Redox

Part - A

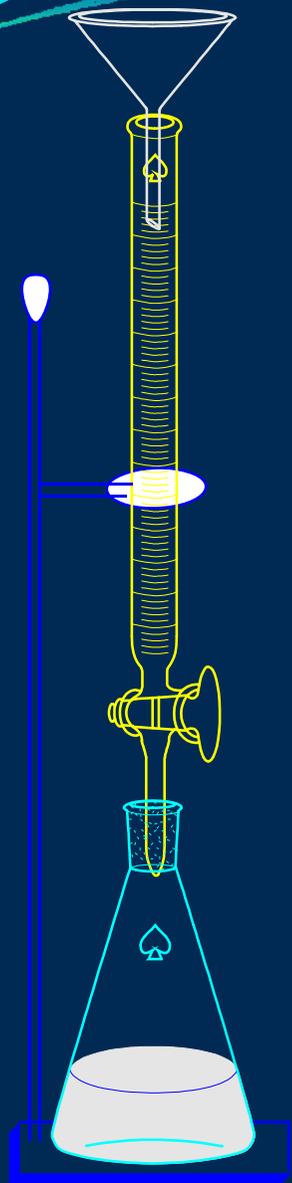**Dr. Apurba Biswas**
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Redox

Reduction

Oxidation

References:
1. Huheey, J. E.; Keiter, E.A. & Keiter, R.L. Inorganic Chemistry, Principles of Structure and Reactivity 4th Ed., Harper Collins 1993, Pearson,2006.
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Topics

Balancing of Redox Reactions by ion-electron method

1. $\overset{+2}{Fe}SO_4 + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3 + \overset{+3}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O$

Oxidation: $Fe^{2+} \longrightarrow Fe^{3+} + e \qquad \times 6$

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reduction: $Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$

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

2.

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

2. $\overset{+2}{Fe}SO_4 + K\overset{+7}{Mn}O_4 + H_2SO_4 \longrightarrow K_2SO_4 + \overset{+2}{Mn}SO_4 + \overset{+3}{Fe_2}(SO_4)_3 + H_2O$

Oxidation: $Fe^{2+} \longrightarrow Fe^{3+} + e \qquad \times 5$

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

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2K_2SO_4 + 2MnSO_4 + 8H_2O$$

3. $\overset{+3}{H_2}C_2O_4 + K\overset{+7}{Mn}O_4 + H_2SO_4 \longrightarrow K_2SO_4 + \overset{+2}{Mn}SO_4 + \overset{+4}{C}O_2 + H_2O$

Oxidation: $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e \qquad \times 5$

reduction: $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O \quad \times 2$

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

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

Equivalent weight of Oxidants & Reductants

Equivalent wt = formula wt/no of electron change occuring per formula species.

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \text{ (strongly acidic cond}^n) \qquad M/5$$

$$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O \text{ (weakly acidic, neutral \& alkaline)} \qquad M/3$$

$$MnO_4^- + e \rightleftharpoons MnO_4^{2-} \text{ (strongly alkaline cond}^n) \qquad M/1$$

$$2S_2O_3^{2-} - 2e \rightleftharpoons S_4O_6^{2-} \text{ (like } I_2) \qquad M/1$$

