Chapter 20

Applications of Oxidation/Reduction Titration
Linus Pauling (1901–1994) was one of the most influential and famous chemists of the twentieth century. His work in chemical bonding, X-ray crystallography, and related areas had a tremendous impact on chemistry, physics, and biology; spanned eight decades; and led to nearly every award available to chemists. He is the only person to receive two unshared Nobel prizes: for chemistry (1954) and, for his efforts to ban nuclear weapons, the peace prize (1962). In his last years, Pauling devoted his immense intellect and energy to the study of various diseases and their cures. He became convinced that vitamin C, or ascorbic acid, was a panacea. His many books and articles on the subject fueled the popularity of alternative therapies and especially the wide use of vitamin C for preventative maintenance of health. This photo of Pauling tossing an orange into the air is symbolic of this work and the importance of being able to determine concentrations of ascorbic acid at all levels in fruits, vegetables, and commercial vitamin preparations. Redox titrations with iodine are widely used to determine ascorbic acid.
The analyte in an oxidation/reduction titration must be in a single oxidation state at the outset. Often, however, the steps that precede the titration, such as dissolving the sample and separating interferences, convert the analyte to a mixture of oxidation states. For example, when a sample containing iron is dissolved, the resulting solution usually contains a mixture of iron(II) and iron(III) ions. If we choose to use a standard oxidant for determining iron, we must first treat the sample solution with an auxiliary reducing agent to convert all of the iron to iron(II). On the other hand, if we plan to titrate with a standard reductant, pretreatment with an auxiliary oxidizing reagent is needed.

Ex. Preadjustment by auxiliary reagent

\[
\begin{align*}
\text{Fe(II), Fe(III)} & \rightarrow \text{Fe(II)} \\
\text{Titration} & \text{Ce}^{4+}
\end{align*}
\]
To be useful as a **preoxidant** or a **prereductant**, a reagent must react quantitatively with the analyte. In addition, any reagent excess must be easily removable because the excess reagent usually interferes with the titration by reacting with the standard solution.

**Preoxidation:** Ammonium Peroxydisulfate (\((NH_4)_2S_2O_8\))
- Sodium bismuthate (\(NaBiO_3\))
- Hydrogen peroxide (\(H_2O_2\))

**Prereduction:** Stannous chloride (\(SnCl_2\))
- Chromous chloride
- Jones reductor (zinc coated with zinc amalgam)
- Walden reductor (solid Ag and 1M HCl)
20A-1 Auxiliary Reducing Reagents

A number of metals are good reducing agents and have been used for the prereduction of analytes. Included among these reductants are zinc, aluminum, cadmium, lead, nickel, copper, and silver (in the presence of chloride ion).

Sticks or coils of the metal can be immersed directly in the analyte solution. After reduction is judged complete, the solid is removed manually and rinsed with water. The analyte solution must be filtered to remove granular or powdered forms of the metal.

An alternative to filtration is the use of a reductor, such as that shown in Figure 20-1. In the reductor, the finely divided metal is held in a vertical glass tube through which the solution is drawn under a mild vacuum. The metal in a reductor is normally sufficient for hundreds of reductions.

A typical 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:

$$2\text{Zn}(s) + \text{Hg}^{2+} \rightarrow \text{Zn}^{2+} + \text{Zn(Hg)}(s)$$
Table 20–1.

Figure 20-1 A Jones reductor.
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.

Table 20-1 lists the principal applications of the Jones reductor. Also listed in this table are reductions that can be accomplished with a 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. Table 20-1 suggests that the Walden reductor is somewhat more selective in its action than is the Jones reductor.
20A-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 NaBiO₃, although its exact composition is somewhat uncertain. Oxidations are performed by suspending the bismuthate in the analyte solution and boiling for a brief period. The unused reagent is then removed by filtration. The half-reaction for the reduction of sodium bismuthate can be written as

\[
\text{NaBiO}_3(s) + 4\text{H}^+ + 2e^- \rightleftharpoons \text{BiO}^+ + \text{Na}^+ + 2\text{H}_2\text{O}
\]

*Ammonium Peroxydisulfate*

Ammonium peroxydisulfate, \((\text{NH}_4)_2\text{S}_2\text{O}_8\), 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

\[
\text{S}_2\text{O}_8^{2-} + 2e^- \rightleftharpoons 2\text{SO}_4^{2-}
\]

The oxidations are catalyzed by traces of silver ion. The excess reagent is easily decomposed by a brief period of boiling:

\[
2\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow 4\text{SO}_4^{2-} + \text{O}_2(g) + 4\text{H}^+
\]
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

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \hspace{1cm} E^0 = 1.78 \text{ V} \]

After oxidation is complete, the solution is freed of excess reagent by boiling:

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2(g) \]
Reagents used in redox titration

Reducing agents

Ferrous salts:
- ammonium iron(II) sulfate hexahydrate (Mohr’s salt) \( \text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \)
- iron(II) ethylene diamine sulfate (Oesper’s salt) \( \text{FeC}_2\text{H}_4(\text{NH}_3)_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \)
- Sodium thiosulfate pentahydrate \( \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \)
- Arsenic trioxide: arsenious oxide \( \text{As}_2\text{O}_3 \)
- Sodium oxalate and oxalic acid dihydrate \( \text{Na}_2(\text{COO})_2 , (\text{COOH})_2 \cdot 2\text{H}_2\text{O} \)
- Titanium trichloride \( \text{TiCl}_3 \)
- Potassium ferrocyanide \( \text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O} \)
20B  Applying Standard Reducing Agents

Standard solutions of most reductants tend to react with atmospheric oxygen. For this reason, reductants are seldom used for the direct titration of oxidizing analytes; indirect methods are used instead. The two most common reductants are iron(II) and thiosulfate ions.

20B-1 Iron(II) Solutions

Solutions of iron(II) are easily prepared from iron(II) ammonium sulfate, Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O (Mohr’s salt), or from the closely related iron(II) ethylenediamine sulfate, FeC$_2$H$_4$(NH$_3$)$_2$(SO$_4$)$_2$·4H$_2$O (Oesper’s salt). Air oxidation of iron(II) takes place rapidly in neutral solutions but is inhibited in the presence of acids, with the most stable preparations being about 0.5 M in H$_2$SO$_4$. Such solutions are stable for no more than one day, if that long. Numerous oxidizing agents are conveniently determined by treatment of the analyte solution with a measured excess of standard iron(II) followed by immediate titration of the excess with a standard solution of potassium dichromate or cerium(IV) (see Sections 20C-1 and 20C-2). Just before or just after the analyte is titrated, the volumetric ratio between the standard oxidant and the iron(II) solution is established by titrating two or three aliquots of iron(II) with the oxidant. This procedure has been applied to the determination of organic peroxides; hydroxylamine; chromium(VI); cerium(IV); molybdenum(VI); nitrate, chlorate, and perchlorate ions; and numerous other oxidants (see for example, Problems 20-20 and 20-21).
Thiosulfate ion ($S_2O_3^{2-}$) is a moderately strong reducing agent that has been widely used to determine oxidizing agents by an indirect procedure in which iodine is an intermediate. With iodine, thiosulfate ion is oxidized quantitatively to tetrathionate ion ($S_4O_6^{2-}$) according to the half-reaction

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$$

The quantitative reaction with iodine is unique. Other oxidants can oxidize the tetrathionate ion to sulfate ion.

