Unit 7 · Study of Heavy Metals

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Inorganic Chemistry (Units 6–7 together): 12 of 75 marks; 2 MCQs and 2 short questions, no long one
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: which ore is concentrated by froth flotation (galena, a sulphide); short: ore X of a Group II metal gives a black oxide on calcination and the metal and a gas on roasting; the gas turns acidified $K_2Cr_2O_7$ green: name the metal, the calcination, the gas's reaction, make the metal's vitriol (copper)
- **MCQ (1 mark)**
  - ores and formulas (malachite, Rinmann's green, white vitriol, cinnabar, calomel, $HgCl_2$, rust, horn silver); chief ores; matte; coinage metals; bell metal
  - purifying blister copper; anode mud; zinc's reducing agent and cathode; quicksilver; sublimes; X in $ZnSO_4$ + BaS and $HgCl_2$ + excess KI
  - blast furnace: ore, reducing agent, flux, hottest zone; open hearth lining; BOP's oxygen; rusting; cyanide process; lunar caustic; indelible ink
- **Short (5 marks, in parts)**
  - give reasons (each metal); preparation and uses of the vitriols, lithopone, Nessler's reagent, calomel, corrosive sublimate, lunar caustic, horn silver
  - what happens: NH_3 into $CuSO_4$; $ZnSO_4$ in an iron vessel; NH_3 on $HgCl_2$; $CuSO_4$ in iron; Cu wire in $AgNO_3$; spelter, spiegeleisen, rusting and its prevention
  - extraction with a diagram (Cu from pyrites, Zn from blende, Hg from cinnabar, Fe from hematite, Ag by cyanide); open hearth vs BOP; quenching and tempering
  - a metal M from its group and Z: identify, ore, extraction, compounds

Key terms

Heavy metals: dense metals (7.1 g/cm^3 Zn to 13.5 Hg); here Cu, Zn, Hg, Fe, Ag.

Matte: molten Cu_2S with some FeS, from smelting copper.

Blister copper: 98–99% Cu; escaping SO_2 leaves blisters.

Self-reduction: a metal's sulphide reduces its oxide ($2Cu_2O + Cu_2S$), no coke.

Poling: stirring molten copper with green wood, which reduces Cu_2O.

Anode mud: less reactive metals (Ag, Au, Pt) that fall below the anode in refining.

Spelter: impure zinc from the retort (Pb, Cd, Fe, As).

Amalgam: an alloy of mercury with another metal.

Pig iron: blast-furnace iron, ~4% C, set in molds.

Spiegeleisen: pig iron rich in Mn (and C), added to steel to remove O and set C.

Passivity: conc. HNO_3 coats iron with Fe_3O_4, which stops further attack.

Corrosion: a metal slowly turned back into a compound by its surroundings; rust $Fe_2O_3 \cdot xH_2O$.

Galvanizing: coating iron with zinc, which corrodes first (sacrificial).

Cupellation: lead in silver oxidized to PbO, absorbed by a bone-ash cupel.

Vitriol: shining crystals of a sulphate: blue $CuSO_4 \cdot 5H_2O$, white $ZnSO_4 \cdot 7H_2O$, green $FeSO_4 \cdot 7H_2O$.

Ores

Metal	Chief ore	Others
Cu	chalcopyrite $CuFeS_2$	Cu_2S (glance), malachite $CuCO_3 \cdot Cu(OH)_2$, cuprite Cu_2O, azurite $2CuCO_3 \cdot Cu(OH)_2$, bornite Cu_5FeS_4
Zn	zinc blende ZnS	calamine $ZnCO_3$, zincite ZnO, willemite Zn_2SiO_4, franklinite $ZnFe_2O_4$
Hg	cinnabar HgS	native droplets
Fe	hematite Fe_2O_3	magnetite Fe_3O_4, limonite $2Fe_2O_3 \cdot 3H_2O$, siderite $FeCO_3$ (pyrites not used: S)
Ag	argentite Ag_2S	horn silver AgCl, ruby silver Ag_3SbS_3, argentiferous galena; by-product of Cu, Zn refining

- sulphide ores ($CuFeS_2$, ZnS, HgS, Ag_2S, galena PbS): **froth flotation** (pine oil, xanthate); NaCN depresses ZnS so PbS floats first
- hematite: **gravity** separation (5.3 against 2.6 g/cm^3)

Copper (7.1)

