An Introduction to Electrochemistry

Redox Reaction

$$ox_1 + red_2 \Leftrightarrow red_1 + ox_2$$

Balancing Redox Equations

half-reaction technique

$$Sn^{2+} + Fe^{3+} \Leftrightarrow Sn^{4+} + Fe^{2+}$$

$$Fe^{2+} + MnO_4^- \Leftrightarrow Fe^{3+} + Mn^{2+}$$

Balancing using the electron change

- 1- balance no of atoms
- 2- determine the e change for the half reaction
- 3- balance the charges -ve (OH^-, alkaline med), +ve (H^+, acidic med)
- 4- balance oxygen and hydrogen by adding H_2O
- (AECO)
- $H_2O_2 + MnO_4^- \rightarrow O_2 + Mn^{2+}$ (acid soln)

- $H_2O_2 \rightarrow O_2$
- $H_2O_2 \rightarrow O_2 + 2e$
- $H_2O_2 \rightarrow O_2 + 2H^+ + 2e$

- X 5

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

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

Balancing without knowledge of oxdn stats

- 1- balance the no of atoms (red/oxd)
- 2- balance oxygen (by adding H_2O)
- 3- balance hydrogen (by adding H+)
- 4- balance the charges (by adding e)
- (AOHC)
- $H_2O_2 + MnO_4^- \rightarrow O_2 + Mn^{2+}$ (acid soln)

- $H_2O_2 \rightarrow O_2$
- $H_2O_2 \rightarrow O_2 + 2H^+$
- $H_2O_2 \rightarrow O_2 + 2H^+ + 2e$
- X 5

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

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

Potassium permenganate

- Oxidising agent for over 100 years.
- Mn (+2,3,4,6,7)
- The most common reaction in acidic soln >= 0.1N

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

- MnO_4^- reacts rapidly with many reducing agents, but some substances require heating or the use of cat to speed up the reaction

- MnO_4^- is a strong agent to oxidise Mn(II) to MnO_2
- $3Mn^{2+} + 2\ MnO_4^- + 2H_2O \rightarrow 5MnO_2(s) + 4H^+$

- The slight excess of MnO_4^- (at ep) ➔ $MnO_2(s)$.
- The reaction is slow ➔ the ppt is formed at the ep

Precautions taken in the prepn of $KMnO_4$ soln

- Traces of MnO_2 (present in $KMnO_4$ or formed by the reaction with traces of reducing agents in H_2O) catalyses the decomposition of $KMnO_4$ soln.

- Dissolve the crystals (heat) → to destroy reducible substances → filter through sintered glass (non reducing filters) → MnO_2 is removed

- → pure soln of $KMnO_4$ → titrate against stand soln
- → keep in the dark → avoid acidifying
- → its concen would be stable for several months

Acidic soln of MnO_4^- is not stable

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

- Slow reaction (dil soln, RT)
- **Never** add excess MnO_4^- to a reducing agent and then raise the temp to hasten oxdn
- ➔ the foregoing reactn will occur at an appreciable rate.

Primary stand for MnO_4^-

- Sod oxalate
- Exact mechan is not clear.
- T=60°C
- The rate increases as Mn(II) is formed
- Autocatalytic reactn

Color Plate 13 The time dependence of the reaction between permanganate and oxalate (see Section 20C-1, page 515).

- Pure sodium oxalte ($Na_2C_2O_4$, mol wt 134) (0.2856 g) in water, H_2SO_4 is added, titrated 70 ^oC
- $KMnO_4$ 45.12 mL
- e.p. overrun
- Extra vol required 1.74 mL 0.0516 M oxalic acid
- Calculate the molarity of $KMnO_4$
- Two solutions NaHA, HA how can you calculate the pH of each solution
- How can you prepare 250 mL, 0.10 M solution NaOH (mol wt 40)

- 5 (M*V) $KMnO_4$ = 2 ((M*V)$Na_2C_2O_4$ + (M*V)$H_2C_2O_4$)
- wt ($Na_2C_2O_4$) = (M*V)oxalate*mol wt/1000
- 0.2856 = (M*V)oxalate * 134 /1000
- (M*V)oxalate = 2.127
- (M*V) oxalic = 0.0516 * 1.74 = 0.0898
- 5 (M*45.12) $KMnO_4$ = 2 (2.127 + 0.0898)
- M ($KMnO_4$) = 0.0197 mmol/ml

- How can you prepare 250 mL, 1.0 M solution NaOH (mol wt 40)
- 40 gm NaOH (in 1.0 L 1000 mL) -------- 1.0 M
- 1000 mL/4 = 250 mL
- 40 gm/4 = 10 gm
- 10 gm NaOH dissolved in 250 mL water = 1.0 M solution NaOH

