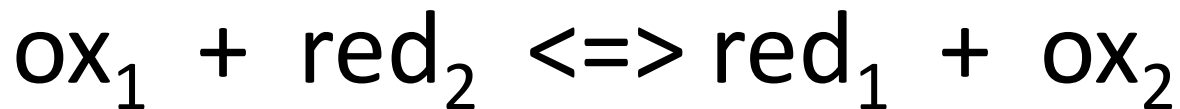


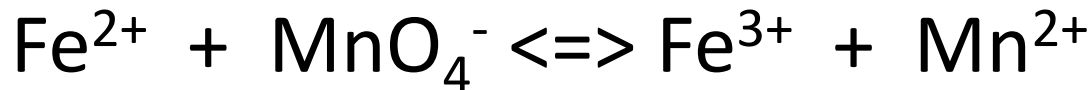
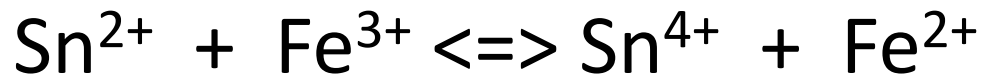
An Introduction to Electrochemistry

Redox Reaction



Balancing Redox Equations

half-reaction technique



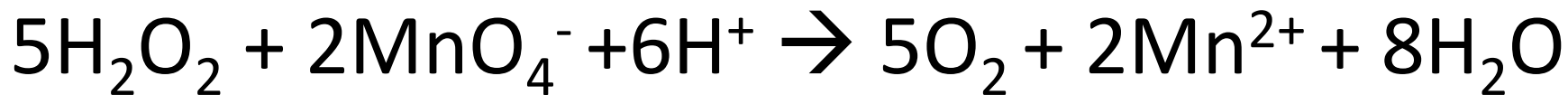
Balancing using the electron change

- 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)
- $\text{H}_2\text{O}_2 + \text{MnO}_4^- \rightarrow \text{O}_2 + \text{Mn}^{2+}$ (acid soln)

- $\text{H}_2\text{O}_2 \rightarrow \text{O}_2$
- $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{e}^-$
- $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$

- X 5

- $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$
- $\text{MnO}_4^- + 5\text{e}^- \rightarrow \text{Mn}^{2+}$
- $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+}$
- $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+}$
- $\qquad\qquad\qquad + 4\text{H}_2\text{O}$
- X 2



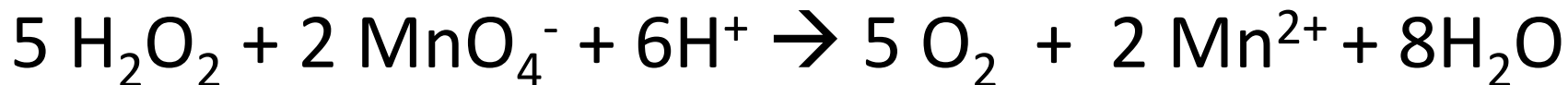
Balancing without knowledge of oxdn stats

- 1- balance the no of atoms (red/oxd)
- 2- balance oxygen (by adding H₂O)
- 3- balance hydrogen (by adding H⁺)
- 4- balance the charges (by adding e)
- (AOHC)
- $\text{H}_2\text{O}_2 + \text{MnO}_4^- \rightarrow \text{O}_2 + \text{Mn}^{2+}$ (acid soln)

- $\text{H}_2\text{O}_2 \rightarrow \text{O}_2$
- $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+$
- $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$

• X 5

- $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$
- $\text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- $\text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- X 2



Potassium permanganate

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



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

- The slight excess of MnO_4^- (at ep) \rightarrow $\text{MnO}_2(\text{s})$.
- The reaction is slow \rightarrow the ppt is formed at the ep

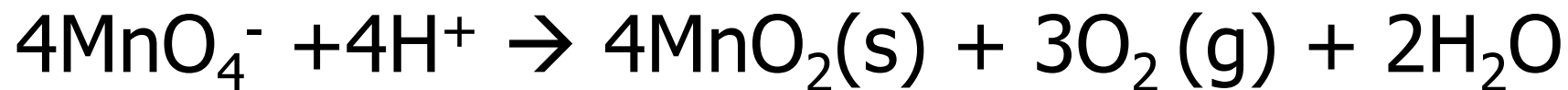
Precautions taken in the prepn of KMnO_4 soln

