Unit 8

Answers: Electrolysis

Quick checks

1 c Molten sodium chloride has free ions, so it conducts and is decomposed into sodium and chlorine: it is an electrolyte in action. A copper wire conducts by free electrons and isn't decomposed; a salt crystal has ions, but they can't move; sugar dissolves as uncharged molecules.

2 d Ethanoic acid (the acid in vinegar) splits only about 1% into ions, so it is weak. Sodium chloride and ammonium chloride are salts and hydrochloric acid a strong acid: all three split almost completely.

3 a In a more dilute solution the ions are farther apart and join back into molecules less often, so a bigger fraction of the acid stays split: from 1.3% at 0.1 mol/L to 4.2% at 0.01 mol/L. It never reaches 100% for a weak acid at any ordinary strength.

4 b Arrhenius's key idea is that an electrolyte splits into ions by itself when it dissolves (or melts). The current only makes the ions, which are already there, move in two directions. (Molten salt is also split into ions, but you don't need to melt it: dissolving is enough.)

5 c A copper anode gives up electrons more easily than any anion in the solution, so it dissolves: $Cu \rightarrow Cu^{2+} + 2e^-$. That is why the solution stays blue: copper ions go in at the anode as fast as they come out at the cathode.

6 c Arrhenius said the ions are there before the current flows (not made by it), that the solution stays neutral, and that weak electrolytes are only partly ionized. With a current, the cations go to the cathode and the anions to the anode.

7 b The object to be plated is always the cathode, where the metal ions (here Ag^+) take electrons and are deposited: $Ag^+ + e^- \rightarrow Ag$. The anode is a plate of silver, and the electrolyte a solution of a silver salt.

8 c Gold and silver are less reactive than copper, so they don't dissolve from the anode. As the copper around them dissolves, they fall to the bottom as anode mud. (Iron, zinc and nickel dissolve but stay in the solution.)

1 a. **c** Glucose dissolves as whole, uncharged molecules, so its solution has no ions and doesn't conduct. Potassium nitrate and sulphuric acid are strong electrolytes, ammonia solution a weak one.

1 b. **b** In a liquid electrolyte, cations move towards the cathode and anions towards the anode; that movement of ions is the current. Free electrons carry the current only in the wires and electrodes.

1 c. **b** Ammonium chloride is a salt and sodium hydroxide a strong base: both ionize almost completely. Ethanoic acid, carbonic acid and ammonia solution are weak electrolytes.

1 d. **a** The anode is positive, so it attracts the negative ions, the anions, which give up electrons there (oxidation).

1 e. **c** Water is split as $2H_2O \rightarrow 2H_2 + O_2$: two volumes of hydrogen for every one of oxygen. Half of 30 cm^3 is 15 cm^3.

1 f. **b** Na^+ is too reactive to be discharged from water, so hydrogen comes off at the cathode. Cl^- is concentrated, so it is discharged at the anode as chlorine. Sodium hydroxide is left in the solution.

1 g. **b** The electrolyte must be a salt of the plating metal, so that its ions can be deposited on the object. The anode is a nickel plate, which dissolves to keep up the supply of Ni^{2+} ions.

1 h. **c** Svante Arrhenius proposed it in 1884 and 1887 and won the Nobel Prize in Chemistry for it in 1903. Faraday, fifty years earlier, had thought the current made the ions.

2 a. In solid sodium chloride the Na^+ and Cl^- ions are held in fixed places in the crystal and can only vibrate, so they can't carry a current. When it dissolves in water (or melts), the ions are free to move: with a current, Na^+ moves to the cathode and Cl^- to the anode, so the solution conducts.

2 b. Sugar is a covalent compound. It dissolves in water as whole, uncharged molecules and doesn't split into ions. With no ions to move, there is nothing to carry a current through the solution, so sugar is a non-electrolyte.

2 c. Whether an electrolyte is strong or weak depends on how much of it splits into ions, not on how much dissolves. Ethanoic acid mixes with water in any amount, but only a small fraction of its molecules ionize (about 1.3% at 0.1 mol/L): $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. With few ions in the solution, it conducts poorly, so it is a weak electrolyte.

