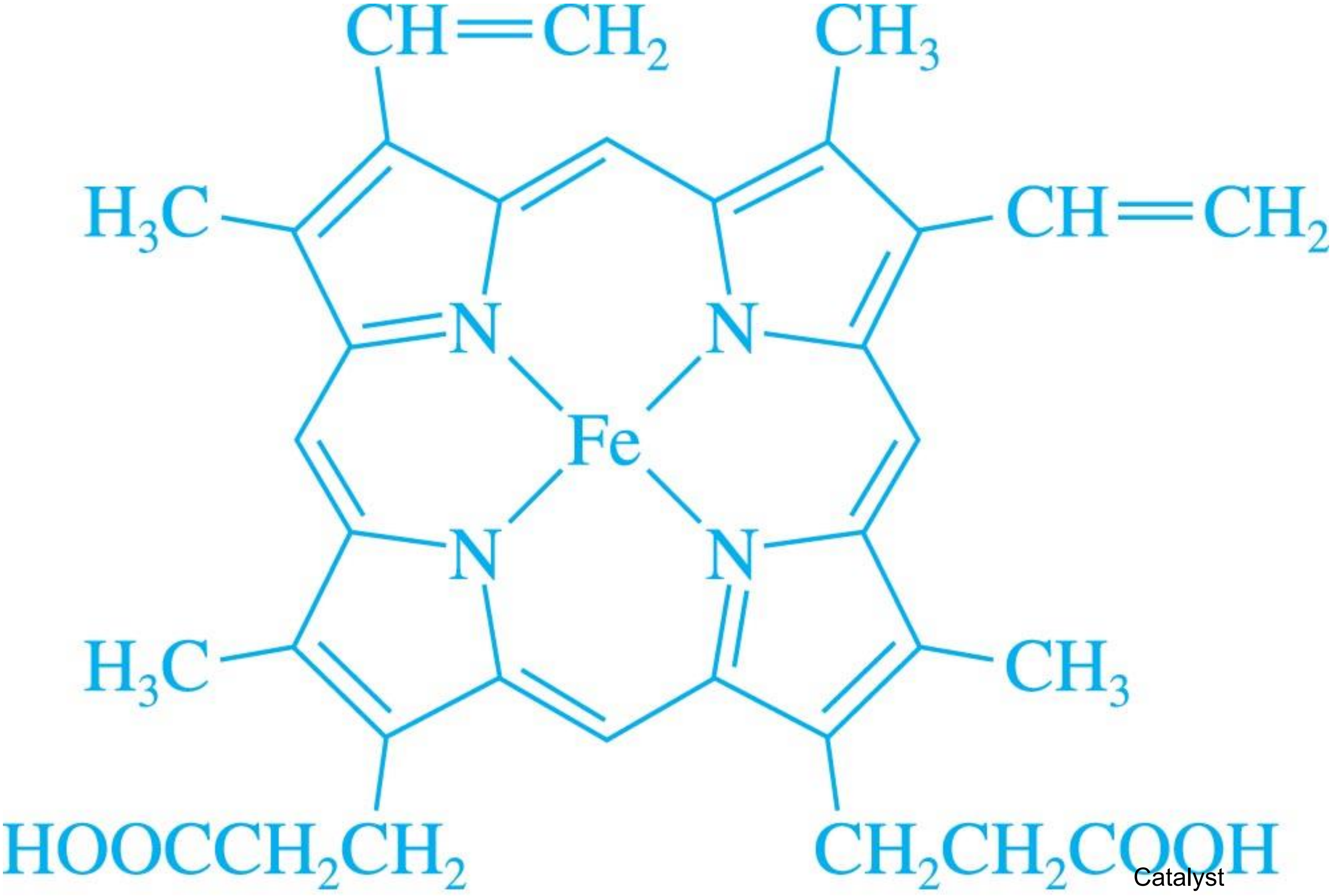


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TABLE 12-2

Some Inorganic Precipitating Agents

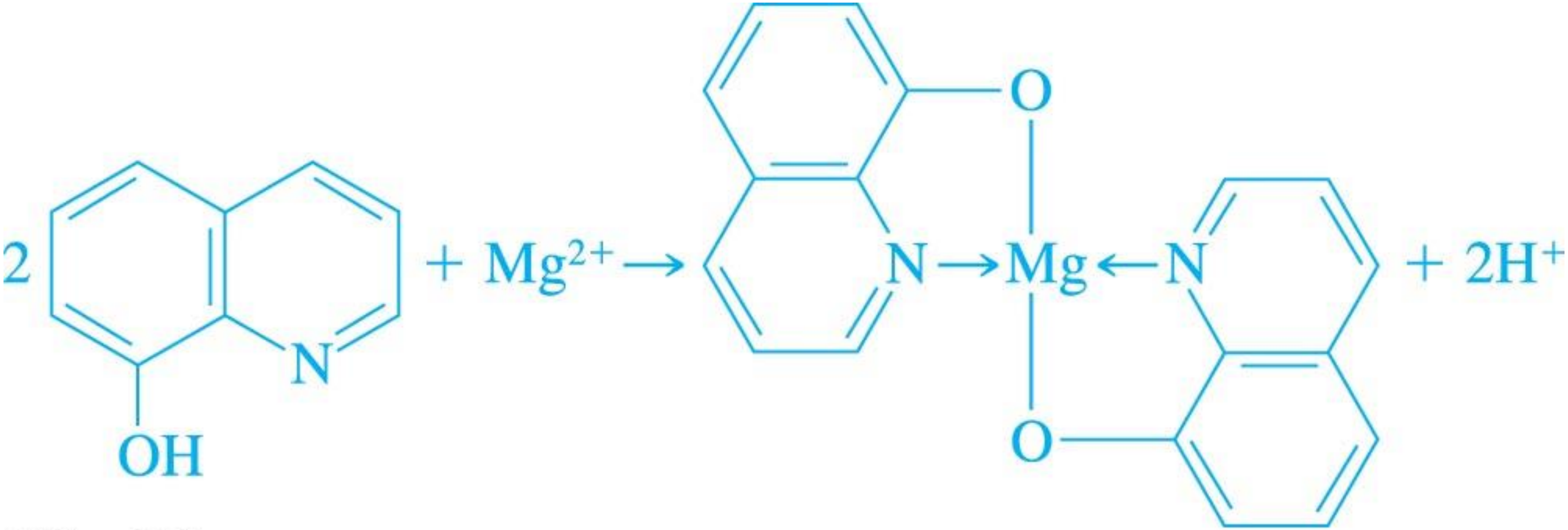
Precipitating Agent	Element Precipitated*
$NH_3(aq)$	**Be** (BeO), **Al** (Al_2O_3), **Sc** (Sc_2O_3), Cr (Cr_2O_3)†, **Fe** (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), **In** (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO)†, **Zn** (ZnO, or $ZnSO_4$), **Ge** (GeO_2), As ($\underline{As_2O_3}$, or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb ($\underline{Sb_2O_3}$), or Sb_2O_5), Bi (Bi_2S_3)
$(NH_4)_2S$	Hg ($\underline{HgS}$), Co (Co_3O_4)
$(NH_4)_2HPO_4$	**Mg** ($Mg_2P_2O_7$), Al ($AlPO_4$), Mn ($Mn_2P_2O_7$), Zn ($Zn_2P_2O_7$), Zr ($Zr_2P_2O_7$), Cd ($Cd_2P_2O_7$), Bi ($BiPO_4$)
H_2SO_4	Li, Mn, **Sr**, **Cd**, **Pb**, **Ba** (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6, or Pt), Rb ($\underline{Rb_2PtCl_6}$), Cs ($\underline{Cs_2PtCl_6}$)
$H_2C_2O_4$	Ca (CaO), Sr (SrO), **Th** (ThO_2)
$(NH_4)_2MoO_4$	Cd ($CdMoO_4$)†, Pb ($\underline{PbMoO_4}$)
HCl	Ag ($AgCl$), Hg (Hg_2Cl_2), Na (as $NaCl$ from butyl alcohol), Si (SiO_2)
$AgNO_3$	**Cl** ($AgCl$), Br ($\underline{AgBr}$), I($\underline{AgI}$)
$(NH_4)_2CO_3$	**Bi** (Bi_2O_3)
NH_4SCN	Cu [$Cu_2(SCN)_2$]
$NaHCO_3$	Ru, Os, Ir (precipitated as hydrous oxides; reduced with H_2 to metallic state)
HNO_3	Sn (SnO_2)
H_5IO_6	Hg [$Hg_5(IO_6)_2$]
$NaCl$, $Pb(NO_3)_2$	F ($PbClF$)
$BaCl_2$	**SO_4^{2-}** ($BaSO_4$)
$MgCl_2$, NH_4Cl	**PO_4^{3-}** ($Mg_2P_2O_7$)

*Boldface type indicates that gravimetric analysis is the preferred method for the element or ion. The weighed form is indicated in parentheses.

†A dagger indicates that the gravimetric method is seldom used. An underscore indicates the most reliable gravimetric method.

From W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis*. New York: Wiley, 1953.

Catalyst



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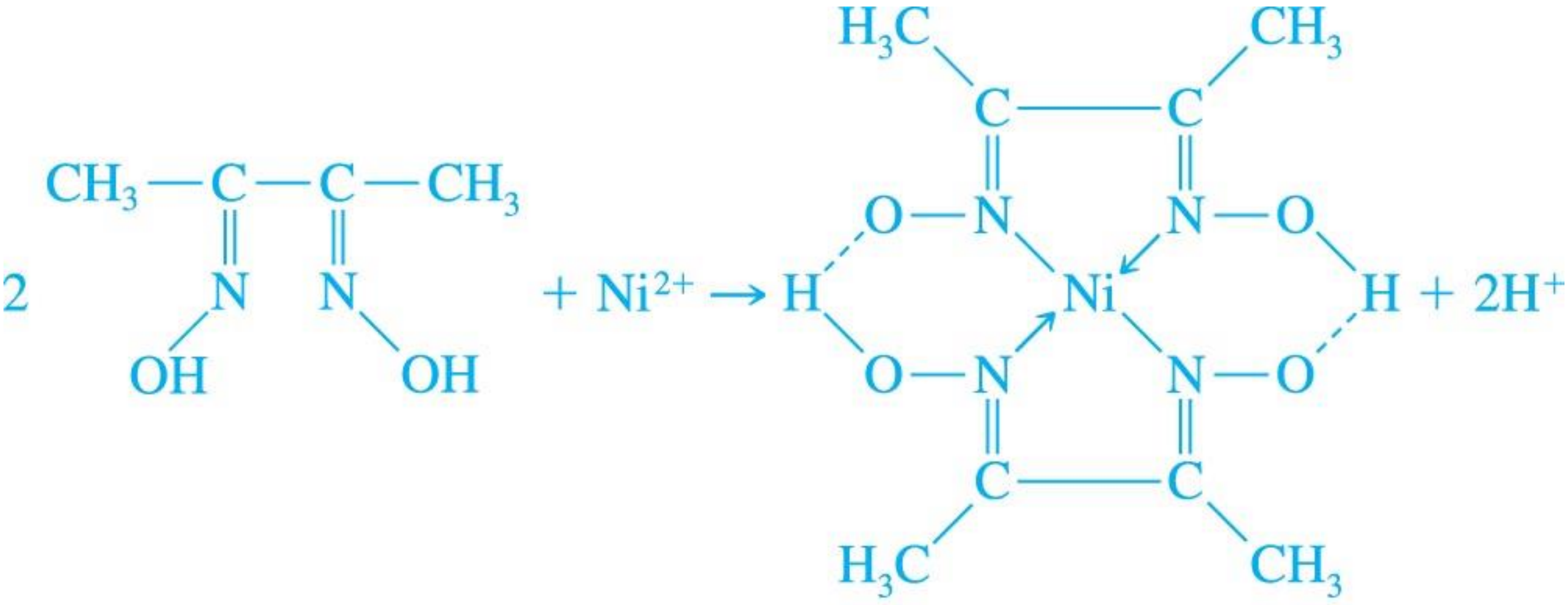

