

CHAPTER 10 REVIEW

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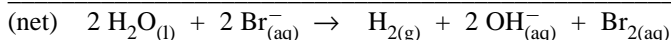
Understanding Concepts

- Electrolysis is the forcing of a possible but nonspontaneous oxidation–reduction reaction by the application of a potential difference from an outside power source.
 - Oxidation (electron loss) occurs at the anode; reduction (electron gain) occurs at the cathode.
 - In electrolysis of molten compounds, water is not present and there are fewer oxidizing agents and reducing agents present (often only one of each). The temperature is usually very high, making container and electrode selection more difficult because they must be able to withstand the temperature conditions. In all other aspects, the process is similar to electrolysis with aqueous electrolytes.
- In both types of cells, the strongest oxidizing agent present undergoes a reduction at the cathode and the strongest reducing agent present undergoes an oxidation at the anode. Both the electrons and ions move in the same direction in electrolytic and galvanic cells.

The major difference between galvanic cells and electrolytic cells is that the most likely redox reaction in electrolytic cells is not spontaneous; thus, the reaction must be driven by the application of potential difference (voltage) from an outside power supply. Electrolytic cells have a negative cell potential and galvanic cells have a positive cell potential. By convention, the positive/negative designation of the electrodes differs as well; in electrolytic cells, the cathode is designated negative and the anode positive. In galvanic cells, the cathode is designated positive and the anode negative.

- Nonspontaneous reaction — external voltage required.
 - Spontaneous reaction — no external voltage required.
 - Spontaneous reaction — no external voltage required.
 - Nonspontaneous reaction — external voltage required.
- $\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode})$
 - $\Delta E^\circ = [(-0.45) - (+0.77)] \text{ V} = -1.22 \text{ V}$
 The minimum potential difference that must be applied to cause a reaction is 1.22 V.
 - $\Delta E^\circ = [(0.00) - (+0.80)] \text{ V} = -0.80 \text{ V}$
 The minimum potential difference that must be applied to cause a reaction is 0.80 V.
 - $\Delta E^\circ = [(-0.14) - (-0.14)] \text{ V} = 0.00 \text{ V}$
 Any potential difference applied will cause tin to dissolve at the anode and to plate out at the cathode, but there is no net chemical reaction. $\Delta E^\circ = 0.00 \text{ V}$ for this cell.

- (cathode) $2 \text{H}_2\text{O}_{(l)} + 2 \text{e}^- \rightarrow \text{H}_{2(g)} + 2 \text{OH}_{(aq)}^-$ $E_r^\circ = -0.83 \text{ V}$
 (anode) $2 \text{Br}_{(aq)}^- \rightarrow \text{Br}_{2(aq)} + 2 \text{e}^-$ $E_r^\circ = +1.07 \text{ V}$

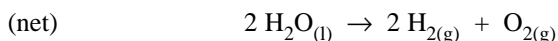


$$\begin{aligned} \Delta E^\circ &= E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\ &= -0.83 \text{ V} - (+1.07 \text{ V}) \end{aligned}$$

$$\Delta E^\circ = -1.90 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 1.90 V.

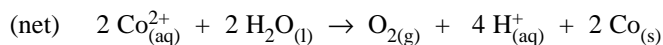
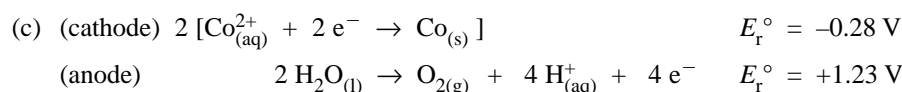
- (cathode) $2 [2 \text{H}_2\text{O}_{(l)} + 2 \text{e}^- \rightarrow \text{H}_{2(g)} + 2 \text{OH}_{(aq)}^-]$ $E_r^\circ = -0.83 \text{ V}$
 (anode) $4 \text{OH}_{(aq)}^- \rightarrow \text{O}_{2(g)} + 2 \text{H}_2\text{O}_{(l)} + 4 \text{e}^-$ $E_r^\circ = +0.40 \text{ V}$



$$\begin{aligned} \Delta E^\circ &= E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\ &= -0.83 \text{ V} - (+0.40 \text{ V}) \end{aligned}$$

$$\Delta E^\circ = -1.23 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 1.23 V.