The scheme used to determine oxidizing agents involves adding an unmeasured excess of potassium iodide to a slightly acidic solution of the analyte. Reduction of the analyte produces a stoichiometrically equivalent amount of iodine. The liberated iodine is then titrated with a standard solution of sodium thiosulfate, $Na_2S_2O_3$, one of the few reducing agents that is stable toward air oxidation. An example of this procedure is the determination of sodium hypochlorite in bleaches. The reactions are

$$OCl^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O \quad \text{(unmeasured excess KI)}$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \quad \text{(20-1)}$$

The quantitative conversion of thiosulfate ion to tetrathionate ion shown in Equation 20-1 requires a pH smaller than 7. If strongly acidic solutions must be titrated, air oxidation of the excess iodide must be prevented by blanketing the solution with an inert gas, such as carbon dioxide or nitrogen.

Sodium thiosulfate is one of the few reducing agents that is not oxidized by air.
Molecular model of thiosulfate ion.

Sodium thiosulfate, formerly called sodium hyposulfite or hypo, is used to “fix” photographic images and to extract silver from ore, as well as an antidote in cyanide poisoning, as a mordant in the dye industry, as a bleaching agent in a variety of applications, as the solute in the supersaturated solution of hot packs, and of course, as an analytical reducing agent.

The action of thiosulfate as a photographic fixer is based on its capacity to form complexes with silver and thus dissolve unexposed silver bromide from the surface of photographic film and paper. Thiosulfate is often used as a dechlorinating agent to make aquarium water safe for fish and other aquatic life.
Detecting End Points in Iodine/Thiosulfate Titrations

A solution that is about $5 \times 10^{-6}$ M in $\text{I}_2$ has a discernible color, which corresponds to less than one drop of a 0.05 M iodine solution in 100 mL. Thus, provided the analyte solution is colorless, the disappearance of the iodine color can serve as the indicator in titrations with sodium thiosulfate.

Most often, iodine titrations are performed with a suspension of starch as an indicator. The deep blue color that develops in the presence of iodine is believed to arise from the absorption of iodine into the helical chain of $\beta$-amylose (see Figure 20-2), a macromolecular component of most starches. The closely related $\alpha$-amylose forms a red adduct with iodine. This reaction is not easily reversible and is thus undesirable. In commercially available soluble starch, the alpha fraction has been removed to leave principally $\beta$-amylose. Indicator solutions are easily prepared from this product.
Figure 20-2 Thousands of glucose molecules polymerize to form huge molecules of \(\beta\)-amylose, as shown schematically in (a). Molecules of \(\beta\)-amylose tend to assume a helical structure. The iodine species \(I_5^-\), as shown in (b), is incorporated into the amylose helix.

Aqueous starch suspensions decompose within a few days, primarily because of bacterial action. The decomposition products tend to interfere with the indicator properties of the preparation and may also be oxidized by iodine. The rate of decomposition can be inhibited by preparing and storing the indicator under sterile conditions and by adding mercury(II) iodide or chloroform as a bacteriostat. Perhaps the simplest alternative is to prepare a fresh suspension of the indicator, which requires only a few minutes, on the day it is to be used.

Starch decomposes irreversibly in solutions containing large concentrations of iodine. Therefore, in titrating solutions of iodine with thiosulfate ion, as in the indirect determination of oxidants, addition of the indicator is delayed until the color of the solution changes from red-brown to yellow; at this point, the titration is nearly complete. The indicator can be introduced at the outset when thiosulfate solutions are being titrated directly with iodine.
When sodium thiosulfate is added to a strongly acidic medium, a cloudiness develops almost immediately as a consequence of the precipitation of elemental sulfur. Even in neutral solution, this reaction proceeds at such a rate that standard sodium thiosulfate must be restandardized periodically.

Stability of Sodium Thiosulfate Solutions

Although sodium thiosulfate solutions are resistant to air oxidation, they do tend to decompose to give sulfur and hydrogen sulfite ion:

\[
S_2O_3^{2-} + H^+ \rightleftharpoons HSO_3^- + S(s)
\]

Variables that influence the rate of this reaction include pH, the presence of microorganisms, the concentration of the solution, the presence of copper(II) ions, and exposure to sunlight. These variables may cause the concentration of a thiosulfate solution to change by several percent over a period of a few weeks. Proper attention to detail will produce solutions that need only occasional restandardization. The rate of the decomposition reaction increases markedly as the solution becomes acidic.

The most important single cause for the instability of neutral or slightly basic thiosulfate solutions is bacteria that metabolize thiosulfate ion to sulfite and sulfate ions as well as to elemental sulfur. To minimize this problem, standard solutions of the reagent are prepared under reasonably sterile conditions. Bacterial activity appears to be at a minimum at a pH between 9 and 10, which accounts, at least in part, for the reagent’s greater stability in slightly basic solutions. The presence of a bactericide, such as chloroform, sodium benzoate, or mercury(II) iodide, also slows decomposition.
Standardizing Thiosulfate Solutions

Potassium iodate is an excellent primary standard for thiosulfate solutions. In this application, weighed amounts of primary-standard-grade reagent are dissolved in water containing an excess of potassium iodide. When this mixture is acidified with a strong acid, the reaction

\[ \text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightleftharpoons 3\text{I}_2 + 3\text{H}_2\text{O} \]

occurs instantaneously. The liberated iodine is then titrated with the thiosulfate solution. The stoichiometry of the reactions is

\[ 1 \text{ mol IO}_3^- = 3 \text{ mol I}_2 = 6 \text{ mol S}_2\text{O}_3^{2-} \]

Other primary standards for sodium thiosulfate are potassium dichromate, potassium bromate, potassium hydrogen iodate, potassium hexacyanoferrate(III), and metallic copper. All these compounds liberate stoichiometric amounts of iodine when treated with excess potassium iodide.
**Standardization of thiosulfate solution:**

Primary standard: potassium iodate (KIO₃), K₂Cr₂O₇, KBrO₃

Titration reactions:

\[
\begin{align*}
KIO_3 + 5KI + 6HCl & \rightarrow 3I_2 + 6KCl + 3 \text{ H}_2\text{O} \\
I_2 + 2Na_2S_2O_3 & \rightarrow 2NaI + Na_2S_4O_6
\end{align*}
\]

\[
KIO_3 \equiv 3I_2 \equiv 6Na_2S_2O_3 \cdot 5\text{H}_2\text{O} \equiv 6 \text{ Equivalent}
\]

\[
\begin{align*}
mw & \quad 214.02 & \quad 248.21 \\
214.02 \text{ g} & \equiv 6 \times 248.21 \text{ g} \\
214.02 \text{ g} / 6 & \equiv 1 \text{ N} \times 1000 \text{ ml} \\
35.67 \text{ g} & \equiv 1 \text{ N} \times 1000 \text{ ml} \\
a \text{ g} & \equiv x \text{ N} \times V \text{ ml}
\end{align*}
\]

\[
x \text{ N} = (a \text{ g} \times 1 \text{ N} \times 1000 \text{ ml}) / (35.67 \text{ g} \times V \text{ ml})
\]

Stabilizer for sodium thiosulfate solution: Na₂CO₃

\[
\begin{align*}
Na_2S_2O_3 + H_2O + CO_2 & \rightarrow Na_2CO_3 + H_2S_2O_3 \\
H_2S_2O_3 & \rightarrow H_2SO_3 + S
\end{align*}
\]
Calculations ✡✡

Equivalent weight = (formula weight) / (e⁻ change)

Equivalents = g / eq. wt.  
meq = mg / eq. Wt.

