Unit 10 · Chemistry of Metals

STUDY NOTES

WHAT NEB'S GRADE 11 EXAM ASKS

- **CDC's grid (2077):** Inorganic Chemistry (Units 9–11 together): 20 of 75 marks
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: order of ease of giving CO_2 when Group 2 carbonates are heated; short: roasting and calcination, the vessel for roasting (reverberatory furnace), two impurities roasting removes; short (with Unit 6): the Downs cell, mass of Na from a current, why Ca is not deposited, why not aqueous NaCl
- **MCQ (1 mark)**: gangue; acidic flux (borax); brass; hematite; Cr by aluminothermy; Ag, Au by hydrometallurgy; calcination is not dressing; collectors in froth flotation; ZnS roasted, $ZnCO_3$ calcined; pure metal at the cathode; ns^1; flame colors; blue in NH_3 from ammoniated electrons; Li no superoxide; Cs lowest m.p.; $CaCl_2$ in the Downs cell; brine gives H_2; least soluble $BaCO_3$, most soluble $BeSO_4$; stability Be < Mg < Ca < Ba
- **Short (5 marks, in parts)**
  - define mineral, ore, alloy, flux, matrix, metalloid, amalgam
  - differentiate: calcination/roasting, the three metallurgies, gangue/flux, poling/liquation, self-/electrochemical reduction, carbon/aluminothermic reduction
  - reasons: ores and minerals; Na not by carbon; sulphides roasted; Na under kerosene; dull in air
  - X = $3s^1$ (Na), Y = $3s^2$ (Mg): with S, water; what happens when (NaOH + $CuSO_4$, Na_2CO_3 + $MgCl_2$, NaOH + CO)
  - Downs cell: $CaCl_2$'s two advantages, electrode reactions, identify A and B; uses of Na, NaOH, Na_2CO_3
- **Long (8 marks)**: the reverberatory furnace (calcination); trends in solubility and thermal stability of Group 2 hydroxides, carbonates, sulphates, nitrates; the calcium flow sheet (X, Y); the blast furnace; uses of CaO, plaster of Paris, Epsom salt, bleaching powder

Key terms

Metallurgy: getting metals from ores, purifying, making them useful; key step a **reduction** ($MC^+ \rightarrow M$). **Pyro-**: by heat and coke (Fe, Cu, Zn, Sn, Pb); **hydro-**: leaching, then displacement (Ag, Au); **electro-**: electrolysis of a melt, metal at the cathode (Na, K, Mg, Ca, Al).

Mineral: natural substance of definite composition in the crust; **ore**: mineral a metal is extracted from **conveniently and profitably**; **native**: uncombined (Au, Ag, Pt).

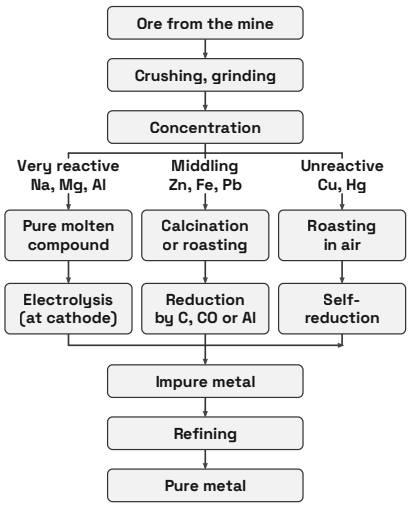
Gangue (matrix): unwanted rock with the ore, often refractory; **flux**: turns it into fusible **slag** (acidic SiO_2, borax for basic gangue; basic CaO, $CaCO_3$, MgO for acidic gangue).

Calcination: heating below the m.p. in **no or limited air**; **roasting**: below the m.p. in **excess air**; **smelting**: oxide + coke + flux → molten metal + slag.

Alloy: mixture of a metal with other metals or a non-metal, made by melting; **amalgam**: alloy of **mercury** (none with Fe: Hg kept in iron flasks).

Metalloid: between metals and non-metals (B, Si, Ge, As, Sb, Te); **anode mud**: unreactive impurities (Ag, Au) below the anode in refining.

