20 Applications of Oxidation/Reduction Titrations

20A AUXILIARY OXIDIZING AND REDUCING REAGENTS

20A-1 Auxiliary Reducing Reagents

Table 20-1 Uses of the Walden Reductor and the Jones Reductor

Walden $Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$	Jones $Zn(Hg)(s) \rightarrow Zn^{2+} + Hg + 2e^-$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$
$Cu^{2+} + e^- \rightarrow Cu^+$	$Cu^{2+} + 2e^- \rightarrow Cu(s)$
$H_2MoO_4 + 2H^+ + e^- \rightarrow MoO_2^+ + 2H_2O$	$H_2MoO_4 + 6H^+ + 3e^- \rightarrow Mo^{3+} + 4H_2O$
$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$	$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$
	$UO_2^{2+} + 4H^+ + 3e^- \rightarrow U^{3+} + 2H_2O$
$V(OH)_4^+ + 2H^+ + e^- \rightarrow VO^{2+} + 3H_2O$	$V(OH)_4^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 4H_2O$
TiO^{2+} not reduced	$TiO^{2+} + 2H^+ + e^- \rightarrow Ti^{3+} + 4H_2O$
Cr^{3+} not reduced	$Cr^{3+} + e^- \rightarrow Cr^{2+}$

20A-2 Auxiliary Oxidizing Reagents

Sodium Bismuthate: $Mn(II) \rightarrow MnO_4^-$

$NaBiO_3(s) + 4H^+ + 2e^- \rightarrow BiO^+ + Na^+ + 2H_2O$

Ammonium Peroxydisulfate, ammonium persulfate, $(NH_4)_2S_2O_8$

in acidic soln: Cr(III) → dichromate
Ce(III) → Ce(IV)
Mn(II) → permanganate

$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ $E^o = 2.01$ V

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

$S_2O_8^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + O_2 + 4H^+$

Sodium Peroxide and Hydrogen Peroxide

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E^o = 1.78$ V

boiling: $H_2O_2 \rightarrow 2H_2O + 2O_2(g)$

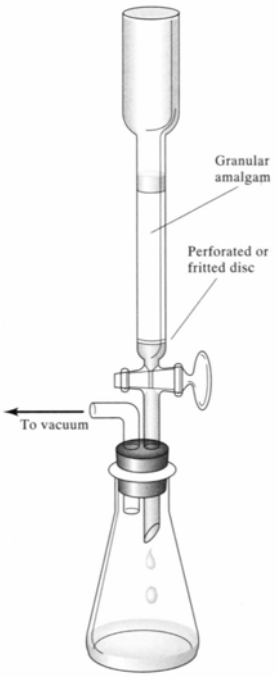


Fig. 20-1
A Jones reductor.

20B APPLING STANDARD REDUCING AGENTS

20B-1 Iron (II) Solutions

iron(II) ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (**Mohr's salt**)

iron(II) ethylenediamine sulfate, $FeC_2H_4(NH_3)_2(SO_4)_2 \cdot 4H_2O$ (**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_2SO_4.

oxidizing agents ← excess of standard Fe(II) ← standard soln of pot. dichromate or Ce(IV).

Application: organic peroxides, hydroxylamine, Cr(VI), Ce(IV), Mo(VI), nitrate, chlorate, perchlorate and numerous other oxidants.

20B-2 Sodium Thiosulfate

iodine ← thiosulfate

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

excess KI

↓ analyte/slightly acidic solution

<u>iodine</u> ← standard solution of $Na_2S_2O_3$

ex: determination of sod. Hypochlorite in bleaches

$Ocl^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O$

(unmeasured excess KI)

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

Detecting End Points in Iodine/Thiosulfate Titrations

1. disappearance of the iodine color

5×10^{-6} M I_2 --- discernible color

2. starch indicator -- deep blue color

Starch undergoes decomposition in solution with high I_2 concentration. In titration of excess I_2 with $Na_2S_2O_3$, addition of the indicator must be deferred until most of the I_2 has been reduced.