$$S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e \text{ (like } MnO_4^-) \qquad M/8$$
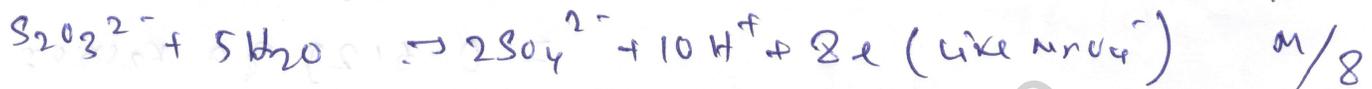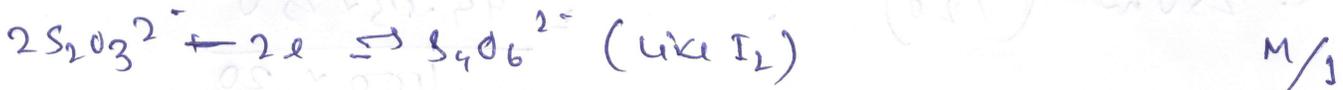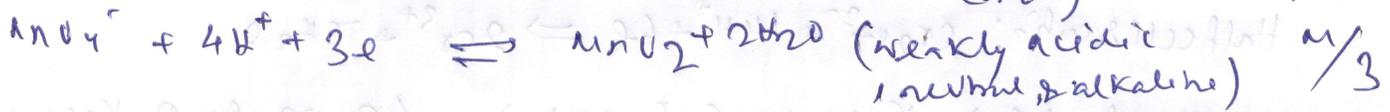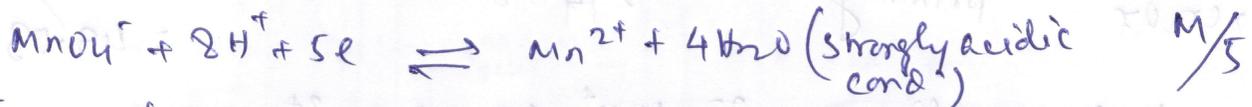
$$Cr_2O_7^- + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \qquad M/6$$
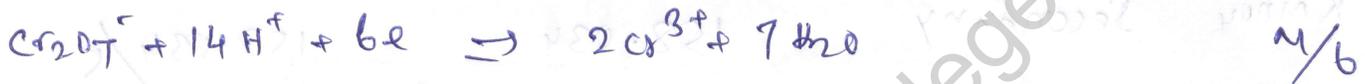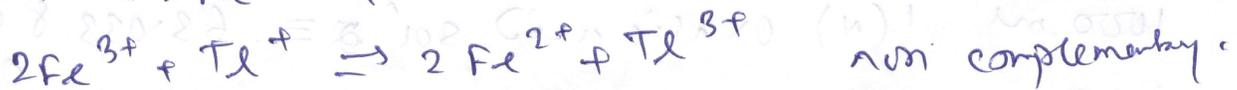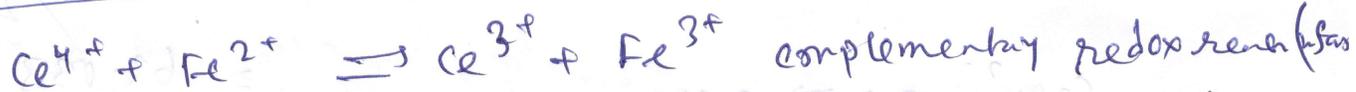
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complementary & non complementary Redox reaction:

If the number of electron change in a redox reaction at each of the centres i,e oxidant & reductant, is the same, then such reactions are referred to as <u>complementary electron transfer reaction</u>.

& If the change is different → <u>non complementary</u> <u>electron transfer reaction</u>

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+} \qquad \text{complementary redox reaction (fast)}$$

$$Sn^{2+} + 2Fe^{3+} \rightleftharpoons Sn^{4+} + 2Fe^{2+} \qquad \text{non complementary (slow)}$$

$$2Fe^{3+} + Tl^+ \rightleftharpoons 2Fe^{2+} + Tl^{3+} \qquad \text{non complementary.}$$

Oxidation state Calculation: perdisulphuric acid (Marshall's acid) $H_2S_2O_8$
Caro acid (H_2SO_5)

equivalent weight of some oxidant & Reduct.

Oxidants	Nature of standard	Formula weight	equivalent wt

1. $K_2Cr_2O_7$ — primary — 294.18 — $294.18/6$ = 49.03

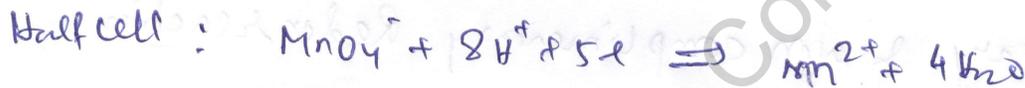Half cell reaction: $Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$
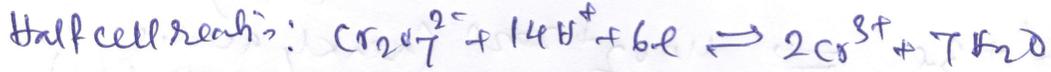
1000 ml 1 (N) $K_2Cr_2O_7$ sol^n contains 49.03 g of $K_2Cr_2O_7$

