

HINTS & SOLUTIONS WORKBOOK - 2

Stoichiometry-II (Redox Reactions)

Daily Tutorial Sheet	Level-0
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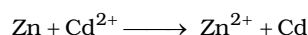
1. Reverse the signs of oxidation potential to get the values of the reduction or electrode potentials. Thus,

$$E_{\text{Zn}|\text{Zn}^{2+}} = 0.763\text{V} \therefore E_{\text{Zn}^{2+}|\text{Zn}} = -0.763\text{V} \text{ and } \therefore E_{\text{Cd}|\text{Cd}^{2+}} = 0.403\text{V}$$

$$\therefore E_{\text{Cd}^{2+}|\text{Cd}} = -0.403\text{V}$$

Since $\text{Zn}^{2+}|\text{Zn}$ electrode is at lower potential, therefore, it acts as the anode while $\text{Cd}^{2+}|\text{Cd}$ electrode with higher potential acts as the cathode.

In other words, Zn loses electrons and Cd^{2+} ion accepts them. Therefore, cell reaction is :



$$\text{And } E_{\text{cell}}^0 = E_{\text{Cd}^{2+}|\text{Cd}}^0 - E_{\text{Zn}^{2+}|\text{Zn}}^0 = -0.403 - (-0.763) = +0.360\text{V}$$

$$2. \quad -0.46 = E_{\text{Cu}^{2+}|\text{Cu}}^0 - E_{\text{Ag}^+|\text{Ag}}^0 \quad \dots(\text{i})$$

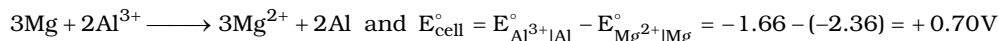
$$1.10 = E_{\text{Cu}^{2+}|\text{Cu}}^0 - E_{\text{Zn}^{2+}|\text{Zn}}^0 \quad \dots(\text{ii})$$

Subtracting equation (i) from equation (ii), we have,

$$E_{\text{cell}}^0 = 1.10 - (-0.46) = E_{\text{Ag}^+|\text{Ag}}^0 - E_{\text{Zn}^{2+}|\text{Zn}}^0 \text{ or } 1.56\text{V} = E_{\text{Ag}^+|\text{Ag}}^0 - E_{\text{Zn}^{2+}|\text{Zn}}^0$$

In other words, E^0 of the cell, $\text{Zn}|\text{Zn}^{2+}(\text{M})||\text{Ag}^+(\text{M})|\text{Ag}$, is 1.56 V.

3. Since, $\text{Mg}^{2+}(\text{aq})|\text{Mg}$ electrode = -2.36V is at a lower potential than $\text{Al}^{3+}(\text{aq})|\text{Al}$ electrode = -1.66V , therefore, $\text{Mg}^{2+}(\text{aq})|\text{Mg}$ electrode acts as the anode and $\text{Al}^{3+}(\text{aq})|\text{Al}$ acts as the cathode. In other words, Mg loses electrons and Al^{3+} ion accepts electrons. Thus, the cell reaction is



$$4. \quad E_{\text{cell}}^0 = E_{\text{Cu}^{2+}|\text{Cu}}^0 - E_{\text{Al}^{3+}|\text{Al}}^0 = 0.34 - (-1.66) = 2.0\text{V}$$

5. If the metal is to react with dil. H_2SO_4 (i.e., H^+ ions) to produce H_2 gas, the metal should have a lower electrode potential than that of standard hydrogen electrode, i.e., 0.0V .

(i) Since, $E_{\text{Cu}^{2+}|\text{Cu}}^0 = 0.34\text{V}$ is higher than $E_{\text{H}^+|\text{H}_2}^0 = 0.0\text{V}$, therefore, Cu will not react with 1N H_2SO_4 to produce H_2 gas.

(ii) Since, $E_{\text{Pb}^{2+}|\text{Pb}}^0 = -0.13\text{V}$ and $E_{\text{H}^+|\text{H}_2}^0 = 0.0\text{V}$, therefore, lead will react with 1N H_2SO_4 to produce H_2 gas.

(iii) Since $E_{\text{Fe}^{2+}|\text{Fe}}^0 = -0.44\text{V}$ and $E_{\text{H}^+|\text{H}_2}^0 = 0.0\text{V}$, therefore iron will react with 1N H_2SO_4 to produce H_2 gas.

6. Since, $E_{\text{Zn}^{2+}|\text{Zn}}^0 = -E_{\text{Zn}|\text{Zn}^{2+}}^0 = -0.76\text{V}$, is at a lower potential than $E_{\text{Cu}^{2+}|\text{Cu}}^0 = 0.34\text{V}$, therefore,

Zn can only lose electrons to Cu^{2+} ions. Conversely, Zn^{2+} cannot accept electrons from Cu and hence the following reaction will not occur. $\text{Zn}^{2+} + \text{Cu} \longrightarrow \text{Zn} + \text{Cu}^{2+}$

In other words, ZnSO_4 solution can be safely stored in a copper vessel.