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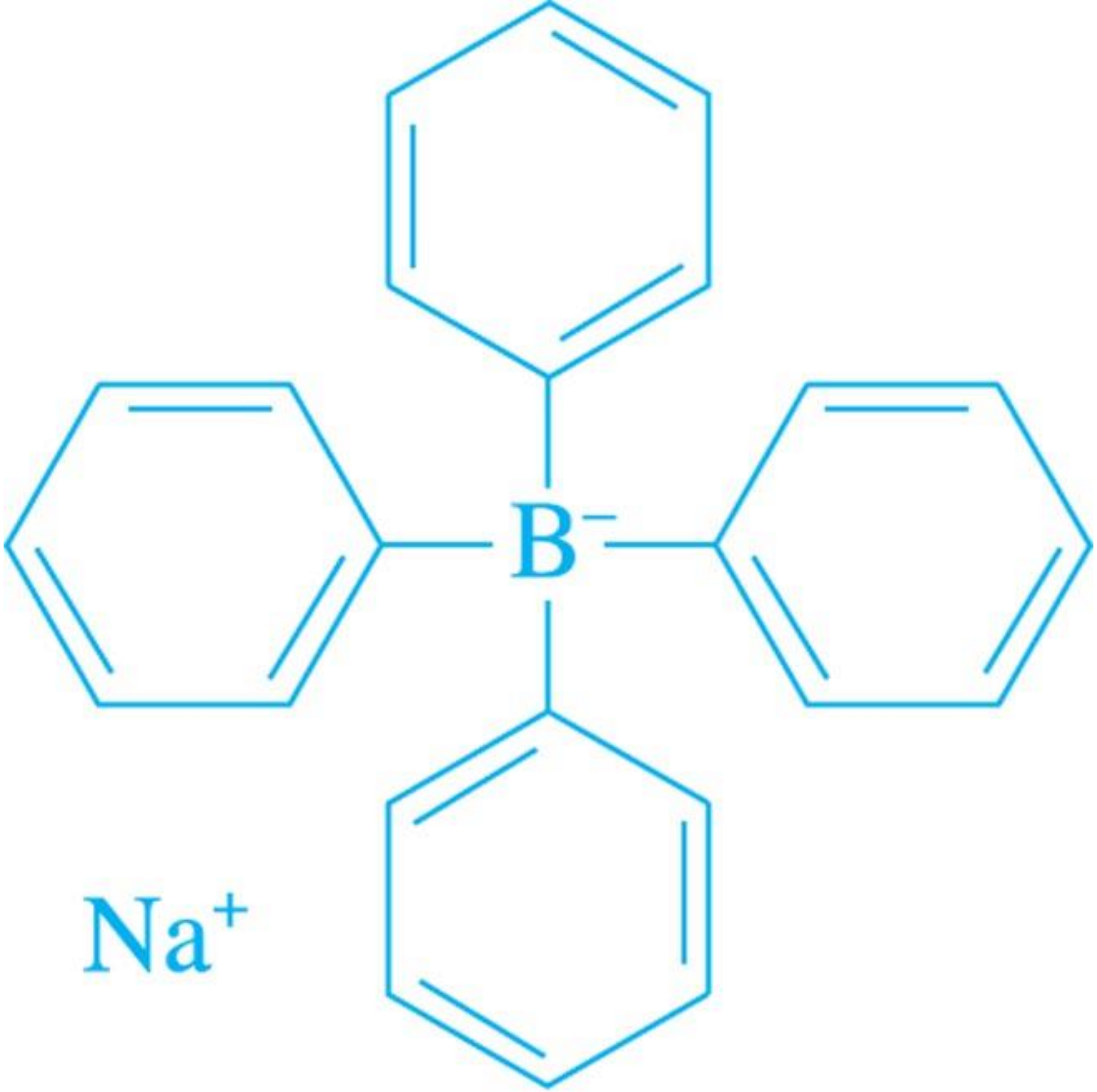

Sodium tetraphenyl borate

Catalyst

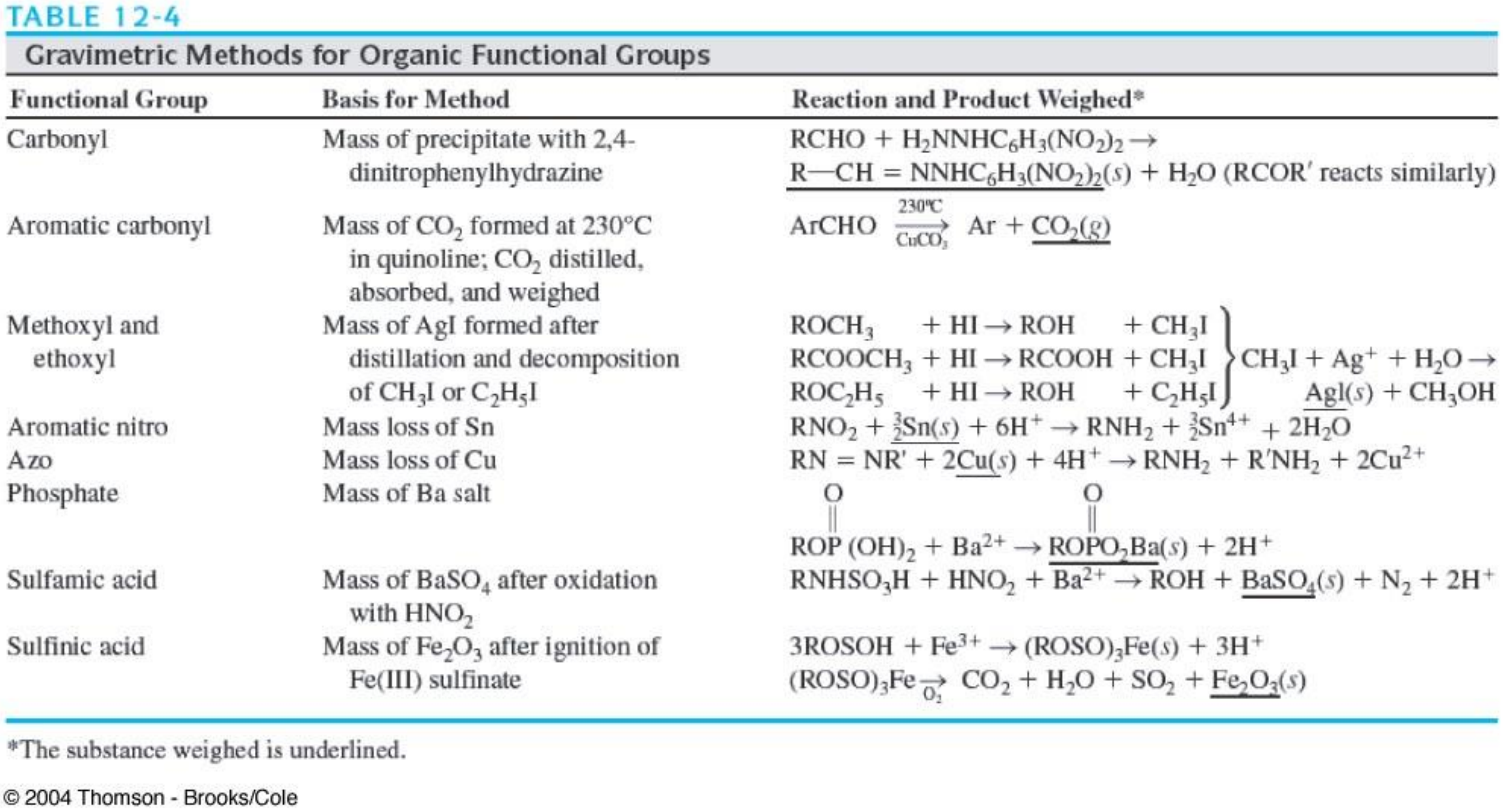

TABLE 12-4

Gravimetric Methods for Organic Functional Groups

Functional Group	Basis for Method	Reaction and Product Weighed*
Carbonyl	Mass of precipitate with 2,4-dinitrophenylhydrazine	$RCHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow$ $\underline{R{-}CH = NNHC_6H_3(NO_2)_2(s)} + H_2O$ (RCOR′ reacts similarly)
Aromatic carbonyl	Mass of CO_2 formed at 230°C in quinoline; CO_2 distilled, absorbed, and weighed	$ArCHO \xrightarrow[CuCO_3]{230°C} Ar + \underline{CO_2(g)}$
Methoxyl and ethoxyl	Mass of AgI formed after distillation and decomposition of CH_3I or C_2H_5I	$\left.\begin{array}{l} ROCH_3 + HI \rightarrow ROH + CH_3I \\ RCOOCH_3 + HI \rightarrow RCOOH + CH_3I \\ ROC_2H_5 + HI \rightarrow ROH + C_2H_5I \end{array}\right\} CH_3I + Ag^+ + H_2O \rightarrow \underline{AgI}(s) + CH_3OH$
Aromatic nitro	Mass loss of Sn	$RNO_2 + \underline{\tfrac{3}{2}Sn(s)} + 6H^+ \rightarrow RNH_2 + \tfrac{3}{2}Sn^{4+} + 2H_2O$
Azo	Mass loss of Cu	$RN = NR' + 2\underline{Cu(s)} + 4H^+ \rightarrow RNH_2 + R'NH_2 + 2Cu^{2+}$
Phosphate	Mass of Ba salt	$R\overset{\overset{O}{\|}}{O}P\,(OH)_2 + Ba^{2+} \rightarrow \underline{RO\overset{\overset{O}{\|}}{P}O_2Ba}(s) + 2H^+$
Sulfamic acid	Mass of $BaSO_4$ after oxidation with HNO_2	$RNHSO_3H + HNO_2 + Ba^{2+} \rightarrow ROH + \underline{BaSO_4}(s) + N_2 + 2H^+$
Sulfinic acid	Mass of Fe_2O_3 after ignition of Fe(III) sulfinate	$3ROSOH + Fe^{3+} \rightarrow (ROSO)_3Fe(s) + 3H^+$ $(ROSO)_3Fe \xrightarrow[O_2]{} CO_2 + H_2O + SO_2 + \underline{Fe_2O_3}(s)$

*The substance weighed is underlined.

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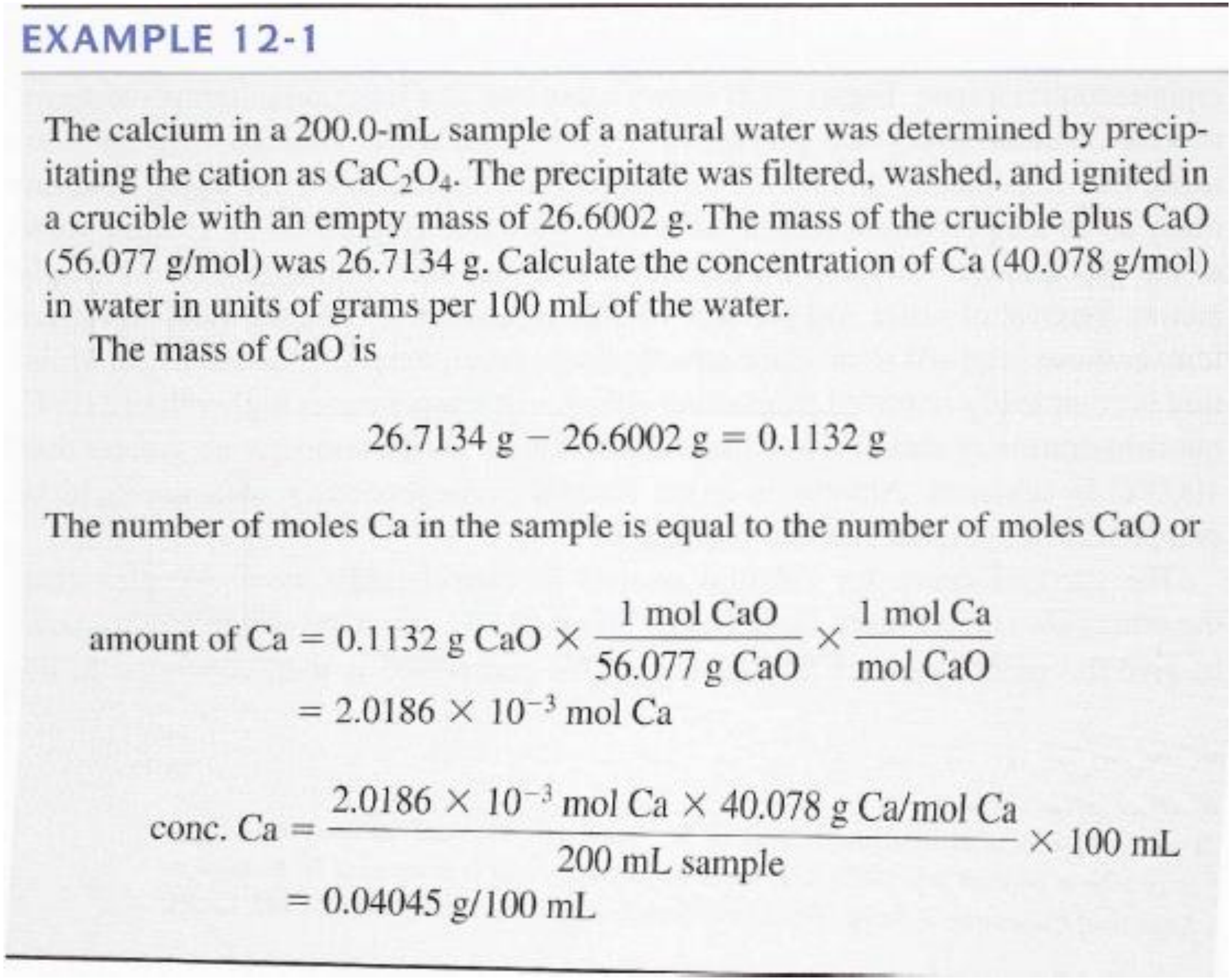


EXAMPLE 12-1

The calcium in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC_2O_4. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO (56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g/mol) in water in units of grams per 100 mL of the water.