∴ 250 ml $(N/20)$ "

$$= \frac{49.03 \times 250}{1000 \times 20}$$

$$= 0.6129 \text{ g of } K_2Cr_2O_7$$

2. $KMnO_4$ — Secondary — 158.034 — $158.034/5$ = 31.6068 g

Half cell : $MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$

1000 ml 1 (N) $KMnO_4$ sol^n contains 31.6068 g $KMnO_4$

∴ 250 ml $N/20$ "
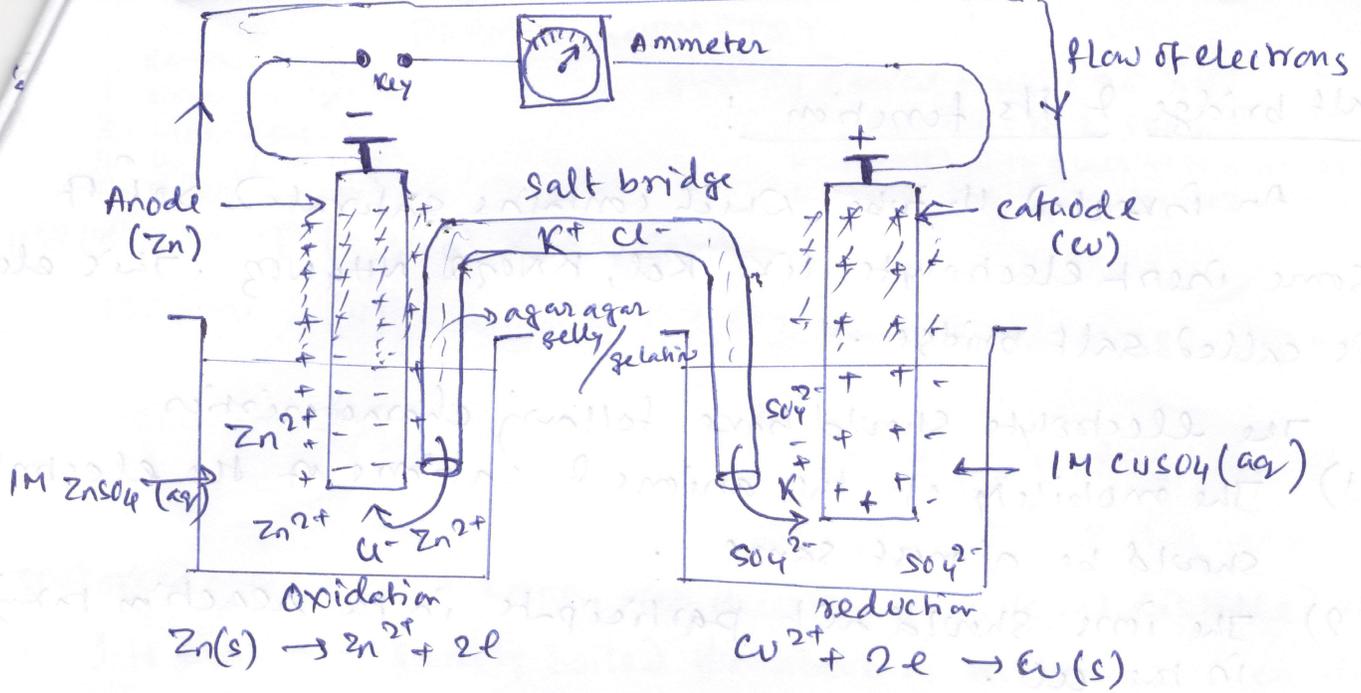
$$= \frac{31.6068 \times 250}{1000 \times 20}$$

