

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

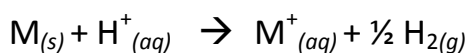
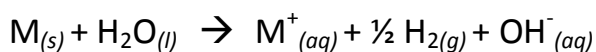
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Notes

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:



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

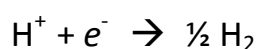


- In simple words, we can say water can act as an oxidising agent as well as a reducing agent.

CASE I: Water as an Oxidant

(i.e., Oxidation of substances by H₂O and reduction of H₂O to H₂)

- When H₂O act as an oxidant, it is reduced to H₂.
- As a matter of fact the reduction of H₂O means the reduction of H⁺_(aq) ions to H_{2(g)}

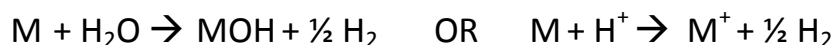


- Reduction half – reaction

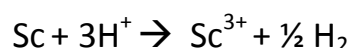
$$\begin{aligned} E_{\text{H}^+ / \frac{1}{2}\text{H}_2} &= E_{\text{H}^+ / \frac{1}{2}\text{H}_2}^{\circ} + 0.0591 \log \frac{1}{[\text{H}^+]} \\ &= 0 - 0.0591 \log [\text{H}^+] \end{aligned}$$

$$\begin{aligned} E_{\text{H}^+ / \frac{1}{2}\text{H}_2} &= -0.0591 \text{ pH} \\ &\text{at } 25^{\circ}\text{C} \end{aligned}$$

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



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

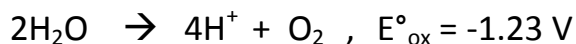


- Consider, the evolution of H₂ at an electrode on which hydrogen overvoltage is, say, 0.60 V.
- Since there is 0.60 V hydrogen overvoltage, E required for the liberation of H₂ would be a little more negative than 0.6591 V at pH = 1 and a little more negative than – 0.6 V at pH = 0.
- This means that 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 H₂O and Oxidation of H₂O to O₂)

When H₂O acts as a reductant, it is oxidised to O₂.



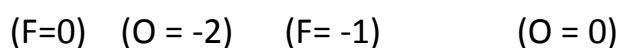
If this oxidation half-reaction is written as reduction half-reaction, then we get:



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

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

Example: When F₂ reacts with H₂O, F₂ is reduced to F⁻ ion and H₂O is oxidised to O₂.



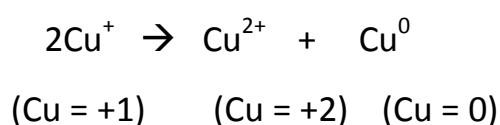
H₂O also reduces Co³⁺ to Co²⁺ and Ce⁴⁺ to Ce³⁺



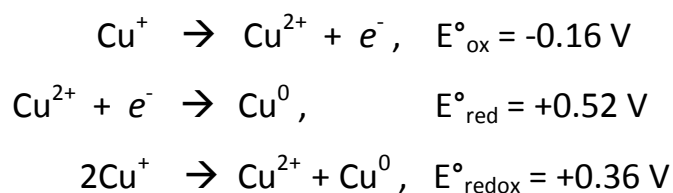
- Let us consider the liberation of O₂ at an electrode on which oxygen overvoltage is, say, 0.27 V.
- Since, there is 0.27 V oxygen overvoltage, E required for the liberation of O₂ would be higher than 1.5 V.
- This means that species with redox potentials higher than +1.5 V at pH = 0.
- As, for example, Co³⁺ (E = +1.82 V) and C⁴⁺ (E = +1.71 V), would get reduced by water which itself gets oxidised to O₂.

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



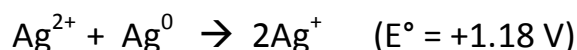
- The two half-reactions are



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

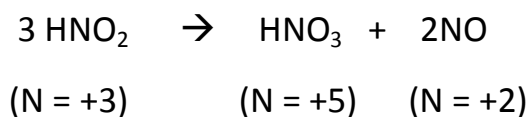
Comproportionation Reactions

- 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



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.



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 an 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.