Primary stand for MnO_4^-

- Iron wire (high degree of purity (dil HCl) ➔ soln ➔ add reducing agent ($SnCl_2$) ➔ redn of Fe(III) ➔ Fe(II)
- If directly titrated against $KMnO_4$ in the presence of Cl^-
- ➔ oxdn of $Cl^- \rightarrow Cl_2$

- **Normally this reaction is slow**
- Presence of iron ➔ catalyse the reaction
- A soln of Mn(II) sulphate, H_2SO_4, and H_3PO_4 (Zimmermann – Reinhardt reagent) called preventive soln.
- It is added to Fe(II) in HCl before titrn with $KMnO_4$

Determination with MnO_4^- : Iron in iron ores

- ***Iron ore*** → add HCl, heat → hot soln Fe (II, III) → add $SnCl_2$ (slight excess to ensure complete redn)
- → Fe(II) soln + $SnCl_2$ (must be removed to avoid reactn with MnO_4^-)

- → cool then add Hg(II) chloride → $Sn^{4+} + Hg_2Cl_2$ (s) + $Fe^{2+} + 2Cl^-$
- Excess **$SnCl_2$ → $Hg_2Cl_2 + Sn^{2+}$ → $2Hg + 2Cl^- + Sn^{4+}$**

- **Addn. of $HgCl_2$ should be slow** and the soln. should be **cold**
- Hg produced in a finely devided state → ppt appears grey to black → sample should be discarded

Oxidation with Potassium Dichromate

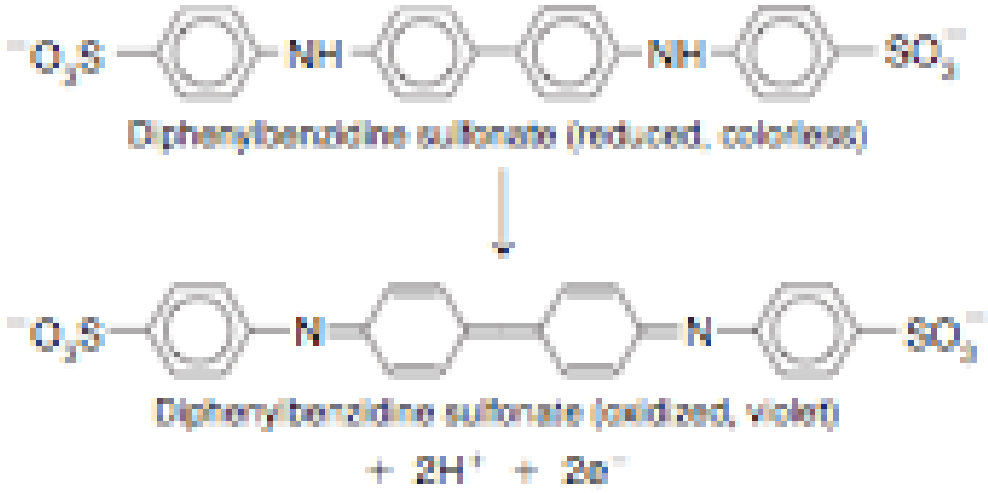
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^\circ = 1.36\ V$$

Dichromate — Chromic

- Is a less powerful oxidizing agent than MnO_4^-. In basic solution, $Cr_2O_7^{2-}$ is converted into yellow chromate ion CrO_4^{2-}
- CrO_4^{2-} oxidizing power is nil

$$CrO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Cr(OH)_3(s, \text{hydrated}) + 5OH^- \qquad E^\circ = -0.12\ V$$

- $K_2Cr_2O_7$, is a primary standard.
- Stable solution and cheap.
- $K_2Cr_2O_7$ is orange
- Cr^{3+} complexes range from green to violet
- ***indicators should be used***
- e.g. diphenylamine sulfonic acid or diphenylbenzidine sulfonic acid



Cr(VI) waste is carcinogenic

- ***$K_2Cr_2O_7$ < MnO_4^- as an oxidant***
- Employed for the determination of Fe(II) and, indirectly, for species that will oxidize Fe(II) to Fe(III).
- ***For indirect analyses***,
- unknown + measured excess Fe(II) .
- unreacted Fe(II) against $K_2Cr_2O_7$.
- e.g. , organic peroxides and ClO_3^-, NO_3^-, MnO_4^-,

Methods Involving Iodine

- When a reducing analyte is titrated with iodine (to produce I^-), the method is called ***iodimetry.***

- In ***iodometry***, an oxidizing analyte is added to excess I^- to produce iodine, which is then titrated with standard thiosulfate solution.