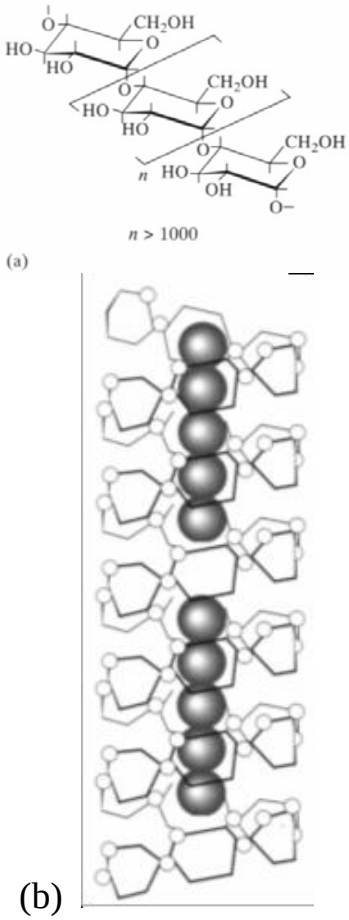


Fig. 20-2 Thousands of glucose molecules polymerize to form huge molecules of β-amylose as shown in (a). Molecules of β-amylose tend to assume a helical structure. The iodine species I_3^- as shown in (b) is incorporated into the amylose helix.

The Stability of Sodium Thiosulfate Solutions

decompose: $S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S(s)$

pH, microorganisms, concentration of the solution, presence of Cu(II) ion and exposure to sunlight.

Standardizing Thiosulfate Solutions

primary standard: pot. iodate/excess KI (pot. dichromate, pot. bromate, pot. hydrogen iodate, pot. ferricyanide and metallic copper)/ excess KI.

$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 2H_2O$

↑ thiosulfate

1 mol IO_3^- = 3 mol I_2 = 6 mol $S_2O_3^{2-}$

Ex. 20-1 A solution of Sod. thiosulfate was standardized by dissolving 0.1210 g KIO_3 (214.00 g/mol) in water, adding a large excess of KI, and acidifying with HCl. The liberated I_2 required 41.64 mL of the thiosulfate soln to decolorize the blue starch/iodine complex. Calculate the molarity of the $Na_2S_2O_3$.

$$\text{amount } Na_2S_2O_3 = 0.1210\text{g } KIO_3 \times \frac{1\,\text{mol}}{0.21400\,\text{g}} \times 6 = 3.3925\,\text{mmol}$$

$$C_{Na_2S_2O_3} = \frac{3.3925\,\text{mmol}}{41.64\,\text{mL}} = 0.08147\,\text{M} \quad \text{or} \quad \frac{\frac{121\,\text{mg}}{214\,\text{mg/mmol}} \times 3 \times 2}{41.64\,\text{mL}} = 0.08147\text{M}$$

Tab 20-2 Applications of Sodium Thiosulfate as Reductant

Analyte	**Half-Reaction**	**Special Condition**
IO_4^-	$IO_4^- + 8H^+ + 7e^- \rightarrow \frac{1}{2} I_2 + 4H_2O$	Acid solution
	$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	Neutral solution
IO_3^-	$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2} I_2 + 3H_2O$	Strong acid
BrO_3^-, ClO_3^-	$XO_3^- + 6H^+ + 6e^- \rightarrow X^- + 3H_2O$	Strong acid
Br_2, Cl_2	$X_2 + 2I^- \rightarrow I_2 + 2X^-$	
NO_2^-	$HNO_2 + H^+ + e^- \rightarrow NO(g) + H_2O$	
Cu^{2+}	$Cu^{2+} + I^- + e^- \rightarrow CuI(s)$	
O_2	$O_2 + 4Mn(OH)_2(s) + 2H_2O \rightarrow 4Mn(OH)_3(s)$	Basic solution
	$Mn(OH)_3(s) + 3H^+ + e^- \rightarrow Mn^{2+} + 3H_2O$	Acidic solution
O_3	$O_3(g) + 2H^+ + 2e^- \rightarrow O_2(g) + H_2O$	
Organic peroxide	$ROOH + 2H^+ + 2e^- \rightarrow ROH + H_2O$	