7. Since, $E^\circ_{\text{Ag}^+|\text{Ag}} = +0.80\text{V}$ is higher than $E^\circ_{\text{Cu}^{2+}|\text{Cu}} = -E^\circ_{\text{Cu}|\text{Cu}^{2+}} = -(-0.34) = +0.34\text{V}$, therefore, Ag^+ ions can easily accept electrons from Cu. In other words, the following reactions will occur.
- $$\text{Cu} + 2\text{Ag}^+ \longrightarrow \text{Cu}^{2+} + 2\text{Ag}$$
- Hence, 1 M AgNO_3 solution cannot be stirred with a copper spoon.
8. Since, Cu will react with Ag^+ ions, as discussed in Ans to Q.7 above, therefore AgNO_3 solution cannot be stored in copper vessel.
9. Since, $E^\circ_{\text{Zn}|\text{Zn}^{2+}} = -E^\circ_{\text{Zn}^{2+}|\text{Zn}} = -0.76\text{V}$ is lower than $E^\circ_{\text{Cu}^{2+}|\text{Cu}}$, therefore, Zn will lose electrons and copper will accept them. In other words, the following reaction will occur, $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$. Since, blue Cu^{2+} ions are consumed and colourless Zn^{2+} ions are produced during the above reaction, therefore, colour of CuSO_4 solution gets discharged when zinc rod is dipped in it.
10. $\text{N} \rightarrow -3 \text{ to } +5$
 $\text{S} \rightarrow -2 \text{ to } +6$
 $\text{Cl} \rightarrow -1 \text{ to } +7$
11. In case of nitric acid, nitrogen is in maximum oxidation state of +5 and therefore, cannot be further oxidized. So, HNO_3 acts as an oxidizing agent only.
 On the other hand, N in HNO_2 is in +3 oxidation state and therefore, can undergo either oxidation or reduction. So, HNO_2 acts both as an oxidizing as well as reducing agent.
12. No. In both $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} , Cr is in +6 oxidation state and therefore, there is no change in oxidation state.
13. (i) $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$; $\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$
 (ii) $2\text{I}^- \longrightarrow \text{I}_2 + 2\text{e}^-$; $2\text{Fe}^{3+} + 2\text{e}^- \longrightarrow \text{Fe}^{2+}$
 (iii) $2\text{Na} \longrightarrow 2\text{Na}^+ + 2\text{e}^-$; $\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$
 (iv) $\text{Mg} \longrightarrow \text{Mg}^{2+} + 2\text{e}^-$; $\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$
 (v) $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$; $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$
14. The electrode to be chosen as the anode should have high oxidation potential.
 So, out of $\text{Zn}|\text{Zn}^{2+}$ and $\text{Fe}|\text{Fe}^{2+}$, the former has higher oxidation potential.
 i.e. $E^\circ_{\text{Zn}|\text{Zn}^{2+}} = 0.76\text{V}$ & $E^\circ_{\text{Fe}|\text{Fe}^{2+}} = 0.44\text{V}$
 The cathode should have higher reduction potential. So, $\text{Cu}^{2+}|\text{Cu}$ can act as cathode.
 So, cell reaction would be
- $$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$$
- $$E_{\text{cell}} = (0.76 + 0.34)\text{V} = 1.10\text{V}$$
- In the internal circuit, the direction of flow of electrons will be from cathode to anode and from anode to cathode in the external circuit.
15. $E_{\text{Fe}|\text{Fe}^{2+}} = 0.44\text{V}$; $E_{\text{Zn}|\text{Zn}^{2+}} = 0.76\text{V}$; $E_{\text{Ni}|\text{Ni}^{2+}} = 0.25\text{V}$
- (i) Since oxidation potential of $\text{Fe}|\text{Fe}^{2+}$ is less than oxidation potential of $\text{Zn}|\text{Zn}^{2+}$,
 \therefore Fe cannot reduce Zn^{2+} ions.
- (ii) Since oxidation potential of $\text{Fe}|\text{Fe}^{2+}$ is higher than that of $\text{Ni}|\text{Ni}^{2+}$, so Fe can reduce Ni^{2+} ions.