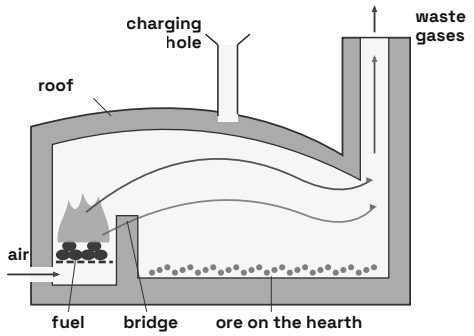
From ore to metal



Routes from ore to metal by reactivity; all end in refining.

- concentration by **density** (gravity, hydraulic washing: SnO_2, Fe_2O_3), **wettability** (froth flotation: sulphides), **magnetism** (SnO_2 from wolframite $FeWO_4$; magnetite), **chemistry** (leaching)
- froth flotation: frother pine oil; collector potassium ethyl xanthate; depressant NaCN (ZnS sinks, PbS floats)
- leaching: $Ag_2S + 4\,NaCN \rightleftharpoons 2\,Na[Ag(CN)_2] + Na_2S$, then Zn displaces Ag; Bayer:
  $Al_2O_3 \cdot 2\,H_2O + 2\,NaOH \longrightarrow 2\,NaAlO_2 + 3\,H_2O$,
  $NaAlO_2 + 2\,H_2O \longrightarrow Al(OH)_3 + NaOH$,
  $2\,Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3\,H_2O$

Calcination and roasting



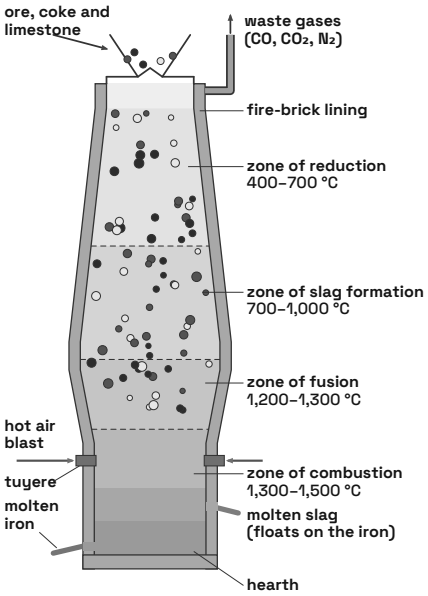
The reverberatory furnace: hot gases from the firebox cross the bridge and the curved roof reflects heat onto the ore on the hearth (air limited for calcination, in excess for roasting).

	Calcination	Roasting
air	none or limited	excess
ores	carbonate, hydrated	sulphide
gives off	CO_2, H_2O	SO_2 (and As_2O_3, Sb_2O_3)

- $ZnCO_3 \longrightarrow ZnO + CO_2$;
  $CuCO_3 \cdot Cu(OH)_2 \longrightarrow 2\,CuO + CO_2 + H_2O$;
  $2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$;
  $2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$
- both: below the m.p., oxide, porous ore; impurities removed: water, organic matter (calcination); **S, As, Sb** as volatile oxides (roasting)

Reduction

- **smelting**: $Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2$;
  $ZnO + C \longrightarrow Zn + CO$; flux:
  $CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$, slag floats on the metal
- **aluminothermic** (Goldschmidt): oxides too stable for C, or forming carbides: $Cr_2O_3 + 2\,Al \longrightarrow 2\,Cr + Al_2O_3$;
  $3\,Mn_3O_4 + 8\,Al \longrightarrow 9\,Mn + 4\,Al_2O_3$; thermite
  $Fe_2O_3 + 2\,Al \longrightarrow 2\,Fe + Al_2O_3$ welds rails; lit by BaO_2 + Mg
- **self-reduction** (Cu, Hg, Pb):
  $2\,Cu_2S + 3\,O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2$,
  $2\,Cu_2O + Cu_2S \longrightarrow 6\,Cu + SO_2$
- **electrochemical** (Na, Mg, Ca, Al): too reactive for C (hold O, Cl firmly; form carbides); **molten** salt, a second salt lowers its m.p.; Al from alumina in cryolite at 950 °C



The blast furnace: ore, coke and limestone in at the top, hot air near the bottom; CO reduces the ore; slag floats on the molten iron; each tapped off.