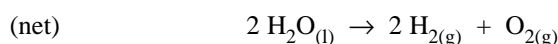
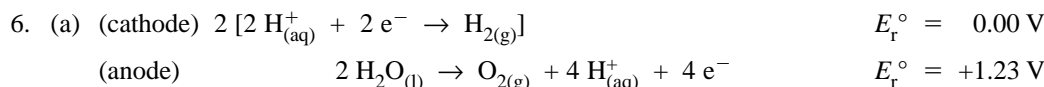


$$\begin{aligned}
 \Delta E^{\circ} &= E_{\text{r}}^{\circ} (\text{cathode}) - E_{\text{r}}^{\circ} (\text{anode}) \\
 &= -0.28 \text{ V} - (+1.23 \text{ V})
 \end{aligned}$$

$$\Delta E^{\circ} = -1.51 \text{ V}$$

Note: If the voltage is slightly higher (1.64 V), the anode product will be predominantly chlorine, because the Cl^- ion oxidation is *very* much faster than that of H_2O molecules.

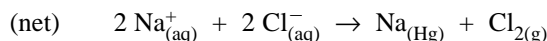
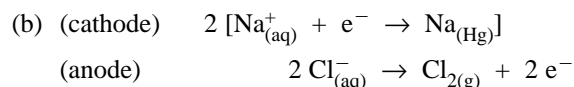
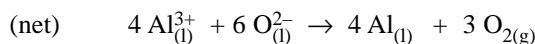
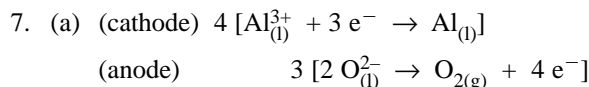
The minimum applied potential difference required to produce a chemical change is 1.51 V.



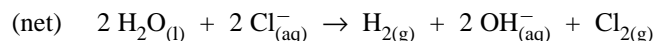
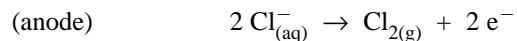
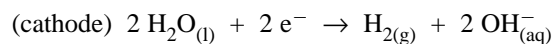
$$\begin{aligned}
 \text{(b)} \quad \Delta E^{\circ} &= E_{\text{r}}^{\circ} (\text{cathode}) - E_{\text{r}}^{\circ} (\text{anode}) \\
 &= 0.00 \text{ V} - (+1.23 \text{ V})
 \end{aligned}$$

$$\Delta E^{\circ} = -1.23 \text{ V}$$

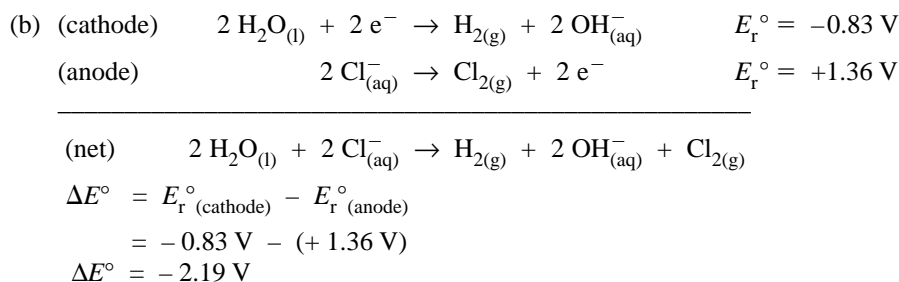
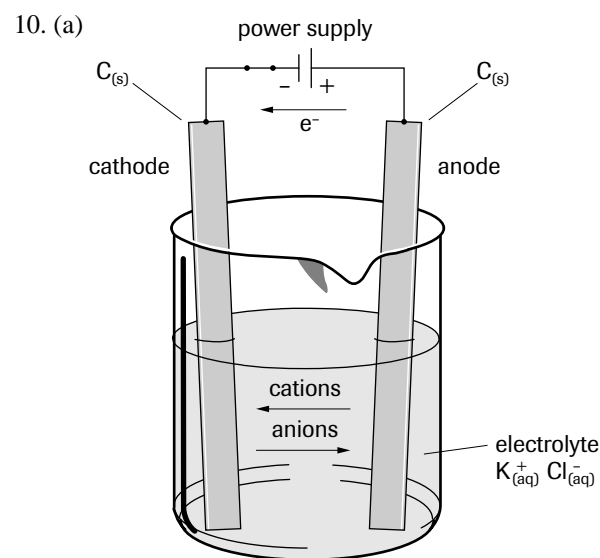
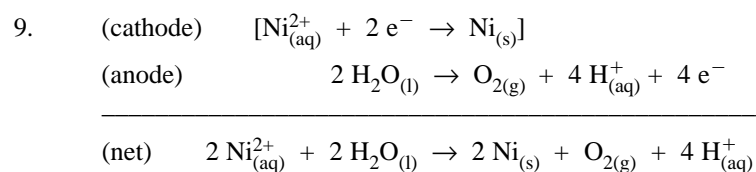
The minimum applied potential difference required to produce a chemical change is 1.23 V.