- I_2 is only slightly soluble in water ($1.3 * 10^{-3}$ M at 20 °C), but its solubility is enhanced by complexation with I^-

- 0.05 M solution of I_3 for titrations is prepared by dissolving 0.12 mol of KI + 0.05 mol of I_2 in 1 L of water
- When iodine is used as a titrant, it means a solution of I_2 + excess I^-.

Use of Starch Indicator

starch is used as an indicator for iodine.

With starch, the limit of detection is extended by about a factor of 10.

- ***In iodimetry (titration with I_3^-),*** starch can be added at the beginning of the titration.
- The first drop of excess I_3^- after the equivalence point causes the solution to turn dark blue.

- ***In iodometry (titration of I_3^-),*** I_3^- is present throughout the reaction up to the *eqc. pt*.
- *Starch should be added just before the eqc. pt.* (fading of the I_3^-).
- If not, iodine would remain bound to starch particles after the *eqc. pt* is reached.

- ***Starch-iodine complexation*** is temperature dependent.
- At 50 ^{0}C, the color is only 1/10 as intense as at 25 ^{0}C ➔ cooling in ice water is recommended.
- Organic solvents ➔ decrease the affinity of iodine for starch

Answer ***all*** questions: (135 Marks) **Date**: 22-06-2016 **Time**: 3hrs.

(Exam in 3 pages)
(Part A: Analytical Chemistry 45 marks)

(1) ***(i)*** **Define the following terms:** ***(8 marks)***

a) Le Chatelier's Principle, ***b)*** Henderson-Hasselbalch Equation,
c) indicator range, ***d)*** Max buffering capacity.

(ii) A typical protein contains 16.20 wt% nitrogen. A 0.500-mL aliquot of protein solution was digested, and the liberated NH_3 was distilled into 10.00 mL of 0.0214 M HCl. Unreacted HCl required 3.26 mL of 0.0198 M NaOH for complete titration. Find the concentration of protein (mg protein/mL) in the original sample.

(5 marks)

(iii) Indicate whether an aqueous solution of the following compounds is acidic, neutral, or basic.
(a) NH_4OAc (b) $NaNO_3$ c) $Na_2C_2O_4$ (d) NaH_2PO_4 ***(2 marks)***

(iv) Identify the principal conjugate acid/base pair of the following:
(a) H_2S (b) H_3AsO_4 (c) H_2CO_3. **(*3 marks*)**

(2) ***(i)*** ***Fill in the gaps using the word or phrase that best completes each statement.*** ***(11 marks)***

a) ---------- solvents undergo self-ionisation, or ----------, to form ----------.

b) A buffered solution resists changes in ----- when ------ and ------ are added or when -------- occurs and it is composed of ----------.

c) The slight excess of MnO_4^- at end point results in the precipitation of ---------. The reaction is ---------- at room temperature.

d) A solution of $MnSO_4$, H_2SO_4, and H_3PO_4 is called ---------- and It is added to Fe(II) in HCl solution before titration with ---------- to ----------.

(Please turn the page)

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a) A solution of $MnSO_4$, H_2SO_4, and H_3PO_4 is called ---------- and It is added to Fe(II) in HCl solution before titration with ---------- to ----------.

(ii)* Calculate the *pH* value of the following solutions: *(9 marks)

(i) A 5.0 mL of 0.100 *M* H_2B solution (weak acid, K_{a1} = 1.0 x 10^{-3} and K_{a2} = 1.0 x 10^{-7}).

(ii) A 40.0 mL of 0.100 *M* H_2B solution (weak acid, K_{a1} = 1.0 x 10^{-3} and K_{a2} = 1.0 x 10^{-7}) and 20.0 mL of 0.100 *M* NaOH solution.

(iii) A 60.0 mL, 0.05 *M* solution of NaOH and 30.0 mL of 0.100 *M* HCl solution.

(iv) A 2 *M* solution of sodium benzoate. *pKa* for benzoic acid is 4.01.

(v) A 5.0 mL, 0.10 *M* NH_3 solution (K_b of NH_3 is 1.8 x 10^{-5}).

(vi) A 1.5 *M* formic acid (*pKa* = 3.751) and 1 *M* sodium formate.

(iii) Tell if each of the following statements is true or false. If false, rew the correct statement.* *(7 marks)

(vii)Ionic compounds are ionized in water and are called non-electrolytes.

(viii)The rate of the reaction of $C_2O_4^{2-}$ with MnO_4^- increases as Mn(II) is formed.

(ix) For a back titration of MnO_4^-, add excess MnO_4^- to a reducing agent and then raise the temperature to hasten oxidation.