Normality (N) = eq / L  =  meq / mL

<table>
<thead>
<tr>
<th>Redox Reaction</th>
<th>eq. wt of reactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺ → Fe³⁺ + e</td>
<td>FW Fe ÷ 1</td>
</tr>
<tr>
<td>KMnO₄ + 5e → Mn²⁺</td>
<td>FW KMnO₄ ÷ 5</td>
</tr>
<tr>
<td>Na₂S₂O₃5H₂O → ½ S₄O₆⁻ + e</td>
<td>FW Na₂S₂O₃5H₂O ÷ 1</td>
</tr>
<tr>
<td>Cr₂O₇²⁻ + 6e → 2 Cr³⁺</td>
<td>FW Cr₂O₇²⁻ ÷ 6</td>
</tr>
</tbody>
</table>
EXAMPLE 20-1

A solution of sodium thiosulfate was standardized by dissolving 0.1210 g KIO₃ (214.00 g/mol) in water, adding a large excess of KI, and acidifying with HCl. The liberated iodine required 41.64 mL of the thiosulfate solution to decolorize the blue starch/iodine complex. Calculate the molar concentration of the Na₂S₂O₃.

Solution

\[
\text{amount Na}_2\text{S}_2\text{O}_3 = 0.1210 \text{ g KIO}_3 \times \frac{1 \text{ mmol KIO}_3}{0.21400 \text{ g KIO}_3} \times \frac{6 \text{ mmol Na}_2\text{S}_2\text{O}_3}{\text{mmol KIO}_3} \\
= 3.3925 \text{ mmol Na}_2\text{S}_2\text{O}_3
\]

\[
\omega_{\text{Na}_2\text{S}_2\text{O}_3} = \frac{3.3925 \text{ mmol Na}_2\text{S}_2\text{O}_3}{41.64 \text{ mL Na}_2\text{S}_2\text{O}_3} = 0.08147 \text{ M}
\]
Table 20-3 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.
Reagents used in redox titration

Oxidizing agents

Potassium permanganate $\text{KMnO}_4$ : Permanganometry
Ceric sulfate / Ceric ammonium sulfate $\text{Ce(SO}_4\text{)}_2\cdot2\text{(NH}_4\text{)}_2\text{SO}_4\cdot4\text{H}_2\text{O}$ : Cerimetry
Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ : Dichrometry
Iodine $\text{I}_2$ : Iodimetry, Iodometry
Potassium iodate $\text{KIO}_3$ : Iodatimetry
Potassium bromate $\text{KBrO}_3$ : Bromatimetry
Sodium nitrite $\text{NaNO}_2$ :
Calcium hypochlorite $\text{Ca(ClO)}_2$ :
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

\[
\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E^0 = 1.51 \text{ V}
\]

\[
\text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+} \quad E^{0'} = 1.44 \text{ V (1 M H}_2\text{SO}_4)\]

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.
Molecular model of permanganate ion, MnO$_4^-$.

In addition to its use as an analytical reagent, usually in the form of its potassium salt, permanganate is very useful as an **oxidizing agent in synthetic organic chemistry**. It is used as a **bleaching agent** with fats, oils, cotton, silk, and other fibers. It has also been used as an **antiseptic** and **anti-infective** and as a component in outdoor survival kits, as well as for destroying organic matter in fish ponds, in manufacturing printed wiring boards, for neutralizing the effects of the pesticide rotenone, and for scrubbing flue gases in the determination of mercury. Solid potassium permanganate reacts violently with organic matter, and this effect is often used as a demonstration in general chemistry courses. To further explore these and other uses of permanganate, use a browser and search *permanganate uses*. 
Color Plate 13. The time dependence of the reaction between permanganate and oxalate (see section 20C-1, page 515)
Comparing the Two Reagents

Solutions of cerium(IV) in sulfuric acid, however, are stable indefinitely, but permanganate solutions decompose slowly and thus require occasional restandardization. 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. 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.

Despite these advantages of cerium solutions over permanganate solutions, the latter are more widely used. One reason is the color of permanganate solutions, which is intense enough to serve as an indicator in titrations. A second reason for the popularity of permanganate solutions is their modest cost. The cost of 1 L of 0.02 M KMnO₄ solution is about one-tenth the cost 1 L of a comparable strength Ce(IV) solution (1/1003 if primary-standard-grade Ce(IV) reagent is used).

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.
Detecting the End Points

A useful property of potassium permanganate solution is its intense purple color, which is sufficient to serve as an indicator for most titrations. If you add as little as 0.01 to 0.02 mL of a 0.02 M solution of permanganate to 100 mL of water, you can perceive the purple color of the resulting solution. If the solution is very dilute, diphenylamine sulfonic acid or the 1,10-phenanthroline complex of iron(II) (see Table 19-3) provides a sharper end point.

The permanganate end point is not permanent because excess permanganate ions react slowly with the relatively large concentration of manganese(II) ions present at the end point, according to the reaction

$$2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons 5\text{MnO}_2(s) + 4\text{H}^+$$

The equilibrium constant for this reaction is about $10^{47}$, indicating that the equilibrium concentration of permanganate ion is incredibly small even in highly acidic media. Fortunately, the rate at which this equilibrium is approached is so slow that the end point fades only gradually over a period of perhaps 30 seconds.

Solutions of cerium(IV) are yellow-orange, but the color is not intense enough to act as an indicator in titrations. Several oxidation/reduction indicators are available for titrations with standard solutions of cerium(IV). The most widely used of these is the iron(II) complex of 1,10-phenanthroline or one of its substituted derivatives (see Table 19-3).
Aqueous solutions of permanganate are not entirely stable because of water oxidation:

\[ 4\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 4\text{MnO}_2(s) + 3\text{O}_2(g) + 4\text{OH}^- \]

Although the equilibrium constant for this reaction indicates that the products are favored, permanganate solutions, when properly prepared, are reasonably stable because the decomposition reaction is slow. It is catalyzed by light, heat, acids, bases, manganese(II), and manganese dioxide.

Moderately stable solutions of permanganate ion can be prepared if the effects of these catalysts, particularly manganese dioxide, are minimized. Manganese dioxide is a contaminant in even the best grade of solid potassium permanganate. Furthermore, this compound forms in freshly prepared solutions of the reagent as a consequence of the reaction of permanganate ion with organic matter and dust present in the water used to prepare the solution. Removal of manganese dioxide by filtration before standardization markedly improves the stability of standard permanganate solutions. Before filtration, the reagent solution is allowed to stand for about 24 hours or is heated for a brief period to hasten oxidation of the organic species generally present in small amounts in distilled and deionized water. Paper cannot be used for filtering because permanganate ion reacts with it to form additional manganese dioxide.
Standardized permanganate solutions should be stored in the dark. Filtration and restandardization are required if any solid is detected in the solution or on the walls of the storage bottle. In any event, restandardization every one or two weeks is a good precautionary measure.

Solutions containing excess standard permanganate should never be heated because they decompose by oxidizing water. This decomposition cannot be compensated for with a blank. It is possible to titrate hot, acidic solutions of reductants with permanganate without error if the reagent is added slowly enough so that large excesses do not accumulate.
EXAMPLE 20-2

Describe how you would prepare 2.0 L of an approximately 0.010 M solution of KMnO₄ (158.03 g/mol).