Note: The cathode half-reaction given is for the original chlor-alkali process, which uses a mercury cathode. The sodium metal produced is reacted with fresh water to produce hydrogen gas and sodium hydroxide. In newer diaphragm and ion-exchange membrane cells, water reacts at the cathode instead of sodium ions as shown below.

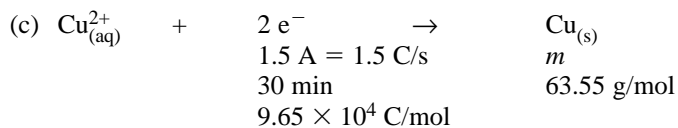
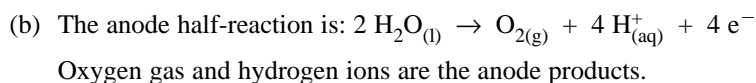


8. (a) In the electrorefining of copper, the anode is impure copper, the cathode is highly pure copper, and the solution contains copper (II) ions.
- (b) In the electrorefining of copper, the silver, gold, and platinum impurities are not oxidized at the anode, and so fall to the bottom of the cell as tiny particles of solid metal, forming a sludge. Iron and zinc impurities are oxidized to ions at the anode, but are not reduced at the cathode because copper(II) ions are a stronger oxidizing agent. This means that unless the voltage applied is too high, the iron and zinc ions will remain in solution.
- (c) High-purity copper is especially important in electronics as an efficient conductor of electric current.



Note: The electrolysis of aqueous potassium chloride should be very similar to that of aqueous sodium chloride. Therefore, chloride ions will be predominantly oxidized over water at the anode, because the $\text{Cl}_{(\text{aq})}^-$ ion oxidation is much faster than that of H_2O molecules.
 The minimum applied potential difference is 2.19 V (versus 2.06 V for water oxidation).

11. (a) The bolt must be attached at the cathode because that is where the copper(II) ions will be reduced to copper metal.



$$t = 30 \cancel{\text{min}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}}$$

$$t = 1.8 \times 10^3 \text{ s}$$

$$n_{\text{e}^-} = \frac{q}{F}$$

$$n_{e^-} = \frac{It}{F}$$

$$= \frac{1.5 \frac{C}{s} \times 1.8 \times 10^3 s}{9.65 \times 10^4 \frac{C}{mol}}$$

$$n_{e^-} = 0.0280 \text{ mol}$$

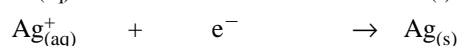
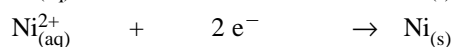
$$n_{Cu} = 0.0280 \text{ mol } e^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-}$$

$$n_{Cu} = 0.0140 \text{ mol}$$

$$m_{Cu} = 0.0140 \text{ mol} \times 63.55 \frac{g}{mol}$$

$$m_{Cu} = 0.889 \text{ g}$$

The mass of copper plated out is 0.889 g.



$$2.50 \text{ A} = 2.50 \text{ C/s}$$

$$45.0 \text{ min}$$

$$9.65 \times 10^4 \text{ C/mol}$$

m (of each metal)