- 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) \rightarrow to destroy reducible substances \rightarrow filter through sintered glass (non reducing filters) \rightarrow MnO_2 is removed

- \rightarrow pure soln of KMnO_4 \rightarrow titrate against stand soln
- \rightarrow keep in the dark \rightarrow avoid acidifying
- \rightarrow its concn would be stable for several months

Acidic soln of MnO_4^- is not stable



- 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.
- $T=60^\circ\text{C}$
- The rate increases as Mn(II) is formed
- Autocatalytic reactn



- Pure sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, mol wt 134) (0.2856 g) in water, H_2SO_4 is added, titrated $70\text{ }^\circ\text{C}$
- 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)

- $5 (M \cdot V) \text{KMnO}_4 = 2 ((M \cdot V)\text{Na}_2\text{C}_2\text{O}_4 + (M \cdot V)\text{H}_2\text{C}_2\text{O}_4)$
- $\text{wt} (\text{Na}_2\text{C}_2\text{O}_4) = (M \cdot V)\text{oxalate} \cdot \text{mol wt} / 1000$
- $0.2856 = (M \cdot V)\text{oxalate} \cdot 134 / 1000$
- $(M \cdot V)\text{oxalate} = 2.127$
- $(M \cdot V) \text{oxalic} = 0.0516 \cdot 1.74 = 0.0898$
- $5 (M \cdot 45.12) \text{KMnO}_4 = 2 (2.127 + 0.0898)$
- $M (\text{KMnO}_4) = 0.0197 \text{ mmol/ml}$

- 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
- $1000 \text{ mL} / 4 = 250 \text{ mL}$
- $40 \text{ gm} / 4 = 10 \text{ gm}$
- 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) \rightarrow soln \rightarrow add reducing agent (SnCl_2) \rightarrow redn of Fe(III) \rightarrow Fe(II)
- If directly titrated against KMnO_4 in the presence of Cl^-
- \rightarrow oxdn of $\text{Cl}^- \rightarrow \text{Cl}_2$

- Normally this reaction is slow
- Presence of iron \rightarrow 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 \rightarrow add HCl, heat \rightarrow hot soln Fe (II, III) \rightarrow add SnCl_2 (slight excess to ensure complete redn)
- \rightarrow Fe(II) soln + SnCl_2 (must be removed to avoid reactn with MnO_4^-)

- \rightarrow cool then add Hg(II) chloride $\rightarrow \text{Sn}^{4+} + \text{Hg}_2\text{Cl}_2 (\text{s}) + \text{Fe}^{2+} + 2\text{Cl}^-$
- Excess $\text{SnCl}_2 \rightarrow \text{Hg}_2\text{Cl}_2 + \text{Sn}^{2+} \rightarrow 2\text{Hg} + 2\text{Cl}^- + \text{Sn}^{4+}$