Solution

\[
\text{mass KMnO}_4 \text{ needed} = 2.0 \text{ L} \times 0.010 \frac{\text{mol KMnO}_4}{\text{L}} \times 158.03 \frac{\text{g KMnO}_4}{\text{mol KMnO}_4} \\
= 3.16 \text{ g KMnO}_4
\]

Dissolve about 3.2 g of KMnO₄ in a little water. After solution is complete, add water to bring the volume to about 2.0 L. Heat the solution to boiling for a brief period and let stand until it is cool. **Filter through a glass filtering crucible and store in a clean dark bottle.**
Permanganate titration

Oxidation with permanganate: Reduction of permanganate

$\text{KMnO}_4$ Powerful oxidant that the most widely used.

In strongly acidic solutions (1M H$_2$SO$_4$ or HCl, pH $\leq$ 1)

$$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad \text{E}^o = 1.51 \text{ V}$$

violet color colorless manganous

$\text{KMnO}_4$ is a self-indicator.

In feebly acidic, neutral, or alkaline solutions

$$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- = \text{MnO}_2 (s) + 2\text{H}_2\text{O} \quad \text{E}^o = 1.695 \text{ V}$$

brown manganese dioxide solid

In very strongly alkaline solution (2M NaOH)

$$\text{MnO}_4^- + \text{e}^- = \text{MnO}_4^{2-} \quad \text{E}^o = 0.558 \text{ V}$$

green manganate
**Standardization of KMnO₄ solution**

Potassium permanganate is not primary standard, because traces of MnO₂ are invariably present.

Standardization by titration of sodium oxalate (primary standard):

\[
2\text{KMnO}_4 + 5 \text{Na}_2(\text{COO})_2 + 8\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 5\text{Na}_2\text{SO}_4 + 10 \text{CO}_2 + 8\text{H}_2\text{O}
\]

\[
\begin{align*}
2\text{KMnO}_4 & \equiv 5 \text{Na}_2(\text{COO})_2 & \equiv 10 \text{ Equivalent} \\
\text{mw 158.03} & \equiv \text{mw 134.01} \\
158.03 \text{ g / 5} & \equiv 134.01 \text{ g / 2} & \equiv 1 \text{ Eq.} \\
31.606 \text{ g} & \equiv 67.005 \text{ g} \\
1\text{N} \times 1000 \text{ ml} & \equiv 67.005 \text{ g} \\
x \text{ N} \times V \text{ ml} & \equiv a \text{ g} \\
x \text{ N} = (a \text{ g} \times 1\text{N} \times 1000 \text{ ml}) / (67.005 \text{ g} \times V \text{ ml})
\end{align*}
\]


**Preparation of 0.1 N potassium permanganate solution**

KMnO₄ is not pure. Distilled water contains traces of organic reducing substances which react slowly with permanganate to form hydrous manganese dioxide. Manganese dioxide promotes the autodecomposition of permanganate.

1) Dissolve about 3.2 g of KMnO₄ (mw=158.04) in 1000ml of water, heat the solution to boiling, and keep slightly below the boiling point for 1 hr. Alternatively, allow the solution to stand at room temperature for 2 or 3 days.

2) Filter the liquid through a sintered-glass filter crucible to remove solid MnO₂.

3) Transfer the filtrate to a clean stoppered bottle freed from grease with cleaning mixture.

4) Protect the solution from evaporation, dust, and reducing vapors, and keep it in the dark or in diffuse light.

5) If in time manganese dioxide settles out, refilter the solution and restandardize it.
Determination of Chromium Species in Water Samples

Chromium is an important metal to monitor in environmental samples. Not only is the total amount of chromium of interest, but the oxidation state in which the chromium is found is quite important. In water, chromium can exist as the Cr(III) or as Cr(VI) species. Chromium(III) is an essential nutrient and nontoxic. Chromium(VI), however, is a known carcinogen. Hence, the determination of the amount of chromium in each of these oxidation states is often of more interest than the total amount of chromium. There are several good methods available for determining Cr(VI) selectively. One of the most popular utilizes the oxidation of the reagent 1,5-diphenylcarbohydrazide (diphenylcarbazide) by Cr(VI) in acid solution. The reaction produces a red-purple chelate of Cr(III) and diphenylcarbazide that can be monitored colorimetrically. The direct reaction of Cr(III) itself and the reagent is so slow that essentially only the Cr(VI) is measured. To determine Cr(III), the sample is oxidized with excess permanganate in alkaline solution to convert all the Cr(III) to Cr(VI). The excess oxidant is destroyed with sodium azide. A new colorimetric measurement is made that now determines total chromium (the original Cr(VI) plus that formed by oxidation of Cr(III)). The amount of Cr(III) present is then obtained by subtracting the amount of Cr(VI) obtained in the original measurement from the amount of total chromium obtained after permanganate oxidation. Note that in this instance permanganate is being used as an auxiliary oxidizing agent.
Chromium has long been prized for its beauty as a polished coating on metals (see photo) and for its anticorrosive properties in stainless steel and other alloys. In trace amounts, chromium(III) is an essential nutrient. Chromium(VI) in the form of sodium dichromate is widely used in aqueous solution as a corrosion inhibitor in large-scale industrial processes. See margin note on page 523 for more details on chromium.
The most widely used compounds for the preparation of solutions of cerium(IV) are listed in Table 20-4. **Primary-standard-grade cerium ammonium nitrate** is available commercially and can be used to prepare standard solutions of the cation directly by mass. More commonly, **less expensive reagent-grade cerium(IV) ammonium nitrate** or ceric hydroxide is used to prepare solutions that are subsequently standardized. In either case, the reagent is dissolved in a solution that is at least 0.1 M in sulfuric acid to prevent the precipitation of basic salts. **Sulfuric acid solutions of cerium(IV) are remarkably stable and can be stored for months or heated at 100°C for prolonged periods without change in concentration.**
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

\[ 2\text{MnO}_4^- + 5\text{H}_2\text{C}_2\text{O}_4 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2(g) + 8\text{H}_2\text{O} \]

The reaction between permanganate ion and oxalic acid is complex and proceeds slowly even at elevated temperature unless manganese(II) is present as a catalyst. Therefore, when the first few milliliters of standard permanganate are added to a hot solution of oxalic acid, several seconds are required before the color of the permanganate ion disappears. As the concentration of manganese(II) builds up, however, the reaction proceeds more and more rapidly as a result of autocatalysis.

**Autocatalysis** is a type of catalysis in which the product of a reaction catalyses the reaction. This phenomenon causes the rate of the reaction to increase as the reaction proceeds.
It has been found that, when solutions of sodium oxalate are titrated at 60°C to 90°C, the consumption of permanganate is from 0.1 to 0.4% less than theoretical, probably due to the air oxidation of a fraction of the oxalic acid. This small error can be avoided by adding 90 to 95% of the required permanganate to a cool solution of the oxalate. After the added permanganate is completely consumed (as indicated by the disappearance of color), the solution is heated to about 60°C and titrated to a pink color that persists for about 30 s. The disadvantage of this procedure is that it requires prior knowledge of the approximate concentration of the permanganate solution so that a proper initial volume can be added. For most purposes, direct titration of the hot oxalic acid solution is adequate (usually 0.2 to 0.3% high). If greater accuracy is required, a direct titration of the hot solution of one portion of the primary standard can be followed by titration of two or three portions in which the solution is not heated until the end.

**Sodium oxalate is also widely used to standardize Ce(IV) solutions.** The reaction between Ce$^{4+}$ and H$_2$C$_2$O$_4$ is

$$2\text{Ce}^{4+} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{Ce}^{3+} + 2\text{CO}_2(g) + 2\text{H}^+$$

Cerium(IV) standardizations against sodium oxalate are usually performed at 50°C in a hydrochloric acid solution containing iodine monochloride as a catalyst.