26.98 g/mol Al; 58.69 g/mol Ni; 107.87 g/mol Ag

$$t = 45.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}}$$

$$t = 2.7 \times 10^3 \text{ s}$$

$$n_{e^-} = \frac{q}{F}$$

$$n_{e^-} = \frac{It}{F}$$

$$= \frac{2.50 \frac{C}{s} \times 2.7 \times 10^3 s}{9.65 \times 10^4 \frac{C}{mol}}$$

$$n_{e^-} = 0.0699 \text{ mol}$$

$$n_{Al} = 0.0699 \text{ mol } e^- \times \frac{1 \text{ mol Al}}{3 \text{ mol } e^-}$$

$$n_{Al} = 0.0233 \text{ mol}$$

$$m_{Al} = 0.0233 \text{ mol} \times 26.98 \frac{g}{mol}$$

$$m_{Al} = 0.629 \text{ g}$$

$$n_{Ni} = 0.0699 \text{ mol } e^- \times \frac{1 \text{ mol Ni}}{2 \text{ mol } e^-}$$

$$n_{Ni} = 0.0350 \text{ mol}$$

$$m_{Ni} = 0.0350 \text{ mol} \times 58.69 \frac{g}{mol}$$

$$m_{Ni} = 2.05 \text{ g}$$

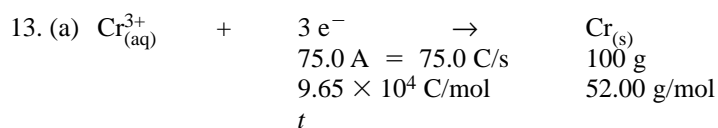
$$n_{Ag} = 0.0699 \text{ mol } e^- \times \frac{1 \text{ mol Ag}}{1 \text{ mol } e^-}$$

$$n_{Ag} = 0.0699 \text{ mol}$$

$$m_{Ag} = 0.0699 \text{ mol} \times 107.87 \frac{g}{mol}$$

$$m_{Ag} = 7.54 \text{ g}$$

Given exactly the same current flow in each cell connected in series, the mass of aluminum plated out is 0.629 g, the mass of nickel plated out is 2.05 g, and the mass of silver plated out is 7.54 g.



$$n_{\text{Cr}} = 100 \text{ g} \times \frac{1 \text{ mol}}{52.00 \text{ g}}$$

$$n_{\text{Cr}} = 1.92 \text{ mol}$$

$$n_{\text{e}^{-}} = 1.92 \text{ mol Cr} \times \frac{3 \text{ mol e}^{-}}{1 \text{ mol Cr}}$$

$$n_{\text{e}^{-}} = 5.77 \text{ mol}$$

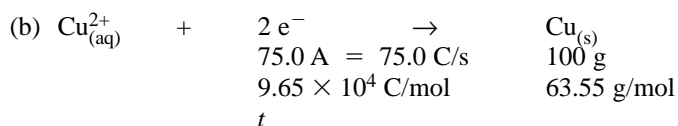
$$n_{\text{e}^{-}} = \frac{q}{F} = \frac{It}{F}$$

$$t = \frac{n_{\text{e}^{-}} F}{I}$$

$$= \frac{5.77 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{75.0 \frac{\text{C}}{\text{s}}}$$

$$t = 7.42 \times 10^3 \text{ s}$$

The time to plate 100 g of chromium is $7.42 \times 10^3 \text{ s}$ (or 2.06 h).



$$n_{\text{Cu}} = 100 \text{ g} \times \frac{1 \text{ mol}}{63.55 \text{ g}}$$

$$n_{\text{Cu}} = 1.57 \text{ mol}$$

$$n_{\text{e}^{-}} = 1.57 \text{ mol Cu} \times \frac{2 \text{ mol e}^{-}}{1 \text{ mol Cu}}$$

$$= 3.15 \text{ mol}$$

$$= \frac{q}{F}$$

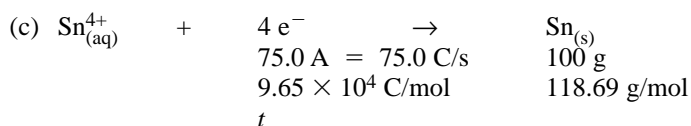
$$n_{\text{e}^{-}} = \frac{It}{F}$$

$$t = \frac{n_{\text{e}^{-}} F}{I}$$

$$= \frac{3.15 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{75.0 \frac{\text{C}}{\text{s}}}$$

$$t = 4.05 \times 10^3 \text{ s}$$

The time to plate 100 g of copper is $4.05 \times 10^3 \text{ s}$ (or 1.12 h).