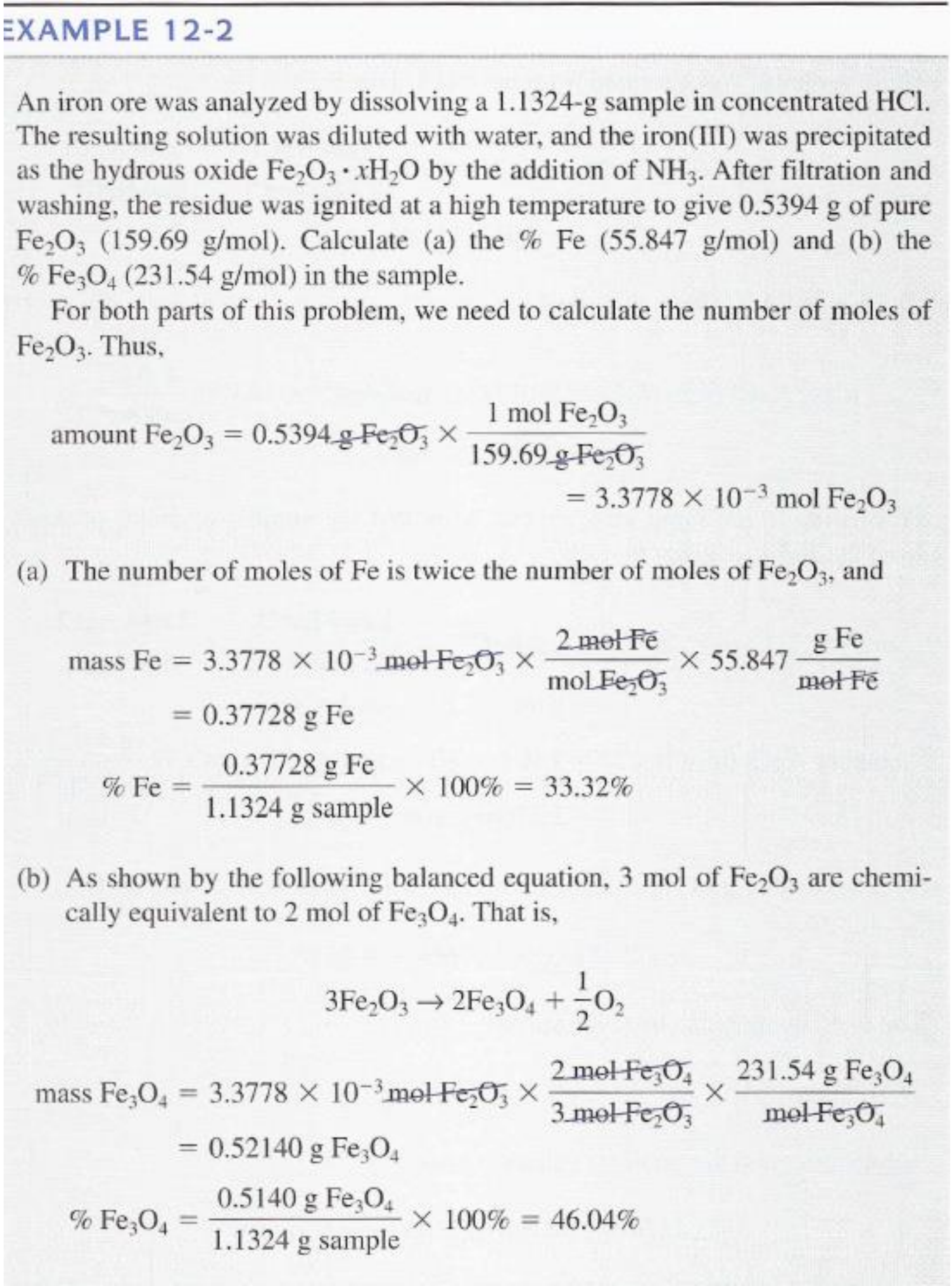
The mass of CaO is

$$26.7134\ \text{g} - 26.6002\ \text{g} = 0.1132\ \text{g}$$

The number of moles Ca in the sample is equal to the number of moles CaO or

$$\begin{aligned}\text{amount of Ca} &= 0.1132\ \text{g CaO} \times \frac{1\ \text{mol CaO}}{56.077\ \text{g CaO}} \times \frac{1\ \text{mol Ca}}{\text{mol CaO}} \\ &= 2.0186 \times 10^{-3}\ \text{mol Ca}\end{aligned}$$

$$\begin{aligned}\text{conc. Ca} &= \frac{2.0186 \times 10^{-3}\ \text{mol Ca} \times 40.078\ \text{g Ca/mol Ca}}{200\ \text{mL sample}} \times 100\ \text{mL} \\ &= 0.04045\ \text{g}/100\ \text{mL}\end{aligned}$$



EXAMPLE 12-2

An iron ore was analyzed by dissolving a 1.1324-g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $Fe_2O_3 \cdot xH_2O$ by the addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe_3O_4 (231.54 g/mol) in the sample.

For both parts of this problem, we need to calculate the number of moles of Fe_2O_3. Thus,

$$\text{amount } Fe_2O_3 = 0.5394\, \cancel{\text{g } Fe_2O_3} \times \frac{1 \text{ mol } Fe_2O_3}{159.69\, \cancel{\text{g } Fe_2O_3}}$$
$$= 3.3778 \times 10^{-3} \text{ mol } Fe_2O_3$$

(a) The number of moles of Fe is twice the number of moles of Fe_2O_3, and

$$\text{mass Fe} = 3.3778 \times 10^{-3}\, \cancel{\text{mol } Fe_2O_3} \times \frac{2\, \cancel{\text{mol Fe}}}{\text{mol}\, \cancel{Fe_2O_3}} \times 55.847 \frac{\text{g Fe}}{\cancel{\text{mol Fe}}}$$
$$= 0.37728 \text{ g Fe}$$

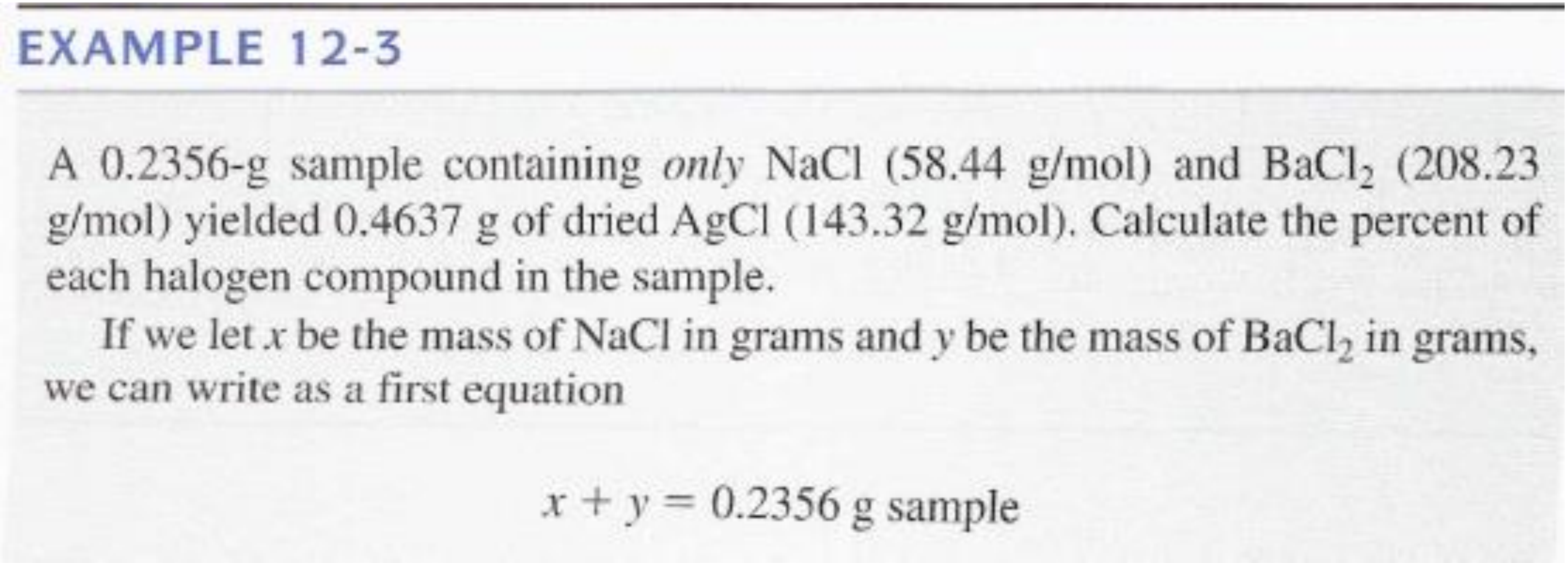
$$\% \text{ Fe} = \frac{0.37728 \text{ g Fe}}{1.1324 \text{ g sample}} \times 100\% = 33.32\%$$

(b) As shown by the following balanced equation, 3 mol of Fe_2O_3 are chemically equivalent to 2 mol of Fe_3O_4. That is,

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$$

$$\text{mass } Fe_3O_4 = 3.3778 \times 10^{-3}\, \cancel{\text{mol } Fe_2O_3} \times \frac{2\, \cancel{\text{mol } Fe_3O_4}}{3\, \cancel{\text{mol } Fe_2O_3}} \times \frac{231.54 \text{ g } Fe_3O_4}{\cancel{\text{mol } Fe_3O_4}}$$
$$= 0.52140 \text{ g } Fe_3O_4$$

$$\% \text{ } Fe_3O_4 = \frac{0.5140 \text{ g } Fe_3O_4}{1.1324 \text{ g sample}} \times 100\% = 46.04\%$$

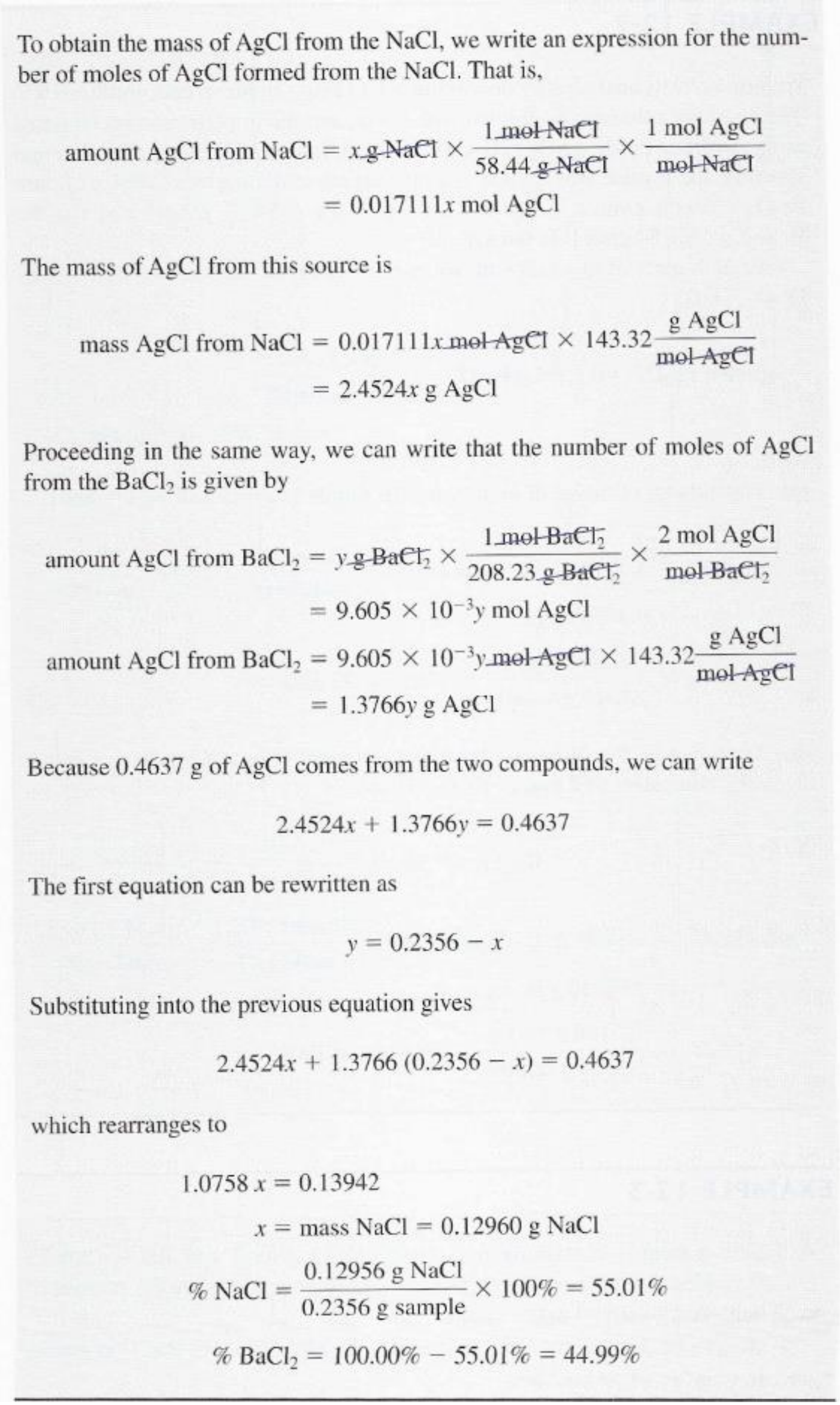


EXAMPLE 12-3

A 0.2356-g sample containing *only* NaCl (58.44 g/mol) and $BaCl_2$ (208.23 g/mol) yielded 0.4637 g of dried AgCl (143.32 g/mol). Calculate the percent of each halogen compound in the sample.