(x) The oxidation of Cl^- by MnO_4^- is a slow reaction and the presence of Fe^{3+} ions catalyses the reaction.

(xi) Strength is expressed as g/L while mg/L is the same as part per million.

(xii)Potassium dichromate can be used as a primary standard material.

A *pH* calculation for a solution of NaHA agrees with that for a weak acid of the type HA.

Preparation and Standardization of I_3^- Solutions

- Triiodide (I_3^-) is prepared by dissolving solid I_2 in excess KI.
- Sublimed I_2 is pure enough to be a primary standard, but it is seldom used as a standard because it evaporates while it is being weighed.
- Instead, the approximate amount is rapidly weighed, and the soln of I_3^- is standardized with a pure sample of analyte or $Na_2S_2O_3$.
- Acidic solutions of I_3^- are unstable because the excess I^- is slowly oxidized by air

$$6I^- + O_2 + 4H^+ \rightarrow 2I_3^- + 2H_2O$$

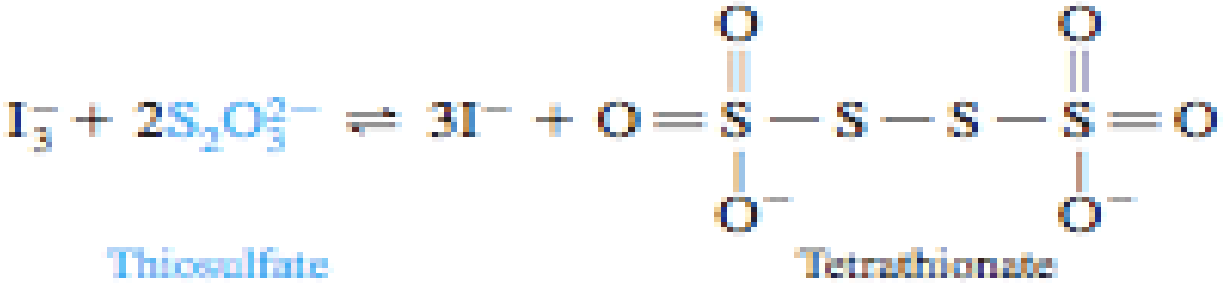
- In neutral solutions, oxidation is insignificant in the absence of heat, light, and metal ions.
- At pH11, I_3^- disproportionates to hypoiodous acid, iodate, and iodide.
- To prepare standard I_3^- ➔ add a weighed quantity of the primary stan- dard potassium iodate (KIO_3) to a small excess of KI. Then add excess strong acid (pH 1) ➔ I_3^- :

$$IO_3^- + 8I^- + 6H^+ \rightleftharpoons 3I_3^- + 3H_2O$$

- Freshly acidified iodate + iodide can be used to standardize thiosulfate.
- I_3^- must be used immediately or it will be oxidized by air.
- The disadvantage of KIO_3 is its low mol wt relative to the number of electrons it accepts ➔ a larger weighing error

Use of Sodium Thiosulfate

- Sodium thiosulfate is the almost universal titrant for triiodide. In neutral or acidic solution, triiodide oxidizes thiosulfate to tetrathionate:



should be carried out below pH 9

In basic solution, I_3^- disproportionates to I^- and HOI, which can oxidize $S_2O_3^{2-}$ to SO_4^{2-}

- The common form of thiosulfate, $Na_2S_2O_3.5H_2O$, is not pure enough to be a primary standard ➔ $S_2O_3^{2-}$ is usually standardized by reaction with a fresh solution of I_3^- (KIO_3 + KI).

- To prepare a stable solution of $S_2O_3^{2-}$ ➔ dissolve $Na_2S_2O_3$ in high-quality, freshly boiled distilled water.
- Dissolved CO_2 makes the solution acidic ➔ dispropor-tionation of $S_2O_3^{2-}$:

$$S_2O_3^{2-} + H^+ \rightleftharpoons \underset{\text{Bisulfite}}{HSO_3^-} + \underset{\text{Sulfur}}{S(s)}$$

- Metal ions catalyze atmospheric oxidation of $S_2O_3^{2-}$:

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

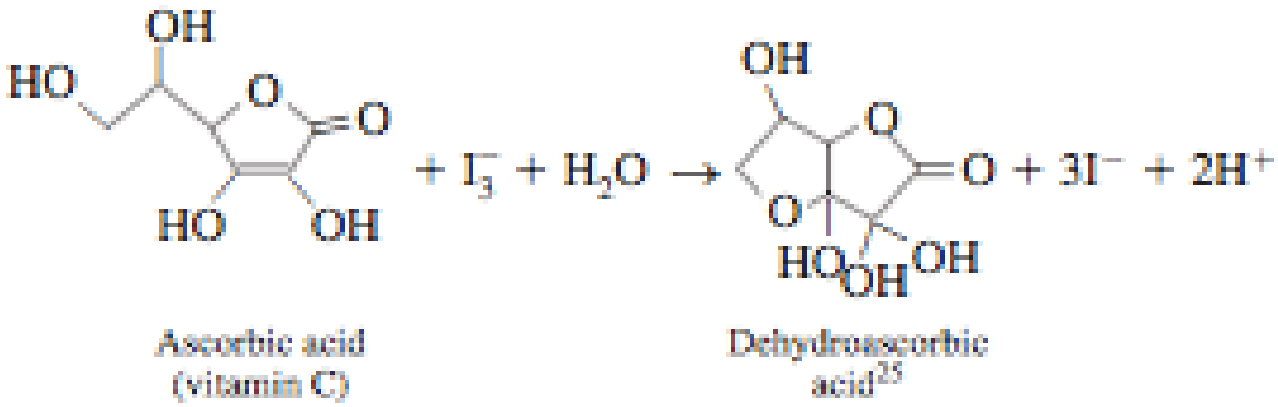
$$2Cu^+ + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O$$

- $S_2O_3^{2-}$ solutions should be stored in the dark.
- Addition of 0.1 g of sodium carbonate per liter maintains the pH in an optimum range for stability of the solution.
- Three drops of chloroform should also be added to each bottle of $S_2O_3^{2-}$ solution to help prevent bacterial growth.
- An acidic solution of $S_2O_3^{2-}$ is unstable, but the reagent can be used to titrate I_3^- in acidic solution because the reaction with I_3^- is faster than:

Analytical Applications of Iodine

- Reducing agents can be titrated directly with standard I_3^- in the presence of starch, until reaching the intense blue starch-iodine end point.
- An example is the iodimetric determination of vitamin C:

- Oxidizing agents can be treated with excess I^- ➔ I_3^-.
- The iodometric analysis is completed by titrating the liberated I_3^- with standard $S_2O_3^{2-}$. Add starch just before e.p.



Ascorbic acid (vitamin C)

Dehydroascorbic acid[25]

Table 16-1 **Oxidizing and reducing agents**

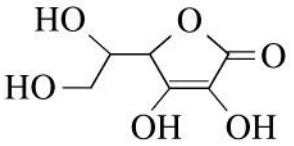
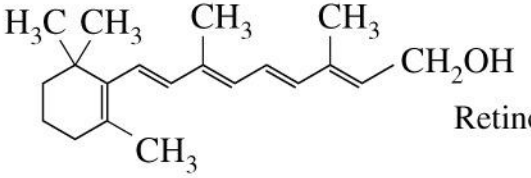
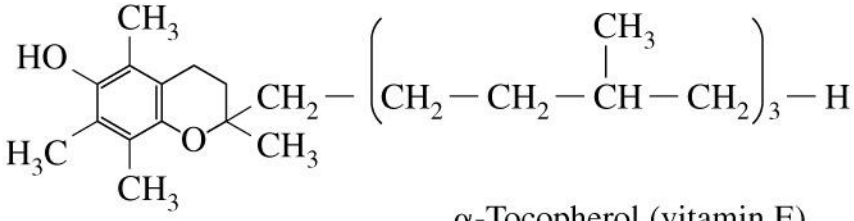
Oxidants		Reductants	
BiO_3^-	Bismuthate		Ascorbic acid (vitamin C)
BrO_3^-	Bromate	BH_4^-	Borohydride
Br_2	Bromine	Cr^{2+}	Chromous
Ce^{4+}	Ceric	$S_2O_4^{2-}$	Dithionite
	Chloramine T	Fe^{2+}	Ferrous
		N_2H_4	Hydrazine
Cl_2	Chlorine		Hydroquinone
ClO_2	Chlorine dioxide	NH_2OH	Hydroxylamine
$Cr_2O_7^{2-}$	Dichromate	H_3PO_2	Hypophosphorous acid
FeO_4^{2-}	Ferrate(VI)		Retinol (vitamin A)
H_2O_2	Hydrogen peroxide		
OCl^-	Hypochlorite		
IO_3^-	Iodate		
I_2	Iodine	Sn^{2+}	Stannous
$Pb(acetate)_4$	Lead(IV) acetate	SO_3^{2-}	Sulfite
HNO_3	Nitric acid	SO_2	Sulfur dioxide
O	Atomic oxygen	$S_2O_3^{2-}$	Thiosulfate
O_3	Ozone		α-Tocopherol (vitamin E)
$HClO_4$	Perchloric acid		
IO_4^-	Periodate		
MnO_4^-	Permanganate		
$S_2O_8^{2-}$	Peroxydisulfate		