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

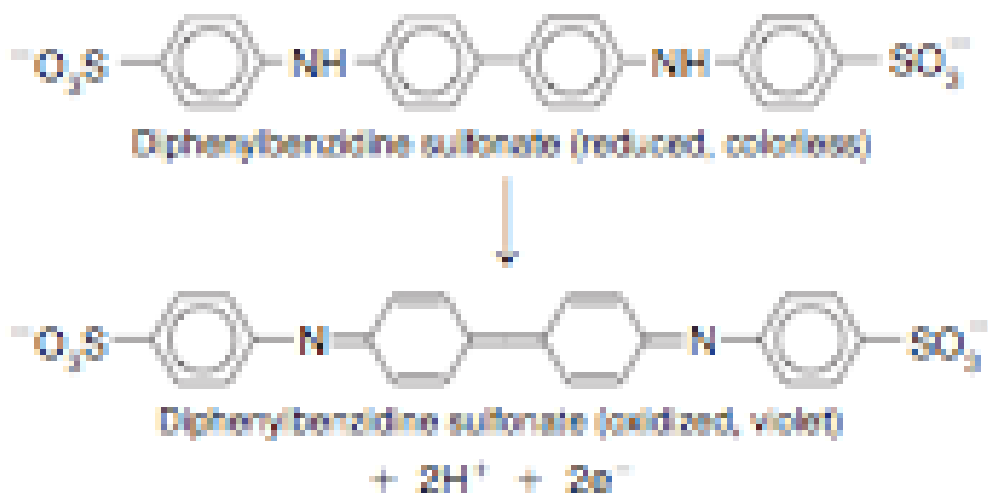
Oxidation with Potassium Dichromate



- Is a less powerful oxidizing agent than MnO_4^- .
In basic solution, $\text{Cr}_2\text{O}_7^{2-}$ is converted into yellow chromate ion CrO_4^{2-}
- CrO_4^{2-} oxidizing power is nil



- $K_2Cr_2O_7$, 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 °C, the color is only 1/10 as intense as at 25 °C
→ cooling in ice water is recommended.
- Organic solvents → decrease the affinity of iodine for starch

(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) $\text{Na}_2\text{C}_2\text{O}_4$ (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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(iii) The slight excess of MnO_4^- at end point results in the precipitation of -----.
The reaction is ----- at room temperature.

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 H₂B solution (weak acid, $K_{a1} = 1.0 \times 10^{-3}$ and $K_{a2} = 1.0 \times 10^{-7}$).

(ii) A 40.0 mL of 0.100 M H₂B solution (weak acid, $K_{a1} = 1.0 \times 10^{-3}$ and $K_{a2} = 1.0 \times 10^{-7}$) 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. pK_a for benzoic acid is 4.01.

(v) A 5.0 mL, 0.10 M NH₃ solution (K_b of NH₃ is 1.8×10^{-5}).

(vi) A 1.5 M formic acid ($pK_a = 3.751$) and 1 M sodium formate.

(iii) Tell if each of the following statements is true or false. If false, rewrite 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



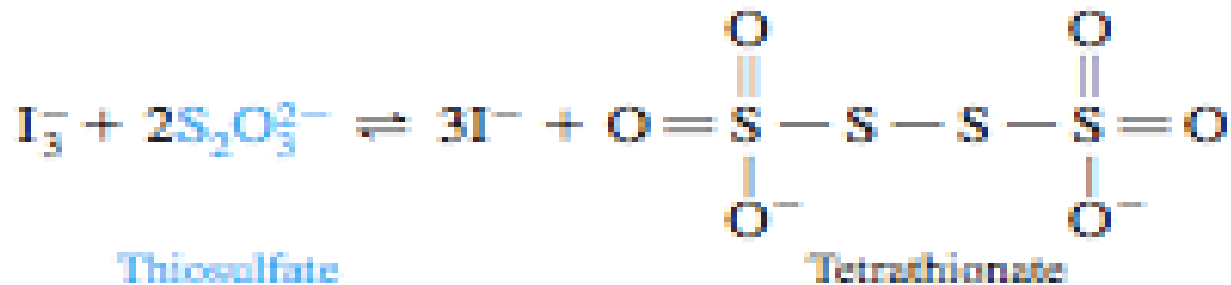
- In neutral solutions, oxidation is insignificant in the absence of heat, light, and metal ions.
- At pH 11, I_3^- disproportionates to hypoiodous acid, iodate, and iodide.
- To prepare standard I_3^- → add a weighed quantity of the primary standard potassium iodate (KIO_3) to a small excess of KI. Then add excess strong acid (pH 1) → I_3^- :



- 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 $\text{S}_2\text{O}_3^{2-}$ to SO_4^{2-}

- The common form of thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, is not pure enough to be a primary standard \rightarrow $\text{S}_2\text{O}_3^{2-}$ is usually standardized by reaction with a fresh solution of I_3^- ($\text{KIO}_3 + \text{KI}$).

- To prepare a stable solution of $\text{S}_2\text{O}_3^{2-}$ \rightarrow dissolve $\text{Na}_2\text{S}_2\text{O}_3$ in high-quality, freshly boiled distilled water.
- Dissolved CO_2 makes the solution acidic \rightarrow disproportionation of $\text{S}_2\text{O}_3^{2-}$:



- Metal ions catalyze atmospheric oxidation of $\text{S}_2\text{O}_3^{2-}$:



- $S_2O_3^{2-}$ 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 $I^- \rightarrow I_3^-$.
- The iodometric analysis is completed by titrating the liberated I_3^- with standard $S_2O_3^{2-}$. Add starch just before

e.p.