If we let x be the mass of NaCl in grams and y be the mass of $BaCl_2$ in grams, we can write as a first equation

$$x + y = 0.2356 \text{ g sample}$$



To obtain the mass of AgCl from the NaCl, we write an expression for the number of moles of AgCl formed from the NaCl. That is,

$$\text{amount AgCl from NaCl} = x\,\cancel{\text{g NaCl}} \times \frac{1\,\cancel{\text{mol NaCl}}}{58.44\,\cancel{\text{g NaCl}}} \times \frac{1\text{ mol AgCl}}{\cancel{\text{mol NaCl}}}$$
$$= 0.017111x\text{ mol AgCl}$$

The mass of AgCl from this source is

$$\text{mass AgCl from NaCl} = 0.017111x\,\cancel{\text{mol AgCl}} \times 143.32\frac{\text{g AgCl}}{\cancel{\text{mol AgCl}}}$$
$$= 2.4524x\text{ g AgCl}$$

Proceeding in the same way, we can write that the number of moles of AgCl from the $BaCl_2$ is given by

$$\text{amount AgCl from BaCl}_2 = y\,\cancel{\text{g BaCl}_2} \times \frac{1\,\cancel{\text{mol BaCl}_2}}{208.23\,\cancel{\text{g BaCl}_2}} \times \frac{2\text{ mol AgCl}}{\cancel{\text{mol BaCl}_2}}$$
$$= 9.605 \times 10^{-3}y\text{ mol AgCl}$$
$$\text{amount AgCl from BaCl}_2 = 9.605 \times 10^{-3}y\,\cancel{\text{mol AgCl}} \times 143.32\frac{\text{g AgCl}}{\cancel{\text{mol AgCl}}}$$
$$= 1.3766y\text{ g AgCl}$$

Because 0.4637 g of AgCl comes from the two compounds, we can write

$$2.4524x + 1.3766y = 0.4637$$

The first equation can be rewritten as

$$y = 0.2356 - x$$

Substituting into the previous equation gives

$$2.4524x + 1.3766\,(0.2356 - x) = 0.4637$$

which rearranges to

$$1.0758\,x = 0.13942$$
$$x = \text{mass NaCl} = 0.12960\text{ g NaCl}$$
$$\%\text{ NaCl} = \frac{0.12956\text{ g NaCl}}{0.2356\text{ g sample}} \times 100\% = 55.01\%$$
$$\%\text{ BaCl}_2 = 100.00\% - 55.01\% = 44.99\%$$

Catalyst

Chapter 13
Titrimetric Methods

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.

Volumetric titrimetry involves measuring the volume of a solution of known concentration that is needed to react essentially completely with the analyte.

Gravimetric titrimetry differs only in that the mass of the reagent is measured instead of its volume.

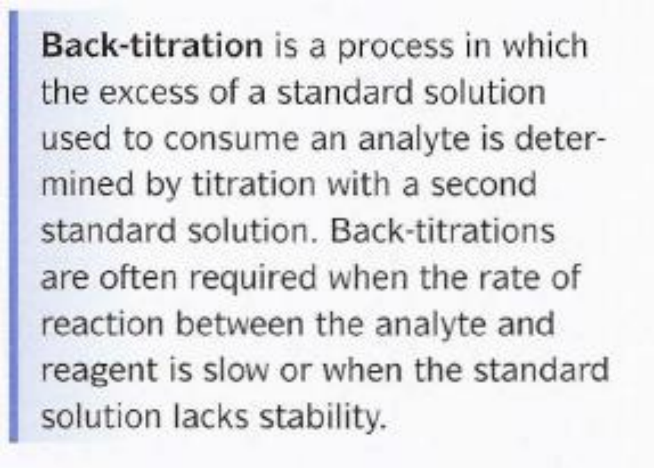
In ***coulometric titrimetry***, the ‘reagent’, is a constant direct electrical current of known magnitude that consumes the analyte.

Defining Some Terms

A ***standard solution*** (or a standard titrant) is a reagent of known concentration that is used to carry out a titrimetric analysis.

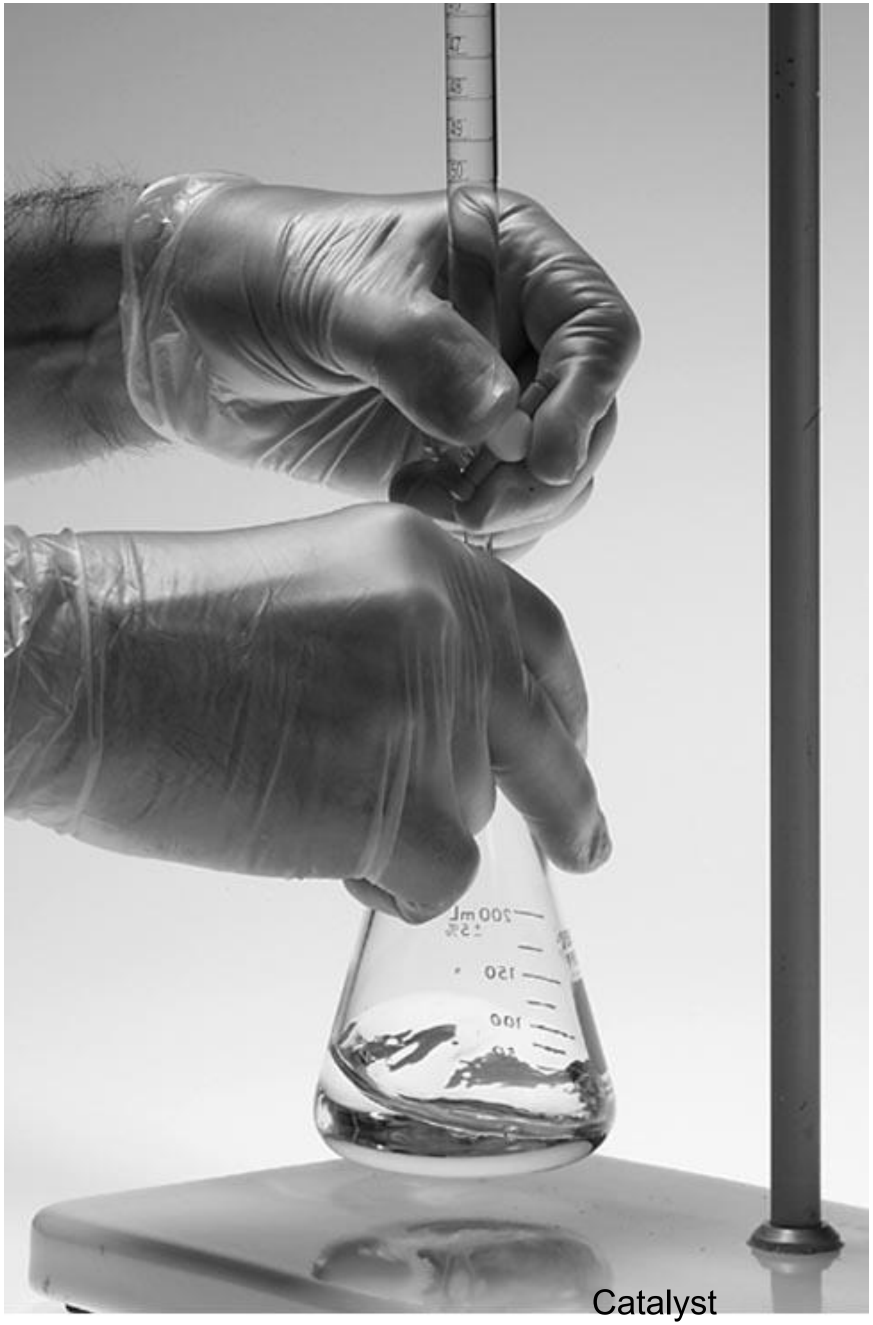
A ***titration*** is performed by adding a standard solution from a buret or other liquid-dispensing device to a solution of the analyte until the reaction between the two is judged complete. The volume of reagent needed to complete the titration is determined from the difference between the initial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

The equivalence point in a titration is reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample.



Back-titration is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution. Back-titrations are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability.

Catalyst



Catalyst

Equivalence Points and End Points

- The equivalence point of a titration cannot be determined experimentally. Instead, we can only estimate its position by observing some physical change associated with the condition of equivalence. This change is called the ***end point*** for the titration.
- Every effort is made to ensure that any volume or mass difference between the equivalence point and the end point is small. Such differences do exist, however, as a result of inadequacies in the physical changes and in our ability to observe them.
- The difference in volume or mass between the equivalence point and the end point is the titration error.
- ***Indicators*** are often added to the analyte solution to give an observable physical change (the end point) at or near the equivalence point. Large changes in the relative concentration of analyte or titrant occur in the equivalence-point region. These concentration changes cause the indicator to change in appearance. Typical indicator changes include the appearance or disappearance of a color, a change in color, or the appearance or disappearance of turbidity.

Primary Standards

A ***primary standard*** is a highly purified compound that serves as a reference material in all volumetric and mass titrimetric methods. The accuracy of a method is critically dependent on the properties of this compound. Important requirements for a primary standard are:

1. High purity
2. Atmospheric stability
3. Absence of hydrate water so that the composition of the solid does not change with variation in relative humidity
4. Ready availability at modest cost
5. Reasonable solubility in the titration medium
6. Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

Desirable Properties of standard Solutions

The ideal standard solution for a titrimetric method will:

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 between additions of reagent is minimized.
3. React completely with the analyte so that satisfactory end points are realized.
4. Undergo a selective reaction with the analyte that can be described by a balanced equation.

Establishing the Concentration of Standard solutions

The accuracy of a titrimetric method can be no better than the accuracy of the concentration of the standard solution used in the titration.

Two basic methods are used to establish the concentration of such solutions. The first is the ***direct method*** in which a carefully weighed quantity of a primary standard is dissolved in a suitable solvent and diluted to a known volume in a volumetric flask. The second is by standardization in which the titrant to be standardized is use to titrate (1) a weighed quantity of a primary standard, (2) a weighed quantity of a secondary standard, or (3) a measured volume of another standard solution.

Expressing the Concentration of Standard Solutions

The concentrations of standard solutions are generally expressed in units of either ***molarity*** c or ***normality*** c_N. The first gives the number of moles of reagent contained in one liter of solution, and the second gives the number of equivalents of reagent in the same volume.

M = moles/L

N = equivalents/L

Examples: 1-3

Some Useful algebraic Relationships

Most volumetric calculations are based on two pairs of fundamental equations that are derived from definitions of millimole, mole, and molar concentration. For the chemical species A, we may write

$$\text{amount A (mol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g / mol)}}$$

$$\text{amount A (mmol)} = \frac{\text{mass A (g)}}{\text{millimolar mass A (g / mmol)}}$$

We may derive a second pair from the definition of molar concentration. That is,

$$\text{amount A (mol)} = \text{volume (L)} \times \text{concentration A} \left(\frac{\text{mol}}{\text{L}}\right)$$

$$\text{amount A (mmol)} = \text{volume (mL)} \times \text{concentration A} \left(\frac{\text{mmol}}{\text{mL}}\right)$$

EXAMPLE 13-1

Describe the preparation of 2.000 L of 0.0500 M $AgNO_3$ (169.87 g/mol) from the primary-standard–grade solid.