Table 16-3 Analytical applications of permanganate titrations

Species analyzed	Oxidation reaction	Notes
Fe^{2+}	$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$	Fe^{3+} is reduced to Fe^{2+} with Sn^{2+} or a Jones reductor. Titration is carried out in 1 M H_2SO_4 or 1 M HCl containing Mn^{2+}, H_3PO_4, and H_2SO_4. Mn^{2+} inhibits oxidation of Cl^- by MnO_4^-. H_3PO_4 complexes Fe^{3+} to prevent formation of yellow Fe^{3+}-chloride complexes.
$H_2C_2O_4$	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Add 95% of titrant at 25°C, then complete titration at 55°–60°C.
Br^-	$Br^- \rightleftharpoons \frac{1}{2}Br_2(g) + e^-$	Titrate in boiling 2 M H_2SO_4 to remove $Br_2(g)$.
H_2O_2	$H_2O_2 \rightleftharpoons O_2(g) + 2H^+ + 2e^-$	Titrate in 1 M H_2SO_4.
HNO_2	$HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-$	Add excess standard $KMnO_4$ and back-titrate after 15 min at 40°C with Fe^{2+}.
As^{3+}	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e^-$	Titrate in 1 M HCl with KI or ICl catalyst.
Sb^{3+}	$H_3SbO_3 + H_2O \rightleftharpoons H_3SbO_4 + 2H^+ + 2e^-$	Titrate in 2 M HCl.
Mo^{3+}	$Mo^{3+} + 2H_2O \rightleftharpoons MoO_2^{2+} + 4H^+ + 3e^-$	Reduce Mo in a Jones reductor, and run the Mo^{3+} into excess Fe^{3+} in 1 M H_2SO_4. Titrate the Fe^{2+} formed.
W^{3+}	$W^{3+} + 2H_2O \rightleftharpoons WO_2^{2+} + 4H^+ + 3e^-$	Reduce W with Pb(Hg) at 50°C and titrate in 1 M HCl.
U^{4+}	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$	Reduce U to U^{3+} with a Jones reductor. Expose to air to produce U^{4+}, which is titrated in 1 M H_2SO_4.
Ti^{3+}	$Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^-$	Reduce Ti to Ti^{3+} with a Jones reductor, and run the Ti^{3+} into excess Fe^{3+} in 1 M H_2SO_4. Titrate the Fe^{2+} that is formed.
Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Co^{2+}, La^{3+}, Th^{4+}, Pb^{2+}, Ce^{3+}, BiO^+, Ag^+	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Precipitate the metal oxalate. Dissolve in acid and titrate the $H_2C_2O_4$.
$S_2O_8^{2-}$	$S_2O_8^{2-} + 2Fe^{2+} + 2H^+ \rightleftharpoons 2Fe^{3+} + 2HSO_4^-$	Peroxydisulfate is added to excess standard Fe^{2+} containing H_3PO_4. Unreacted Fe^{2+} is titrated with MnO_4^-.
PO_4^{3-}	$Mo^{3+} + 2H_2O \rightleftharpoons MoO_2^{2+} + 4H^+ + 3e^-$	$(NH_4)_3PO_4 \cdot 12MoO_3$ is precipitated and dissolved in H_2SO_4. The Mo(VI) is reduced (as above) and titrated.

Table 16-3 **Analytical applications of permanganate titrations**

Species analyzed	Oxidation reaction	Notes
W^{3+}	$W^{3+} + 2H_2O \rightleftharpoons WO_2^{2+} + 4H^+ + 3e^-$	Reduce W with Pb(Hg) at 50°C and titrate in 1 M HCl.
U^{4+}	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$	Reduce U to U^{3+} with a Jones reductor. Expose to air to produce U^{4+}, which is titrated in 1 M H_2SO_4.
Ti^{3+}	$Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^-$	Reduce Ti to Ti^{3+} with a Jones reductor, and run the Ti^{3+} into excess Fe^{3+} in 1 M H_2SO_4. Titrate the Fe^{2+} that is formed.
Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Co^{2+}, La^{3+}, Th^{4+}, Pb^{2+}, Ce^{3+}, BiO^+, Ag^+	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Precipitate the metal oxalate. Dissolve in acid and titrate the $H_2C_2O_4$.
$S_2O_8^{2-}$	$S_2O_8^{2-} + 2Fe^{2+} + 2H^+ \rightleftharpoons 2Fe^{3+} + 2HSO_4^-$	Peroxydisulfate is added to excess standard Fe^{2+} containing H_3PO_4. Unreacted Fe^{2+} is titrated with MnO_4^-.
PO_4^{3-}	$Mo^{3+} + 2H_2O \rightleftharpoons MoO_2^{2+} + 4H^+ + 3e^-$	$(NH_4)_3PO_4 \cdot 12MoO_3$ is precipitated and dissolved in H_2SO_4. The Mo(VI) is reduced (as above) and titrated.