20C APPLYING STANDARD OXIDING AGENTS

Table 20-3 Some common oxidants used as standard solutions

Reagent and Formula	Reduction product	Standard Potential, V	Standardized with	Indicator*	Stability#
$KMnO_4$	Mn^{2+}	1.51†	$Na_2C_2O_4$, Fe, As_2O_3	MnO_4^-	(b)
$KBrO_3$	Br^-	1.44†	$KBrO_3$	(1)	(a)
Ce(IV), Ce^{4+}	Ce^{3+}	1.44†	$Na_2C_2O_4$, Fe, As_2O_3	(2)	(a)
$K_2Cr_2O_7$	Cr^{3+}	1.33†	$K_2Cr_2O_7$, Fe	(3)	(a)
I_2	I^-	0.536†	$BaS_2O_3 \cdot H_2O$, $Na_2S_2O_3$	starch	(c)

* (1) α-Naphthoflavone; (2) 1,10-phenanthroline iron(II) complex (ferroin); (3) diphenylamine sulfonic acid.

 # (a) Indefinitely stable;
(b) moderately stable, requires periodic standardization;
(c) somewhat unstable, require frequent standardization.

† $E^{o'}$ in H_2SO_4.

20C-1 The Strong Oxidants-Potassium Permanganate and Cerium(IV)

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^o = 1.51$ V (in $\geqq$ 0.1 M strong acid)

$Ce^{4+} + e^- \rightarrow Ce^{3+}$ $E^{o\prime} = 1.44$ V (1M H_2SO_4) = 1.70 V (1M $HClO_4$) = 1.61 V (1M HNO_3)

Comparison of the Two Reagents

	Ce^{4+}	**MnO_4^-**
in sulfuric acid	stable	decompose slowly
	not oxidize Cl^- --	oxidize Cl^-
HCl soln of analyte	can be used	cannot be used
primary-standard-grade salt	available	
self-indicator	no	color of MnO_4^-
cost (1L 0.02 M soln)	\$ 2.20 (4.40)	\$ 0.08
in < 0.1 M strong acid	tendency to form ppt	

Detecting the End Points

indicators: $KMnO_4$ solution -- intense purple color

diphenylamine sulfonic acid

1, 10-phenanthroline complex of Fe(II)

$2MnO_4^- + 3Mn^{2+} + H_2O \rightarrow 5MnO_2(s) + 4H^+$

$K = 10^{47}$ $\rightarrow$ *equilibrium* [**MnO_4^-**] $\downarrow$

rate: slow $\rightarrow$ end point fades only gradually over 30s.

in Ce(IV) titration:

indicator: Fe(II) complex of 1,10-phenanthroline or one of its substitute derivatives (Table 20-3)

$C_{12}H_8N_2 + Fe^{2+} \rightarrow Fe(C_{12}H_8N_2)_3^{2+} \rightarrow Fe(C_{12}H_8N_2)_3^{3+} + e^-$

Ferrous complex Ferric complex

(Ferroin) red (Ferriin) weak blue

The Preparation and Stability of Standard Solutions

$KMnO_4$ soln: not entirely stable

$4MnO_4^- + 2H_2O \rightarrow 4MnO_2(s) + 3O_2(g) + 4OH^-$

decomposition reaction is slow -- catalyzed by **light**, heat, acids, bases, Mn(II) and MnO_2.

Ex. 20-2 Described how you would prepare 2.0 L of an approximately 0.010 M soln of $KMnO_4$ (158.03 g/mol).

$KMnO_4$ needed = 2.0 L× 0.010 M × 158.03 g/mol = 3.16 g

Dissolve about 3.2 g of $KMnO_4$ 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 stored in a clean dark bottle.

Analytically Useful Cerium(IV) Compounds

Name	Formula	Molar Mass
Cerium(IV) ammonium nitrate	$Ce(NO_3)_4 \cdot 2NH_4NO_3$	548.2
Cerium(IV) ammonium sulfate	$Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$	632.6
Cerium(IV) hydroxide	$Ce(OH)_4$	208.1
Cerium(IV) hydrogen sulfate	$Ce(HSO_4)_4$	528.4

Primary Standards

Sodium Oxalate.