Solutions of KMnO$_4$ and Ce$^{4+}$ can also be standardized with electrolytic iron wire or with potassium iodide.
EXAMPLE 20-3

You wish to standardize the solution in Example 20-2 against primary Na$_2$C$_2$O$_4$ (134.00 g/mol). If you want to use between 30 and 45 mL of the reagent for the standardization, what range of masses of the primary standard should you weigh out?

Solution

For a 30-mL titration,

\[
\text{amount KMnO}_4 = 30 \text{ mL KMnO}_4 \times 0.010 \frac{\text{mmol KMnO}_4}{\text{mL KMnO}_4} = 0.30 \text{ mmol KMnO}_4
\]

\[
\text{mass Na}_2\text{C}_2\text{O}_4 = 0.30 \text{ mmol KMnO}_4 \times \frac{5 \text{ mmol Na}_2\text{C}_2\text{O}_4}{2 \text{ mmol KMnO}_4} \times 0.134 \frac{\text{g Na}_2\text{C}_2\text{O}_4}{\text{mmol Na}_2\text{C}_2\text{O}_4} = 0.101 \text{ g Na}_2\text{C}_2\text{O}_4
\]

Proceeding in the same way, we find for a 45-mL titration,

\[
\text{mass Na}_2\text{C}_2\text{O}_4 = 45 \times 0.010 \times \frac{5}{2} \times 0.134 = 0.151 \text{ g Na}_2\text{C}_2\text{O}_4
\]

Thus, you should weigh between 0.10 and 0.15 g samples of the primary standard.
EXAMPLE 20-4

A 0.1278-g sample of primary-standard Na$_2$C$_2$O$_4$ required exactly 33.31 mL of the permanganate solution in Example 20-2 to reach the end point. What was the molar concentration of the KMnO$_4$ reagent?

Solution

\[
\text{amount } \text{Na}_2\text{C}_2\text{O}_4 = 0.1278 \text{ g Na}_2\text{C}_2\text{O}_4 \times \frac{1 \text{ mmol Na}_2\text{C}_2\text{O}_4}{0.13400 \text{ g Na}_2\text{C}_2\text{O}_4} = 0.95373 \text{ mmol Na}_2\text{C}_2\text{O}_4
\]

\[
\text{c}_{\text{KMnO}_4} = 0.95373 \text{ mmol Na}_2\text{C}_2\text{O}_4 \times \frac{2 \text{ mmol KMnO}_4}{5 \text{ mmol Na}_2\text{C}_2\text{O}_4} \times \frac{1}{33.31 \text{ mL KMnO}_4} = 0.01145 \text{ M}
\]
Applications of permanganometry

(1) H₂O₂

\[ \text{2KMnO}_4 + 5 \text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 5\text{O}_2 + 8\text{H}_2\text{O} \]

(2) NaNO₂

\[ \text{2NaNO}_2 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{HNO}_2 \]

\[ \text{2KMnO}_4 + 5 \text{HNO}_2 + 3\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 5\text{HNO}_3 + 3\text{H}_2\text{O} \]

(3) FeSO₄

\[ \text{2KMnO}_4 + 5 \text{10 FeSO}_4 + 8\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} \]

(4) CaO

\[ \text{CaO} + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} \]

\[ \text{CaCl}_2 + \text{H}_2\text{C}_2\text{O}_4 = \text{CaC}_2\text{O}_4 + 2\text{HCl} \quad \text{(excess oxalic acid)} \]

\[ \text{2KMnO}_4 + 5 \text{H}_2\text{C}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O} \quad \text{(back tit)} \]

(5) Calcium gluconate

\[ [\text{CH}_2\text{OH(CHOH)_4COO}]_2\text{Ca} + 2\text{HCl} = \text{CaCl}_2 + 2\text{CH}_2\text{OH(CHOH)_4COOH} \]

\[ (\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{CaCl}_2 = \text{CaC}_2\text{O}_4 + 2\text{NH}_4\text{Cl} \]

\[ \text{CaCl}_2 + \text{H}_2\text{SO}_4 = \text{H}_2\text{C}_2\text{O}_4 + \text{CaSO}_4 \]

\[ \text{2KMnO}_4 + 5 \text{H}_2\text{C}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O} \]
Applications of cerimetry

(1) Menadione (2-methylnaphthoquinon: vitamin K₃)

\[
\text{HCl, Zn}
\]

\[
\text{Reduction}
\]

\[
2 \text{Ce(SO}_4\text{)}_2
\]

(2) Iron

\[
2\text{FeSO}_4 + 2(\text{NH}_4)_4\text{Ce(SO}_4\text{)}_4 = \text{Fe}_2(\text{SO}_4)_3 + \text{Ce}_2(\text{SO}_4)_3 + 4(\text{NH}_4)_2\text{SO}_4
\]
EXAMPLE 20-5

Aqueous solutions containing approximately 3% (w/w) \( \text{H}_2\text{O}_2 \) are sold in drug stores as a disinfectant. Propose a method for determining the peroxide content of such a preparation using the standard solution described in Examples 20-3 and 20-4. Assume that you wish to use between 30 and 45 mL of the reagent for a titration. The reaction is

\[
5\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 5\text{O}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}
\]

Solution

The amount of \( \text{KMnO}_4 \) in 35 to 45 mL of the reagent is between

\[
\text{amount } \text{KMnO}_4 = 35 \text{ mL } \text{KMnO}_4 \times 0.01145 \frac{\text{mmol } \text{KMnO}_4}{\text{mL } \text{KMnO}_4} = 0.401 \text{ mmol } \text{KMnO}_4
\]

and

\[
\text{amount } \text{KMnO}_4 = 45 \times 0.01145 = 0.515 \text{ mmol } \text{KMnO}_4
\]
The amount of $\text{H}_2\text{O}_2$ consumed by 0.401 mmol of $\text{KMnO}_4$ is

$$\text{amount } \text{H}_2\text{O}_2 = 0.401 \text{ mmol } \text{KMnO}_4 \times \frac{5 \text{ mmol } \text{H}_2\text{O}_2}{2 \text{ mmol } \text{KMnO}_4} = 1.00 \text{ mmol } \text{H}_2\text{O}_2$$

and

$$\text{amount } \text{H}_2\text{O}_2 = 0.515 \times \frac{5}{2} = 1.29 \text{ mmol } \text{H}_2\text{O}_2$$

We, therefore, need to take samples that contain from 1.00 to 1.29 mmol $\text{H}_2\text{O}_2$.

$$\text{mass sample} = 1.00 \text{ mmol } \text{H}_2\text{O}_2 \times 0.03401 \frac{\text{g } \text{H}_2\text{O}_2}{\text{mmol } \text{H}_2\text{O}_2} \times \frac{100 \text{ g sample}}{3 \text{ g } \text{H}_2\text{O}_2}$$

$$= 1.1 \text{ g sample}$$

to

$$\text{mass sample} = 1.29 \times 0.03401 \times \frac{100}{3} = 1.5 \text{ g sample}$$

Thus, our samples should weigh between 1.1 and 1.5 g. These should be diluted to perhaps 75 to 100 mL with water and made slightly acidic with dilute $\text{H}_2\text{SO}_4$ before titration.
Antioxidants

Oxidation can have deleterious effects on the cells and tissues of the human body. There is a considerable body of evidence that reactive oxygen and nitrogen species, such as superoxide ion $\text{O}_2^-$, hydroxyl radical $\text{OH}^•$, peroxyl radicals $\text{RO}_2^•$, alkoxyl radicals $\text{RO}^•$, nitric oxide $\text{NO}^•$, and nitrogen dioxide $\text{NO}_2^•$, damage cells and other body components. A group of compounds known as antioxidants can help counteract the influence of reactive oxygen and nitrogen species. Antioxidants are reducing agents that are so easily oxidized that they can protect other compounds in the body from oxidation. Typical antioxidants include Vitamins A, C, and E; minerals, such as selenium; and herbs, such as ginkgo, rosemary, and milk thistle.