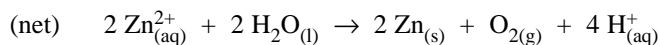
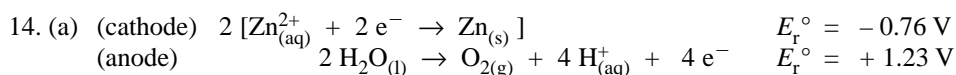
$$n_{\text{Sn}} = 100 \text{ g} \times \frac{1 \text{ mol}}{118.69 \text{ g}}$$

$$n_{\text{Sn}} = 0.843 \text{ mol}$$

$$\begin{aligned}
 n_{e^-} &= 0.843 \cancel{\text{mol Sn}} \times \frac{4 \text{ mol } e^-}{1 \cancel{\text{mol Sn}}} \\
 n_{e^-} &= 3.37 \text{ mol} \\
 n_{e^-} &= \frac{q}{F} \\
 n_{e^-} &= \frac{It}{F} \\
 t &= \frac{n_{e^-} F}{I} \\
 &= \frac{3.37 \cancel{\text{mol}} \times 9.65 \times 10^4 \frac{\cancel{\text{C}}}{\cancel{\text{mol}}}}{75.0 \frac{\text{C}}{\text{s}}}
 \end{aligned}$$

$$t = 4.34 \times 10^3 \text{ s}$$

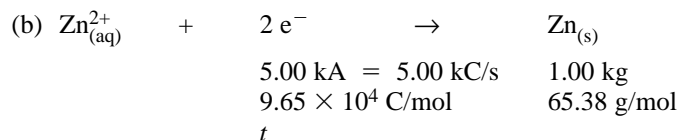
The time to plate 100 g of tin is $4.34 \times 10^3 \text{ s}$ (or 1.20 h).



$$\begin{aligned}
 \Delta E^\circ &= E_{r(\text{cathode})}^\circ - E_{r(\text{anode})}^\circ \\
 &= -0.76 \text{ V} - (+1.23 \text{ V})
 \end{aligned}$$

$$\Delta E^\circ = -1.99 \text{ V}$$

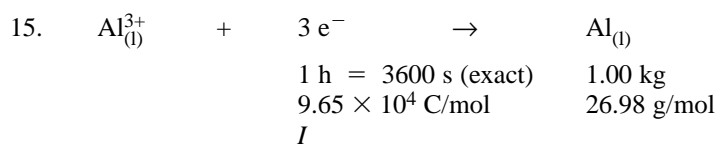
The minimum applied potential difference required for the electrolysis is 1.99 V.



$$\begin{aligned}
 n_{\text{Zn}} &= 1.00 \cancel{\text{kg}} \times \frac{1 \text{ mol}}{65.38 \cancel{\text{g}}} \\
 n_{\text{Zn}} &= 0.0153 \text{ kmol} = 15.3 \text{ mol} \\
 n_{e^-} &= 15.3 \cancel{\text{mol Zn}} \times \frac{2 \text{ mol } e^-}{1 \cancel{\text{mol Zn}}} \\
 n_{e^-} &= 30.6 \text{ mol} \\
 n_{e^-} &= \frac{q}{F} \\
 n_{e^-} &= \frac{It}{F} \\
 t &= \frac{n_{e^-} F}{I} \\
 &= \frac{30.6 \cancel{\text{mol}} \times 9.65 \times 10^4 \frac{\cancel{\text{C}}}{\cancel{\text{mol}}}}{5.00 \times 10^3 \frac{\text{C}}{\text{s}}}
 \end{aligned}$$

$$t = 590 \text{ s}$$

The time to plate 1.00 kg of zinc is 590 s (or 9.84 min).