$$\approx 0.4 \text{ g} \qquad "$$

3. **Reductant**

1. Oxalic acid — primary — 126.066 — $126.066/2$ = 63.033
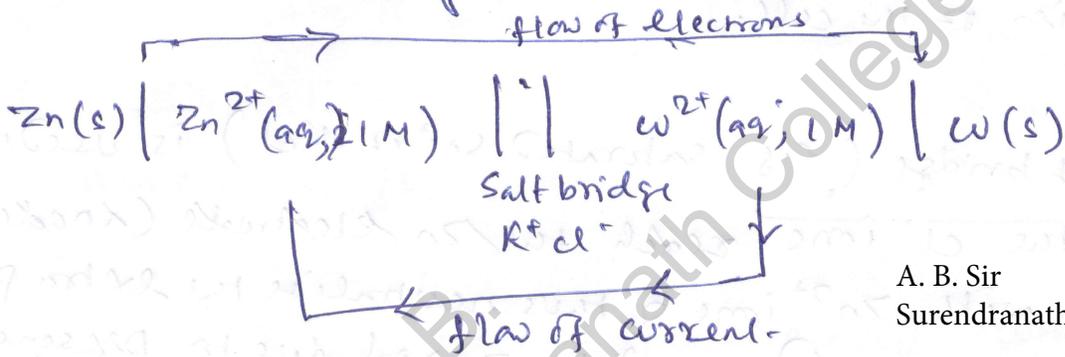
$$C_2O_4^{2-} - 2e \rightleftharpoons 2CO_2$$
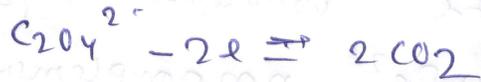
1000 ml 1 (N) oxalic acid sol^n ≡ 63.033 g of crystalline Oxalic acid

∴ 250 ml $N/20$ " ≡ $\frac{63.033 \times 250}{1000 \times 20}$

= 0.7879 g

2. $Na_2S_2O_3 \cdot 5H_2O$ — Secondary — 248.186 — $248.186/1$ = 248.186 g

a. $2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e$ — 250 ml $N/20$ → n3.4 g

3. Mohr salt sol^n — Secondary — 392.143

Working of a Daniell cell

$$Zn(s) \mid Zn^{2+}(aq, 1M) \mid \mid Cu^{2+}(aq, 1M) \mid Cu(s)$$

Salt bridge
$K^+ Cl^-$

flow of current

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Electrochemical cell or galvanic cell

Electrochemical cell is a device in which oxidation & reduction takeplace in two separate containers & electrical energy is produced during this reactions. Electrochemical cell is also called voltaic cell.

1. Zn metal plate placed in a soln containing Zn^{2+} ions

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e$$

electron thus generated get accumulated on the Zn plate & hence make the plate negatively charged, A electrical layer develops a definite potential diff bet^n the Zn & Zn^{2+} (aq) ions of the soln. This potential is called electrode potential

Salt bridge & Its function :

An inverted U-tube which contains saturated soln of some inert electrolyte like KCl, KNO₃ & NH₄NO₃. This elect. is called salt bridge.

The electrolyte should have follwing charactereistics

1) The mobility of the anions & cations of the electrolyte should be almost same.

2) The ions should not participate in the reaction takisphe in the cell.

3) The ions of the electrolyte should not react with the species of the cell.

If a salt bridge (e.g saturated soln of KCl) is used in Daniell cell, the cl⁻ ions reach the Zn electrode (anode) reacts with Zn^{2+} ions & thus neutralise the extra positive charge accumulated round the Zn rod due to presence of Zn^{2+} ions. Similarly K^+ ions neutralise charge created due to the presence of SO_4^{2-} ions.

If salt bridge not used :

After sometime extra positive charge due to the presence of Zn^{2+} ions is accumulated in the soln round the Zn rode (anode) The accumulation of +ve charge round the Zn rod prevents the flow of electrons from Zn rod to Cu rod.

Similarly, -ve charge round the Cu rod prevents the flow of electrons to Cu^{2+} ions. The flow of electrons will takes place only for a moment & the cell will stop