

Question 20. Write four informations about the reaction:

 $(CN)_2(g) + 2OH^-(ag) \rightarrow CN^-(ag) + CNO^-(ag) + H_2O(l)$

Answer: Let x be the O.N. of C.

O.N. of C in cyanogen, $(CN)_2 = 2(x - 3) = 0$ or x = +3

O.N. of C in cyanide ion, $CN^- = x - 3 = -1$ or x = +2

O.N. of C in cyanate ion, CNO = x - 3 - 2 = -1 or x = +4

The four information about the reaction are:

- (i) The reaction involves decomposition of cyanogen, (CN)₂ in the alkaline medium to cyanide ion, CN and cyanate ion, CNO⁻.
- (ii) The O.N. of C decreases from +3 in $(CN)_2$ to +2 in CN^- ion and increases from +3 in $(CN)_2$ to +4 in CNO^- ion. Thus, cyanogen is simultaneously reduced to cyanide ion and oxidised to cyanate ion. (iii) It is an example of a redox reaction in general and a disproportionation reaction in particular.
- (iv) Cyanogen is a pseudohalogen (behaves like halogens) while cyanide ion is a pseudohalide ion (behaves like halide ion).

Question 21. The ${\rm Mn}^{3+}$ ion is unstable in solution and undergoes disproportionation to give ${\rm Mn}^{2+}$, ${\rm MnO}_2$ and ${\rm H}^+$ ion. Write a balanced ionic equation for the reaction.

Answer:

The skeletal equation is:

 $Mn^{3+}(aq) \longrightarrow Mn^{2+}(aq) + MnO_2(s) + H^+(aq).$

Oxidation half equation:

$$Mn^{3+}(aq) \longrightarrow MnO_2(s)$$

Balance O.N. by adding electrons,

 $Mn^{3+}(aq) \longrightarrow MnO_2(s) + e^{-}$

Balance charge by adding 4H+ ions,

$$Mn(aq) \longrightarrow MnO_2(s) + 4H^+(aq) + e^-$$

Balance O atoms by adding 2H₂O:

$$Mn(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + 4H^{\dagger}(aq) + e^{-}$$
 ...(i)

Reduction half equation:

$$\stackrel{+3}{\text{Mn}}^{3+} \longrightarrow \stackrel{+2}{\text{Mn}}^{2+}$$

Balance O.N. by adding electrons:

Mn³⁺(aq) +
$$e^- \longrightarrow \text{Mn}^{2+}(aq)$$
 ...(ii)

Adding Eq. (i) and Eq. (ii), the balanced equation for the disproportionation reaction is

$$2Mn^{3+}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + Mn^{2+}(aq) + 4H^+(aq)$$

Question 22. Consider the elements: Cs, Ne, I, F

- (a) Identify the element that exhibits -ve oxidation state.
- (b) Identify the element that exhibits +ve oxidation state.
- (c) Identify the element that exhibits both +ve and -ve oxidation states.
- (d) Identify the element which neither exhibits -ve nor +ve oxidation state.

Answer:

- (a) F. Fluorine being the most electronegative element shows only a -ve oxidation state of -1.
- (b) Cs. Alkali metals because of the presence of a single electron in the valence shell, exhibit an oxidation state of +1.
- (c) I. Because of the presence of seven electrons in the valence shell, I shows an oxidation state of -1 (in compounds of I with more electropositive elements such as H, Na, K, Ca, etc.) or an oxidation

state of +1 compounds of I with more electronegative elements, i.e., O, F, etc.) and because of the presence of d-orbitals it also exhibits +ve oxidation states of +3, +5 and +7.

(d) Ne. It is an inert gas (with high ionization enthalpy and high positive electron gain enthalpy) and hence it neither exhibits -ve nor +ve oxidation states.

Question 23. Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess chlorine is removed by treating with sulphur dioxide. Present a balanced equation for the reaction for this redox change taking place in water.

