

Redox Reactions

ANSWERS

- 1. Decomposition reaction
- 2. Salt bridge
- **3.** Oxygen difluoride (OF₂)

4. (b) : NH₄NO₃ may be rewritten as NH₄⁺NO₃⁻ In NH₄⁺, O. N. of N is : x + 4 = +1 *i.e.*, x = -3In NO₃⁻, O. N. of N is : x + (-6) = -1 *i.e.*, x = +5

5. (d) :

Peroxomonosulphuric acid (H_2SO_5) 1 + x + 2(-1) + 2(-2) + (-2) + 1 = 0 x = +6H - O - O - S = OH

6. (a) : E.M.F. = $E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = +0.80 - (-0.76) = 1.56 \text{ V}$ The maximum e.m.f. of the cell is obtained when the electrode potential of the anode is minimum and that of the cathode is maximum.

7. (a): $N_1V_1 = N_2V_2 \Rightarrow 0.08 \times 30 = N_2 \times 20$ (KMnO₄) (H₂O₂) $N_2 = 0.12$ N

Strength of H_2O_2 = Normality × eq. wt. of H_2O_2 = 0.12 × 17 = 2.04 gL⁻¹

8. (**b**) : Zn is more reactive than Ag and hence precipitates Ag from $AgNO_3$ solution. As Ag is less reactive than Zn, $ZnSO_4$ solution can be stirred with a silver spoon.

9. (a)

10. (a)

11. (b) : Fe is a stronger reducing agent than H_2 or E° of Fe is less than that of H_2 . Hence, liberates H_2 gas when Fe reacts with HCl.

12. (a)
13.
$$Cl_{2(g)}^{0} + 2OH_{(aq)}^{-} \longrightarrow ClO_{(aq)}^{-} + Cl_{(aq)}^{-1} + H_2O_{(f)}$$

Here, the Cl atom undergoes both oxidation +1 and reduction -1. Therefore, it is a disproportionation reaction.

14. (i)
$$F_2 + 2e^- \longrightarrow 2F^-$$
 (Oxidant)
 $BrO_3^- \longrightarrow BrO_4^- + 2e^-$ (Reductant)

(ii) $I_2 \longrightarrow NalO_3 + 5e^-$ (Reductant) NaClO₃ + 5 $e^- \longrightarrow Cl_2$ (Oxidant)

15. Oxidation number of Cl in HClO \Rightarrow 1 + x - 2 = 0 or x = +1 ClO₄⁻ \Rightarrow x + 4 (-2) = -1 or x = +7 CaOCl₂ \Rightarrow +2 + (-2) + 2x = 0 or x = 0 ClO₂ \Rightarrow x + 2 (-2) = 0 or x = +4

OR

(a) Na₂S₂O₃ Structure of Na₂S₂O₃ is

The oxidation state of S¹ is -2. Let oxidation state of S² be x. $2 \times (+1) + 3(-2) + x + 1 \times (-2) = 0$ (For Na) (For O) (For coordinate S)

$$+2-6+x-2=0$$

 $x = +6$

Thus, the oxidation states of two S atoms in $\rm Na_2S_2O_3$ are -2 and +6.

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 $S_{(3)} = 0$

 $S_{(4)} = +5$

(b)
$$Na_2S_4O_6$$

From the left, $S_{(1)} = (-2 + (-2) + (-2) + (+1) = +5$ $S_{(2)} = 0$

(c) Na_2SO_3 $2 \times (+1) + x + 3 (-2) = 0$ x = +4(d) Na_2SO_4 +2 + x + (-8) = 0

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16. We rewrite the two equation in the reduction form $Sn_{(eq)}^{2+} + 2e^{-} \longrightarrow Sn_{(s)}$; $E^{\circ} = -0.14 \text{ V}$

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$$Ag^{+}_{(eq)} + e^{-} \longrightarrow Ag_{(s)}; \qquad E^{\circ} = +0.80 \text{ V}$$
$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = 0.80 - (-0.14) = +0.94 \text{ V}$$

17. E° value of Fe²⁺/Fe (- 0.44 V) is lower than that of Ag⁺ / Ag (+ 0.80 V) electrode, therefore, Ag⁺ gets reduced and Fe gets oxidised. As a result, concentration of Ag⁺ ions decrease while that of NO₃⁻ ions remains unchanged.

