Redox titration

By **Dr/Amira Al.Enna**

Demonstrator at Pharmaceutical Analytical Chemistry department

Oxidation

- Electron loss
- Increase in oxidation no

Oxidation half reaction

$Fe^{2+} = Fe^{3+} + e^{-}$

Fe^{2+} is reducing agent or reductant (electron donor)

Reduction

- Electron gain
- decrease in oxidation no

Reduction half reaction

$Ce^{4+} + e^{-} = Ce^{3+}$

Ce^{4+} is oxidizing agent or oxidant (electron acceptor)

Overall redox reaction

$Fe^{2+} = Fe^{3+} + e^-$ Oxidation half reaction

$Ce^{4+} + e^- = Ce^{3+}$ Reduction half reaction

Overall redox reaction

$$Fe^{2+} = Fe^{3+} + \cancel{e^-}$$ Oxidation half reaction

$$Ce^{4+} + \cancel{e^-} = Ce^{3+}$$ Reduction half reaction

$$Fe^{2+} + Ce^{4+} = Fe^{3+} + Ce^{3+}$$ Overall redox reaction

Oxidizing agents

- $KMnO_4 \longrightarrow Mn^{2+}$
- $K_2Cr_2O_7 \longrightarrow Cr^{3+}$
- $I_2 \longrightarrow I^-$
- $Ce^{4+} \longrightarrow Ce^{3+}$

Reducing agents

- Oxalic acid $\longrightarrow CO_2$
- $Na_2S_2O_3 \longrightarrow Na_2S_4O_6$
- $Fe^{2+} \longrightarrow Fe^{3+}$
- $AsO_3^{3-} \longrightarrow AsO_4^{3-}$

How to balance redox equations

Example 1: oxidation of Fe^{2+} by $Cr_2O_7^{2-}$

Oxidation half equation

$Fe^{2+} = Fe^{3+}$

Oxidation half equation

$Fe^{2+} = Fe^{3+}$ M.B.

Oxidation half equation

$Fe^{2+} = Fe^{3+}$ C.B.

+2 +3

Oxidation half equation

$Fe^{2+} = Fe^{3+} + e^{-}$ C.B.

+2

$+3 - 1 = +2$

Reduction half equation

$Cr_2O_7^{2-} = Cr^{3+}$

Reduction half equation

$Cr_2O_7^{2-} = Cr^{3+}$

M.B.

1. Cr
2. O $\rightarrow$ H_2O
3. H $\rightarrow$ H^+

Reduction half equation

$Cr_2O_7^{2-} = 2Cr^{3+}$

M.B.

1.Cr

2.$O \longrightarrow H_2O$

3.$H \longrightarrow H^+$

Reduction half equation

$Cr_2O_7^{2-} = 2Cr^{3+} + 7H_2O$

M.B.

1. Cr
2. **O $\rightarrow$ H_2O**
3. H $\rightarrow$ H^+

Reduction half equation

$Cr_2O_7^{2-} + 14H^+ = 2Cr^{3+} + 7H_2O$

M.B.

1. Cr
2. O $\longrightarrow$ H_2O
3. **H $\longrightarrow$ H^+**

Reduction half equation

$Cr_2O_7^{2-} + 14H^+ = 2Cr^{3+} + 7H_2O$ C.B.

-2 + 14 = +12

+6

Reduction half equation

$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$ C.B.

$-2 + 14 - 6 = +6$

$+6$

$$Fe^{2+} = Fe^{3+} + e^{-} \quad \times 6$$

$$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} = 2Cr^{3+} + 7H_2O$$

$6Fe^{2+} = 6Fe^{3+} + 6e^-$ Oxidation half equation

$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$ Reduction half equation

$$6Fe^{2+} = 6Fe^{3+} + \cancel{6e^-}$$

Oxidation half equation

$$Cr_2O_7^{2-} + 14H^+ + \cancel{6e^-} = 2Cr^{3+} + 7H_2O$$

Reduction half equation

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

$6Fe^{2+} = 6Fe^{3+} + \cancel{6e^-}$ Oxidation half equation

$Cr_2O_7^{2-} + 14H^+ + \cancel{6e^-} = 2Cr^{3+} + 7H_2O$ Reduction half equation

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$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ = 6Fe^{3+} + 2Cr^{3+} + 7H_2O$ **M.B.**

$\boxed{+12 - 2 + 14 = +24}$ $\boxed{18 + 6 = +24}$ **C.B.**

Overall redox equation:

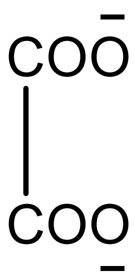
$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ = 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

How to balance redox equations

Example 2: oxidation of oxalate by MnO_4^-

Oxidation half equation

$C_2O_4^{2-} = CO_2$



Oxidation half equation

$C_2O_4^{2-} = CO_2$

M.B.