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2(g) + 8H_2O$$

Mn(II) as a catalyst (autocatalysis)

$$2Ce^{4+} + H_2C_2O_4 \rightarrow 2Ce^{3+} + 2H^+ + 2CO_2$$

Ex. 20-3 You wish to standardize the soln in Ex.20-2 against pure $Na_2C_2O_4$ (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?

for a 30-mL titration:

amount $KMnO_4$ = 30 mL × 0.010 M = 0.30 mmol

mass $Na_2C_2O_4$ = 0.30 mmol × 5/2 × 0.134 = 0.101 g

for a 45-mL titration:

mass $Na_2C_2O_4$ = 45 × 0.010 × 5/2 × 0.134 = 0.151 g

Ex. 20-4 A 0.1278-g sample of primary-standard $Na_2C_2O_4$ required exactly 33.31 mL of the $KMnO_4$ solution in Ex. 20-2 to reach the end point. What was the molarity of the $KMnO_4$ reagent?

amount $Na_2C_2O_4$ = 0.1278 g × 1 mmol/0.134 g = 0.95373 mmol

C_{KMnO_4} = 0.95373 mmol × (2/5) × (1/33.31 = 0.01145 M

Using Potassium Permanganate and Cerium(IV) Solutions: Table 20-5

Ex. 20-5 Aqueous solution containing approximately 3% (w/w) H_2O_2 are sold in drug stores as a disinfectant. propose a method for determining the peroxide content of such a preparation using the standard soln described in Exs.20-3 and 4. Assume that you wish to use between 35 and 45 mL of the reagent for a titration.

$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$

35 - 45 mL reagent:

amount $KMnO_4$ = (35 ~ 45) mL × 0.01145 M = 0.401~0.515 mmol

amount H_2O_2 = (0.401 ~ 0.515) mmol × (5/2) = 1.00~1.29 mmol

mass sample = (1.00 ~ 1.29) × 0.03401 × (100/3) = 1.1 ~1.5 g

Thus we could weigh out from 1.1 to 1.5 g samples. These should be diluted to perhaps 75 to 100 mL with water and made slightly acidic with dilute H_2SO_4 before titration.

20C-2 Potassium Dichromate

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $E^o = 1.33$ V

orange green

in 1 M HCl or H_2SO_4 $E^{o'} = 1.0 \sim 1.1$ V

Advantages: stable, can be boiled without decomposition and do not react with HCl, primary-standard reagent is available and at a modest cost.

Disadvantage: lower electrode potential and the slowness reaction.

Preparing Dichromate Solutions

reagent-grade $K_2Cr_2O_7$ dried at 150℃ to 200℃ before being weighed

indicator: diphenylamine sulfonic acid,

violet (oxidized) → colorless (reduced)

Applying Potassium Dichromate Solutions

1. titration of Fe(II): in moderate conc. of HCl

   $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

2. indirect determination of oxidizing agents (nitrate, chlorate, permanganate, dichromate and organic peroxides):

   analyte/acidic solution + measured excess Fe(II) →

   back-titrated excess Fe(II)

Ex. 20-6 A 5.00-mL sample of brandy was diluted to 1.000 L in a volumetric flask. The ethanol(C_2H_5OH) in a 25.00-mL aliquot of the diluted soln was distilled into 50.00 mL of 0.02000 M $K_2Cr_2O_7$, and oxidized to acidic acid with heating.

$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$

After cooling, 20.00 mL of 0.1253 M Fe^{2+} were pipetted into the flask. The excess Fe^{2+} was then titrated with 7.46 mL of the standard $K_2Cr_2O_7$ to a diphenylamine sulfonic acid end point. Calculate the percent (w/v) C_2H_5OH (46.07 g/mol) in the brandy.

amount $K_2Cr_2O_7$ = (50.00 + 7.46) mL × 0.02000 = 1.1492 mmol

$K_2Cr_2O_7$ consumed by Fe^{2+} = 20.00 × 0.1253 × 1/6 = 0.41767 mmol

$K_2Cr_2O_7$ consumed by C_2H_5OH = 1.1492 - 0.41767 = 0.73153 mmol

mass C_2H_5OH = 0.73153 × (3/2) × 0.04607 = 0.050552 g

percent C_2H_5OH = 0.050552/(5.00 × 25.00/1000) × 100 % = 40.44 %

20C-3 Iodine

weak oxidizing agents: determination of strong reductants

$I_3^- + 2e^- \rightarrow 3I^-$ $E^o = 0.536$ V

advantages: selectivity, sensitive and reversible indicator

disadvantage: lack stability

Properties of Iodine Solutions

$I_2(s) + I^- \rightarrow I_3^-$ $K = 7.1 \times 10^2$

lack stability: volatility of iodine, slowly attacks most organic materials, air-oxidation of iodide ion (↑ conc.). **$4I^- + O_2(g) + 4H^+ \rightarrow 2I_2 + 2H_2O$**