Several mechanisms for antioxidant action have been proposed. The presence of antioxidants may result in the decreased formation of the reactive oxygen and nitrogen species in the first place. Antioxidants may also scavenge the reactive species or their precursors. Vitamin E is an example of this latter behavior in its inhibition of lipid oxidation by its reaction with radical intermediates generated from polyunsaturated fatty acids. Some antioxidants can bind the metal ions needed to catalyze the formation of the reactive oxidants. Other antioxidants can repair oxidative damage to biomolecules or can influence enzymes that catalyze repair mechanisms.
Vitamin E, or α-tocopherol, is thought to deter atherosclerosis, accelerate wound healing, and protect lung tissue from inhaled pollutants. It may also reduce the risk for heart disease and prevent premature skin aging. Researchers suspect that Vitamin E has several other beneficial effects ranging from alleviating rheumatoid arthritis to preventing cataracts. Most of us get enough Vitamin E through our diet and do not require supplements. **Dark-green leafy vegetables, nuts, vegetable oils, seafood, eggs, and avocados are food sources rich in Vitamin E.**

Selenium has antioxidant effects that complement those of Vitamin E. It is a required constituent of several enzymes that remove reactive oxidants. The metal may support the immune function and neutralize some heavy metal poisons. It may also aid in deterring heart disease and some cancers. **Good sources of selenium in the diet are whole grains, asparagus, garlic, eggs, mushrooms, lean meats, and seafood.** Usually diet alone provides sufficient selenium for good health. Supplements should be taken only if prescribed by a doctor because high doses can be toxic.
Potassium Dichromate

In its analytical applications, dichromate ion is reduced to green chromium(III) ion:

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

\[ E^0 = 1.33 \text{ V} \]

Dichromate titrations are generally carried out in solutions that are about 1 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.

Preparing Dichromate Solutions

For most purposes, reagent-grade potassium dichromate is sufficiently pure to permit the direct preparation of standard solutions, the solid simply being dried at 150°C to 200°C before being weighed.

The orange color of a dichromate solution is not intense enough for use in endpoint detection. However, diphenylamine sulfonic acid (see Table 19-3) is an excellent indicator for titrations with this reagent. The oxidized form of the indicator is violet, and its reduced form is essentially colorless; thus, the color change observed in a direct titration is from the green of chromium(III) to violet.
Molecular model of dichromate ion.

For many years, dichromate in the form of its ammonium, potassium, or sodium salts was used in nearly all areas of chemistry as a powerful oxidizing agent.

In addition to its use as a primary standard in analytical chemistry, it has been used as an oxidizing agent in synthetic organic chemistry; as a pigment in the paint, dye, and photographic industries; as a bleaching agent; and as a corrosion inhibitor. Chromic acid solution made from sodium dichromate and sulfuric acid was once the reagent of choice for thorough cleaning of glassware. Dichromate has been used as the analytical reagent in the alcohol Breathalyzer®, but in recent years, these devices have largely been replaced by analyzers based on the absorption of infrared radiation. Early color photography utilized the colors produced by chromium compounds in the so-called gum bichromate process, but this process has been replaced by silver bromide-based processes. The use of chromium compounds in general and dichromate in particular has decreased over the last decade because of the discovery that chromium compounds are carcinogenic. In spite of this danger, many millions of pounds of chromium compounds are manufactured and consumed by industry each year. Before using dichromate in laboratory work, read the MSDS for potassium dichromate (see the Web Works for this chapter) and explore its chemical, toxicological, and carcinogenic properties. Observe all precautions in handling this useful but potentially hazardous chemical either in the solid form or in solution.
Applying Potassium Dichromate Solutions

The principal use of dichromate is for the volumetric titration of iron(II) based on the reaction

$$\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$$

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 (see Section 20B-1). Standardization of the iron(II) solution by titration with the dichromate is performed concurrently with the determination because solutions of iron(II) tend to be air oxidized. 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.
Ex. Redox titration (hydroquinone vs dichromate standard solution)

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e} \leftrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E^\circ = 1.33
\]

\[
3 \left[ \begin{array}{c}
\text{HO} - \\
\text{OH}
\end{array} \right] \leftrightarrow \begin{array}{c}
\text{O} \\
\equiv
\end{array} \text{O} + 2\text{H}^+ + 2\text{e} \quad E^\circ = 0.700
\]

\[
3 \text{HO} - \\
\text{OH} + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \leftrightarrow 3 \begin{array}{c}
\text{O} \\
\equiv
\end{array} \text{O} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

\[
E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.33 - 0.700 = 0.63 \text{ V}
\]

\[
K = 10^{nE^\circ/0.05916} = 10^{6(0.63)/0.05916} = 10^{64}
\]

redox indicator: diphenylamine

colorless to violet

Very large: quantitative: complete reaction
EXAMPLE 20-6

A 5.00-mL sample of brandy was diluted to 1.000 L in a volumetric flask. The ethanol (C\textsubscript{2}H\textsubscript{5}OH) in a 25.00-mL aliquot of the diluted solution was distilled into 50.00 mL of 0.02000 M K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} and oxidized to acetic acid with heating:

\[3\text{C}_2\text{H}_5\text{OH} + 2\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 3\text{CH}_3\text{COOH} + 11\text{H}_2\text{O}\]

After cooling, 20.00 mL of 0.1253 M Fe\textsuperscript{2+} was pipetted into the flask. The excess Fe\textsuperscript{2+} was then titrated with 7.46 mL of the standard K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} to a diphenylamine sulfonic acid end point. Calculate the percent (w/v) C\textsubscript{2}H\textsubscript{5}OH (46.07 g/mol) in the brandy.

Solution

total amount K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}

\[= (50.00 + 7.46) \text{ mL K}_2\text{Cr}_2\text{O}_7 \times 0.02000 \frac{\text{mmol K}_2\text{Cr}_2\text{O}_7}{\text{mL K}_2\text{Cr}_2\text{O}_7}\]

\[= 1.1492 \text{ mmol K}_2\text{Cr}_2\text{O}_7\]
amount $\text{K}_2\text{Cr}_2\text{O}_7$ consumed by $\text{Fe}^{2+}$

$$= 20.00 \text{ mL Fe}^{2+} \times 0.1253 \frac{\text{mmol Fe}^{2+}}{\text{mL Fe}^{2+}} \times \frac{1 \text{ mmol K}_2\text{Cr}_2\text{O}_7}{6 \text{ mmol Fe}^{2+}}$$

$$= 0.41767 \text{ mmol K}_2\text{Cr}_2\text{O}_7$$

amount $\text{K}_2\text{Cr}_2\text{O}_7$ consumed by $\text{C}_2\text{H}_5\text{OH} = (1.1492 - 0.41767) \text{ mmol K}_2\text{Cr}_2\text{O}_7$

$$= 0.73153 \text{ mmol K}_2\text{Cr}_2\text{O}_7$$

mass $\text{C}_2\text{H}_5\text{OH}$

$$= 0.73153 \text{ mmol K}_2\text{Cr}_2\text{O}_7 \times \frac{3 \text{ mmol C}_2\text{H}_5\text{OH}}{2 \text{ mmol K}_2\text{Cr}_2\text{O}_7} \times 0.04607 \frac{\text{g C}_2\text{H}_5\text{OH}}{\text{mmol C}_2\text{H}_5\text{OH}}$$

$$= 0.050552 \text{ g C}_2\text{H}_5\text{OH}$$

percent $\text{C}_2\text{H}_5\text{OH} = \frac{0.050552 \text{ g C}_2\text{H}_5\text{OH}}{5.00 \text{ mL sample} \times 25.00 \text{ mL/1000 mL}} \times 100\%$$

$$= 40.4\% \text{ C}_2\text{H}_5\text{OH}$$
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

\[ I_3^- + 2e^- \rightleftharpoons 3I^- \quad E^0 = 0.536 \, \text{V} \]