 $2Ag^+_{(aq)} + Fe_{(s)} \longrightarrow 2Ag_{(s)} + Fe^{2+}_{(aq)}$

18. Element (D) is the strongest oxidising agent since its electrode potential is the highest while element A is the strongest reducing agent since its electrode potential is the lowest.

19. The given representation is wrong Mg^{2+}/Mg electrode with lower E° value will act as anode and Zn^{2+}/Zn electrode with higher E° value will act as cathode.

The correct representation is: Mg | Mg^{2+} (1M) || Zn^{2+} (1M) | Zn

OR

(a) (i) $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Galvanic cell corresponding to the above redox reaction may be depicted as :

Zn|Zn²⁺_(aq) (1 M) ||Cu²⁺_(aq) (1 M) |Cu

(ii) The two half-cells reactions are,

 $Zn \longrightarrow Zn^{2+} + 2e^{-}$

(oxidation-half reaction at anode)

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

(reduction-half reaction at cathode) Therefore, Zn acts as anode while Cu acts as cathode.

20. $2K_2Cr_2O_7 + 3Sn + 28HCI \longrightarrow 4KCI + 4CrCl_3 + 3SnCl_4 + 14H_2O$

 2×294 3×118.7 (M. M. of K₂Cr₂O₇ = 294 = 588 g = 356.1g and At. wt. of Sn = 118.7)

356.1 g Sn react with $K_2Cr_2O_7 = 588$ g

1 g Sn react with
$$K_2Cr_2O_7 = \frac{588}{356.1} = 1.65g$$

Eq. wt of $K_2Cr_2O_7 = \frac{Mol.wt}{6} = \frac{294}{6} = 49$

A decinormal $K_2Cr_2O_7$ solution means 1000 mL. Solution contains 4.9 g $K_2Cr_2O_7$ *i.e.,* 4.9 g $K_2Cr_2O_7$ present in 1000 mL solution

 \therefore 1.65 g K₂Cr₂O₇ will be present in

$$=\frac{1000}{4.9}$$
 × 1.65 = 336.7 mL

21. $\operatorname{Cr}_2\operatorname{O}_7^{2-} + \operatorname{6S}_2\operatorname{O}_3^{2-} + 14\operatorname{H}^+ \to 2\operatorname{Cr}^{3+} + 3\operatorname{S}_4\operatorname{O}_6^{2-} + 7\operatorname{H}_2\operatorname{O}$ $\frac{M_1V_1}{n_1}(\operatorname{Cr}_2\operatorname{O}_7^{2-}) = \frac{M_2V_2}{n_2}(\operatorname{S}_2\operatorname{O}_3^{2-}) \Longrightarrow \frac{M_1 \times 2\operatorname{O}}{1} = \frac{1 \times 16}{25 \times 6}$

$$M_{1} = \frac{16}{6 \times 25 \times 20} \mod L^{-1}$$

Conc. of K₂Cr₂O₇ in g/L⁻¹ = $\frac{16 \times 294}{6 \times 25 \times 20} = 1.568$ g

22. (i) $3HCI + HNO_3 \longrightarrow CI_2 + NOCI + 2H_2O$

O.N. of N decreases from 5 to 3 and O.N. of Cl increases from -1 to 0.

HNO₃ is oxidising agent and HCl is reducing agent.