Answer: The skeletal equation is:

This represents the balanced redox reaction.

$$\begin{array}{c} \operatorname{Cl}_2(aq) + \operatorname{SO}_2(aq) + \operatorname{H}_2\mathrm{O}(l) &\longrightarrow \operatorname{Cl}^-(aq) + \operatorname{SO}_4^{2-}(aq) \\ \operatorname{Reduction\ half\ equation:} & \operatorname{Cl}_2(aq) &\longrightarrow \operatorname{Cl}^-(aq) \\ \\ \operatorname{Balance\ Cl\ atoms,} & \operatorname{Cl}_2(aq) &\longrightarrow \operatorname{2Cl}^-(aq) \\ \\ \operatorname{Balance\ O.N.\ by\ adding\ electrons:} & \operatorname{Cl}_2(aq) + 2e^- &\longrightarrow \operatorname{2Cl}^-(aq) \\ \\ \operatorname{Oxidation\ half\ equation:} & \overset{+6}{\operatorname{SO}_2(aq)} &\longrightarrow \overset{+6}{\operatorname{SO}_4^2}(aq) + 2e^- \\ \\ \operatorname{Balance\ O.N.\ by\ adding\ electrons:} & \operatorname{SO}_2(aq) &\longrightarrow \operatorname{SO}_4^{2-}(aq) + 2e^- \\ \\ \operatorname{Balance\ charge\ by\ adding\ 4H^+\ ions:} & \operatorname{SO}_2(aq) &\longrightarrow \operatorname{SO}_4^{2-}(aq) + 4H^+(aq) + 2e^- \\ \\ \operatorname{Balance\ O\ atoms\ by\ adding\ 2H}_2\mathrm{O}, & \operatorname{SO}_2(aq) + 2H_2\mathrm{O}(l) &\longrightarrow \operatorname{SO}_4^{2-}(aq) + 4H^+(aq) + 2e^- \\ \\ \operatorname{Adding\ Eq.\ (i)\ and\ Eq.\ (ii)\ , we\ have,} & \dots (ii) \\ \end{array}$$

Question 24. Refer to the periodic table given in your book and now answer the following questions.

- (a) Select the possible non-metals that can show disproportionation reaction.
- (b) Select three metals that show disproportionation reaction. Answer:

 $Cl_2(aq) + SO_2(aq) + 2H_2O(l) \longrightarrow 2Cl^-(aq) + SO_4^{2-}(aq) + 4H^+(aq)$

(a) The non-metals are:
$$P_4$$
, Cl_2 and S_8 .
(i) $P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$
(ii) $Cl_2(g) + 2OH^-(aq) \xrightarrow{cold} Cl^-(aq) + ClO^-(aq) + H_2O(l)$
or $3Cl_2(g) + 6OH^-(aq) \xrightarrow{hot} 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$
(iii) $S_8(s) + 12OH^- \longrightarrow 4S^{2-}(aq) + 2S_2O_3^{2-}(aq) + 6H_2O(l)$
(b) The metals are: Cu^+ , Ga^+ , In^+ , Mn^{3+} , etc.

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

$$3Ga^{+}(aq) \longrightarrow Ga^{3+}(aq) + 2\overset{0}{G}a(s)$$

$$3In^{+}(aq) \longrightarrow In^{3+}(aq) + 2\overset{0}{In}(s)$$

$$2\overset{3+}{Mn}(aq) + 2H_{2}O(l) \longrightarrow MnO_{2}(s) + Mn(aq) + 4H^{+}(aq)$$

Question 25. In Ostwald's process for the manufacture of nitric add, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum wight of nitric oxide that can be obtained starting only with 10.0 g of ammonia and 20.0 g of oxygen?

Answer: The balanced equation for the reaction is:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

 $4 \times 17 \qquad 5 \times 32 \qquad 4 \times 30$
 $= 68 g \qquad = 160 g \qquad = 120 g$

Here, 68 g of NH_3 will react will $O_2 = 160$ g

$$\therefore 10 \text{ g of NH}_3 \text{ will react with } O_2 = \frac{160 \text{ g}}{68g} \times 10g = 23.6 \text{ g}$$

But the amount of $\rm O_2$ which is actually available is 20.0 g which is less than the amount which is needed. Therefore, $\rm O_2$ is the limiting reagent and hence calculations must be based upon the amount of

 O_2 taken and not on the amount of NHz taken. From the equation, 160 g of O_2 produce NO = 120 g 20 g of O_2 will produce NO =120/160 x 20 = 15 g

Question 26. Using the standard electrode potentials given in the Table 8.1, predict if the reaction between the following is feasible:

- (a) Fe^{3+} (aq) and I-(aq)
- (b) Ag^{+} (aq) and Cu(s)
- (c) Fe^{3+} (aq) and Cu(s)
- (d) Ag(s) and $Fe^{3+}(ag)$
- (e) Br_2 (aq) and Fe^{3+} (aq).

