

CHAPTER 20

Applications of Oxidation/Reduction Titrations

In this chapter, we describe the preparation of standard solutions of oxidants and reductants and their applications in analytical chemistry. In addition, auxiliary reagents that convert an analyte to a single oxidation state are discussed.¹

AUXILIARY OXIDIZING AND REDUCING REAGENTS

20A

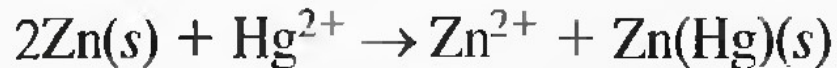
The analyte in an oxidation/reduction titration must be in a single oxidation state at the outset. Often, however, the steps that precede the titration, such as dissolving the sample and separating interferences, convert the analyte to a mixture of oxidation states. For example, when a sample containing 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 to determine iron, we must first treat the sample solution with an auxiliary reducing agent to convert all of the iron to iron(II). If we plan to titrate with a standard reductant, however, pretreatment with an auxiliary oxidizing reagent is needed.²

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.

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 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 20-1.³ Here, 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 ordinarily 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:



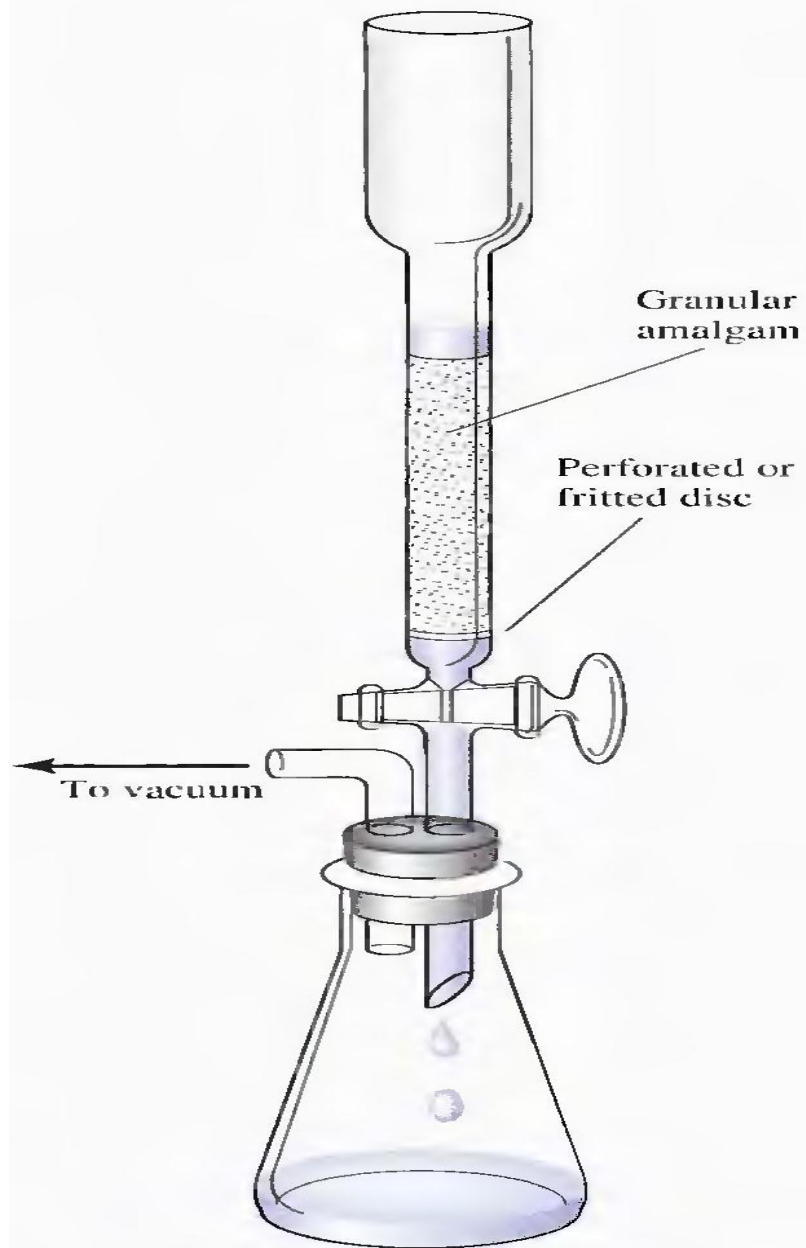


Figure 20-1 A Jones reductor.

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

TABLE 20-1

Uses of the Walden Reductor and the Jones Reductor*

Walden	Jones
$\text{Ag}(s) + \text{Cl}^- \rightarrow \text{AgCl}(s) + e^-$	$\text{Zn}(\text{Hg})(s) \rightarrow \text{Zn}^{2+} + \text{Hg} + 2e^-$
$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$
$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}(s)$
$\text{H}_2\text{MoO}_4 + 2\text{H}^+ + e^- \rightarrow \text{MoO}_2^+ + 2\text{H}_2\text{O}$	$\text{H}_2\text{MoO}_4 + 6\text{H}^+ + 3e^- \rightleftharpoons \text{Mo}^{3+} + 3\text{H}_2\text{O}$
$\text{UO}_2^{2+} + 4\text{H}^+ + 2e^- \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O}$	$\text{UO}_2^{2+} + 4\text{H}^+ + 2e^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$
	$\text{UO}_2^{2+} + 4\text{H}^+ + 3e^- \rightleftharpoons \text{U}^{3+} + 2\text{H}_2\text{O}^\dagger$
$\text{V}(\text{OH})_4^+ + 2\text{H}^+ + e^- \rightarrow \text{VO}^{2+} + 3\text{H}_2\text{O}$	$\text{V}(\text{OH})_4^+ + 4\text{H}^+ + 3e^- \rightleftharpoons \text{V}^{2+} + 4\text{H}_2\text{O}$
TiO^{2+} not reduced	$\text{TiO}^{2+} + 2\text{H}^+ + e^- \rightleftharpoons \text{Ti}^{2+} + \text{H}_2\text{O}$
Cr^{3+} not reduced	$\text{Cr}^{3+} + e^- \rightleftharpoons \text{Cr}^{2+}$

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, prereducations 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

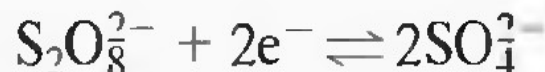
Sodium Bismuthate

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 NaBiO_3 , 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



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

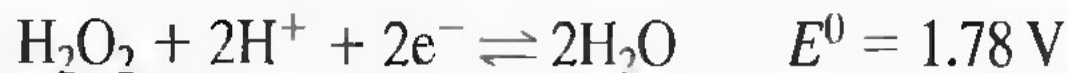


The oxidations are catalyzed by traces of silver ion. The excess reagent is easily decomposed by a brief period of boiling:

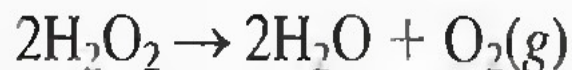


Sodium Peroxide and Hydrogen Peroxide

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



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



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, iron(II) and thiosulfate ions, are discussed in the paragraphs that follow.