2 d. Pure water is a very weak electrolyte: only about 2 molecules in a billion are ionized, so it hardly conducts and its electrolysis would be extremely slow. Sulphuric acid is a strong electrolyte; a little of it provides plenty of ions to carry the current. The sulphate ions are not discharged, so only the water is decomposed, into hydrogen and oxygen, and the acid is not used up.

2 e. The metal ions in the electrolyte are positive (Cu^{2+}, Ag^+, Ni^{2+}), so they move to the cathode, where they take electrons and are deposited as metal atoms, for example $Ag^+ + e^- \rightarrow Ag$. So the object must be the cathode for the coat to form on it. At the anode, the metal would dissolve instead.

2 f. The blue color is due to Cu^{2+} ions. With carbon electrodes, Cu^{2+} ions are deposited as copper on the cathode and nothing replaces them (oxygen comes off the anode), so the solution gets paler. With copper electrodes, the copper anode dissolves, $Cu \rightarrow Cu^{2+} + 2e^{-}$, putting back Cu^{2+} ions as fast as they are deposited at the cathode, so the color stays the same.

3 i.

Electrolyte	Non-electrolyte
Conducts electricity when molten or in solution.	Doesn't conduct, molten or in solution.
Forms ions.	Stays as uncharged molecules.
Is decomposed by the current.	Is not decomposed.
Acids, bases and salts.	Mostly covalent compounds.
Examples: NaCl, $CuSO_4$, HCl.	Examples: sugar, glucose, alcohol.

3 ii.

Strong electrolyte	Weak electrolyte
Ionizes almost completely in solution.	Ionizes only partly.
Its solution has many ions and hardly any whole molecules.	Its solution has a few ions among many molecules.
Conducts well.	Conducts poorly.
One arrow: $NaCl \rightarrow Na^{+} + Cl^{-}$.	Double arrow: $CH_3COOH \rightleftharpoons CH_3COO^{-} + H^{+}$.
Examples: HCl, NaOH, NaCl, NH_4Cl.	Examples: CH_3COOH, H_2CO_3, NH_4OH.

3 iii.

Metallic conduction	Electrolytic conduction
Carried by free electrons.	Carried by positive and negative ions.
The conductor is not changed chemically.	The electrolyte is decomposed.
No matter moves through the conductor.	Ions travel through the liquid.
Happens in metals and graphite.	Happens in molten ionic compounds and solutions of electrolytes.
Resistance rises when heated.	Resistance falls when heated.

3 iv.

Electroplating	Electrorefining
Coats an object with a thin layer of another metal.	Purifies an impure metal.
The object is the cathode.	A thin sheet of pure metal is the cathode.
A pure plate of the coating metal is the anode.	The impure metal is the anode.
For protection or decoration.	For metal 99.99% pure.
Example: chromium plating a bicycle handlebar.	Example: refining copper.

4 a. An electrolyte is a substance that conducts electricity in the molten state or in solution, by means of ions, and is decomposed by the current. Strong electrolytes: sodium chloride, hydrochloric acid (also NaOH, NH_4Cl, $CuSO_4$). Weak electrolytes: ethanoic acid, ammonia solution (also carbonic acid).

4 b. The degree of ionization is the fraction of the total number of molecules of an electrolyte dissolved that is split into ions: α = number of molecules ionized ÷ total number of molecules dissolved. It depends on:

1. the nature of the electrolyte (strong electrolytes nearly 100%, weak ones a few percent);
2. the concentration (a more dilute solution is more ionized);
3. the temperature (it increases a little with temperature for most weak electrolytes).

4 c.

1. On dissolving in water or melting, an electrolyte splits into positive ions (cations) and negative ions (anions), without any current.
2. The total positive charge equals the total negative charge, so the solution is electrically neutral.
3. The ions move freely and at random through the solution.
4. Ionization is reversible: ions join back into molecules while molecules split, $AB \rightleftharpoons A^+ + B^-$.
5. The degree of ionization depends on the nature of the electrolyte, its concentration and the temperature; strong electrolytes are almost completely ionized, weak ones only partly.
6. When a current is passed, cations move to the cathode and anions to the anode.
7. At the electrodes, the ions are discharged: cations gain electrons at the cathode and anions lose electrons at the anode, forming the products of electrolysis.
8. The properties of the solution of an electrolyte are the properties of its ions.

4 d.

