Unit 8 · Electrolysis

STUDY NOTES

Key terms

Electrolyte: conducts when molten or in solution, by ions, and is decomposed.

Non-electrolyte: doesn't conduct, molten or in solution; stays as whole molecules.

Electrolysis: current through an electrolyte, decomposing it.

Electrode: plate or rod (metal, carbon) where the current enters or leaves. **Inert**: Pt, C. **Active**: takes part (Cu anode).

Anode: joined to **+**; **cathode**: joined to **−**. ("PANIC"; electrolysis only.)

Anion: − ion, goes to the anode; **cation**: + ion, goes to the cathode.

Voltameter: electrolytic cell.

Degree of ionization α: fraction of dissolved molecules split into ions.

Strong electrolyte: splits almost completely. **Weak**: only partly.

Discharged: ion loses its charge at an electrode.

Electroplating: thin coat of another metal, by electrolysis.
Electrorefining: purifying a metal by electrolysis.
Electrotyping: copy made by depositing metal on a mold.

Formulas

$\alpha = \dfrac{\text{molecules split}}{\text{molecules dissolved}}$	also as a %; each molecule that splits into a pair gives 2 ions **Use:** how far it ionizes
$Q = It$	Q charge (C), I current (A), t time (s) **Use:** charge passed; electrons = $Q \div 1.6 \times 10^{-19}$ C

- Cu^{2+} takes 2 electrons per atom; mass deposited $\propto$ charge (Faraday): 300 C $\rightarrow$ 9.4×10^{20} atoms, about 0.1 g copper
- water
  - $2H_2O \rightarrow 2H_2 + O_2$
  - hydrogen : oxygen = 2 : 1 by volume
  - water is 1/9 hydrogen by mass

8.1 Electrolytes and non-electrolytes

Metallic conduction	Electrolytic conduction
free electrons	positive and negative ions
metals, graphite	molten ionic compounds; solutions of acids, bases, salts
not changed chemically	decomposed; new substances at the plates
no matter moves	ions travel
resistance rises when heated	resistance falls when heated

Electrolyte	Non-electrolyte
conducts molten or in solution	doesn't
forms ions	whole, uncharged molecules
decomposed	not decomposed
acids, bases, salts: NaCl, $CuSO_4$, HCl, NaOH	mostly covalent: sugar, glucose, urea, ethanol, glycerin, kerosene, petrol

- **solid NaCl doesn't conduct**: ions locked, only vibrate; melt (801 °C) or dissolve $\rightarrow$ free to move
- NaCl $\rightarrow$ $Na^+ + Cl^-$; $CuSO_4$ $\rightarrow$ $Cu^{2+} + SO_4^{2-}$
- pure water
  - about 2 molecules in a billion split
  - conducts about a million times worse than seawater
  - tap water has salts
- Faraday's words, 1834; he thought the current made the ions

8.2 Strong and weak electrolytes

Strong	Weak
splits almost completely	only partly
many ions, hardly any molecules	few ions among many molecules
conducts well	conducts poorly
one arrow: $HCl \rightarrow H^+ + Cl^-$	double arrow: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
HCl, H_2SO_4, HNO_3, NaOH, KOH, nearly all salts (NaCl, **NH_4Cl**, $CuSO_4$, KNO_3, CH_3COONa)	CH_3COOH, H_2CO_3, citric, formic acid, NH_4OH, water

- **strong ≠ concentrated**; **weak ≠ dilute**: strong/weak = how completely it splits; concentrated/dilute = how much is dissolved
- 0.1 mol/L: NaCl conducts about 20 × better than ethanoic acid
- **NH_4Cl is strong**: a salt; NH_4OH is the weak one

α of a weak electrolyte depends on

- nature
- concentration (more dilute $\rightarrow$ more ionized): ethanoic acid
  - 0.1 mol/L: 1.3%
  - 0.01 mol/L: 4.2%
  - 0.001 mol/L: 12.5%
- temperature: warmer $\rightarrow$ a little more

8.3 Arrhenius theory

- thesis at Uppsala, 1884; full theory 1887; Nobel Prize in Chemistry, 1903

Postulates

1. dissolved or melted: splits into cations and anions, **without any current**
2. total + charge = total − charge: solution neutral
3. ions move freely, at random
4. reversible: $AB \rightleftharpoons A^+ + B^-$
5. α: nature, concentration, temperature

6. current: cations → cathode; anions → anode (this is the current)
7. at electrodes ions **discharged**, become atoms or molecules
8. solution's properties = its ions' (blue = Cu^{2+}; sour = H^+)