(ii)
$$\underset{\text{HgCl}_2}{\overset{+2}{}} + \underset{2\text{Kl}}{\overset{+1-1}{}} \xrightarrow{\overset{+2}{}} \underset{\text{Hgl}_2}{\overset{+2}{}} + \underset{2\text{KC}}{\overset{+1-1}{}}$$

No change in oxidation number. So it is not a redox reaction.

(iii)
$$Fe_2O_3^{-2} + 3CO \xrightarrow{A} 2Fe + 3CO_2^{-2}$$

O.N. of Fe decreases from +3 to 0 hence, Fe₂O₃ is oxidising agent. O.N. of C increases from +2 to +4 hence, CO is reducing agent.

OR

(i)
$$+3-1 + 1-2 + 1-1 + 1+3-2$$

 $PCl_3 + 3H_2O \longrightarrow 3HCl + H_3PO_3$

No change in oxidation number. So, it is not a redox reaction.

(ii)
$$-3 + 1 = 0 = 0 + 1 - 2$$

 $4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$

O.N. of N increases from -3 to 0 hence, NH₃ acts as a reducing agent. O.N. of O decreases from 0 to -2 hence, O₂ acts as an oxidising agent.

(iii)
$$Cl_2 + 2OH^- \longrightarrow ClO^- + Cl^- + H_2O$$

Oxidation number of Cl increase from 0 to +1. Hence Cl₂ act as reducing agent oxidation number of Cl decrease from 0 to -1. Hence Cl₂ act as oxidising agent.

23. The balanced redox reactions involving oxidation of Fe²⁺ ions by $Cr_2O_{7(aq)}^{2-}$ and $MnO_{4(aq)}^{-}$ respectively are :

$$Cr_{2}O_{7}^{2-} + 6Fe^{2+} + 14H^{+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_{2}O$$

$$MnO_{4}^{-} + 5Fe^{2+} + 8H^{+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_{2}O$$

$$\frac{M_{1}V_{1}}{n_{1}}(Cr_{2}O_{7}^{2-}) = \frac{M_{2}V_{2}}{n_{2}}(Fe^{2+})$$

Here, we suppose V_2 cm³ of M_2 Fe²⁺ is titrated against 24.50 cm³ of 0.1 M Cr₂O₇²⁻ and V_1 cm³ of 0.1 M MnO₄⁻ solution. $\frac{24.5 \times 0.1}{1} (Cr_2O_7^{2-}) = \frac{M_2V_2}{6} (Fe^{2+}) ...(i)$

$$\frac{V_1 \times 0.1}{1} (MnO_4^{-}) = \frac{M_2 V_2}{5} (Fe^{2+}) \qquad ...(ii)$$

On equating eq. (i) and (ii), $V_1 = 24.5 \times \frac{6}{5} = 29.4 \text{ cm}^3$ **24.** The Cu⁺ undergoes disproportionation to form Cu²⁺ and Cu. $2Cu^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

Thus, Cu^+ or Cu_2O acts as both oxidant as well as reductant.

- (i) When heated in air, Cu₂O is oxidised to CuO $\begin{array}{c} +1+2 & 0 \\ Cu_2O + 1/2O_2 \longrightarrow 2CuO \\ i.e., Cu_2O \text{ acts as a reductant and reduces } O_2 \text{ to } O^{2-}. \end{array}$
- (ii) When heated with Cu_2S , it oxidises S^{2-} to SO_2 and hence Cu_2O act as an oxidant. $\begin{array}{c} +1-2 & +1-2 \\ 2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2 \end{array}$
- Cu₂O is reduced to Cu.