Since the volume is in liters, we base our calculations on the mole rather than the millimole. Thus, to obtain the amount of $AgNO_3$ needed, we write

$$\begin{aligned}\text{amount AgNO}_3 &= V_{\text{soln}}(\text{L}) \times c_{\text{AgNO}_3}(\text{mol/L})\\ &= 2.000\,\cancel{\text{L}} \times \frac{0.0500\text{ mol Na}_2\text{CO}_3}{\cancel{\text{L}}} = 0.1000\text{ mol AgNO}_3\end{aligned}$$

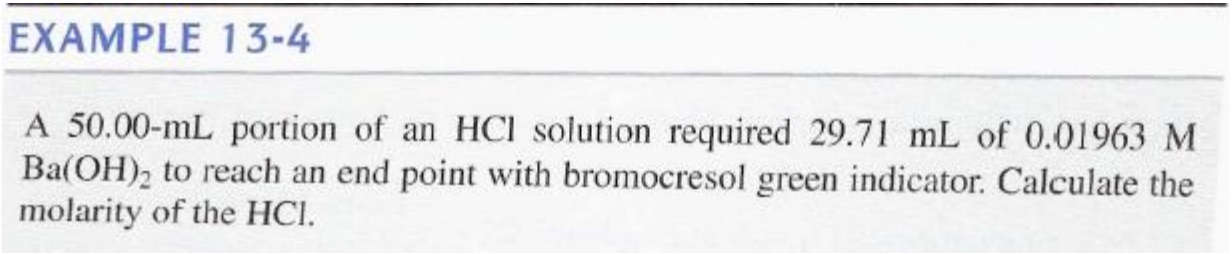
To obtain the mass of $AgNO_3$, we rearrange Equation 13-2 to give

$$\begin{aligned}\text{mass AgNO}_3 &= 0.1000\,\cancel{\text{mol AgNO}_3} \times \frac{169.87\text{ g AgNO}_3}{\cancel{\text{mol AgNO}_3}}\\ &= 16.98\text{ g AgNO}_3\end{aligned}$$

Therefore, the solution is prepared by dissolving 16.98 g of $AgNO_3$ in water and diluting to exactly 2.000 L.

Treating Titration Data

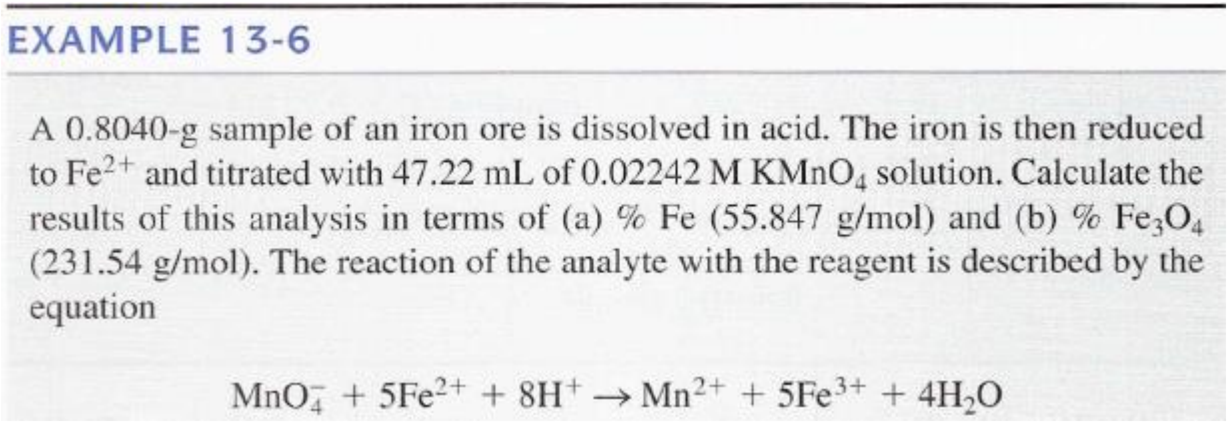
- *Calculating Molaritles from Standardization on Data*



EXAMPLE 13-4

A 50.00-mL portion of an HCl solution required 29.71 mL of 0.01963 M $Ba(OH)_2$ to reach an end point with bromocresol green indicator. Calculate the molarity of the HCl.

- *Calculating the Quantity* of *Analyte from Titration Data*



EXAMPLE 13-6

A 0.8040-g sample of an iron ore is dissolved in acid. The iron is then reduced to Fe^{2+} and titrated with 47.22 mL of 0.02242 M $KMnO_4$ solution. Calculate the results of this analysis in terms of (a) % Fe (55.847 g/mol) and (b) % Fe_3O_4 (231.54 g/mol). The reaction of the analyte with the reagent is described by the equation

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

Examples: 4-9

Catalyst

GRAVIMETRIC TITRIMETRY

- The *mass* of titrant is measured rather than the volume.
  - Balance and a weighable solution dispenser are substituted for a buret and its markings.

TITRATION CURVES

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

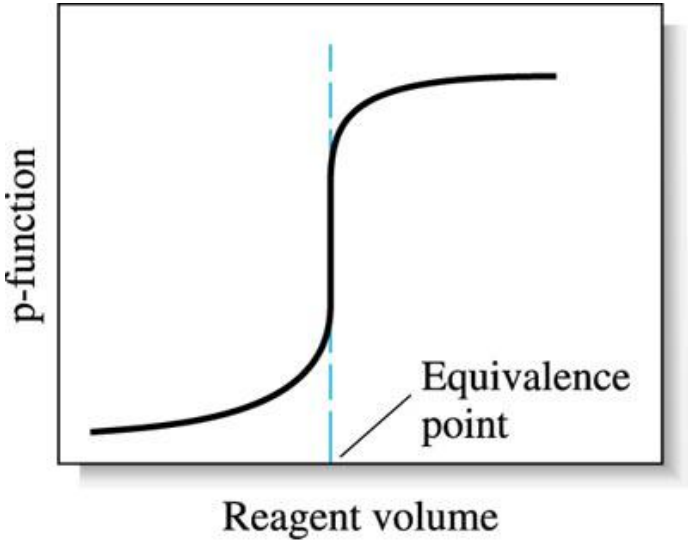
1. changes in color due to the reagent, the analyte, or an indicator and
2. a change in potential of an electrode that responds to the concentration of the reagent or the analyte.

To understand the detection of end points and the sources of titration errors, we will construct ***titration curves*** for the system under consideration.

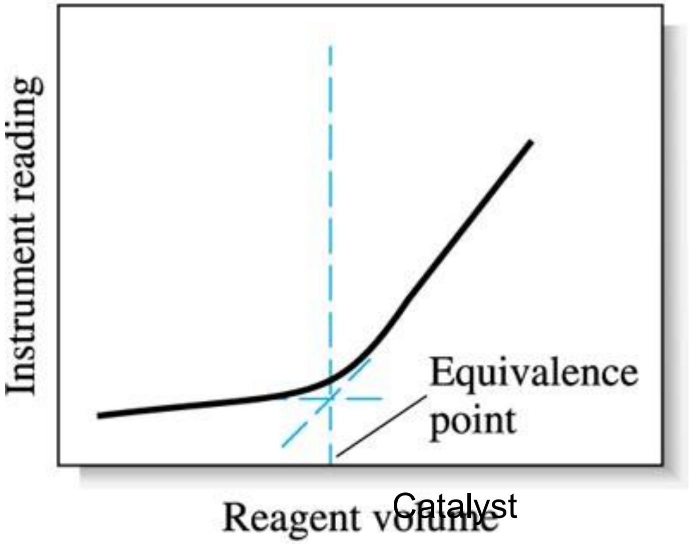
Titration curves consist of a plot of reagent volume on the horizontal axis and some function of the analyte or reagent concentration on the vertical axis.

Types of Titration Curves

- **Sigmoidal curve**, in which the p-function of analyte (or sometimes the reagent) is plotted as a function of reagent volume.
- **Linear segment curve**, measurements are made on both sides of, *but well away from*, the equivalence point.
  - Measurements near equivalence are avoided.
  - 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

$$Ag^+ + SCN^- \rightarrow AgSCN_{(s)}$$

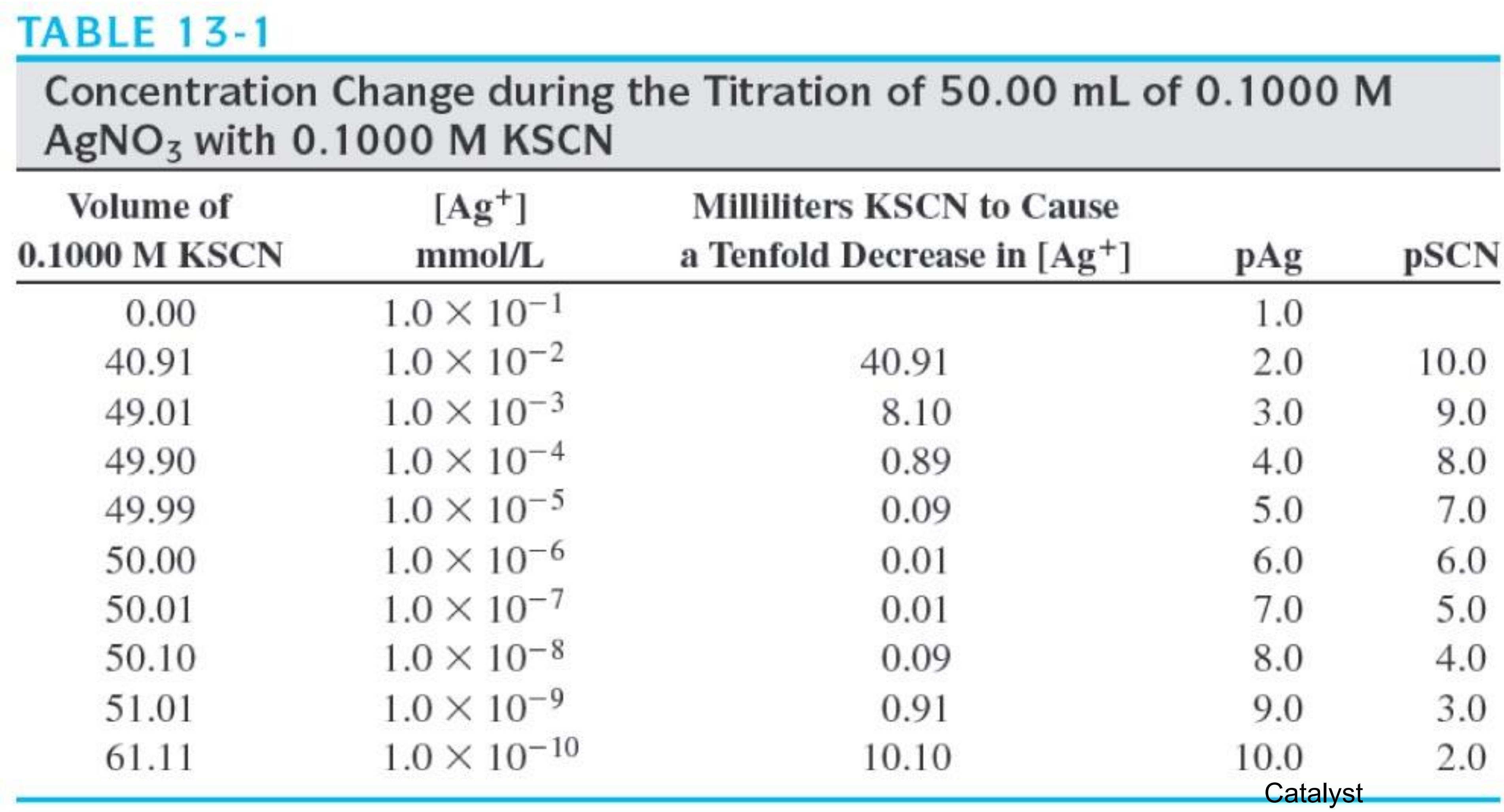
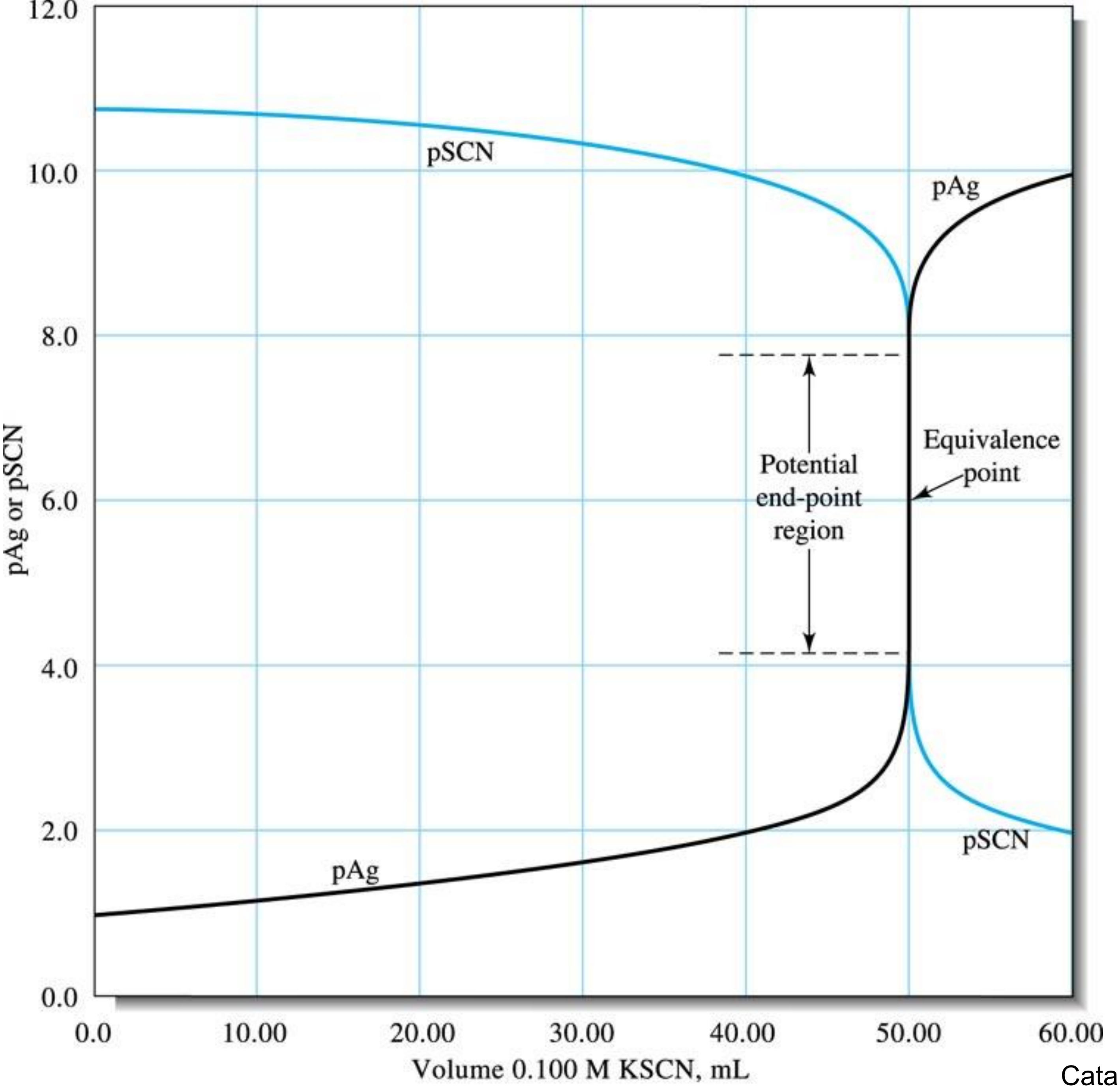