Refining

- **poling** (Cu, Pb with their oxides): green poles' gases reduce them: $4\,Cu_2O + CH_4 \longrightarrow 8\,Cu + CO_2 + 2\,H_2O$
- **liquation**: low-melting metal (Sn, Pb, Bi) melts down a sloping hearth; **distillation**: low-boiling Zn, Hg
- **oxidation**: air blown through pig iron (C, Si, P out → steel)
- **electrolytic** (Cu, Ag, Zn, Ni): impure anode, pure cathode; Cu in $CuSO_4 + H_2SO_4$: $Cu \longrightarrow Cu^{2+} + 2\,e^-$ at the anode, $Cu^{2+} + 2\,e^- \longrightarrow Cu$ at the cathode (99.99%); Ag, Au fall as anode mud

Alloys and ores

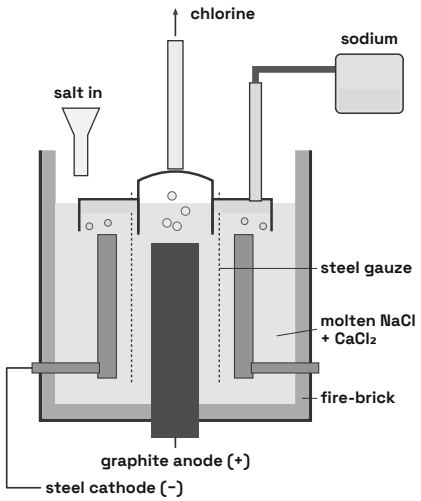
- steel Fe + C 0.1–2%; stainless Fe, Cr 18, Ni 8; invar Fe 64, Ni 36; nichrome Ni 80, Cr 20; brass **Cu + Zn**; bronze Cu + Sn; bell metal (kansa) Cu 80, Sn 20; German silver Cu, Zn, Ni; solder Sn + Pb
- Fe: hematite Fe_2O_3, magnetite Fe_3O_4, siderite $FeCO_3$; Cu: **chalcopyrite $CuFeS_2$ (chief ore)**, copper glance Cu_2S, cuprite Cu_2O, malachite; Zn: zinc blende ZnS, calamine $ZnCO_3$; Al: bauxite $Al_2O_3 \cdot 2H_2O$, cryolite Na_3AlF_6; Sn: cassiterite SnO_2; Cr: chromite $FeO \cdot Cr_2O_3$; Pb: galena PbS; Hg: cinnabar HgS; Ag: argentite Ag_2S, horn silver AgCl; Na: rock salt, Chile saltpeter $NaNO_3$, borax; Mg, Ca: magnesite, dolomite $MgCO_3 \cdot CaCO_3$, limestone, gypsum $CaSO_4 \cdot 2H_2O$, carnallite

Alkali metals (Group 1, ns^1)

	Li	Na	K	Rb	Cs
radius (pm)	152	186	227	248	265
density (g/cm^3)	0.53	0.97	0.89	1.53	1.93
m.p. (°C)	181	98	63	39	28
IE_1 (kJ/mol)	520	496	419	403	376
E° (V)	−3.04	−2.71	−2.93	−2.98	−3.03
flame	crimson	golden yellow	lilac	red-violet	blue-violet

- down the group: radius ↑, IE ↓, m.p. ↓, reactivity ↑; density **Li < K < Na < Rb < Cs**; soft (one electron each to the metallic bond); always +1; strongest reducing agent in water **Li** (Li^+'s large hydration energy)
- burning: $4\,Li + O_2 \longrightarrow 2\,Li_2O$ oxide, $2\,Na + O_2 \longrightarrow Na_2O_2$ peroxide, $K + O_2 \longrightarrow KO_2$ superoxide (K, Rb, Cs; not Li)
- water: $2\,M + 2\,H_2O \longrightarrow 2\,MOH + H_2$ (Li steady, K catches fire); $2\,Na + H_2 \longrightarrow 2\,NaH$; $2\,Na + S \longrightarrow Na_2S$; kept under kerosene
- in liquid NH_3: deep **blue** (ammoniated electrons), conducting, reducing; $2\,Na + 2\,NH_3 \longrightarrow 2\,NaNH_2 + H_2$

Sodium



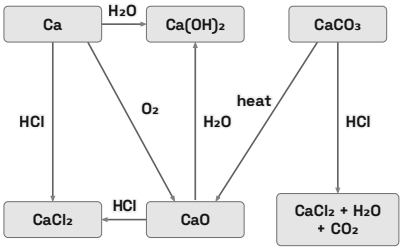
The Downs cell: graphite anode in the middle, ring-shaped steel cathode, steel gauze between; Cl_2 up over the anode, molten Na up round the cathode.

