Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Paper Code: CHC-106

Paper Title: Inorganic Chemistry (Section B)

Unit: 6 (Oxidation and Reduction)

Module Name: Redox stability in water

Name of the Presenter: Dr. Rita N. Jyai

Notes

Redox Stability in Water

- The stability of an ion or a molecule in a solution depends upon the solvent and on other solutes including oxygen that may be present in the solution.
- This is because the ion or the molecule may be destroyed by oxidation or reduction brought about by the solvent or by the other species present in the solution.
- For instance,

a) Metals such as Na, K, Ca, Sc, etc., get oxidised by water or H^+ ions liberating hydrogen:

$$M_{(s)} + H_2O_{(l)} \rightarrow M^+_{(aq)} + \tfrac{1}{2} H_{2(g)} + OH^-_{(aq)}$$

$$M_{(s)} + H^+_{(aq)} \rightarrow M^+_{(aq)} + \tfrac{1}{2} H_{2(g)}$$

b) And ions such as Co^{3+} get reduced by water liberating oxygen:

$$Co^{3+}_{(aq)} + 2H_2O_{(l)} \rightarrow Co^{2+}_{(aq)} + 4H^+_{(aq)} + O_{2\,(g)}$$

- In simple words, we can say water can act as an oxidising agent as well as a reducing agent.

CASE I: Water as an Oxidant

(i.e., Oxidation of substances by H_2O and reduction of H_2O to H_2)

- When H_2O act as an oxidant, it is reduced to H_2.
- As a matter of fact the reduction of H_2O means the reduction of $H^+_{(aq)}$ ions to $H_{2(g)}$

$$H^+ + e^- \rightarrow ½\, H_2$$

- Reduction half – reaction

$$E_{H^+/½H_2} = E^o_{H^+/½H_2} + 0.0591 \log \frac{1}{[H^+]}$$

$$= 0 - 0.0591 \log [H^+]$$

$$\underset{\text{at } 25^oC}{E_{H^+/½H_2}} = - 0.0591\ pH$$

Example: Alkali or alkaline earth metals (except Be),

$$M + H_2O \rightarrow MOH + ½\, H_2 \quad \text{OR} \quad M + H^+ \rightarrow M^+ + ½\, H_2$$

Metals of first transition series like Sc, Ti, V, Cr, Mn etc.

$$Sc + 3H^+ \rightarrow Sc^{3+} + ½\, H_2$$

- Consider, the evolution of H_2 at an electrode on which hydrogen overvoltage is, say, 0.60 V.
- Since there is 0.60 V hydrogen overvoltage, E required for the liberation of H_2 would be a little more negative than 0.6591 V at pH = 1 and a little more negative than – 0.6 V at pH = 0.
- This means that the species with redox potentials more negative than -0.6591 V at pH=1.
- As, for example, Na (E = -2.71 V), Ca (E = -2.87 V), Li (E = -3.04 V), would get oxidised by water or H^+ ions with the evolution of H.

CASE II: Water as a Reductant

(i.e., Reduction of substances by H_2O and Oxidation of H_2O to O_2)

When H_2O acts as a reductant, it is oxidised to O_2.

$$2H_2O \rightarrow 4H^+ + O_2 \ , \ E°_{ox} = -1.23 \text{ V}$$

If this oxidation half-reaction is written as reduction half-reaction, then we get:

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \ , \ E°_{red} = +1.23 \text{ V}$$

For this reduction half-reaction, $E = E°_{red} - 0.0591 \text{ pH}$

$$\text{At pH 0, } E = 1.23 - 0.0591 \times 0 = 1.23\text{V}$$

Example: When F_2 reacts with H_2O, F_2 is reduced to F^- ion and H_2O is oxidised to O_2.

$$2F_2 + 2H_2O \rightarrow 4F^- + 4H^+ + O_2$$

$$(F=0) \quad (O = -2) \quad (F= -1) \qquad (O = 0)$$

H_2O also reduces Co^{3+} to Co^{2+} and Ce^{4+} to Ce^{3+}

$$4Co^{3+} + 2H_2O \rightarrow 4Co^{2+} + 4H^+ + O_2$$

$$4Ce^{4+} + 2H_2O \rightarrow 4Ce^{3+} + 4H^+ + O_2$$

- Let us consider the liberation of O_2 at an electrode on which oxygen overvoltage is, say, 0.27 V.
- Since, there is 0.27 V oxygen overvoltage, E required for the liberation of O_2 would be higher than 1.5 V.
- This means that species with redox potentials higher than +1.5 V at pH = 0.
- As, for example, Co^{3+} (E = +1.82 V) and C^{4+} (E = +1.71 V), would get reduced by water which itself gets oxidised to O_2.

CASE III: Disproportionation Reactions

- It is a redox reaction in which the oxidation number (O.N.) of an element increases as well as decreases simultaneously.
- This leads to the formation of two products one of which has the element in lower oxidation state and the other product has the element in higher oxidation state.
- In other words the species which undergoes disproportionation acts as an oxidant as well as a reductant.
- Example: Cu^+ acts as an oxidant as well as a reductant

$$\underset{(Cu = +1)}{2Cu^+} \rightarrow \underset{(Cu = +2)}{Cu^{2+}} + \underset{(Cu = 0)}{Cu^0}$$

- The two half-reactions are

$$Cu^+ \rightarrow Cu^{2+} + e^-, \quad E°_{ox} = -0.16\ V$$

$$Cu^{2+} + e^- \rightarrow Cu^0, \quad E°_{red} = +0.52\ V$$

$$2Cu^+ \rightarrow Cu^{2+} + Cu^0, \quad E°_{redox} = +0.36\ V$$

- Since, $E°_{redox}$ is positive, the disproportionation reaction is spontaneous.

Comproportionation Reactions

- These are simply the reverse of disproportionation reactions.
- In these reactions an element in its two different oxidation states combine together to form a product which has the element in intermediate oxidation state.
- The following reaction is a spontaneous comproportionation reaction

$$Ag^{2+} + Ag^0 \rightarrow 2Ag^+ \quad (E° = +1.18\ V)$$

Auto-oxidation

- It is a process in which a substance undergoes oxidation and reduction both by itself.
- It may be noted that in disproportionation reaction the same thing happens but in case of auto-oxidation this reaction occurs slowly without the action of heat, light or electricity.

$$3\,HNO_2 \rightarrow HNO_3 + 2NO$$

$$(N = +3) \qquad (N = +5) \qquad (N = +2)$$

Summary

- The compounds may evolve H_2 by reacting with H_2O. In these reactions the compounds are oxidised by H_2O and H_2O itself is reduced to H_2. Thus, in these reactions H_2O acts as on oxidising agent.
- The compounds may evolve O_2 by reacting with H_2O. In these reactions the compounds are reduced and H_2O itself is oxidised to O_2. Thus, in these reactions H_2O acts as a reducing agent.
- The compounds may undergo disproportionation forming compounds of higher and lower oxidation states.