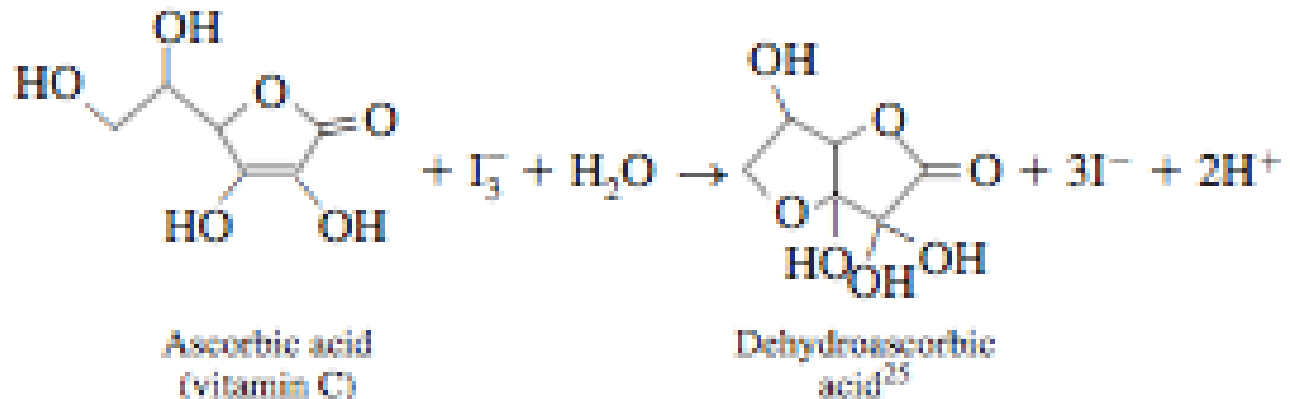


Table 16-1 Oxidizing and reducing agents

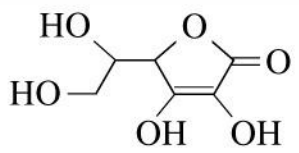

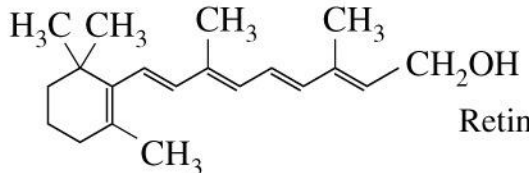
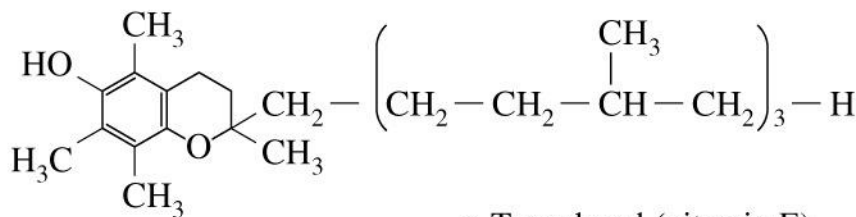
Oxidants		Reductants	
BiO_3^-	Bismuthate		Ascorbic acid (vitamin C)
BrO_3^-	Bromate	BH_4^-	Borohydride
Br_2	Bromine	Cr^{2+}	Chromous
Ce^{4+}	Ceric	$\text{S}_2\text{O}_4^{2-}$	Dithionite
$\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{NCl}^-$	Chloramine T	Fe^{2+}	Ferrous
Cl_2	Chlorine	N_2H_4	Hydrazine
ClO_2	Chlorine dioxide		Hydroquinone
$\text{Cr}_2\text{O}_7^{2-}$	Dichromate	NH_2OH	Hydroxylamine
FeO_4^{2-}	Ferrate(VI)	H_3PO_2	Hypophosphorous acid
H_2O_2	Hydrogen peroxide		Retinol (vitamin A)
OCl^-	Hypochlorite	Sn^{2+}	Stannous
IO_3^-	Iodate	SO_3^{2-}	Sulfite
I_2	Iodine	SO_2	Sulfur dioxide
$\text{Pb}(\text{acetate})_4$	Lead(IV) acetate	$\text{S}_2\text{O}_3^{2-}$	Thiosulfate
HNO_3	Nitric acid		$\alpha\text{-Tocopherol (vitamin E)}$
O	Atomic oxygen		
O_3	Ozone		
HClO_4	Perchloric acid		
IO_4^-	Periodate		
MnO_4^-	Permanganate		
$\text{S}_2\text{O}_8^{2-}$	Peroxydisulfate		