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. On the other hand, iodine solutions lack stability and must be restandardized regularly.
Properties of Iodine Solutions

Iodine is not very soluble in water (0.001 M). To prepare solutions having analytically useful concentrations of the element, iodine is usually dissolved in moderately concentrated solutions of potassium iodide. In this medium, iodine is reasonably soluble as a consequence of the reaction

\[ \text{I}_2(s) + \text{I}^- \rightleftharpoons \text{I}_3^- \quad K = 7.1 \times 10^2 \]

Iodine dissolves only very slowly in solutions of potassium iodide, particularly if the iodide concentration is low. To ensure complete solution, the iodine is always dissolved in a small volume of concentrated potassium iodide, care being taken to avoid dilution of the concentrated solution until the last trace of solid iodine has disappeared. Otherwise, the concentration of the diluted solution gradually increases with time. This problem can be avoided by filtering the solution through a sintered glass crucible before standardization.

Iodine solutions lack stability for several reasons, one being the volatility of the solute. Losses of iodine from an open vessel occur in a relatively short time even in the presence of an excess of iodide ion. In addition, iodine slowly attacks most organic materials. Therefore, cork or rubber stoppers are never used to close containers of the reagent, and precautions must be taken to protect standard solutions from contact with organic dusts and fumes.

Air oxidation of iodide ion also causes changes in the concentration of an iodine solution:

\[ 4\text{I}^- + \text{O}_2(g) + 4\text{H}^+ \rightarrow 2\text{I}_2 + 2\text{H}_2\text{O} \]

In contrast to the other effects, this reaction causes the concentration of the iodine to increase. Air oxidation is promoted by acids, heat, and light.
Standardizing and Using 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 is discussed in detail in Section 20B-2. Often, solutions of iodine are standardized against solutions of sodium thiosulfate that have in turn been standardized against potassium iodate or potassium dichromate (see Section 20B-2). Table 20-6 summarizes methods that use iodine as an oxidizing agent.
**Iodimetry and iodometry**

**Iodimetry**: a reducing analyte is titrated directly with iodine.

**Iodometry**: an oxidizing analyte is added to excess iodide to produce iodine, which is then titrated with standard thiosulfate solution.

Its solubility is enhanced by complexation with iodide.

\[ I_2 + I^- = I_3^- \quad K = 7 \times 10^2 \]
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. Direct titrations with potassium bromate are relatively few. Instead, the reagent is a convenient and widely used stable source of bromine. In this application, an unmeasured excess of potassium bromide is added to an acidic solution of the analyte. When a measured volume of standard potassium bromate is introduced, a stoichiometric quantity of bromine is produced.

\[ \text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O} \]

This indirect generation circumvents the problems associated with the use of standard bromine solutions, which lack stability.

The primary use of standard potassium bromate is for the determination of organic compounds that react with bromine. Few of these reactions are rapid enough to make direct titration feasible. Instead, a measured excess of standard bromate is added to the solution that contains the sample plus an excess of potassium bromide. 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:

\[ 2\text{I}^- + \text{Br}_2 \rightarrow \text{I}_2 + 2\text{Br}^- \]

The liberated iodine is then titrated with standard sodium thiosulfate (Equation 20-1).
Substitution Reactions

Bromine is incorporated into an organic molecule either by substitution or by addition. In halogen substitution, a hydrogen in an aromatic ring is replaced by a halogen. Substitution methods have been successfully applied to the determination of aromatic compounds that contain strong ortho-para-directing groups, particularly amines and phenols.

An important example of the use of a bromine substitution reaction is the determination of 8-hydroxyquinoline:

\[
\text{OH} \quad \text{Br} \quad + \quad 2\text{Br}_2 \quad \rightarrow \quad \text{OH} \quad \text{Br} \quad + \quad 2\text{HBr}
\]
In contrast to most bromine substitutions, this reaction takes place rapidly enough in hydrochloric acid solution to make direct titration feasible. The titration of 8-hydroxyquinoline with bromine is particularly significant because the former is an excellent precipitating reagent for cations (see Section 12C-3). For example, aluminum can be determined according to the sequence

\[ \text{Al}^{3+} + 3\text{HOC}_9\text{H}_6\text{N} \xrightarrow{\text{pH 4-9}} \text{Al(OC}_9\text{H}_6\text{N)}_3(s) + 3\text{H}^+ \]

\[ \text{Al(OC}_9\text{H}_6\text{N)}_3(s) \xrightarrow{\text{hot 4 M HCl}} 3\text{HOOC}_9\text{H}_6\text{N} + \text{Al}^{3+} \]

\[ 3\text{HOOC}_9\text{H}_6\text{N} + 6\text{Br}_2 \rightarrow 3\text{HOOC}_9\text{H}_4\text{NBr}_2 + 6\text{HBr} \]

The stoichiometric relationships in this case are

\[ 1 \text{ mol } \text{Al}^{3+} = 3 \text{ mol } \text{HOOC}_9\text{H}_6\text{N} = 6 \text{ mol } \text{Br}_2 = 2 \text{ mol } \text{KBrO}_3 \]
Addition Reactions

In addition reactions, olefinic double bonds are opened. For example, 1 mole of ethylene reacts with 1 mole of bromine in the reaction

\[
\text{H} - \text{C} = \text{C} - \text{H} + \text{Br}_2 \rightarrow \text{H} - \text{C} - \text{C} - \text{H}
\]

\[
\text{Br} \quad \text{Br}
\]

The literature contains numerous references to the use of bromine for the estimation of olefinic unsaturation in fats, oils, and petroleum products. A method for the determination of ascorbic acid in vitamin C tablets is given in Section 38I-3.
EXAMPLE 20-7

A 0.2981-g sample of an antibiotic powder was dissolved in HCl and the solution diluted to 100.0 mL. A 20.00-mL aliquot was transferred to a flask and followed by 25.00 mL of 0.01767 M KBrO₃. An excess of KBr was added to form Br₂, and the flask was stoppered. After 10 min, during which time the Br₂ brominated the sulfanilamide, an excess of KI was added. The liberated iodine titrated with 12.92 mL of 0.1215 M sodium thiosulfate. The reactions are

\[ \text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O} \]

\[ \text{SO}_2\text{NH}_2 \]

sulfanilamide

\[ \text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2 \quad \text{(excess KI)} \]

\[ \text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{S}_4\text{O}_6^{2-} + 2\text{I}^- \]

Calculate the percent sulfanilamide (\(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2\), 172.21 g/mol) in the powder.
Solution

total amount $\text{Br}_2 = 25.00 \text{ mL KBrO}_3 \times 0.01767 \frac{\text{mmol KBrO}_3}{\text{mL KBrO}_3} \times 3 \frac{\text{mmol Br}_2}{\text{mmol KBrO}_3}$