Answer:

(a) It may be noted that for oxidation reactions, i.e., Eq. (i), the sign of the electrode potential as given in Table 8.1 is reversed. To get the equation for the overall reaction, the number of electrons lost in Eq. (i) and gained in Eq. (ii) must be cancelled. To do so, Eq. (ii) is multiplied by 2 and added to Eq. (i). Further, it may be noted that whenever any half reaction equation is multiplied by any integer, its electrode potential is not multiplied by that integer. Thus,

Overall reaction: $2Fe^{3+}$ (ag) + $2I^{-}$ (ag) $\rightarrow 2Fe^{2+}$ (ag) + I_{2} (s); E° = + 0.23

Since the EMF for the above reaction is positive, therefore, the above reaction is feasible.

(b) The possible reaction between $Ag^{+}(aq)$ and Cu(s) is Cu(s) + $2Aq^{+}$ (aq) $\rightarrow Cu^{2+}$ (aq) + 2Ag(s)

The above redox reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from Table 8.1, we have,

Oxidation: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-};$ $E^{\circ} = -0.34 \text{ V}$ $Ag^{+}(aq) + e^{-} \longrightarrow Ag(s) \times 2; \quad E^{\circ} = +0.80 \text{ V}$

Overall reaction: $Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$; $E^{\circ} = +0.46 \text{ V}$ Since the EMF of the above reaction comes out to be positive, therefore, the above

(c) Suppose the reaction between Fe3+(aq) and Cu(s) occurs according to the following equation.

 $Cu(s) + 2Fe^{3+}(aq) \longrightarrow 3Cu^{2+}(aq) + 2Fe^{2+}(aq)$

The above reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from Table 8.1, we have,

Cu(s) \longrightarrow Cu²⁺(aq) + 2e⁻; E° = -0.34 V Fe³⁺(aq) + e⁻ \longrightarrow Fe²⁺(aq)] × 2; E° = +0.77 V Oxidation: Reduction:

Overall reaction: $Cu(s) + 2Fe^{3+}(aq) \longrightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$; $E^{\circ} = +0.43 \text{ V}$ Since the EMF of the reaction is positive, therefore, the above reaction is feasible. Alternatively, if the reaction between Fe³⁺(aq) and Cu(s) occurs according to the following equation.

 $3Cu(s) + 2Fe^{3+}(aq) \longrightarrow 3Cu^{2+}(aq) + 2Fe(s)$

The EMF of the reaction comes out to be -ve, i.e., -0.376 V (-0.34 V -0.036 V) and hence this reaction is not feasible.

(d) Suppose the reaction between Ag(s) and Fe3+(aq) occurs according to the following equation:

 $Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^{+}(aq) + Fe^{2+}(aq)$

The above reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from Table 8.1, we have,

Oxidation: $Ag(s) \longrightarrow Ag^{+}(aq) + e^{-}; E^{\circ} = -0.80 \text{ V}$ $Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq); E^{\circ} = +0.77$ \rightarrow Fe²⁺(aq); E° = +0.77 V Reduction:

Overall reaction: $Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^{+}(aq) + Fe^{2+}(aq)$; $E^{\circ} = -0.03 \text{ V}$ Since the EMF of the reaction is negative, therefore, the above reaction is not feasible

Alternatively, the reaction between Ag(s) and Fe3+(aq) may occur according to the following equation

 $3Ag(s) + Fe^{3+}(aq) \longrightarrow 3Ag^{+}(aq) + Fe(s)$

On similar lines, we can calculate the e.m.f. of this reaction comes to be even more negative, i.e., -0.836 V, and hence this redox reaction is also not feasible.