25. (i)
$$Z_{n}^{0} + H^{+} + NO_{3}^{-} \longrightarrow Z_{n}^{2+} + NH_{4}^{-3+1} + H_{2}^{+1-2}$$

$$\xrightarrow{Oxidation} \\ Z_{n}^{0} + HNO_{3} \longrightarrow Z_{n}^{2+} + NH_{4}^{+} + H_{2}O$$

$$Zn \longrightarrow Zn^{2+} + 2e^{-} \times 4 \xrightarrow{\text{Reduction}} 10H^{+} + NO_{3}^{-} + 8e^{-} \longrightarrow NH_{4}^{+} + 3H_{2}O$$
$$4Zn + NO_{3}^{-} + 10H^{+} \longrightarrow 4Zn^{2+} + NH_{4}^{+} + 3H_{2}O$$

(ii)
$$l_2^{0} + s_2^{0} 0_3^{2-} \longrightarrow l^- + s_4^{+2.5} 0_6^{2-}$$

Total decrease in O.N. =
$$0.5 \times 4 =$$

To equalise O.N. multiply
$$S_2O_3^{2-}$$
 and Γ by 2
 $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

(i) $H_2S + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + S$ Oxidation half reaction:

 $H_2S \longrightarrow 2H^+ + S + 2e^-$

Reduction half reaction: $Fe^{3+} + e^- \longrightarrow Fe^{2+}$...(ii)

Multiplying equation (ii) by 2 and adding it to equation (i), we have

$$\begin{array}{l} H_2S + 2Fe^{3+} \longrightarrow 2Fe^{2+} + 2H^+ + S \\ (ii) \quad C_{1_2}^0 \longrightarrow C_{1^-}^{-1} \qquad (Reduction half-reaction) \\ C_{1_2} + 2e^- \longrightarrow 2CI^- \qquad \dots (i) \\ B_r^{+5}O_3^- \longrightarrow B_r^{+7}O_4^{--} \qquad (Oxidation half-reaction) \end{array}$$

$$BrO_3^- \longrightarrow BrO_4^-$$
 (Oxidation half-reaction
 $BrO_3^- \longrightarrow BrO_4^- + 2e^-$

$$BrO_{3}^{-} + 2OH^{-} \longrightarrow BrO_{4}^{-} + 2e^{-} + H_{2}O \qquad ...(ii)$$

Adding (i) and (ii)
$$Cl_{2} + BrO_{3}^{-} + 2OH^{-} \longrightarrow BrO_{4}^{-} + 2Cl^{-} + H_{2}O$$

26. (i) In this redox reaction, H in LiAlH₄ gets oxidised because of the addition of oxygen atom that leads to the formation of OH⁻. Propan-2-ol (CH₃COCH₃) gets reduced because of addition of hydrogen atom to propan-2-ol (CH₃CH(OH)CH₃).

(ii) This is not a redox reaction as neither hydrogen or oxygen or e^- is removed or added.

(iii) This is not a redox reaction as neither hydrogen or oxygen or e^- is removed or added.

27. (a)
$$Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

(b) Zn | ZnSO₄(1M) || CuSO₄(1M)|Cu

(c) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.34 - (-0.76) = 1.1 \text{ V}$

(d) Zn electrode will act as anode as oxidation takes place in the electrode. Cu electrode will act as the cathode as reduction takes place in this electrode.

(e) The direction of electrons flow is from anode to cathode *i.e.*, from Zn electrode to copper electrode. The direction of current flow is from cathode to anode *i.e.*, from Cu electrode to Zn electrode.

OR

(a) A reaction in which a particular species simultaneously gets oxidised and reduced, is known as disproportionation reaction.

e.g.,
$$H_{g_2}^{\dagger}Cl_2 \longrightarrow H_{g_2}^{0}H_{g_2}^{\dagger}H_{g_2}^{\dagger}Cl_2$$

In this reaction, Hg₂Cl₂ is getting oxidised to HgCl₂ and also getting reduced to Hg.