- 29, [Ar] $3d^{10}\ 4s^1$, coinage metal; mp 1085 °C, 8.96 g/cm^3; second best conductor
- **roasting** (reverberatory, excess air): $2\,CuFeS_2 + O_2 \longrightarrow Cu_2S + 2\,FeS + SO_2$; $2\,FeS + 3\,O_2 \longrightarrow 2\,FeO + 2\,SO_2$; S, As, P burn off
- **smelting** (blast furnace, coke + silica): $Cu_2O + FeS \longrightarrow Cu_2S + FeO$; $FeO + SiO_2 \longrightarrow FeSiO_3$ (slag); matte below
- **Bessemer**: FeS → FeO → slag; then $2\,Cu_2S + 3\,O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2$, $2\,Cu_2O + Cu_2S \longrightarrow 6\,Cu + SO_2$
- **refining**: poling ($Cu_2O + C \longrightarrow 2\,Cu + CO$) to 99.5%; electrolytic: impure anode, pure cathode, $CuSO_4 + H_2SO_4$; Ag, Au to the anode mud
- moist air: green **patina** $CuCO_3{\cdot}Cu(OH)_2$; heat: black CuO, above 1100 °C red Cu_2O
- below H: no H_2; dilute HCl, H_2SO_4 only with air; hot conc. $H_2SO_4 \rightarrow SO_2$
- conc. $HNO_3 \rightarrow NO_2$; dil. (1 : 1) → NO: $3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$
- displaces Ag; with NH_3 and air, deep blue $[Cu(NH_3)_4]^{2+}$
- alloys: brass Cu–Zn; bronze Cu–Sn; bell metal Cu 78, Sn 22; gun metal Cu–Sn–Zn; German silver Cu–Zn–Ni (no silver)
- **blue vitriol**: CuO, $Cu(OH)_2$, $CuCO_3$ (or Cu + air) in dil. H_2SO_4, crystallized
  - heat: blue → $CuSO_4{\cdot}H_2O$ (pale, ~100 °C) → white $CuSO_4$ (~250 °C) → black CuO + SO_3 (~750 °C)
  - NaOH: pale blue $Cu(OH)_2$; NH_3: same, then deep blue $[Cu(NH_3)_4]SO_4$
  - KI: $2\,CuSO_4 + 4\,KI \longrightarrow Cu_2I_2 + I_2 + 2\,K_2SO_4$ (iodometry); Zn, Fe displace Cu; H_2S: black CuS
  - uses: Bordeaux mixture, Fehling's and Benedict's, electrolyte, anhydrous tests for water
- CuO (black): finds C and H in organic compounds; Cu_2O (red): red glass, anti-fouling paint
- model paper: malachite calcined, $CuCO_3 \cdot Cu(OH)_2 \longrightarrow 2\,CuO + CO_2 + H_2O$ (black W); Cu_2S roasted to Cu + SO_2
- SO_2 turns acidified dichromate orange → green:

$$K_2Cr_2O_7 + H_2SO_4 + 3\,SO_2$$

$$\longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

Zinc (7.2)

- 30, $3d^{10}\ 4s^2$, **non-typical**: only +2, white compounds; mp 420, bp 907 °C
- **roasting** at ~900 °C: $2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$ ($ZnSO_4$ formed is broken up again)
- **reduction** in a vertical retort, coke, 1400 °C: $ZnO + C \longrightarrow Zn(g) + CO$; vapor condensed; closed, as Zn boils below 1100 °C
- spelter purified: fractional distillation (Cd 767, Zn 907, Pb 1749 °C) or electrolysis ($ZnSO_4$, pure Zn or Al cathode), 99.99%
- brittle; malleable at 100–150 °C; moist air: basic zinc carbonate, protective
- burns: ZnO (philosopher's wool), yellow hot, white cold; with $Co(NO_3)_2$, **Rinmann's green** $CoZnO_2$; red-hot Zn + steam → $ZnO + H_2$
- above H: dil. acids → H_2; HNO_3 more dilute → NO_2, NO, N_2O, NH_4NO_3: $4\,Zn + 10\,HNO_3 \longrightarrow 4\,Zn(NO_3)_2 + NH_4NO_3 + 3\,H_2O$
- amphoteric: $Zn + 2\,NaOH \longrightarrow Na_2ZnO_2 + H_2$
- uses: **galvanizing** (half of all Zn), dry cells, brass, zinc dust for Ag and Au
- **white vitriol** $ZnSO_4{\cdot}7H_2O$: efflorescent; heat → $ZnSO_4{\cdot}H_2O$ (~100) → $ZnSO_4$ (~280) → ZnO + SO_3 (~800 °C)
  - NaOH: white $Zn(OH)_2$, dissolves in excess; BaS: **lithopone** ZnS + $BaSO_4$ (white paint); $K_4[Fe(CN)_6]$: white $Zn_2[Fe(CN)_6]$
  - uses: zinc for soils (Terai rice), galvanizing bath, lithopone, eye lotion (past)

Mercury (7.3)