Standardizing and Appling Iodine Solutions

Standardization: anhydrous Na thiosulfate or Ba thiosulfate

<u>Iodimetry</u>: (direct method)

I_2 → *reducing agents* (ex: thiosulfate or arsenites)

<u>Iodometry</u>: (indirect method)

oxidizing agents + excess KI → **I_2** ← **thiosulfate**

<u>Indicator</u>:

1. Starch indicator solution

$I_2 + I^-$ → I_3^- + starch → **I_3^--starch** complex (**blue-purple)**

2. CCl_4, $HCCl_3$, CS_2

I_2 in CCl_4, $HCCl_3$, CS_2 → **violet** color

Preparation of 0.1 N Iodine solution

12.7 g I_2 + 40 g KI/20 mL H_2O →adding H_2O to 1 L

Standardization- **Primary standard: Arsenic (III) oxide, As_2O_3**

$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$

$Na_3AsO_3 + 3HCl \rightarrow H_3AsO_3 + 3NaCl$

$H_3AsO_3 + H_2O + I_2 \rightarrow H_3AsO_4 + 2HI$

pH ↓ : $H_3AsO_3 + H_2O + I_2 \leftarrow H_3AsO_4 + 2H^+ + 2I^-$

pH ↑ : $I_2 + 2OH^- \rightarrow IO^- + I^- + H_2O$

$3IO^- \rightarrow IO_3^- + 2I^-$

strong oxidizing agent

滴定中加入 $NaHCO_3$ [pH: 7～8]

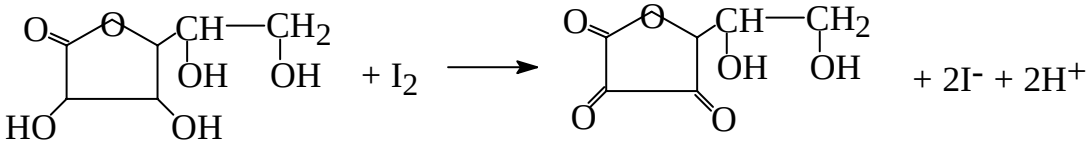
$Na_3AsO_3 + I_2 + 2NaHCO_3 \rightarrow Na_3AsO_4 + 2NaI + 2CO_2 \uparrow + H_2O$

Calculation: $$\text{N of Iodine} = \frac{\frac{\text{mg } As_2O_3}{197.8/4}}{\text{mL Iodine}}$$

(1) Direct Iodimetric Titration

a. $H_3AsO_3 + H_2O + I_2 \rightarrow H_3AsO_4 + 2H^+ + 2I^-$

b. Assay of Ascorbic Acid (Vit C)



(enediol) (α-diketone)

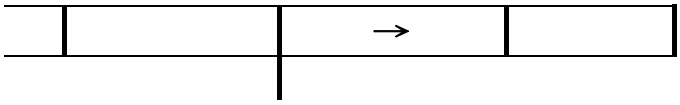
(2) Residual Titration (I_2- $Na_2S_2O_3$)

$NaHSO_3 + I_2 + H_2O \rightarrow NaHSO_4 + 2HI$

$I_2 + 2\ Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

(3) Iodometry:

Sample + KI (excess) → I2 ← Na2S2O3



(+2) ($1e^-$) (+1)

a. $CuSO_4 + 4KI \rightarrow 2CuI \downarrow + I_2 + 2K_2SO_4$

$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

b. Assay of sodium hypochlorite solution (NaOCl)

$$\mathbf{NaOCl + H^+ \rightarrow HOCl}$$

$$\mathbf{\overset{(+1)}{HOCl} + 2KI + HOAc \rightarrow \overset{(2e^-)}{I_2} + \overset{(-1)}{KCl} + KOAc + H_2O}$$

