SOLUTION DPP–6

Electrolytic Cell (Qualitative)

Chapter: Electrochemistry

TYPE–1 : Products of Electrolysis

Solution 1

Explanation

Fused CaH_2 contains Ca^{2+} and H^- ions. During electrolysis, H^- (anion) migrates to the anode and gets oxidised: $2\,H^- \longrightarrow H_2 + 2\,e^-$. So hydrogen is produced at the **anode**.

Approach

Trick question! Normally we associate H_2 with the cathode (from H^+ reduction). But here hydrogen is present as H^- (hydride) — it's an anion, like Cl^-. Anions always go to anode. Think: "Negative guests always go to the positive party (anode)."

Answer

(2) Anode

Solution 2

Explanation

Na_2SO_4 (aq) with inert electrodes: Na^+ and ${SO_4}^{2-}$ won't discharge because water is easier to electrolyse. At cathode: $2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$. At anode: $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$. Products: Cathode = H_2, Anode = O_2.

Approach

Na^+ is too lazy to get reduced (very negative $E°$), and ${SO_4}^{2-}$ is too stable to get oxidised. So water does all the work at both electrodes — like when the boss and manager both skip work, the intern (water) handles everything!

Answer

(4) H_2, O_2

Solution 3

Explanation

H_2 at cathode means H^+/H_2O is reduced (not the metal cation). Cl_2 at anode means Cl^- is oxidised. This combination is possible only with NaCl (aq) — Na^+ won't reduce in water, and Cl^- is present to give Cl_2.

Approach

Cathode gives H_2 ⇒ metal cation is too strong to reduce (like Na). Anode gives Cl_2 ⇒ Cl^- must be present. Only NaCl(aq) ticks both boxes. $CuCl_2$ would deposit Cu at cathode, not H_2.

Answer

(3) NaCl (aq.)

Solution 4

Explanation

NaBr (aq) with inert electrodes: Na^+ won't reduce (water reduces instead giving H_2). Br^- is easier to oxidise than water, so Br_2 forms at anode. The leftover Na^+ and OH^- give NaOH in solution.

Approach

Na^+ is a couch potato — refuses to get reduced. Water steps in to give H_2 at cathode. But Br^- is an eager volunteer at anode (halides except F^- are easy to oxidise). Remaining ions form NaOH. This is actually how the chlor-alkali process works!

Answer

(3) H_2, Br_2 and NaOH

Solution 5

Explanation

Metals with very negative $E°$ values (Na, K, Ca, Al, Mg) cannot be deposited from aqueous solutions because water gets reduced first. Ca ($E° = -2.87$ V) falls in this category. Cu, Cr, Ag all have sufficiently positive $E°$ to deposit from aqueous solution.

Approach

Imagine a queue at a bank. Water is always standing in line. If the metal is "more desperate" than water (more negative $E°$), water cuts in and gets reduced first. Ca is way more desperate than water, so it never gets its turn. Cu, Cr, Ag are chill enough to get their turn.

Answer

(4) Ca

Solution 6

Explanation

Same as Q2. Na_2SO_4 (aq) with inert electrodes: water electrolyses at both electrodes. Anode = O_2, Cathode = H_2. (Note: this question asks anode first, then cathode.)

Approach

Same logic as Q2 — the intern (water) does all the work. Just be careful with the order asked: anode product first, then cathode.

Answer

(1) O_2, H_2

Solution 7

Explanation

Dilute H_2SO_4: At anode, water is oxidised to give O_2. At cathode, H^+ ions are reduced to give H_2. ${SO_4}^{2-}$ is too stable to discharge. Order asked: anode then cathode.

Approach

Dilute acid = lots of water + some H^+ and ${SO_4}^{2-}$. Sulphate is the "untouchable" ion — never gets discharged in dilute solution. So anode = O_2 (from water), cathode = H_2 (from H^+).

Answer

(3) O_2, H_2

TYPE–2 : pH Change During Electrolysis

Solution 8

Explanation

KCl (aq) electrolysis: Cathode produces H_2 and OH^- (from water reduction). Anode produces Cl_2 (from Cl^- oxidation). Net effect: OH^- accumulates in solution ⇒ pH increases above 7.

Approach

Think of it like removing acid-makers (Cl^- leaves as Cl_2) while adding base-makers (OH^- from cathode). The solution becomes more and more basic — like a party where all the troublemakers leave and only the calm people remain.

Answer

(1) pH > 7

Solution 9

Explanation

KBr (aq) with Pt electrodes: Cathode reduces water → $H_2 + OH^-$. Anode oxidises Br^- → Br_2. Net result: KOH forms in solution, making it basic. pH > 7.