- 16.** The standard reduction potential of the four metallic elements – A, B, C and D have been given. Higher the reduction potential, lesser will be the electropositive character.
 \therefore Decreasing order of electropositive character is – B > C > D > A
- 17.** Since the reduction potential of Br_2 ($E^\circ_{\text{Br}_2|\text{Br}^-} = 1.09 \text{ V}$) is higher than that of I_2 ($E^\circ_{\text{I}_2|\text{I}^-} = 0.54 \text{ V}$), so, Br_2 will get reduced while I^- ions will undergo oxidation. So, the reaction would be
- $$\text{Br}_2 + 2\text{I}^- \longrightarrow 2\text{Br}^- + \text{I}_2 \quad (E^\circ = 0.55 \text{ V})$$
- 18. (i)** $E_{\text{Zn}^{2+}|\text{Zn}}^\circ = -0.76 \text{ V}$ and $E_{\text{Cu}^{2+}|\text{Cu}}^\circ = 0.34 \text{ V}$
 Zinc will displace copper from its salt solution, copper sulphate solution should not be stored in a zinc vessel.
- (ii)** Since reduction potential of $\text{Ag}^+|\text{Ag}$ is higher than $\text{Cu}^{2+}|\text{Cu}$, so, copper ion will not be reduced. So, copper sulphate solution can be stored in silver vessel.
- (iii)** Similar to the case of silver vessel, copper sulphate solution can be stored in gold vessel.
- 19.** In case of Cu_2O , Cu is in +1 oxidation state. So, it can undergo both oxidation as well as reduction. That is why it can act both as an oxidant and reductant.
 As an oxidant
- $$\begin{array}{ccccccc} \text{Cu}_2\text{O} & + & \text{H}_2 & \longrightarrow & 2\text{Cu} & + & \text{H}_2\text{O} \\ 0.5 & & +1 & & 0 & & \end{array} \quad \text{As a reductant}$$
- 20.** Reduction $2\text{MnO}_4^- + 6\text{e}^- \longrightarrow 2\text{MnO}_2$
 Oxidation $\text{Br}^- \longrightarrow \text{BrO}_3^- + 6\text{e}^-$
 Complete redox reaction would be $2\text{MnO}_4^- + \text{Br}^- + \text{H}_2\text{O} \longrightarrow 2\text{MnO}_2 + \text{BrO}_3^- + 2\text{OH}^-$
- 21.** $2\text{MnO}_4^- + 6\text{I}^- + 4\text{H}_2\text{O} \longrightarrow 2\text{MnO}_2 + 3\text{I}_2 + 8\text{OH}^-$
- 22. (a)** $\text{KI}_3 \longrightarrow +1 + 3(x) = 0$
 $\therefore x = +1/3$
- (b)** $\text{H}_2\text{S}_4\text{O}_6 \longrightarrow 2(+1) + 4(x) + 6(-2) = 0$
 $\Rightarrow 4x - 10 = 0 \Rightarrow x = 10/4$
- (c)** $\text{Fe}_3\text{O}_4 \longrightarrow 3(x) + 4(-2) = 0$
 $\therefore x = +8/3$
- (d)** $\overset{1}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\text{OH} \longrightarrow 2(x) + 6(+1) + 1(-2) = 0$
 $\Rightarrow 2x + 4 = 0 \Rightarrow 2x = -4$
 So, sum of 0.5. of both carbon atoms is -4.
 Oxidation number of C-1 = -3
 Oxidation number of C-2 = -1
- (e)** $\overset{1}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{OOH} \longrightarrow 2(x) + 4(+1) + 2(-2) = 0$
 $\Rightarrow 2x = 0 \Rightarrow x = 0$
 So, sum of oxidation states of both carbon atoms is zero.
 Oxidation number of C-1 = -3
 Oxidation number of C-2 = +3

- 23.** Compounds in which elements are in higher oxidation states are unstable. So, they act as oxidizing agents. Here, Ag in AgF_2 is in unstable + 2 oxidation states.
- 24.** Alcohol will act as a solvent for toluene which is insoluble in aqueous medium.
- (a) $\text{C}_6\text{H}_5\text{CH}_3 + 2\text{KMnO}_4 \longrightarrow \text{C}_6\text{H}_5\text{COOH} + 2\text{MnO}_2 + 2\text{KOH}$
- (b) (i) $\text{H}_2\text{SO}_4 + \text{Cl}^- \longrightarrow \text{HCl} \uparrow + \text{HSO}_4^-$
(pungent smell)
- (ii) $\text{H}_2\text{SO}_4 + \text{Br}^- \longrightarrow \text{HBr} + \text{HSO}_4^-$
- $\text{H}_2\text{SO}_4 + 2\text{HBr} \longrightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
(OA)
- 25.** Higher the standard electrode potential, higher will be the reducing power.
- \therefore Increasing order of reducing power is $\text{K}^+ < \text{Mg}^{2+} < \text{Cr}^{3+} < \text{Hg}_2^{2+} < \text{Ag}^+$