Table 16-3 Analytical applications of permanganate titrations

Species analyzed	Oxidation reaction	Notes
Fe ²⁺	$\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{e}^{-}$	Fe ³⁺ is reduced to Fe ²⁺ with Sn ²⁺ or a Jones reductor. Titration is carried out in 1 M H ₂ SO ₄ or 1 M HCl containing Mn ²⁺ , H ₃ PO ₄ , and H ₂ SO ₄ . Mn ²⁺ inhibits oxidation of Cl ⁻ by MnO ₄ ⁻ . H ₃ PO ₄ complexes Fe ³⁺ to prevent formation of yellow Fe ³⁺ -chloride complexes.
H ₂ C ₂ O ₄	$\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^{-}$	Add 95% of titrant at 25°C, then complete titration at 55°–60°C.
Br ⁻	$\text{Br}^{-} \rightleftharpoons \frac{1}{2}\text{Br}_2(\text{g}) + \text{e}^{-}$	Titrate in boiling 2 M H ₂ SO ₄ to remove Br ₂ (g).
H ₂ O ₂	$\text{H}_2\text{O}_2 \rightleftharpoons \text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^{-}$	Titrate in 1 M H ₂ SO ₄ .
HNO ₂	$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_3^{-} + 3\text{H}^+ + 2\text{e}^{-}$	Add excess standard KMnO ₄ and back-titrate after 15 min at 40°C with Fe ²⁺ .
As ³⁺	$\text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^{-}$	Titrate in 1 M HCl with KI or ICl catalyst.
Sb ³⁺	$\text{H}_3\text{SbO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{SbO}_4 + 2\text{H}^+ + 2\text{e}^{-}$	Titrate in 2 M HCl.
Mo ³⁺	$\text{Mo}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{MoO}_2^{2+} + 4\text{H}^+ + 3\text{e}^{-}$	Reduce Mo in a Jones reductor, and run the Mo ³⁺ into excess Fe ³⁺ in 1 M H ₂ SO ₄ . Titrate the Fe ²⁺ formed.
W ³⁺	$\text{W}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{WO}_2^{2+} + 4\text{H}^+ + 3\text{e}^{-}$	Reduce W with Pb(Hg) at 50°C and titrate in 1 M HCl.
U ⁴⁺	$\text{U}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^{-}$	Reduce U to U ³⁺ with a Jones reductor. Expose to air to produce U ⁴⁺ , which is titrated in 1 M H ₂ SO ₄ .
Ti ³⁺	$\text{Ti}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{TiO}^{2+} + 2\text{H}^+ + \text{e}^{-}$	Reduce Ti to Ti ³⁺ with a Jones reductor, and run the Ti ³⁺ into excess Fe ³⁺ in 1 M H ₂ SO 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 ⁺	$\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^{-}$	Precipitate the metal oxalate. Dissolve in acid and titrate the H ₂ C ₂ O ₄ .
S ₂ O ₈ ²⁻	$\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} + 2\text{H}^+ \rightleftharpoons 2\text{Fe}^{3+} + 2\text{HSO}_4^{-}$	Peroxydisulfate is added to excess standard Fe ²⁺ containing H ₃ PO ₄ . Unreacted Fe ²⁺ is titrated with MnO ₄ ⁻ .
PO ₄ ³⁻	$\text{Mo}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{MoO}_2^{2+} + 4\text{H}^+ + 3\text{e}^{-}$	(NH ₄) ₃ PO ₄ ·12MoO ₃ is precipitated and dissolved in H ₂ SO 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⁺	$\text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^-$	Titrate directly in NaHCO ₃ solution with I ₃ ⁻ .