(e) Suppose the reaction between Br₂(aq) and Fe²⁺(aq) occurs according to the

 \rightarrow 2Br⁻(aq) + 2Fe³⁺(aq) $Br_2(aq) + 2Fe^{2+}(aq) -$

The above reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from the Table **8.1,** we have **Oxidation:** $\operatorname{Fe}^{2^+}(aq) \longrightarrow \operatorname{Fe}^{3^+}(aq) + e^-] \times 2$; $\operatorname{E}^{\circ} = -0.77 \, \operatorname{V}$

Reduction: $Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq); E^\circ = +1.09 \text{ V}$

Overall reaction: $2\text{Fe}^{2+}(aq) + \text{Br}_2(aq) \longrightarrow 2\text{Fe}^{3+}(aq) + 2\text{Br}^-(aq)$; $\text{E}^\circ = +0.32 \text{ V}$ Since the EMF for the above reaction is positive, therefore, this reaction is feasible. Question 27. Predict the products of electrolysis in each of the folloxving:

- (i) An aqueous solution of AgNO₃ with silver electrodes.
- (ii) An aqueous solution of silver nitrate with platinum electrodes.
- (iii) A dilute solution of H₂SO₄with platinum electrodes.
- (iv) An aqueous solution of CuCl₂ with platinum electrodes.

Answer: (i) In aqueous solution, AgNO₃ ionises to give $Ag^+(aq)$ and $NO_3^-(aq)$ ions.

$$AgNO_3(aq) \rightarrow Ag^+(aq) + NO_3^-(aq)$$

Thus, when electricity is passed, $Ag^+(aq)$ ions move towards the cathode while NO_3^- ions move towards the anode. In other words, at the cathode, either $Ag^+(aq)$ ions or H_2O molecules may be reduced. Which of these will actually get discharged would depend upon their electrode potentials which are given below:

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s); E^{\circ} = +0.80 \text{ V ...(i)}$$

 $2H_{2}O(Z) + 2e^{-} \rightarrow H_{2}(g) + 2OH^{-}(aq); E^{\circ} = -0.83 \text{ V ...(ii)}$

Since the electrode potential (i.e., reduction potential of Ag⁺(aq) ions is higher than that of H₂O molecules, therefore, at the cathode,

it is the ${\rm Ag^+}({\rm aq})$ ions (rather than ${\rm H_2O}$ molecules) which are reduced.

Similarly, at the anode, either Ag metal of the anode or H_2O molecules may be oxidised. Their electrode potentials are:

$$Ag(s) \rightarrow Ag^{+}(aq) + e^{-}; E^{\circ} = -0.80 \text{ V ...(iii)}$$

$$2H_2O(1) \rightarrow O_2(g) + 4H + (aq) + 4e^-$$
; $E^\circ = -1.23 \text{ V ...(iv)}$

Since the oxidation potential of Ag is much higher than that of $\rm H_2O$, therefore.

at the anode, it is the Ag of the silver anode which gets oxidised and not the $\rm H_2O$ molecules. It may, however, be mentioned here that the oxidation potential of $\rm NO_3^-$ ions is even lower than that of $\rm H_2O$ since more bonds are to broken during reduction of $\rm NO_3$ ions than those in $\rm H_2O$.

Thus, when an aqueous solution of AgNO₃ is electrolysed, Ag from Ag anode dissolves while Ag⁺(aq) ions present in the solution get reduced and get deposited on the cathode.

(ii) If, however, electrolysis of $AgNO_3$ solution is carried out using platinum electrodes, instead of silver electrodes, oxidation of water occurs at the anode since Pt being a noble metal does not undergo oxidation easily. As a result, O_2 is liberated at the anode according to equation (iv).

Thus, when an aqueous solution of $AgNO_3$ is electrolysed using platinum electrodes, Ag^+ ions from the solution get deposited on the cathode while O_2 is liberated at the anode.

(iii) In aqueous solution, H_2SO_4 ionises to give $H^+(aq)$ and $SO_4^{2-}(aq)$ ions.

$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^-(aq)$$

Thus, when electricity is passed, H⁺ (aq) ions move towards cathode while $SO_4^{2^-}$ (aq) ions move towards anode. In other wode either H⁺(aq) ions or H₂O molecules are reduced. Their electrode potentials are:2H⁺(aq)2e⁻ \rightarrow H₂(q); E° = 0.0 V

$$H_2O(aq) + 2e^- \rightarrow H_2(g) + 2OH^-((aq); E^\circ = -0.83 \text{ V}$$

Since the electron potential (i.e., reduction potential) of H⁺(aq) ions is higher than that of H₂O, therefore, at the cathode, it is H⁺(aq) ions (rather than H₂O molecules) which are reduced to evolve H₂ gas. Similarly at the anode, either SO_4^{2-} (aq) ions or H₂O molecules are oxidised. Since the oxidation potential of SO_4 is expected to be much lower (since it involved cleavage of many bonds as

compared to those in H20) than that of H_2O molecules, therefore, at the anode, it is H_2O molecules (rather than SO_4^{2-} ions) which are oxidised to evolve O_2 gas.