TABLE 13-1

Concentration Change during the Titration of 50.00 mL of 0.1000 M $AgNO_3$ with 0.1000 M KSCN

Volume of 0.1000 M KSCN	$[Ag^+]$ mmol/L	Milliliters KSCN to Cause a Tenfold Decrease in $[Ag^+]$	pAg	pSCN
0.00	1.0×10^{-1}		1.0	
40.91	1.0×10^{-2}	40.91	2.0	10.0
49.01	1.0×10^{-3}	8.10	3.0	9.0
49.90	1.0×10^{-4}	0.89	4.0	8.0
49.99	1.0×10^{-5}	0.09	5.0	7.0
50.00	1.0×10^{-6}	0.01	6.0	6.0
50.01	1.0×10^{-7}	0.01	7.0	5.0
50.10	1.0×10^{-8}	0.09	8.0	4.0
51.01	1.0×10^{-9}	0.91	9.0	3.0
61.11	1.0×10^{-10}	10.10	10.0	2.0

Catalyst


12.0
10.0
8.0
6.0
4.0
2.0
0.0
pAg or pSCN
pSCN
pAg
Potential end-point region
Equivalence point
pAg
pSCN
0.0
10.00
20.00
30.00
40.00
50.00
60.00
Volume 0.100 M KSCN, mL

Catalyst

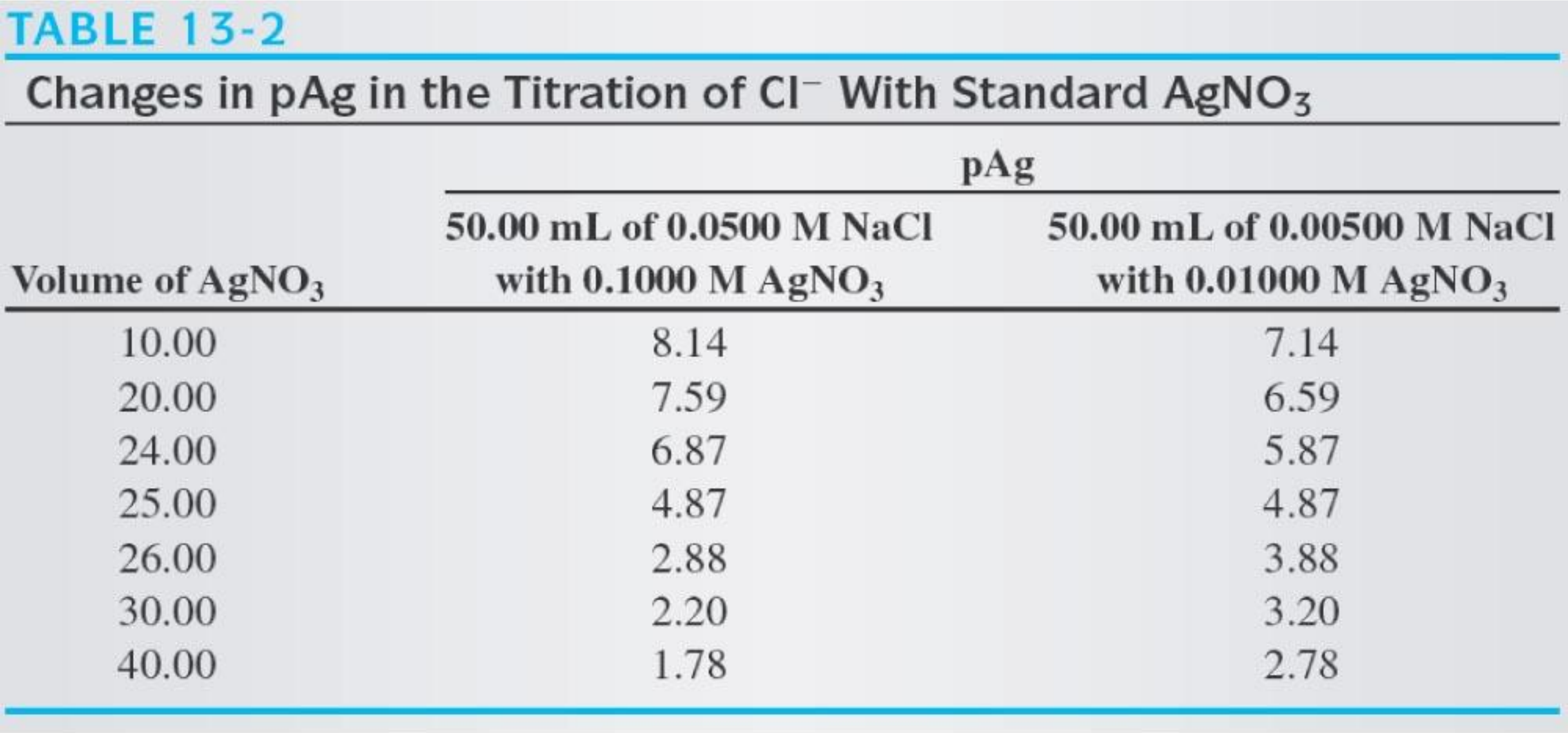


TABLE 13-2

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

Catalyst

PRECIPITATION TITRIMETRY

- is based on reactions that yield ionic compounds of limited solubility.
- Because of the slow rate of formation of most precipitates, however, there are only a few precipitating agents that can be used in titrimetry.
  - Most widely used and most important precipitating reagent is silver nitrate. It is used for halides, the halide-like anions (SCN-, CN-, CNO-), mercaptans, fatty acids, and several divalent and trivalent inorganic anions. **(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.
- 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, three type of calculations are required, each of which corresponds to a distinct stage in the reaction:
  1. preequivalence,
  2. Equivalence
  3. postequivalence

EXAMPLE 13-10

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, $K_{sp} = 1.82 \times 10^{-10}$).

$$\text{Reaction:} \qquad Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

(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,

$$c_{NaCl} = \frac{\text{original number of mmol NaCl} - \text{no. mmol } AgNO_3 \text{ added}}{\text{total volume solution}}$$

(continued)

But

$$\text{original number of mmol NaCl} = 50.00\ \cancel{\text{mL}} \times 0.0500\ \frac{\text{mmol NaCl}}{\cancel{\text{mL}}} = 2.500$$

$$\text{number of mmol } AgNO_3 \text{ added} = 10.00\ \cancel{\text{mL}} \times 0.1000\ \frac{\text{mmol } AgNO_3}{\cancel{\text{mL}}} = 1.000$$

$$\text{no. mmol NaCl remaining} = 1.500$$

$$c_{NaCl} = \frac{1.500 \text{ mmol NaCl}}{(50.00 + 10.00)\text{ mL}} = 0.02500\ \frac{\text{mmol NaCl}}{\text{mL}} = 0.02500\text{ M}$$

$$[Cl^-] = 0.02500\text{ M}$$

$$[Ag^+] = K_{sp}/[Cl^-] = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9}\text{ M}$$

$$pAg = -\log(7.28 \times 10^{-9}) = 8.14$$

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,

$$[Ag^+] = [Cl^-] \qquad \text{and} \qquad [Ag^+][Cl^-] = 1.82 \times 10^{-10} = [Ag^+]^2$$

$$[Ag^+] = 1.349 \times 10^{-5}\text{ M} \qquad \text{and} \qquad pAg = -\log(1.349 \times 10^{-5}) = 4.87$$

(3) **Postequivalence-Point Data**

At 26.00 mL $AgNO_3$ added, Ag^+ is in excess, so

$$[Ag^+] = c_{AgNO_3} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{50.00 - 26.00} = 1.316 \times 10^{-3}\text{ M}$$

$$pAg = -\log(1.316 \times 10^{-3}) = 2.88$$

Additional postequivalence-point data are obtained in the same way and are shown in Table 13-2.

TABLE 13-2

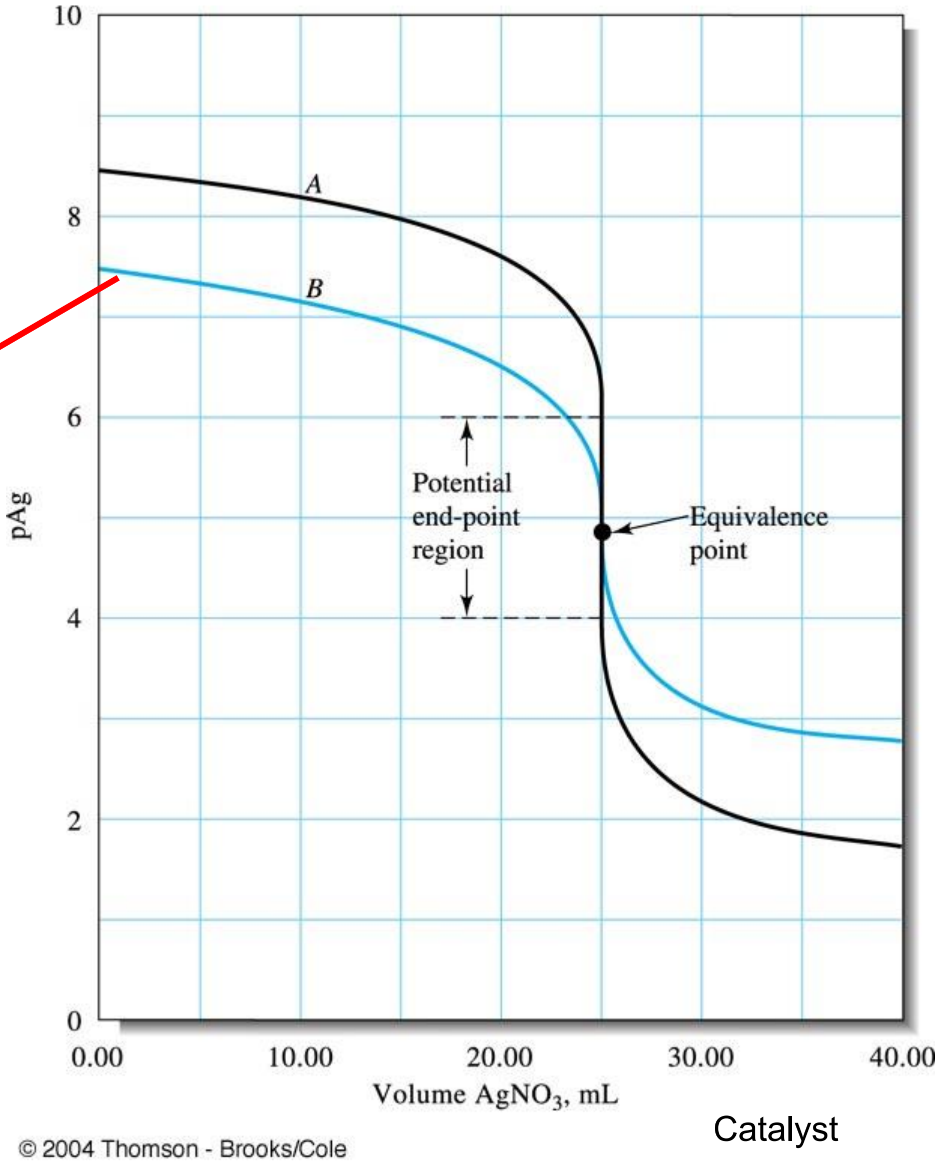
Changes in pAg in the Titration of Cl^- With Standard $AgNO_3$

	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

Catalyst

The Effect of Concentration on Titration Curves

For the more dilute chloride solution, the change in pAg in the equivalence-point region would be too small to be detected precisely with a visual indicator.