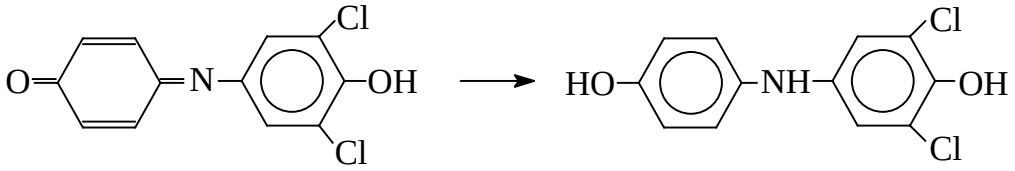
$$\mathbf{I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6}$$

Table 20-6 Some Applications of Iodine Solutions

Analyte	Half-Reaction
As	$H_3ASO_3 + H_2O \rightarrow H_3AsO_4 + 2H^+ + 2e^-$
Sb	$H_3SbO_3 + H_2O \rightarrow H_3SbO_4 + 2H^+ + 2e^-$
Sn	$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$
H_2S	$H_2S \rightarrow S(s) + 2H^+ + 2e^-$
SO_2	$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$
$S_2O_3^{2-}$	$2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$
N_2H_4	$N_2H_4 \rightarrow N_2(g) + 4H^+ + 4e^-$
Ascorbic acid	$C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e^-$

**** <u>Dichloroindophenol Titration</u>**

--Determination of *Ascorbic acid Preparation*



***Blue* in basic sol'n** **colorless**

***Pink* in acid sol'n**

End point: pink (self-indicator)

Vit C titration in metaphosphoric acid and acetic acid sol'n

20C-4 Potassium Bromate as a Source of Bromine

Primary-standard $KBrO_3$ is available, stable

standard 0.1 N Bromine sol'n (Koppeschaar's sol'n): (3 g $KBrO_3$ + 15 g KBr)/1 L H_2O

Assay of sample: aniline, phenol, salicylic acid, resorcinol etc.

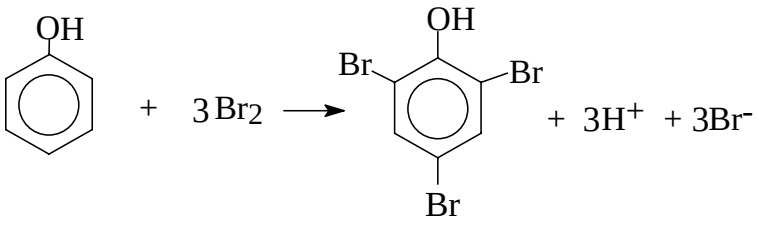
$$\mathbf{BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O}$$

standard soln excess

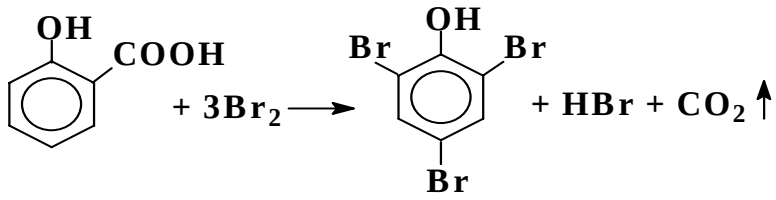
1 mol $KBrO_3$ = 3 mol Br_2

$2I^- + Br_2 \rightarrow I_2 + 2Br^-$ (excess KI)

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$



(ppt) soluble in $CHCl_3$

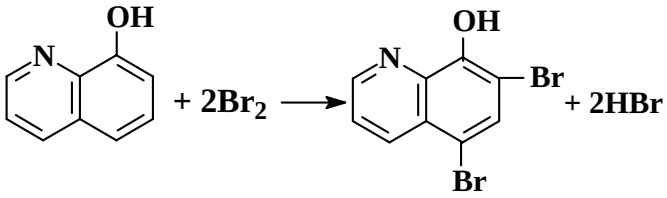


Substitution Reactions

halogen substitution: replacement of H in an aromatic ring by a halogen.

determination of aromatic compound that contain strong ortho-para-directing groups, particularly amines and phenols.