From the above discussion, it follows that during electrolysis of an aqueous solution of H_2SO_4 only the electrolysis of H_2O occurs liberating H_2 at the cathode and O_2 at the anode.

(iv) In aqueous solution, CuCl₂ ionises as follows:

$$CuCl_2(aq) \rightarrow CU^{2+}(aq) + 2Cl^{-}(aq)$$

On passing electricity, $Cu^{2+}(aq)$ ions move towards cathode and $Cu^{2+}(aq)$ ions move towards anode.

Thus, at cathode, either ${\rm Cu}^{2+}({\rm aq})$ or ${\rm H}_2{\rm O}$ molecules are reduced. Their electrode potentials are:

$$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$$
; $E^{\circ} = +0.34 \text{ V}$

$$H_2O(1) + 2e^- \rightarrow H_2(g) + 2OH^-; E^\circ = -0.83 \text{ V}$$

Since the electrode potential of $Cu^{2+}(aq)$ ions is much higher than that of H_2O , therefore, at the cathode, it is $Cu^{2+}(aq)$ ions which are reduced and not H_2O molecules.

Similarly, at the anode, either ${\rm Cl}^{\text{-}}({\rm aq})$ ions or ${\rm H}_2{\rm O}$ molecules are oxidised. Their oxidation potentials

$$2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}; \Delta E^{\circ} = -1.36 \text{ V}$$

$$2H_2O(1) \rightarrow O_2(g) + 4H^+(aq) + 4e^-; \Delta E^\circ = -1.23 \text{ V}$$

Although oxidation potential of H₂O molecules is higher than that of

 ${\rm Cl}^-$ ions, nevertheless, oxidation of ${\rm Cl}^-$ (aq) ions occurs in preference to H₂O since due to overvoltage much lower potential than -1.36 V is needed for the oxidation of H₂O molecules.

Thus, when an aqueous solution of CuCl₂ is electrolysed, Cu metal is liberated at the cathode while Cl₂ gas is evolved at the anode.

Question 28. Arrange the following metals in the order in which they displace each other from the solution of their salts.Al, Cu, Fe, Mg and Zn.

Answer: It is based upon the relative positions of these metals in the activity series. The correct order is Mg, Al, Zn, Fe, Cu .

Question 29. Given the standard electrode potentials,

$$K^+/K = -2.93 \text{ V}, \text{Ag}^+/\text{Ag} = 0.80 \text{ V}, \text{Hg}^{2+}/\text{Hg} = 0.79 \text{ V}, \text{Mg}^{2+}/\text{Mg} = -2.37 \text{ V},$$

 $Cr^{3+}/Cr = -0.74$ V. Arrange these metals in increasing order of their reducing power.

Answer: Lower the electrode potential, better is the reducing agent. Since the electrode potentials increase in the oder; K^+/K (-2.93 V), Mg^{2+}/Mg (-2.37 V), Cr^{3+}/Cr (-0.74 V), Hg^{2+}/Hg (0.79 V), Ag^{+}/Ag (0.80 V), therefore, reducing power of metals decreases in the same order, i.e., K, Mg, Cr, Hg, Ag.

Question 30. Depict the galvanic cell in which the reaction, Zn(s) +

$$2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

takes place. Further show:

- (i) which of the electrode is negatively charged.
- (ii) the carriers of current in the cell and
- (iii) individual reaction at each electrode.

Answer: The given redox reaction is $Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$

Since Zn gets oxidised to Zn²⁺ ions, and Ag⁺ gets reduced to Ag metal, therefore,

oxidation occurs at the zinc electrode and reduction occurs at the silver electrode. Thus, galvanic cell corresponding to the above redox reaction may be depicted as:

$$Zn | Zn^{2+}(aq) \parallel Ag^{+}(aq) | Ag$$

- | Zn | Zn²⁺(aq) | Ag * (aq) | Ag (i) Since oxidation occurs at the zinc electrode, therefore, electrons accumulate on the zinc electrode and hence, zinc electrode is negatively charged.

 (ii) The ions carry current. The electrons flow from Zn to Ag electrode while the
- current flows from Ag to Zn electrode.

 (iii) The reactions occurring at the two electrodes are: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$ $Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$

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

 $Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$

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