(b) **Step 1** : The skeletal ionic equation is

$$\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-}_{(aq)} + \operatorname{SO}_{3}^{2-}_{(aq)} \longrightarrow \operatorname{Cr}_{(aq)}^{3+} + \operatorname{SO}_{4}^{2-}_{(aq)}$$

Step 2 : Assign oxidation numbers for Cr and S

$$\operatorname{Cr}_{2}^{+\circ} \operatorname{Or}_{7}^{2-}_{(aq)} + \operatorname{SO}_{3}^{+\circ}_{(aq)} \longrightarrow \operatorname{Cr}^{+3}_{(aq)} + \operatorname{SO}_{4}^{+\circ} \operatorname{Or}_{4}^{2-}_{(aq)}$$

This indicates that the dichromate ion is the oxidant and the sulphite ion is the reductant.

Step 3 : Calculate the increase and decrease of oxidation number, and make them equal :

$$\overset{+6}{\text{Cr}_{2}^{0}\text{C}_{7}^{2-}}_{(aq)} + \overset{+4-2}{3\text{SO}_{3}^{2-}}_{(aq)} \longrightarrow 2\text{Cr}^{3+}_{(aq)} \overset{+6-2}{+} \overset{-2}{3\text{SO}_{4}^{2-}}_{(aq)}$$

...(i)

Step 4 : As the reaction occurs in the acidic medium, and further the ionic charges are not equal on both the sides, add $8H^+$ on the left to make ionic charges equal.

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+ \longrightarrow 2Cr_{(aq)}^{3+} + 3SO_4^{2-}(aq)$$

Step 5: Finally, count the hydrogen atoms, and add appropriate number of water molecules (*i.e.*, 4H₂O) on the right to achieve balanced redox change.

$$\operatorname{Cr}_2\operatorname{O}_{7(aq)}^{2-} + \operatorname{3SO}_{3(aq)}^{2-} + \operatorname{8H}_{(aq)}^+ \longrightarrow \operatorname{2Cr}_{(aq)}^{3+} + \operatorname{3SO}_{4(aq)}^{2-} + \operatorname{4H}_2\operatorname{O}_{(l)}$$

(c) Skeleton equation :

$$^{+7}_{MnO_{4}^{-2}} + ^{+4-2}_{SO_{2}} \longrightarrow ^{+2}_{Mn} ^{2+} + ^{+1+6-2}_{HSO_{4}^{-}}$$

Oxidation half : SO₂ \longrightarrow HSO₄
Reduction half : MnO₄⁻ \longrightarrow Mn²⁺
Oxidation half :
SO₂ \longrightarrow HSO₄⁻ + 2e⁻
(Add 2H₂O molecules to balance O atoms)

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 $SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2e^-$...(i) Reduction half : $MnO_4^- + 5e^- \longrightarrow Mn^{2+}$ (Add $4H_2O$ molecules to balance O atoms and H atoms)

 $MnO_{4}^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O$

Overall reaction, adding eq. (i) \times 5, eq. (ii) \times 2, Now $2MnO_4^- + 5SO_2 + 2H_2O + H^+ \rightarrow 5HSO_4^- + 2Mn^{2+}$...(ii)

28. (a) The potential difference set up between the metal and its own ions in the solution is called electrode potential. In general, it is the tendency of an electrode to gain or lose electrons.

(b) Smaller the reduction potential, more easily the substance is oxidised and hence acts as a strong reducing agent. Therefore, order of increasing reducing power will be Ag < Mg < K.

(c)
$$E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Ag^{+}/Ag} = -0.46$$
 ...(i)

$$E^{\circ}_{Cu}^{2+}/_{Cu} - E^{\circ}_{Zn}^{2+}/_{Zn} = 1.10$$
 ...(ii)

Subtracting eq. (i) from eq. (ii) we get

 $E^{\circ}_{cell} = E^{\circ}_{Ag^+, Ag} - E^{\circ}_{Zn^{2+}, Zn} = 1.10 - (-0.46) = 1.56 \text{ V}$ The E° value for the cell Zn/Zn²⁺(1M) || Ag⁺(1M) | Ag is 1.56 V.

OR

(a) EMF of a cell is used to predict the spontaneity of a redox reaction. If the EMF comes out to be positive, the reaction takes place, and if the EMF comes out to be negative, the reaction will not take place.