Catalyst

The Effect of Reaction Completeness on Titration Curves

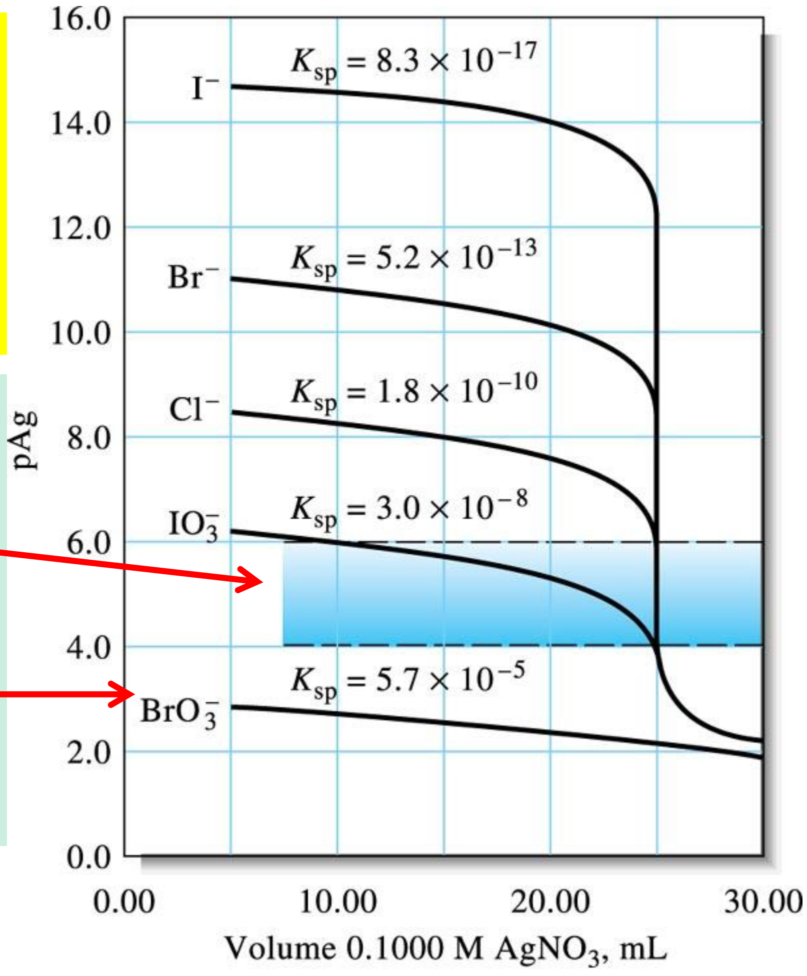
Clearly, the change in pAg at the equivalence point becomes greater as the solubility products become smaller, that is, as the reaction between the analyte and silver nitrate becomes more complete.

By careful choice of indicator -*one that changes color in the region of pAg from 4 to 6*- titration of chloride ion should be possible with a minimal titration error.

Note that ions forming precipitates with K_{sp} much larger than ~10^{-10} do not yield satisfactory end points.

*You can derive a useful relationship for silver chloride,

$$\begin{aligned} -\log K_{sp} &= -\log([Ag^+][Cl^-]) \\ &= -\log[Ag^+] - \log[Cl^-] \\ pK_{sp} &= pAg + pCI \\ &= -\log(1.82 \text{ X } 10^{-10}) \\ 9.74 &= pAg + pCI \end{aligned}$$



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Titration Curves for Mixtures of Anions

- The methods developed in the previous section for deriving titration curves can be extended to mixtures that form precipitates of different solubilities.
- Silver chloride has greater Ksp than silver iodide
  - ✓ AgCl does not begin to precipitate until well into the titration.

- How much iodide is precipitated before appreciable amounts of silver chloride form.

$$\frac{\cancel{[Ag^+]}[I^-]}{\cancel{[Ag^+]}[Cl^-]} = \frac{8.3 \times 10^{-17}}{1.82 \times 10^{-10}} = 4.56 \times 10^{-7}$$

$$[I^-] = (4.56 \times 10^{-7})\,[Cl^-]$$

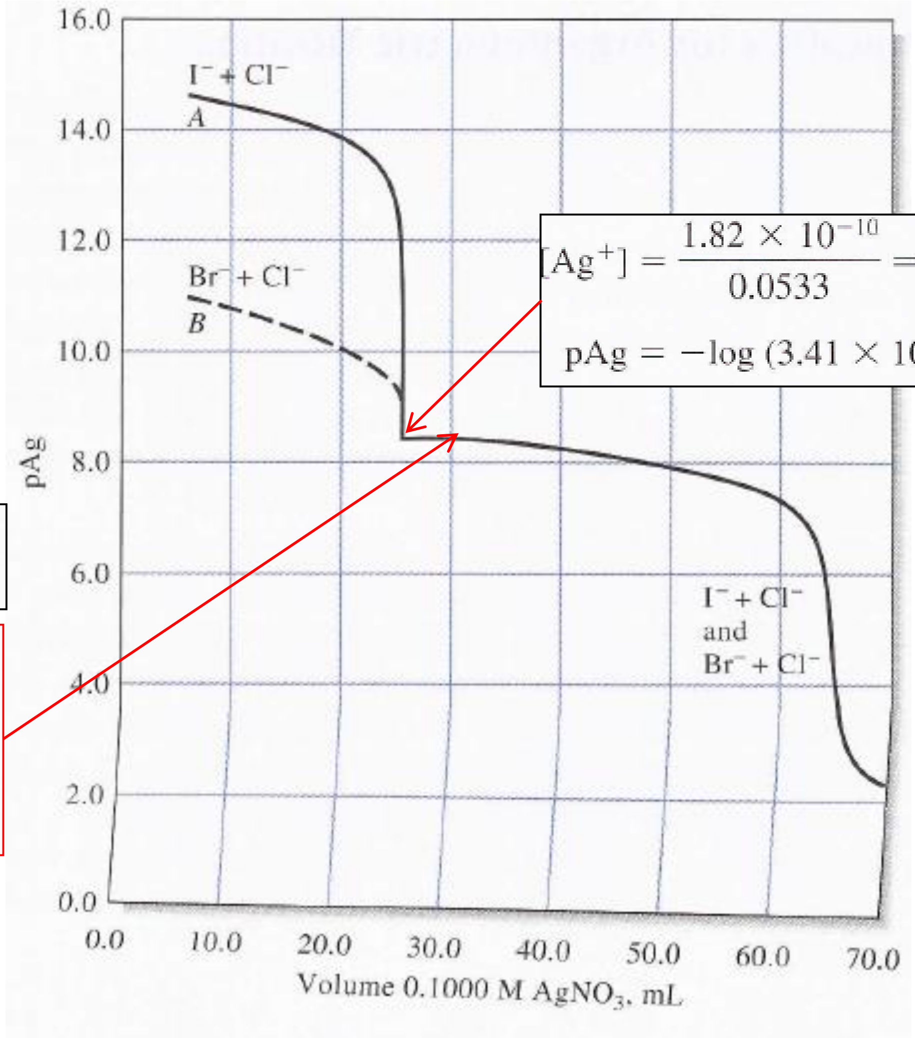
- So for all practical purposes, AgCl forms only after 25.00 mL of titrant have been added in this titration. At this point, the chloride ion concentration is approximately

$$c_{Cl} = [Cl^-] = \frac{50.00 \times 0.0800}{50.00 + 25.00} = 0.0533\ \mathrm{M}$$

Substituting into the previous equation yields

$$[I^-] = 4.56 \times 10^{-7} \times 0.0533 = 2.43 \times 10^{-8}\ \mathrm{M}$$

Figure 13-6 Titration curves for 50.00 mL of a solution 0.0800 M in Cl^- and 0.0500 M in I^- or Br^-.



$$[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0533} = 3.41 \times 10^{-9}$$

$$pAg = -\log(3.41 \times 10^{-9}) = 8.47$$

$$c_{Cl} = [Cl^-] = \frac{50.00 \times 0.0800 + 50.00 \times 0.0500 - 30.00 \times 0.100}{50.00 + 30.00}$$

$$[Cl^-] = 0.0438 \text{ M}$$

$$[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0438} = 4.16 \times 10^{-9}$$

$$pAg = 8.38$$

Indicators for Argentometric Titrations

1. **chemical**, Three chemical indicators, consists of a color change or, occasionally, the appearance or disappearance of turbidity in the solution being titrated.
   - The requirements for an indicator for a precipitation titration are that
     1. the color change should occur over a limited range in p-function of the reagent or the analyte
     2. the color change should take place within the steep portion of the titration curve for the analyte.

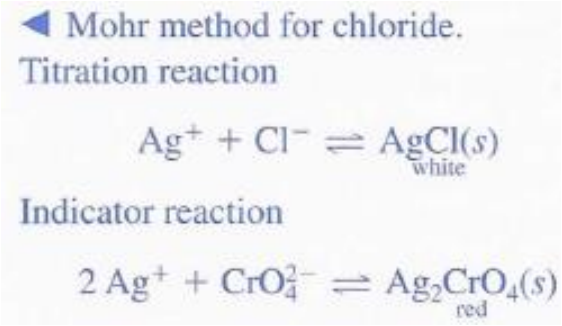
The titration of iodide with any indicator providing a signal in the pAg range of about 4.0 to 12.0 should give a satisfactory end point. In contrast, the end-point signal for the reaction of chloride ions would be limited to a pAg of about 4.0 to 6.0.

2. **potentiometric**, end points are obtained by measuring the potential between a silver electrode and a reference electrode whose potential is constant and independent of the added reagent. (Figures 13-3, 13-4, and 13-5)
3. **amperometric**, end point, the current generated between a pair of silver microelectrodes in the solution of the analyte is measured and plotted as a function of reagent volume.

Chemical indecators

1. 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.



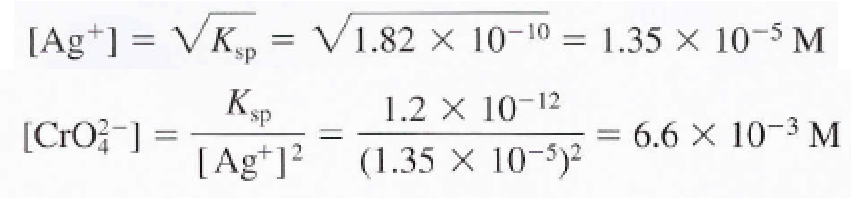
◀ Mohr method for chloride.