1. It says electrolytes form ions on dissolving, but ionic compounds such as NaCl are made of ions even in the solid state; dissolving only sets the ions free.
2. It says strong electrolytes are not fully ionized at higher concentrations, but they are completely ionized at every concentration; their conductivity falls because the crowded ions attract each other.

(Also: the ions are surrounded by water molecules, and H^+ exists as H_3O^+.)

4 e. Draw Hofmann's voltameter as in Figure 8.2: two graduated side tubes with taps, joined to a middle tube with a reservoir, a platinum electrode at the foot of each, joined to a battery. It is filled with water containing a little dilute sulphuric acid, which provides ions to carry the current. When the current flows, H^+ ions move to the cathode and OH^- ions to the anode:
Cathode: $4H^+ + 4e^- \rightarrow 2H_2$. Anode: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$. Overall: $2H_2O \rightarrow 2H_2 + O_2$.
Hydrogen collects over the cathode and oxygen over the anode, 2 volumes to 1.
Tests: hydrogen burns with a pop when a lighted splint is brought to it; oxygen relights a glowing splint.

4 f. Electroplating is coating a metal object with a thin layer of another metal by electrolysis. Draw as in Figure 8.3. The clean iron spoon is made the cathode (joined to −), a copper plate the anode (joined to +), and both hang in copper sulphate solution. A small, steady direct current is passed. Cu^{2+} ions move to the spoon and are deposited as copper: $Cu^{2+} + 2e^- \rightarrow Cu$. The copper anode dissolves to replace them: $Cu \rightarrow Cu^{2+} + 2e^-$. The spoon gets an even coat of copper and the solution stays blue.

4 g. In electrorefining, a thick slab of impure copper is the anode, a thin sheet of pure copper the cathode, and copper sulphate solution with some sulphuric acid the electrolyte. With the current, copper from the anode dissolves, $Cu \rightarrow Cu^{2+} + 2e^-$, and pure copper is deposited on the cathode, $Cu^{2+} + 2e^- \rightarrow Cu$. More reactive impurities (iron, zinc, nickel) dissolve but stay in the solution; less reactive ones (gold, silver) don't dissolve and fall below the anode as anode mud. The cathode copper is 99.99% pure.

4 h. Electrotyping is making an exact metal copy of an object, such as a printing block, coin or medal, by depositing metal on a mold of it by electrolysis. Steps:

1. a mold of the object is made in wax;
2. its face is coated with graphite to make it conduct;
3. it is made the cathode in copper sulphate solution, with a copper anode, and copper is deposited on it;
4. the copper shell is removed and backed with a cheaper metal.

Uses: making printing plates for books and newspapers; making copies of coins, medals and museum objects (and, as electroforming, the masters that press CDs).

5 a.

$$\alpha = \frac{0.0042}{0.1} = 0.042 = 4.2\%$$

4.2%. (Ethanoic acid is ionized this much at 0.01 mol/L: here, 0.1 mol of it made up to 10 liters.)

5 b.

$$10{,}000 \times \frac{1.3}{100} = 130$$

130 molecules are ionized, giving **260 ions** (130 CH_3COO^- and 130 H^+). The other 9,870 stay whole.

5 c.

i. **Hydrogen** (H^+ ions are discharged at the cathode).

ii. Oxygen is half the volume of hydrogen: $24 \div 2 = $ **12 cm³**.

iii. $24 + 12 = $ **36 cm³**.

5 d. One part is $45 \div 3 = 15$ cm³. Hydrogen is 2 parts, **30 cm³**; oxygen 1 part, **15 cm³**.

5 e.

i. $t = 25 \times 60 = 1{,}500$ s, so $Q = It = 0.2 \times 1{,}500 = $ **300 C**.

ii.

$$n = \frac{300}{1.6 \times 10^{-19}} = 1.875 \times 10^{21}$$

iii. $Cu^{2+} + 2e^- \rightarrow Cu$, so the number of copper atoms is half the number of electrons: $1.875 \times 10^{21} \div 2 \approx$ **9.4×10^{20} atoms** (about 0.1 g of copper).

5 f.

$$= 2 \times \frac{18}{2} = 18$$

18 kg, about **18 liters** of water a day. A real station uses a little more (about 10 L per kg of hydrogen, so about 20 L), since some water is lost and the water must be purified first.