$$n_{\text{Al}} = 1.00 \text{ kg} \times \frac{1 \text{ mol}}{26.98 \text{ g}}$$

$$n_{\text{Al}} = 0.0371 \text{ kmol} = 37.1 \text{ mol}$$

$$n_{\text{e}^{-}} = 37.1 \text{ mol Al} \times \frac{3 \text{ mol e}^{-}}{1 \text{ mol Al}}$$

$$= 111 \text{ mol}$$

$$n_{\text{e}^{-}} = \frac{q}{F}$$

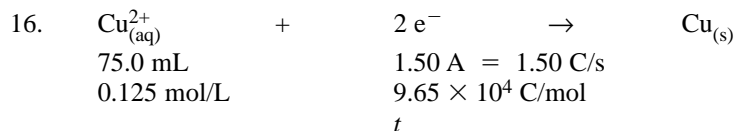
$$n_{\text{e}^{-}} = \frac{It}{F}$$

$$I = \frac{n_{\text{e}^{-}} F}{t}$$

$$= \frac{111 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{3600 \text{ s}}$$

$$I = 2.98 \times 10^3 \text{ C/s} = 2.98 \text{ kA}$$

The current required to produce 1.00 kg of aluminum per hour is 2.98 kA.



$$n_{\text{Cu}^{2+}} = Cv$$

$$= 0.125 \frac{\text{mol}}{\text{L}} \times 0.0750 \text{ L}$$

$$n_{\text{Cu}^{2+}} = 0.00938 \text{ mol}$$

$$n_{\text{e}^{-}} = 0.00938 \text{ mol Cu}^{2+} \times \frac{2 \text{ mol e}^{-}}{1 \text{ mol Cu}^{2+}}$$

$$n_{\text{e}^{-}} = 0.0188 \text{ mol}$$

$$n_{\text{e}^{-}} = \frac{q}{F}$$

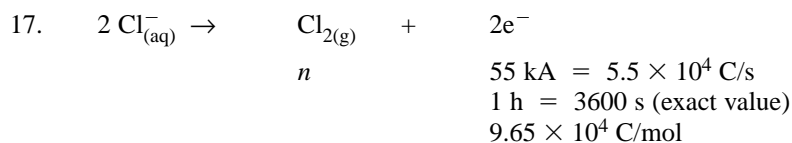
$$n_{\text{e}^{-}} = \frac{It}{F}$$

$$t = \frac{n_{\text{e}^{-}} F}{I}$$

$$= \frac{0.0188 \text{ mol} \times 9.65 \times 10^4 \frac{\text{C}}{\text{mol}}}{1.50 \frac{\text{C}}{\text{s}}}$$

$$t = 1.21 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 20.1 \text{ min}$$

The time for the copper to plate from solution is 20.1 min.



$$n_{e^-} = \frac{q}{F}$$

$$n_{e^-} = \frac{It}{F}$$

$$n_{e^-} = \frac{5.5 \times 10^4 \frac{\cancel{C}}{\cancel{s}} \times 3600 \cancel{s}}{9.65 \times 10^4 \frac{\cancel{C}}{\text{mol}}}$$

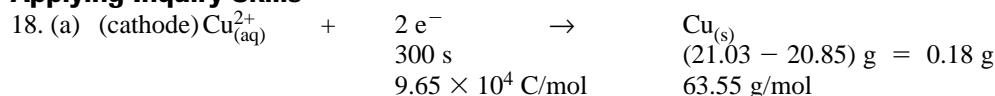
$$n_{e^-} = 2.1 \times 10^3 \text{ mol} = 2.1 \text{ kmol}$$

$$n_{\text{Cl}_2} = 2.1 \text{ kmol } e^- \times \frac{1 \text{ mol Cl}_2}{2 \text{ mol } e^-}$$

$$n_{\text{Cl}_2} = 1.0 \text{ kmol}$$

The chlorine gas is produced at a rate of 1.0 kmol/h.