Approach

Same logic as KCl. Halide leaves at anode, OH^- builds up at cathode. Solution turns basic. Remember: whenever a halide salt (except HF type) is electrolysed, pH goes up!

Answer

(1) pH > 7

Solution 10

Explanation

Dilute HNO_3: NO_3^- is very stable and won't discharge. At cathode: $2\,H^+ + 2\,e^- \longrightarrow H_2$. At anode: $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$. So O_2 is formed at anode.

Approach

NO_3^- is the "VIP ion" — sits comfortably and never participates. It's too stable. Water takes over at anode to give O_2, and H^+ takes over at cathode to give H_2.

Answer

(2) O_2 gas is formed at anode

Solution 11

Explanation

pH increases near an electrode ⇒ OH^- is produced there ⇒ this happens at the cathode when water is reduced: $2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$. This occurs when the metal cation gets deposited instead of H^+ being reduced. In $CuCl_2$, Cu^{2+} deposits at cathode while water still produces some OH^-. But more importantly, in KCl, K^+ won't deposit so water reduction dominates, producing large amounts of OH^-.

Approach

Which solution makes pH go up near an electrode? We need OH^- production at cathode. In KCl, the cathode reaction is purely water reduction → massive OH^- production. In $CuCl_2$, Cu deposits and consumes the cathode's attention, less OH^- forms.

Answer

(1) KCl

Solution 12

Explanation

$CuSO_4$ (aq) electrolysis with inert electrodes: At cathode, Cu^{2+} deposits (not water). At anode, water is oxidised: $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$. H^+ ions accumulate ⇒ pH decreases.

Approach

Cathode: Cu^{2+} happily deposits (no OH^- produced). Anode: water breaks down and dumps H^+ into solution. More H^+ = lower pH. It's like someone adding lemon juice to the solution from the anode side!

Answer

(2) A decrease in pH

TYPE–3 : Electrode Behaviour & Special Cases

Solution 13

Explanation

If the anode is removed, there is no electrode to complete the circuit. Without a complete circuit, no current flows. However, ions that were already moving due to the electric field will continue moving briefly due to inertia before coming to rest. So current flows for a short time.

Approach

Think of it like a conveyor belt carrying boxes (ions). If you suddenly remove one end of the belt (anode), the boxes already on the belt keep sliding for a moment before stopping. The "current" continues briefly due to momentum of the already-moving ions.

Answer

(3) Current will continue to flow for sometime

Solution 14

Explanation

At Hg cathode, the overpotential for H_2 evolution is very high. This means more voltage is needed to reduce H^+ at mercury surface compared to Pt. Since H^+ reduction becomes difficult, Na^+ gets reduced instead and dissolves in Hg forming sodium amalgam.

Approach

Imagine two doors to exit a building. At Pt cathode, the "H_2 door" opens easily, so hydrogen escapes first. At Hg cathode, the "H_2 door" is jammed (high overpotential) — so sodium has no choice but to take the other exit and dissolve into mercury. The mercury makes hydrogen's life harder!

Answer

(2) More voltage is required to reduce H^+ at Hg than at Pt

TYPE–4 : Concentrated Acid Electrolysis

Solution 15

Explanation

50% concentrated H_2SO_4: At high concentration, ${SO_4}^{2-}$ ions can get oxidised at the anode instead of water. The reaction is: $2\,{SO_4}^{2-} \longrightarrow {S_2O_8}^{2-} + 2\,e^-$. This produces the peroxodisulphate ion (${S_2O_8}^{2-}$).

Approach

In dilute acid, sulphate is the "lazy ion" that never participates. But when concentration is high (50%), there are SO many sulphate ions crowding the anode that they finally get forced to react — like a shy person who gets pushed onto the dance floor when the room is too crowded. They combine to form ${S_2O_8}^{2-}$.

Answer

(3) $S_2O_8{}^{2-}$

Solution 16

Explanation

Concentrated H_2SO_4 electrolysis at anode: Same concept as Q15. $SO_4{}^{2-}$ ions get oxidised at anode to form peroxodisulphic acid ($H_2S_2O_8$): $2\,SO_4{}^{2-} \longrightarrow S_2O_8{}^{2-} + 2\,e^-$, which combines with H^+ to give $H_2S_2O_8$.

Approach

Concentrated = sulphate ions finally participate. Marshall's acid ($H_2S_2O_8$) forms. This is actually how $H_2S_2O_8$ is industrially manufactured — by electrolysis of concentrated H_2SO_4!

Answer

(4) $H_2S_2O_8$