Sn ²⁺	$\text{SnCl}_4^{2-} + 2\text{Cl}^- \rightleftharpoons \text{SnCl}_6^{2-} + 2\text{e}^-$	Sn(IV) is reduced to Sn(II) with granular Pb or Ni in 1 M HCl and titrated in the absence of oxygen.
N ₂ H ₄ SO ₂	$\text{N}_2\text{H}_4 \rightleftharpoons \text{N}_2 + 4\text{H}^+ + 4\text{e}^-$ $\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$ $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$	Titrate in NaHCO ₃ solution. Add SO ₂ (or H ₂ SO 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 ₂ S	$\text{H}_2\text{S} \rightleftharpoons \text{S}(s) + 2\text{H}^+ + 2\text{e}^-$	Add H ₂ S to excess I ₃ ⁻ in 1 M HCl and back-titrate with thiosulfate.
Zn ²⁺ , Cd ²⁺ , Hg ²⁺ , Pb ²⁺	$\text{M}^{2+} + \text{H}_2\text{S} \rightarrow \text{MS}(s) + 2\text{H}^+$ $\text{MS}(s) \rightleftharpoons \text{M}^{2+} + \text{S} + 2\text{e}^-$	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	$2\text{RSH} \rightleftharpoons \text{RSSR} + 2\text{H}^+ + 2\text{e}^-$	Titrate the sulfhydryl compound at pH 4–5 with I ₃ ⁻ .
HCN	$\text{I}_2 + \text{HCN} \rightleftharpoons \text{ICN} + \text{I}^- + \text{H}^+$	Titrate in carbonate-bicarbonate buffer, using <i>p</i> -xylene as an extraction indicator.
H ₂ C=O	$\text{H}_2\text{CO} + 3\text{OH}^- \rightleftharpoons \text{HCO}_2^- + 2\text{H}_2\text{O} + 2\text{e}^-$	Add excess I ₃ ⁻ plus NaOH to the unknown. After 5 min, add HCl and back-titrate with thiosulfate.
Glucose (and other reducing sugars)	$\begin{array}{c} \text{O} \\ \\ \text{RCH} \end{array} + 3\text{OH}^- \rightleftharpoons \text{RCO}_2^- + 2\text{H}_2\text{O} + 2\text{e}^-$	Add excess I ₃ ⁻ plus NaOH to the sample. After 5 min, add HCl and back-titrate with thiosulfate.
Ascorbic acid (vitamin C)	$\text{Ascorbate} + \text{H}_2\text{O} \rightleftharpoons$ dehydroascorbate + 2H ⁺ + 2e ⁻	Titrate directly with I ₃ ⁻ .
H ₃ PO ₃	$\text{H}_3\text{PO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{PO}_4 + 2\text{H}^+ + 2\text{e}^-$	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) $\underline{\text{MnO}_4^-} + 5e^- \rightarrow \underline{\text{Mn}^{2+}}$ (manganous ion)
- \rightarrow eq wt of potassium permanganate is 1/5th gram-mol wt 31.61 g.
- ($\text{KMnO}_4 : 1/5 \times 158.05 = 31.61$)
- (2) $\underline{\text{Cr}_2\text{O}_7^{2-}} + 6e^- \rightarrow \underline{2\text{Cr}^{3+}}$ (chromous ion)
- \rightarrow eq wt of potassium dichromate is 1/6 gram-mol wt 49.03 g.
- ($\text{K}_2\text{Cr}_2\text{O}_7 : 1/6 \times 294.18 = 49.03$)
- (3) $\underline{\text{I}_2} + 2e^- \rightarrow \underline{2\text{I}^-}$ (iodide ion)
- \rightarrow eq wt of iodine is 1 gram-mol wt 126.90 g. (I_2 : Molecular Weight = 126.90)
- (4) $\underline{\text{BrO}_3^-} + 6e^- \rightarrow \underline{\text{Br}^-}$ (bromide ion)
- \rightarrow eq wt of potassium bromate is 1/6 gram-mol wt 27.83 g. ($\text{KBrO}_3 : 1/6 \times 167.01 = 27.83$)