Applying Inquiry Skills



$$n_{\text{Cu}} = 0.18 \cancel{\text{g}} \times \frac{1 \text{ mol}}{63.55 \cancel{\text{g}}}$$

$$n_{\text{Cu}} = 0.00283 \text{ mol}$$

$$n_{e^-} = 0.00283 \text{ mol Cu} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Cu}}$$

$$= 0.00566 \text{ mol}$$

$$n_{e^-} = \frac{q}{F}$$

$$n_{e^-} = \frac{It}{F}$$

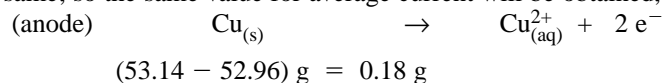
$$I = \frac{n_e F}{t}$$

$$= \frac{0.00566 \cancel{\text{mol}} \times 9.65 \times 10^4 \frac{\cancel{\text{C}}}{\cancel{\text{mol}}}}{300 \text{ s}}$$

$$I = 1.8 \text{ C/s} = 1.8 \text{ A}$$

The average current required to reduce 0.18 g of copper at the cathode is 1.8 A.

Note: The mass loss at the anode is the same value as the mass gain at the cathode, and the half-reaction ratios are the same; so the same value for average current will be obtained, if calculated from the anode mass change.



The average current required to oxidize 0.18 g of copper at the anode is 1.8 A.

- (b) The primary source of experimental error in this case is the precision of the balance, which limits the mass value used to only two significant digits. One could also say that the size of the mass change is too small because doing the experiment for ten times as long would give mass changes of three significant digits. Another likely source of error is the usual variation in the current flow over time as the cell operates, which requires constant adjustment of the current used by the experimenter.

$$\begin{aligned} \text{(c) \% difference} &= \frac{|\text{experimental value} - \text{predicted value}|}{\text{predicted value}} \times 100\% \\ &= \frac{|1.8 \text{ A} - 1.85 \text{ A}|}{1.85 \text{ A}} \times 100\% \end{aligned}$$

$$\% \text{ difference} = 2\%$$

The ammeter accuracy appears reasonably good. However, this is a tentative conclusion because the precision of the experiment is poor.

Making Connections

19. (a) The plastic is made conductive by a chemical dipping of the cleaned/treated plastic to make an adhering layer of copper or nickel/palladium.
- (b) The surface must be thoroughly cleaned and etched by removing some surface plastic molecules. In one process for ABS plastic, the initial layer is catalytic palladium, which is then covered with a layer of nickel. In other processes, copper is deposited first. In all cases, several other layers of metal are then added, usually by electrolysis, to produce the final plated product.
- (c) An important limitation is the ability to create molecular-size pits in the plastic surface to adhere the initial metal layer. Metal plating plastics makes them less flexible and the plating may crack. As a general rule, if the object has to bend, then it should not be plated. Selective plating may be used with some objects.
20. Chromium from electroplating waste solutions can be removed by first reducing the chromium from the +6 oxidation state to the +3 state using a reducing agent such as sodium bisulfite. The chromium(III) ions are then precipitated as a nontoxic chromium(III) hydroxide.

UNIT 5 PERFORMANCE TASK: ELECTROPLATING

(Page 762)

Purpose

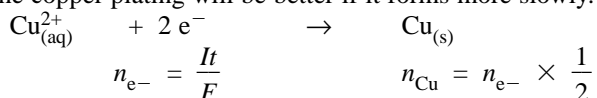
The purpose is to create a process for plating copper onto a metal object.

Question

What design produces a smooth layer of copper metal that adheres to a metal object?

Prediction

- (a) According to the redox concepts in this unit and some Internet research, a metal object can be plated at the cathode of a copper(II) sulfate electrolytic cell. The key independent variable is the electric current. The best plating should occur at relatively low currents because this produces a relatively low rate of plating. The assumption is that the quality of the copper plating will be better if it forms more slowly.

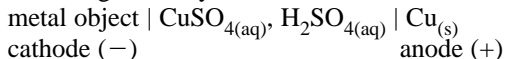


The amount of copper formed depends directly on the amount of electrons transferred. The amount of electrons per unit of time depends directly on the current.

Experimental Design

A small metal object is carefully cleaned and plated with copper. The dependent variable is the quality of the copper plating as determined by its thickness, appearance, and adherence to the object.

- (b) The following electrolytic cell is constructed.



Based on other copper-plating cells, copper(II) sulfate is acidified with a sulfuric cell.

- (c) The independent variable used is the electric current. Other potential variables that are held constant are: surface area of the metal in the solution; cleaning of the metal surface; distance between the electrodes; charge transferred ($q = It$); and the composition, concentration, and temperature of the electrolyte.