Ex: 1. Determination of 8-hydroxyquinoline



2. Determination of aluminum

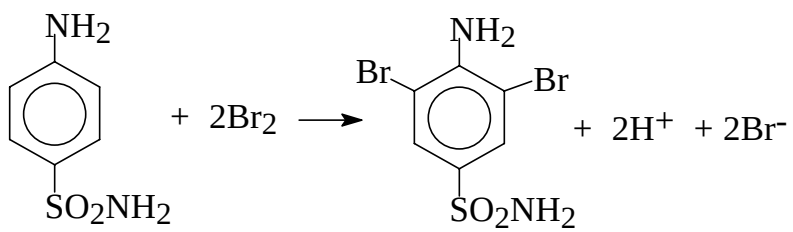
$$Al^{3+} + 3HOC_9H_6N \xrightarrow{\text{pH 4-9}} Al\left(OC_9H_6N\right)_3(S) + 3H^+$$

$$Al\left(OC_9H_6N\right)_3(S) \xrightarrow{\text{hot 4M HCl}} 3HOC_9H_6N + Al^{3+}$$

$$3HOC_9H_6N + 6Br_2 \rightarrow 3HOC_9H_4NBr_2 + 6HBr$$

Ex. 20-7 A 0.2891-g sample of an antibiotic powder containing sulfanilamide was dissolved in HCl and the solution diluted to 100.0 mL. A 20.00-mL aliquot was transferred to a stoppered flask and 25.00 mL of 0.01767 M $KBrO_3$ added. About 10 g of KBr was added to form Br_2, which brominated the sulfanilamide in the sample. After 10 min, an excess of KI was added and the liberated iodine titrated with 12.92 mL of 0.1215 M sodium thiosulfate. The reaction are

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$



$Br_2 + 2I^- \rightarrow 2Br^- + I_2$ (excess KI)

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$

Calculate the % $NH_2C_6H_4SO_2NH_2$ (172.21 g/mol) in the powder.

total amount Br_2 = 25.00 mL × 0.01767 M × 3 = 1.32525 mmol

amount excess Br_2 = amount I_2 = 12.92 mL × 0.1215 M × (1/2) = 0.78489 mmol

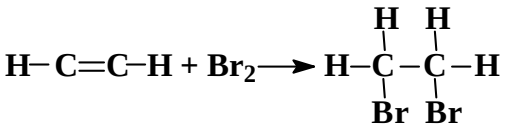
The amount of Br_2 consumed by the sample = 1.32525 – 0.78489 = 0.54036 mmol

mass analyte = 0.54036 × (1/2) × 0.17221 = 0.046528 g

$$\%\ \text{analyte} = \frac{0.046528}{0.2891 \times \frac{20.00mL}{100mL}} \times 100\% = 80.47\%$$

or $$\frac{(0.01767 \times 3 \times 2 \times 25 - 0.1215 \times 12.92) \times \frac{172.21}{4} \times 5}{289.1} \times 100\% = 80.47\%$$

Addition Reactions



20C-5 Determining Water with the Karl Fischer Reagent

Karl Fischer Reagent: I_2, SO_2, organic base such as pyridine (C_5H_5N) or imidazole /CH_3OH or low-molecular-mass alcohol

In aprotic solvent: $I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$ 2 mol $H_2O \rightarrow$ 1 mol I_2

Classical chemistry: use anhydrous methanol as solvent, and excess pyridine

$C_5H_5N{\cdot}I_2 + C_5H_5N{\cdot}SO_2 + C_5H_5N + H_2O \rightarrow 2C_5H_5N{\cdot}HI + C_5H_5N{\cdot}SO_3$

$C_5H_5N^+{\cdot}SO_3^- + CH_3OH \rightarrow C_5H_5N(H)SO_4CH_3$

1 mol $H_2O \rightarrow$ 1 mol I_2, 1 mol SO_2, 3 mol C_5H_5N

Pyridine-free chemistry

Replaced by other amines: imidazole

(1) Solvolysis: $2ROH + SO_2 \rightarrow RSO_3^- + ROH_2^+$

(2) Buffering: $B + RSO_3^- + ROH_2^+ \rightarrow BH^+SO_3R^- + ROH$

(3) Redox: $B{\cdot}I_2 + BH^+SO_3R^- + B + H_2O \rightarrow BH^+SO_4R^- + 2BH^+I^-$

1 mol $H_2O \rightarrow$ 1 mol I_2

Interfering reactions