(b) $Zn_{(s)} + H_2SO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + H_{2(g)}$

The cell is represented as :

 $Zn_{(s)} | Zn^{2+}_{(aq)} || H^{+}_{(aq)} | H_{2(g)} (Pt_{(s)})$

 $E_{\text{cell}}^{\circ} = E_{\text{H}^+/\text{H}_2}^{\circ} - E_{\text{Zn}^2+/\text{Zn}}^{\circ} = 0 - (-0.76) = +0.76 \text{ V}$

Now, the E_{cell}° is positive, hence the reaction takes place. Yes, zinc on reaction with 1M sulphuric acid will liberate hydrogen gas.

(c) $E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Ni}^{+2}/\text{Ni}}^{\circ} = 0.34 \text{ V} - (-0.25 \text{ V}) = 0.59 \text{ V}$ Hence, E_{cell}° comes out to be positive. The reaction will take place. Therefore, CuSO₄ solution cannot be stored in a nickel vessel.

29. (a) The arrangement of various elements in order of their increasing reduction potential (with respect to standard hydrogen electrode) is called electrochemical series. We can

compare the relative activity of elements by this series because activity can be compared in terms of oxidation potential.

The redox reaction of an electrochemical cell is feasible if EMF of the cell is positive. If the EMF comes out to be negative then the reverse reaction would be feasible.

(b) Reduction half :
$$Zn^{2+} + 2e^{-} \longrightarrow Zn$$

Oxidation half : $Cd \longrightarrow Cd^{2+} + 2e^{-}$
 $E_{cell}^{\circ} = E_{Zn/Zn^{2+}}^{\circ} - E_{Cd^{2+}/Cd}^{\circ} = 0.763 - 0.403 = 0.36 \text{ V}$
OR

(a) Electrode potential is defined as the tendency of an electrode to either lose or gain electrons *i.e.*, tendency to get either oxidised or reduced when it is in contact with a solution of its own ions is known as electrode potential.

We can determine the reducing power of an element by electrode potential. If a substance has

- (i) a negative E° , it is stronger reducing agent than H₂.
- (ii) a positive E° , it is stronger oxidising agent than H₂.

(b) Mg^{2+}/Mg electrode has lower potential it act as anode and Al^{3+}/Al electrode has higher potential it act as cathode. The cell reaction is : $3Mg + 2Al^{3+} \longrightarrow 3Mg^{2+} + 2Al$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -1.66 - (-2.36) = +0.70 \text{ V}$$

30. (i) The electrode with higher reduction potential has a strong tendency to gain electrons and hence acts as the cathode while the electrode with lower reduction potential has a strong tendency to set oxidised and hence acts as the anode. Cr with lower electrode potential ($E^{\circ} = -0.74 \text{ V}$) acts as the anode while Fe with higher electrode potential ($E^{\circ} = -0.74 \text{ V}$) acts as the cathode.

(ii)
$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$$

= -0.44 - (-0.74) = +0.30 V
(iii) $2Cr_{co} + 3Fe^{2+} \longrightarrow 2Cr_{co}^{3+} + 3Fe^{2+}$

(iii) $2Cr_{(s)} + 3Fe_{(aq)}^{2+} \longrightarrow 2Cr_{(aq)}^{3+} + 3Fe_{(s)}$ $Cr_{(s)} | Cr_{(1M)}^{3+} || Fe_{(1M)}^{2+} | Fe_{(s)}$

(iv)
$$Cr_{(s)} \longrightarrow Cr_{(aq)}^{3+} + 3e^{-}$$
 (Oxidation)
 $Fe_{(aq)}^{2+} + 2e^{-} \longrightarrow Fe_{(s)}$ (Reduction)

(v)
$$E_{\text{cell}}^{\circ} = -0.036 - (-0.74) = +0.704 \text{ V}$$

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