Limitations

- ionic solids already made of ions; dissolving only sets them free
- strong electrolytes fully ionized at every concentration; conductivity falls because crowded ions pull on each other (Debye and Hückel, 1923)
- ions hydrated; H^+ exists as H_3O^+
- only water solutions and melts

Electrode equations

- cathode: cation **gains** e^-, on the left: **reduction**
- anode: anion **gives up** e^-, on the right: **oxidation**
- charges balance; electrons gained = electrons given up
- molten NaCl: $Na^+ + e^- \rightarrow Na$; $2Cl^- \rightarrow Cl_2 + 2e^-$ (Downs cell, $CaCl_2$ lowers melting to about 600 °C)
- molten $PbBr_2$: $Pb^{2+} + 2e^- \rightarrow Pb$; $2Br^- \rightarrow Br_2 + 2e^-$

Which ion is discharged

- **activity series**
  - Cu^{2+}, Ag^+ before H^+
  - K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+} not from water (H_2 instead)
  - OH^- before SO_4^{2-}, NO_3^-
- **concentration**: brine: Cl^- before OH^-; very dilute salt: oxygen
- **electrode**: Cu anode dissolves; no anion discharged

Cell	Cathode	Anode	After
water + a little H_2SO_4, Pt	$4H^+ + 4e^- \rightarrow 2H_2$	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	2 : 1; acid not used up
brine, C	$2H^+ + 2e^- \rightarrow H_2$	$2Cl^- \rightarrow Cl_2 + 2e^-$	equal volumes; NaOH left
$CuSO_4$, C	$Cu^{2+} + 2e^- \rightarrow Cu$	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	blue fades; dilute H_2SO_4
$CuSO_4$, Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	$Cu \rightarrow Cu^{2+} + 2e^-$	blue stays; copper moves
$AgNO_3$ dilute, Pt	$Ag^+ + e^- \rightarrow Ag$	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	dilute HNO_3

Electrolysis of water (Hofmann's voltameter)

- a little dilute H_2SO_4
  - ions to carry the current
  - SO_4^{2-} not discharged
  - not salt: chlorine at the anode
- **hydrogen** over cathode, burns with a pop; **oxygen** over anode, relights a glowing splint
- early reading above 2 : 1: oxygen dissolves at first; run longer
- Kathmandu University, Dhulikhel (2024): about 2 kg H_2 a day; about 10 L water, 40–45 units per kg

8.4 Applications

Electroplating

- **cathode**: the clean object
- **anode**: the coating metal
- **electrolyte**: its salt
- copper on an iron spoon
  - $Cu^{2+} + 2e^- \rightarrow Cu$ on the spoon; $Cu \rightarrow Cu^{2+} + 2e^-$ at the plate
  - blue stays; only the part under the liquid is plated
- **small, steady d.c.**: large current → rough, loose coat
- to protect, to look better
  - chromium over nickel (taps, handlebars)
  - tin (food cans)
  - zinc (bolts)
  - silver
  - gold
- iron in $CuSO_4$ coats itself with no current: $Fe + CuSO_4 \rightarrow FeSO_4 + Cu$ (loose, powdery)
- Patan: fire gilding with gold-mercury paste, fumes poisonous

Electrorefining (copper: 99% → 99.99%)

- **anode**: thick impure slab
- **cathode**: thin pure sheet
- **electrolyte**: $CuSO_4$ + some H_2SO_4
- more reactive (Fe, Zn, Ni): dissolve, stay in solution
- less reactive (Au, Ag, Pt): fall as **anode mud**

Electroplating	Electrorefining
coats an object	purifies a metal
cathode: the object	cathode: pure sheet
anode: pure plating metal	anode: impure metal
protects or decorates	gets 99.99% pure

Electrotyping (Jacobi, 1838)

1. press object into wax → mold
2. brush the face with graphite, so it conducts
3. mold = cathode in $CuSO_4$, copper anode
4. lift off the shell; back with cheaper metal

- Printing plates
- museum copies
- as electroforming, CD masters

Other uses

- reactive metals from molten compounds
  - Na
  - K
  - Ca
  - Mg
  - Al (Hall–Héroult, 1886)
- chlor-alkali: Cl_2, NaOH, H_2 from brine
- anodizing: aluminium as **anode** in dilute H_2SO_4; oxide skin thickens, can be dyed

COMMON MISTAKES

✗ salt crystal conducts because it has ions
✓ ions must be free to move.

✗ current makes the ions
✓ they are there before it flows.

✗ weak = dilute
✓ weak = partly split; a dilute strong acid is still strong.

✗ electrons on the wrong side
✓ cathode left, anode right.

✗ Na at the cathode from brine
✓ hydrogen; Na only from a melt.

✗ 2 : 1 by mass
✓ by **volume**.