Titration reaction

$$Ag^+ + Cl^- \rightleftharpoons \underset{\text{white}}{AgCl(s)}$$

Indicator reaction

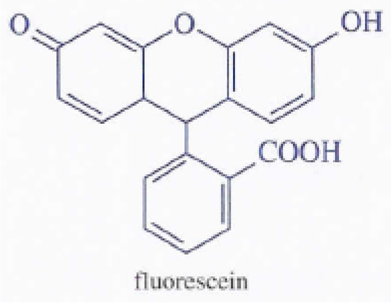
$$2\,Ag^+ + CrO_4^{2-} \rightleftharpoons \underset{\text{red}}{Ag_2CrO_4(s)}$$



$$[Ag^+] = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}\ M$$

$$[CrO_4^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{1.2 \times 10^{-12}}{(1.35 \times 10^{-5})^2} = 6.6 \times 10^{-3}\ M$$

2. *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). e.g., Fluorescein

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.*

In the early stages of the titration of chloride ion with silver nitrate, the colloidal silver chloride particles are **–ve** charged because of adsorption of excess chloride ions. The dye anions are repelled from this surface by electrostatic repulsion and impart a yellow-green color to the solution. Beyond the equivalence point, however, the silver chloride particles strongly adsorb silver ions and thereby acquire a **+ve** charge. Fluoresceinate anions are now attracted *into the counter-ion layer* that surrounds each colloidal silver chloride particle. The net result is the appearance of the red color of silver fluoresceinate *in the surface layer of the solution surrounding the solid.*

3. Iron(lII) Ion; The Volhard Method

▶ Volhard method for chloride.

$$\underset{\text{excess}}{Ag^+} + Cl^- \rightleftharpoons \underset{\text{white}}{AgCl(s)}$$

$$SCN^- + Ag^+ \rightleftharpoons \underset{\text{white}}{AgSCN(s)}$$

$$Fe^{3+} + SCN^- \rightleftharpoons \underset{\text{red}}{Fe(SCN)^{2+}}$$

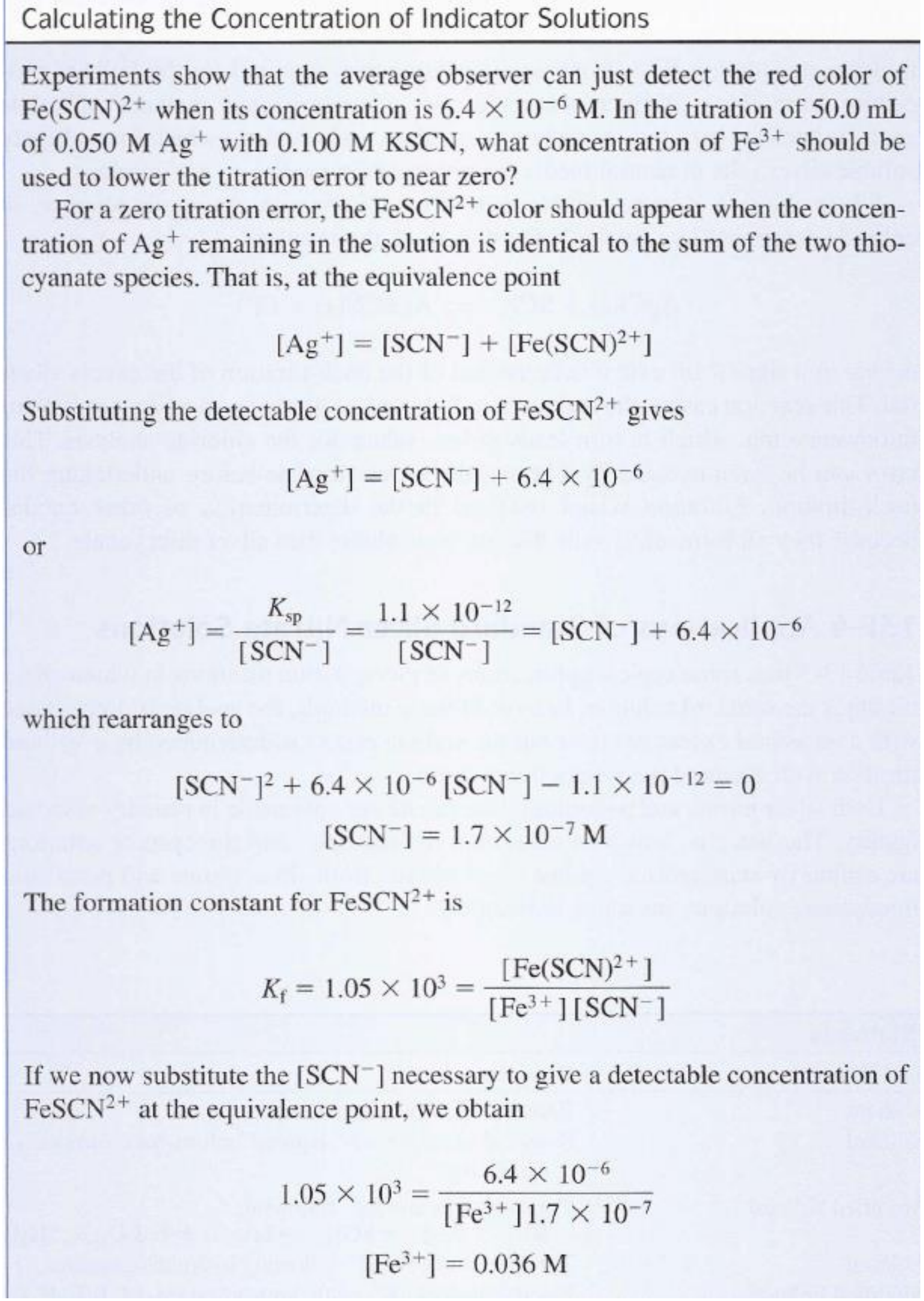
Silver ions are titrated with a standard solution of thiocyanate ion:

$$Ag^+ + SCN^- \rightleftharpoons AgSCN(s)$$

lron(III) serves as the indicator. The solution turns red with the first slight excess of thiocyanate ion:

$$Fe^{3+} + SCN^- \rightleftharpoons \underset{\text{red}}{FeSCN^{2+}} \qquad K_f = 1.05 \times 10^3 = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$$

The titration must be carried out in acidic solution to prevent precipitation of iron(III) as the hydrated oxide.



Calculating the Concentration of Indicator Solutions

Experiments show that the average observer can just detect the red color of $Fe(SCN)^{2+}$ when its concentration is 6.4×10^{-6} M. In the titration of 50.0 mL of 0.050 M Ag^+ with 0.100 M KSCN, what concentration of Fe^{3+} should be used to lower the titration error to near zero?

For a zero titration error, the $FeSCN^{2+}$ color should appear when the concentration of Ag^+ remaining in the solution is identical to the sum of the two thiocyanate species. That is, at the equivalence point

$$[Ag^+] = [SCN^-] + [Fe(SCN)^{2+}]$$

Substituting the detectable concentration of $FeSCN^{2+}$ gives

$$[Ag^+] = [SCN^-] + 6.4 \times 10^{-6}$$

or

$$[Ag^+] = \frac{K_{sp}}{[SCN^-]} = \frac{1.1 \times 10^{-12}}{[SCN^-]} = [SCN^-] + 6.4 \times 10^{-6}$$

which rearranges to

$$[SCN^-]^2 + 6.4 \times 10^{-6}[SCN^-] - 1.1 \times 10^{-12} = 0$$

$$[SCN^-] = 1.7 \times 10^{-7} \text{ M}$$

The formation constant for $FeSCN^{2+}$ is

$$K_f = 1.05 \times 10^3 = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$$

If we now substitute the $[SCN^-]$ necessary to give a detectable concentration of $FeSCN^{2+}$ at the equivalence point, we obtain

$$1.05 \times 10^3 = \frac{6.4 \times 10^{-6}}{[Fe^{3+}]1.7 \times 10^{-7}}$$

$$[Fe^{3+}] = 0.036 \text{ M}$$

Catalyst

Applications of Standard Silver Nitrate Solutions

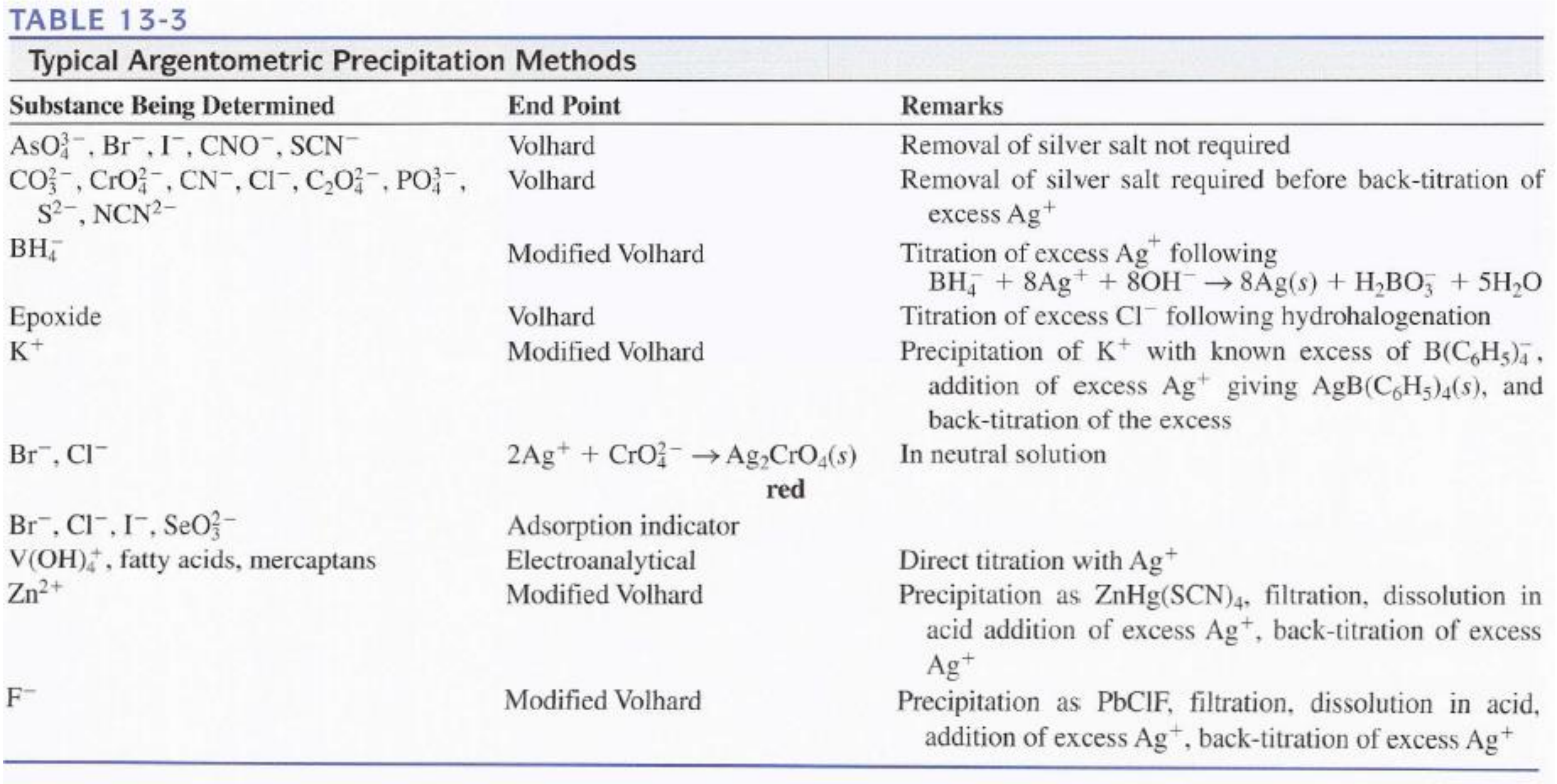


TABLE 13-3

Typical Argentometric Precipitation Methods

Substance Being Determined	End Point	Remarks
AsO_4^{3-}, Br^-, I^-, CNO^-, SCN^-	Volhard	Removal of silver salt not required
CO_3^{2-}, CrO_4^{2-}, CN^-, Cl^-, $C_2O_4^{2-}$, PO_4^{3-}, S^{2-}, NCN^{2-}	Volhard	Removal of silver salt required before back-titration of excess Ag^+
BH_4^-	Modified Volhard	Titration of excess Ag^+ following $BH_4^- + 8Ag^+ + 8OH^- \rightarrow 8Ag(s) + H_2BO_3^- + 5H_2O$
Epoxide	Volhard	Titration of excess Cl^- following hydrohalogenation
K^+	Modified Volhard	Precipitation of K^+ with known excess of $B(C_6H_5)_4^-$, addition of excess Ag^+ giving $AgB(C_6H_5)_4(s)$, and back-titration of the excess
Br^-, Cl^-	$2Ag^+ + CrO_4^{2-} \rightarrow \underset{\textbf{red}}{Ag_2CrO_4(s)}$	In neutral solution
Br^-, Cl^-, I^-, SeO_3^{2-}	Adsorption indicator	
$V(OH)_4^+$, fatty acids, mercaptans	Electroanalytical	Direct titration with Ag^+
Zn^{2+}	Modified Volhard	Precipitation as $ZnHg(SCN)_4$, filtration, dissolution in acid addition of excess Ag^+, back-titration of excess Ag^+
F^-	Modified Volhard	Precipitation as PbClF, filtration, dissolution in acid, addition of excess Ag^+, back-titration of excess Ag^+