- **Downs process**: molten NaCl + **$CaCl_2$** (lowers the m.p. from 801 to about 600 °C, less Na boils off or dissolves in the melt)
- cathode $Na^+ + e^- \longrightarrow Na$; anode $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$; Ca not deposited: Na^+ more easily reduced (−2.71 vs −2.87 V)
- not by carbon (Na holds O, Cl more firmly); not from brine (H_2 at the cathode, Na would react with water)
- **NaOH**: $CuSO_4 + 2\,NaOH \longrightarrow Cu(OH)_2\downarrow + Na_2SO_4$ (blue); $Zn(OH)_2$, $Al(OH)_3$ dissolve in excess ($Zn(OH)_2 + 2\,NaOH \longrightarrow Na_2ZnO_2 + 2\,H_2O$); $NaOH + CO \longrightarrow HCOONa$ (210 °C, pressure); soap, paper
- **Na_2CO_3** (washing soda $\cdot 10H_2O$ **effloresces** to $\cdot H_2O$): $Na_2CO_3 + CO_2 + H_2O \longrightarrow 2\,NaHCO_3$; $MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + 2\,NaCl$ (softens hard water); glass, soap, paper

Alkaline earth metals (Group 2, ns^2)

	Be	Mg	Ca	Sr	Ba
radius (pm)	112	160	197	215	222
IE_1 (kJ/mol)	899	738	590	549	503
E° (V)	−1.85	−2.37	−2.87	−2.89	−2.91
flame	none	none	brick red	crimson	apple green

- vs Group 1: smaller, harder, denser, higher m.p. (two electrons each), higher IE, less reactive, always +2; Be mostly covalent
- $2\,Mg + O_2 \longrightarrow 2\,MgO$ (dazzling white; with Mg_3N_2); Ca, Sr, Ba with cold water, Mg with steam: $Mg + H_2O \longrightarrow MgO + H_2$; $3\,Mg + N_2 \longrightarrow Mg_3N_2$
- **quicklime** CaO: $CaCO_3 \xrightarrow{900\,^\circ C} CaO + CO_2$; cement, glass, basic flux, drying, liming soils; **bleaching powder** Ca(OCl)Cl: Cl_2 over slaked lime, disinfectant
- **plaster of Paris** $CaSO_4\cdot\frac{1}{2}H_2O$ (gypsum at 120 °C) sets with water to $CaSO_4\cdot 2H_2O$: casts, statues; **Epsom salt** $MgSO_4\cdot 7H_2O$: laxative; **magnesia** MgO: furnace linings, antacid



CDC's calcium flow sheet, filled in: X = $CaCO_3$, Y = $Ca(OH)_2$.

Solubility (dissolves if hydration energy ≥ lattice energy)

- **hydroxides** (small OH^-, lattice energy falls fast): more soluble down: $Be(OH)_2 < \ldots < Ba(OH)_2$
- **carbonates, sulphates** (large anion, lattice energy nearly constant, hydration energy falls): less soluble down: $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

Thermal stability of carbonates, nitrates, sulphates **increases** down: $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$ (so $BeCO_3$ gives CO_2 most easily)

- small, highly charged cation **polarizes** the large anion's electron cloud and weakens its bonds
- $MCO_3 \longrightarrow MO + CO_2$; $2\,M(NO_3)_2 \longrightarrow 2\,MO + 4\,NO_2 + O_2$; $MSO_4 \longrightarrow MO + SO_3$

COMMON MISTAKES

✗ cuprite, richest in Cu, is the chief ore
✓ **chalcopyrite**: an ore is chosen by abundance and cost.

✗ calcination in excess air
✓ **no or limited air**; roasting in excess.

✗ sodium from salt water
✓ brine gives **H_2**; Na from **molten** NaCl + $CaCl_2$.

✗ Cs the strongest reducing agent in water
✓ **Li**.

✗ carbonates, sulphates more soluble down Group 2
✓ **less**; only hydroxides more.