1. C
2. O $\rightarrow$ H_2O
3. H $\rightarrow$ H^+

Reduction half equation

$C_2O_4^{2-} = 2CO_2$

M.B.

1.C

2.O $\longrightarrow$ H_2O

3.H $\longrightarrow$ H^+

Reduction half equation

$C_2O_4^{2-} = 2CO_2$

M.B.

1.Cr

2.O $\rightarrow$ H_2O

3.H $\rightarrow$ H^+

Oxidation half equation

$C_2O_4^{2-} = 2CO_2$ C.B.

-2

zero

Oxidation half equation

$C_2O_4^{2-} = 2CO_2 + 2e^-$ C.B.

-2

0 – 2 = -2

Reduction half equation

$MnO_4^- = Mn^{2+}$

Reduction half equation

$MnO_4^- = Mn^{2+}$

M.B.

1. Mn
2. O $\rightarrow$ H_2O
3. H $\rightarrow$ H^+

Reduction half equation

$MnO_4^- = Mn^{2+}$

M.B.

1.Mn

2.O $\longrightarrow$ H_2O

3.H $\longrightarrow$ H^+

Reduction half equation

$MnO_4^- = Mn^{2+} + 4H_2O$

M.B.

1. Cr
2. **O $\rightarrow$ H_2O**
3. H $\rightarrow$ H^+

Reduction half equation

$MnO_4^- + 8H^+ = Mn^{2+} + 4H_2O$

M.B.

1. Cr
2. O $\rightarrow$ H_2O
3. **H $\rightarrow$ H^+**

Reduction half equation

$MnO_4^- + 8H^+ = Mn^{2+} + 4H_2O$ C.B.

-1 + 8 = +7

+2

Reduction half equation

$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$ C.B.

-1 + 8 - 5 = +2

+2

$C_2O_4^{2-} = 2CO_2 + 2e^-$ $\times 5$

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

$$5C_2O_4^{2-} = 10CO_2 + 10e^-$$

Oxidation half equation

$$2MnO_4^- + 16H^+ + 10e^- = 2Mn^{2+} + 8H_2O$$

Reduction half equation

$$5C_2O_4^{2-} = 10CO_2 + \cancel{10e^-}$$

Oxidation half equation

$$2MnO_4^- + 16H^+ + \cancel{10e^-} = 2Mn^{2+} + 8H_2O$$

Reduction half equation

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ = 10CO_2 + 2Mn^{2+} + 8H_2O$$

$5C_2O_4^{2-} = 10CO_2 + \cancel{10e^-}$ Oxidation half equation

$2MnO_4^- + 16H^+ + \cancel{10e^-} = 2Mn^{2+} + 8H_2O$ Reduction half equation

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$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ = 10CO_2 + 2Mn^{2+} + 8H_2O$

M.B.

$\boxed{\mathbf{-10 - 2 + 16 = +4}}$ $\boxed{\mathbf{+4}}$

C.B.

Overall redox equation:

$$5C_2O_4^{2-} + 2MnO_4^{-} + 16H^{+} = 10CO_2 + 2Mn^{2+} + 8H_2O$$

Detection of E.P in redox titration

1) **Specific indicators:**

e.g$_1$. starch with iodine

e.g$_2$. SCN^- with Fe^{3+}

2) **self indicators:**

e.g. $KMnO_4 \longrightarrow Mn^{2+}$

purple colorless

3) Redox indicators:

They have 2 forms with 2 different colors:

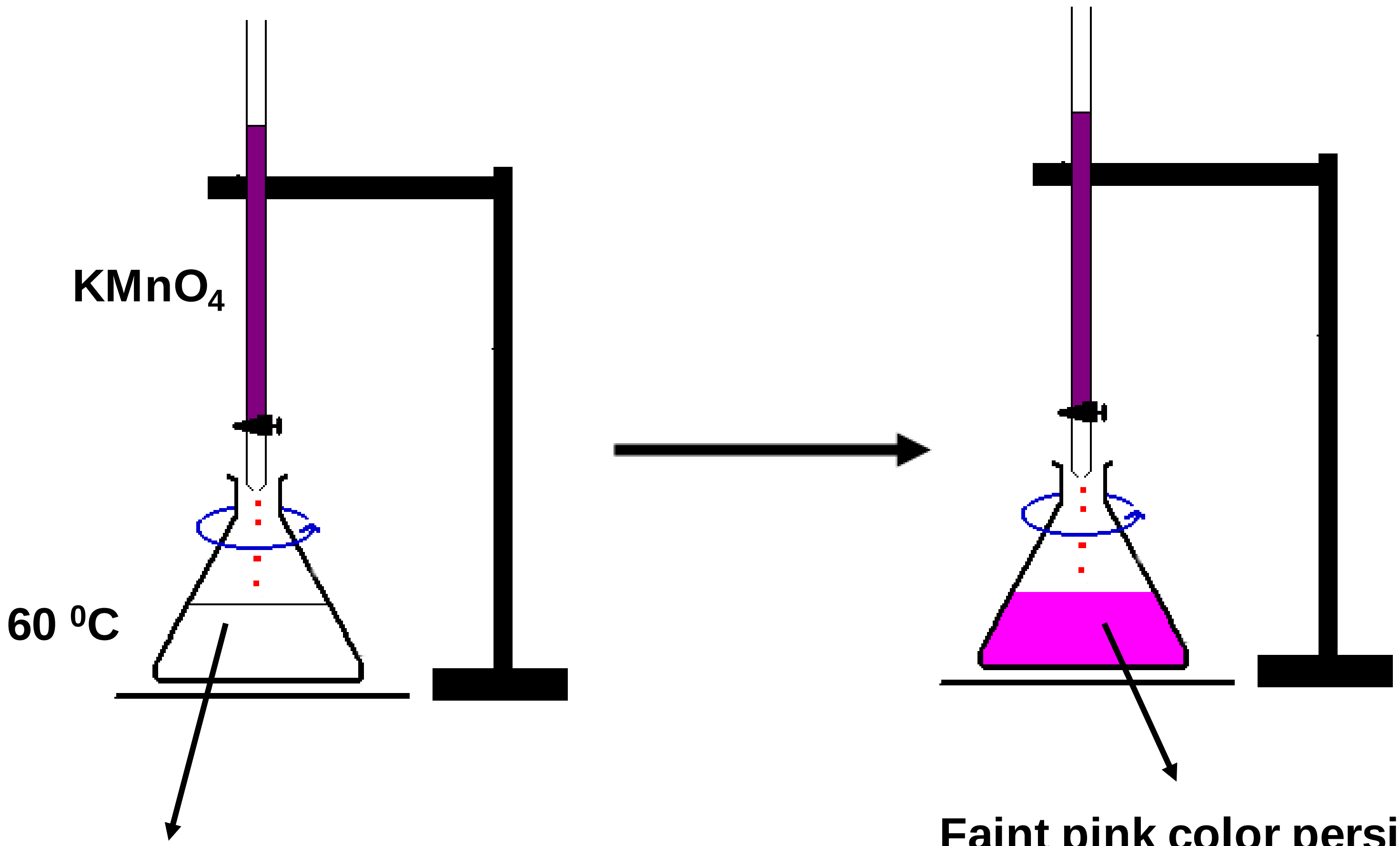
Oxidized form & reduced form

e.g. **1.Diphenyl amine**

2.O-phenanthroline-iron complexes

Standardization of 0.1 N $KMnO_4$ by 0.1 N sodium oxalate

$$5C_2O_4^{2-} + 2MnO_4^{-} + 6H^{+} = 10CO_2 + 2Mn^{2+} + 8H_2O$$



20 ml 0.1N sodium oxalate + 5 ml 6*M* H_2SO_4

Faint pink color persists for about ½ min after shaking

Calculations

$$N \,.\, V = N` .\, V`$$

Sodium oxalate	**$KMnO_4$**
N = 0.1	**N` = ?**
V = 20	**V` = E.P**

N.B.1. at the beginning of titration, the oxidation of oxalic acid by $KMnO_4$ proceeds very slowly until enough manganous ions are formed to catalyse the subsequent oxidation. Then, the reaction between oxalic acid & $KMnO_4$ proceeds relatively rapidly

N.B.2. the permanganate end point is not permanent, the pink color fades slowly, because the reducing matter in the water, dust particles,etc…, reduce this slight excess of permanganate & the color of the E.P fades away

Thank you