Table 16-4 Titrations with standard triiodide (iodimetric titrations)

Species analyzed	Oxidation reaction	Notes
As^{3+}	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e^-$	Titrate directly in $NaHCO_3$ solution with I_3^-.
Sn^{2+}	$SnCl_4^{2-} + 2Cl^- \rightleftharpoons SnCl_6^{2-} + 2e^-$	Sn(IV) is reduced to Sn(II) with granular Pb or Ni in 1 M HCl and titrated in the absence of oxygen.
N_2H_4	$N_2H_4 \rightleftharpoons N_2 + 4H^+ + 4e^-$	Titrate in $NaHCO_3$ solution.
SO_2	$SO_2 + H_2O \rightleftharpoons H_2SO_3$ $H_2SO_3 + H_2O \rightleftharpoons SO_4^{2-} + 4H^+ + 2e^-$	Add SO_2 (or H_2SO_3 or HSO_3^- or SO_3^{2-}) to excess standard I_3^- in dilute acid and back-titrate unreacted I_3^- with standard thiosulfate.
H_2S	$H_2S \rightleftharpoons S(s) + 2H^+ + 2e^-$	Add H_2S to excess I_3^- in 1 M HCl and back-titrate with thiosulfate.
Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}	$M^{2+} + H_2S \rightarrow MS(s) + 2H^+$ $MS(s) \rightleftharpoons M^{2+} + S + 2e^-$	Precipitate and wash metal sulfide. Dissolve in 3 M HCl with excess standard I_3^- and back-titrate with thiosulfate.
Cysteine, glutathione, thioglycolic acid, mercaptoethanol	$2RSH \rightleftharpoons RSSR + 2H^+ + 2e^-$	Titrate the sulfhydryl compound at pH 4–5 with I_3^-.
HCN	$I_2 + HCN \rightleftharpoons ICN + I^- + H^+$	Titrate in carbonate-bicarbonate buffer, using *p*-xylene as an extraction indicator.
$H_2C{=}O$	$H_2CO + 3OH^- \rightleftharpoons HCO_2^- + 2H_2O + 2e^-$	Add excess I_3^- plus NaOH to the unknown. After 5 min, add HCl and back-titrate with thiosulfate.
Glucose (and other reducing sugars)	$RCH(=O) + 3OH^- \rightleftharpoons RCO_2^- + 2H_2O + 2e^-$	Add excess I_3^- plus NaOH to the sample. After 5 min, add HCl and back-titrate with thiosulfate.
Ascorbic acid (vitamin C)	Ascorbate + $H_2O \rightleftharpoons$ dehydroascorbate + $2H^+ + 2e^-$	Titrate directly with I_3^-.
H_3PO_3	$H_3PO_3 + H_2O \rightleftharpoons H_3PO_4 + 2H^+ + 2e^-$	Titrate in $NaHCO_3$ solution.