$= 1.32525 \text{ mmol Br}_2$

We next calculate how much $\text{Br}_2$ was in excess over that required to brominate the analyte:

amount excess $\text{Br}_2 = \text{amount I}_2$

$= 12.92 \text{ mL Na}_2\text{S}_2\text{O}_3 \times 0.1215 \frac{\text{mmol Na}_2\text{S}_2\text{O}_3}{\text{mL Na}_2\text{S}_2\text{O}_3} \times 1 \frac{\text{mmol I}_2}{2 \text{ mmol Na}_2\text{S}_2\text{O}_3}$

$= 0.78489 \text{ mmol Br}_2$

The amount of $\text{Br}_2$ consumed by the sample is given by

$\text{amount Br}_2 = 1.32525 - 0.78489 = 0.54036 \text{ mmol Br}_2$

mass analyte $= 0.54036 \text{ mmol Br}_2 \times 1 \frac{\text{mmol analyte}}{2 \text{ mmol Br}_2} \times 0.17221 \frac{\text{g analyte}}{\text{mmol analyte}}$

$= 0.046528 \text{ g analyte}$

percent analyte $= \frac{0.046528 \text{ g analyte}}{0.2891 \text{ g sample} \times 20.00 \text{ mL/100 mL}} \times 100\%$

$= 80.47\%$ sulfanilamide
20C-5 Determining water with the Karl Fisher Reagent

The Karl Fischer reaction is based on the oxidation of sulfur dioxide by iodine.

\[ \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4 \]

For the determination of small amount of water, Karl Fischer (1935) proposed a reagent prepared as an anhydrous methanolic solution containing iodine, sulfur dioxide and anhydrous pyridine in the mole ratio 1:3:10. In the first step, \( \text{I}_2 \) and \( \text{SO}_2 \) react in the presence of pyridine and water to form pyridinium sulfite and pyridinium iodide:

\[ \text{C}_5\text{H}_5\text{N}\cdot\text{I}_2 + \text{C}_5\text{H}_5\text{N}\cdot\text{SO}_2 + \text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightarrow 2\text{C}_5\text{H}_5\text{N}\cdot\text{HI} + \text{C}_5\text{H}_5\text{N}\cdot\text{SO}_3 \quad (20-2) \]

\[ \text{C}_5\text{H}_5\text{N}^+\cdot\text{SO}_3^- + \text{CH}_3\text{OH} \rightarrow \text{C}_5\text{H}_5\text{N}(\text{H})\text{SO}_4\text{CH}_3 \quad (20-3) \]

Pyridinium sulfite can also consume water.

\[ \text{C}_5\text{H}_5\text{N}^+\cdot\text{SO}_3^- + \text{H}_2\text{O} \rightarrow \text{C}_5\text{H}_5\text{NH}^+\text{SO}_4\text{H}^- \quad (20-4) \]

This last reaction is undesirable because it is not as specific for water. It can be prevented completely by having a large excess of methanol present. Note that the stoichiometry is 1 mole of \( \text{I}_2 \) per mole of \( \text{H}_2\text{O} \) present. The end point can be detected either by visual (at the end point, the color changes from dark brown to yellow) or electrometric, or photometric (absorbance at 700 nm) titration methods. For coulometric methods (see Chapter 22), the Karl Fischer reagent contains KI instead of \( \text{I}_2 \) since, as we will see, the \( \text{I}_2 \) is generated electrochemically.
Pyridine free Karl Fisher reagent

In recent years, pyridine, and its objectionable odor, have been replaced in the Karl Fisher reagent by other amines, particularly imidazole.

(1) Solvolysis \[ 2\text{ROH} + \text{SO}_2 \leftrightarrow \text{RSO}_3^- + \text{ROH}_2^+ \]

(2) Buffering \[ \text{B} + \text{RSO}_3^- + \text{ROH}_2^+ \leftrightarrow \text{BH}^+\text{SO}_3\text{R}^- + \text{ROH} \]

(3) Redox \[ \text{B} \cdot \text{I}_2 + \text{BH}^+\text{SO}_3\text{R}^- + \text{B} + \text{H}_2\text{O} \leftrightarrow \text{BH}^+\text{SO}_4\text{R}^- + 2 \text{BH}^+\text{I}^- \]

Note that the stoichiometry is again one mole of I\(_2\) consumed for each mole of H\(_2\)O present in the sample.
**Interfering Reactions.** There are several reactions that can occur that cause interferences in the Karl Fischer titration. These undesired reactions can cause results to be too high, too low, or just imprecise. Oxidation of iodide in the coulometric reagent by oxidizing agents such as Cu(II), Fe(III), nitrite, Br₂, Cl₂, or quinones produces I₂, which can react with H₂O and cause low results since not as much generated I₂ is needed. The carbonyl groups on aldehydes and ketones can react with SO₂ and H₂O to form bisulfite complexes. Since this reaction consumes water, the titration results are again too low. Substitution of a weaker base like pyridine for imidazole can lessen the problem.

The iodine generated coulometrically or present in the reagent can be reduced by oxidizable species such as ascorbic acid, ammonia, thiols, Tl⁺, Sn²⁺, In⁺, hydroxyl amines, and thiosulfite. This reduction results in consumption of I₂ and water determinations that are too high. Phenolic derivatives and bicarbonates also cause reduction of I₂.

Some interfering compounds react to produce water, which causes the water results to be too high. Carboxylic acids can react with alcohols to produce an ester and water. To minimize this problem, the alcohol can be eliminated in the reagent, or an alcohol that reacts at a slower rate than methanol can be used. The pH of the reagent can be increased because the formation of esters is usually acid catalyzed. Ketones and aldehydes can react with alcoholic solvents to form ketals and acetics with the production of water according to

\[
R_2C\equiv O + 2\text{CH}_3\text{OH} \rightarrow R_2C(\text{OCH}_3)_2 + \text{H}_2\text{O}
\]
Aromatic ketones are less reactive than aliphatic ketones. Aldehydes are much more reactive than ketones. Some commercial reagent preparations have been formulated to minimize this problem by using alcohols that react slowly and a higher pH.

Silanols and cyclic siloxanes also can react with alcohols to produce ethers and water. Some metal oxides, hydroxides, and carbonates can react with HI to produce water. All of these reactions increase the amount of I$_2$ consumed and produce results that are too high.

**Detecting the End Point**

An end point in a Karl Fischer titration can be observed visually based on the brown color of the excess reagent. More commonly, however, end points are obtained by electroanalytical measurements. Several instrument manufacturers offer automatic or semiautomatic instruments for performing Karl Fischer titrations. All of these instruments are based on electrometric end point detection.
Reagent Properties

Karl Fischer reagent decomposes on standing. Because decomposition is particularly rapid immediately after preparation, it is common practice to prepare the reagent a day or two before it is to be used. Its strength must be established at least daily against a standard solution of water in methanol. A proprietary commercial Karl Fischer reagent reported to require only occasional restandardization is now available.

It is obvious that great care must be exercised to keep atmospheric moisture from contaminating the Karl Fischer reagent and the sample. All glassware must be carefully dried before use, and the standard solution must be stored out of contact with air. It is also necessary to minimize contact between the atmosphere and the solution during the titration.
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.
Summary

Preoxidation
Oxidizing agent
Reducing agent
Redox titration
Permanganometry
Cerimetry
Dichrometry
Iodimetry
Iodometry
Iodatimetry
Bromatimetry

Redox indicator
Iodine starch indicator
Self indicator
Karl Fisher titration
Karl Fisher reagent