Table 16-5 **Titration of I_3^- produced by analyte (iodometric titrations)**

Species analyzed	Reaction	Notes
Cl_2	$Cl_2 + 3I^- \rightleftharpoons 2Cl^- + I_3^-$	Reaction in dilute acid.
HOCl	$HOCl + H^+ + 3I^- \rightleftharpoons Cl^- + I_3^- + H_2O$	Reaction in 0.5 M H_2SO_4.
Br_2	$Br_2 + 3I^- \rightleftharpoons 2Br^- + I_3^-$	Reaction in dilute acid.
BrO_3^-	$BrO_3^- + 6H^+ + 9I^- \rightleftharpoons Br^- + 3I_3^- + 3H_2O$	Reaction in 0.5 M H_2SO_4.
IO_3^-	$2IO_3^- + 16I^- + 12H^+ \rightleftharpoons 6I_3^- + 6H_2O$	Reaction in 0.5 M HCl.
IO_4^-	$2IO_4^- + 22I^- + 16H^+ \rightleftharpoons 8I_3^- + 8H_2O$	Reaction in 0.5 M HCl.
O_2	$O_2 + 4Mn(OH)_2 + 2H_2O \rightleftharpoons 4Mn(OH)_3$ $2Mn(OH)_3 + 6H^+ + 6I^- \rightleftharpoons 2Mn^{2+} + 2I_3^- + 6H_2O$	The sample is treated with Mn^{2+}, NaOH, and KI. After 1 min, it is acidified with H_2SO_4, and the I_3^- is titrated.
H_2O_2	$H_2O_2 + 3I^- + 2H^+ \rightleftharpoons I_3^- + 2H_2O$	Reaction in 1 M H_2SO_4 with NH_4MoO_3 catalyst.
O_3[a]	$O_3 + 3I^- + 2H^+ \rightleftharpoons O_2 + I_3^- + H_2O$	O_3 is passed through neutral 2 wt % KI solution. Add H_2SO_4 and titrate.
NO_2^-	$2HNO_2 + 2H^+ + 3I^- \rightleftharpoons 2NO + I_3^- + 2H_2O$	The nitric oxide is removed (by bubbling CO_2 generated in situ) prior to titration of I_3^-.
As^{5+}	$H_3AsO_4 + 2H^+ + 3I^- \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$	Reaction in 5 M HCl.
$S_2O_8^{2-}$	$S_2O_8^{2-} + 3I^- \rightleftharpoons 2SO_4^{2-} + I_3^-$	Reaction in neutral solution. Then acidify and titrate.
Cu^{2+}	$2Cu^{2+} + 5I^- \rightleftharpoons 2CuI(s) + I_3^-$	NH_4HF_2 is used as a buffer.
$Fe(CN)_6^{3-}$	$2Fe(CN)_6^{3-} + 3I^- \rightleftharpoons 2Fe(CN)_6^{4-} + I_3^-$	Reaction in 1 M HCl.
MnO_4^-	$2MnO_4^- + 16H^+ + 15I^- \rightleftharpoons 2Mn^{2+} + 5I_3^- + 8H_2O$	Reaction in 0.1 M HCl.
MnO_2	$MnO_2(s) + 4H^+ + 3I^- \rightleftharpoons Mn^{2+} + I_3^- + 2H_2O$	Reaction in 0.5 M H_3PO_4 or HCl.
$Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 9I^- \rightleftharpoons 2Cr^{3+} + 3I_3^- + 7H_2O$	Reaction in 0.4 M HCl requires 5 min for completion and is particularly sensitive to air oxidation.
Ce^{4+}	$2Ce^{4+} + 3I^- \rightleftharpoons 2Ce^{3+} + I_3^-$	Reaction in 1 M H_2SO_4.

a. The pH must be ≥7 when O_3 is added to I^-. In acidic solution each O_3 produces 1.25 I_3^-, not 1 I_3^-.

[N. V. Klassen, D. Marchington, and H. C. E. McGowan, *Anal. Chem.* **1994**, *66*, 2921.]

Table 16-2 Redox indicators

Indicator	Color		E°
	Oxidized	Reduced	
Phenosafranine	Red	Colorless	0.28
Indigo tetrasulfonate	Blue	Colorless	0.36
Methylene blue	Blue	Colorless	0.53
Diphenylamine	Violet	Colorless	0.75
4′-Ethoxy-2,4-diaminoazobenzene	Yellow	Red	0.76
Diphenylamine sulfonic acid	Red-violet	Colorless	0.85
Diphenylbenzidine sulfonic acid	Violet	Colorless	0.87
Tris(2,2′-bipyridine)iron	Pale blue	Red	1.120
Tris(1,10-phenanthroline)iron (ferroin)	Pale blue	Red	1.147
Tris(5-nitro-1,10-phenanthroline)iron	Pale blue	Red-violet	1.25
Tris(2,2′-bipyridine)ruthenium	Pale blue	Yellow	1.29

- (1) $\underline{MnO_4^- + 5e^- \rightarrow Mn^{2+}}$ (manganous ion)
- → eq wt of potassium permanganate is 1/5th gram-mol wt 31.61 g.
- ($KMnO_4$: 1/5 × 158.05 = 31.61)
  (2) $\underline{Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+}}$ (chromous ion)
- → eq wt of potassium dichromate is l/6 gram-mol wt 49.03 g.
- ($K_2Cr_2O_7$: 1/6 × 294.18 = 49.03)
  $\underline{(3)\ I_2 + 2e^- \rightarrow 2I^-}$ (iodide ion)
- → eq wt of iodine is 1 gram-mol wt 126.90 g. (I_2 : Molecular Weight = 126.90)
- (4) $\underline{BrO_3^- + 6e^- \rightarrow Br-}$ (bromide ion)
  → eq wt of potassium bromate is 1/6 gram-mol wt 27.83 g. ($KBrO_3$: 1/6 × 167.01 = 27.83)