- the only liquid metal: mp −38.83, bp 356.73 °C, 13.53 g/cm^3; poisonous vapor
- concentration: froth flotation (or gravity); **roast and distill** in one shaft furnace: $HgS + O_2 \longrightarrow Hg + SO_2$ (no reducing agent)
- purify: squeeze through chamois leather; drop through 5% HNO_3 (Zn, Pb, Cu displace Hg from $Hg_2(NO_3)_2$); vacuum distillation
- 350 °C in air: red HgO; above 450 °C back to Hg + O_2
- below H; cold dil. HNO_3 (Hg excess): $6\,Hg + 8\,HNO_3 \longrightarrow 3\,Hg_2(NO_3)_2 + 2\,NO + 4\,H_2O$; hot conc.: $Hg(NO_3)_2 + NO_2$
- aqua regia (1 HNO_3 : 3 HCl, nascent Cl) → $HgCl_2$; hot conc. $H_2SO_4 \rightarrow HgSO_4 + SO_2$
- ozone: Hg_2O film, **tailing**; amalgams with Na, Au, Ag, Sn
- uses: thermometers, barometers (going), amalgams, Hg cells, lamps; **Minamata Convention** (2013; Nepal signed, not ratified)
- **calomel** Hg_2Cl_2 (Hg–Hg, +1): $Hg_2(NO_3)_2 + 2\,HCl \longrightarrow Hg_2Cl_2 + 2\,HNO_3$; $Hg + HgCl_2 \longrightarrow Hg_2Cl_2$; $2\,HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$
  - heat: $Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$; NaOH: black Hg_2O; NH_3: **black** Hg + $Hg(NH_2)Cl$; $SnCl_2$: gray Hg
  - uses: calomel electrode, laxative (past)
- **corrosive sublimate** $HgCl_2$: $Hg + Cl_2 \longrightarrow HgCl_2$; $HgO + 2\,HCl \longrightarrow HgCl_2 + H_2O$; $HgSO_4$ + 2NaCl (MnO_2) → sublimes
  - soluble, sublimes (mp 276), very poisonous

- NaOH: **yellow** HgO; NH_3: **white** $Hg(NH_2)Cl$; KI: **scarlet** HgI_2, excess → colorless $K_2[HgI_4]$
- **Nessler's reagent**: $K_2[HgI_4]$ + KOH; brown with NH_3 (ammonia in water)

Iron (7.4)

- 26, [Ar] $3d^6\ 4s^2$; 7.87 g/cm³, mp 1538 °C; ferromagnetic below 770 °C
- **calcination** (air): $2\,Fe_2O_3 \cdot 3\,H_2O \longrightarrow 2\,Fe_2O_3 + 3\,H_2O$; $FeCO_3 \longrightarrow FeO + CO_2$, $4\,FeO + O_2 \longrightarrow 2\,Fe_2O_3$ (FeO would go to slag); S, P, As off; ore porous
- **blast furnace**: burden ore : coke : limestone ≈ 8 : 4 : 1; air at ~1000 °C (Cowper stoves) through tuyeres

Zone	°C	Reaction
combustion (hottest)	1300–1500	$C + O_2 \longrightarrow CO_2$, −393 kJ
fusion	1200–1300	$CO_2 + C \longrightarrow 2\,CO$, +172 kJ; iron melts, takes C
slag formation	700–1000	$CaCO_3 \longrightarrow CaO + CO_2$; $CaO + SiO_2 \longrightarrow CaSiO_3$
reduction	400–700	$Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2$ (CO the reducing agent)

- cast iron 2–4.5% C (brittle); steel 0.1–2% (tough, malleable); wrought iron under 0.1% (soft)
- rust $4\,Fe + 3\,O_2 + 2x\,H_2O \longrightarrow 2\,Fe_2O_3 \cdot x\,H_2O$; burns to Fe_3O_4; red-hot + steam: $3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2$
- dil. HCl, $H_2SO_4 \rightarrow Fe^{2+} + H_2$; hot conc. $H_2SO_4 \rightarrow Fe_2(SO_4)_3 + SO_2$; conc. HNO_3: **passive**; cold dil. HNO_3: $Fe(NO_3)_2 + NH_4NO_3$
- displaces Cu, Ag; $Fe + 5\,CO \longrightarrow Fe(CO)_5$ (pure iron); not attacked by alkali
- **open hearth** (Siemens–Martin, regenerative heating, 8–10 h): pig iron + scrap + hematite
  - acidic (silica) lining for low P, S: Fe_2O_3 oxidizes C, Si, Mn, S; $MnO + SiO_2 \rightarrow MnSiO_3$
  - basic (dolomite, magnesite) lining + lime: $5\,Fe_2O_3 + 6\,P \longrightarrow 10\,Fe + 3\,P_2O_5$, $3\,CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2$ (basic slag, fertilizer)
  - spiegeleisen added at the end; good control, uses scrap; slow, fuel-hungry, now under 1%
- **basic oxygen (LD)**: pure O_2 by a lance onto molten pig iron (+ ¼ scrap), lime added; C → CO, Si, Mn, P oxidized
  - **autogenous** (no fuel), 30–45 min, ~70% of the world's steel, low N, P, S
- quenching: red-hot steel into water: hard, brittle; tempering: reheated to 200–600 °C: tough
- **rusting** needs O_2 and water; salt, acid speed it; electrochemical theory:
  - anode $Fe \longrightarrow Fe^{2+} + 2\,e^-$; cathode $O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$; $4\,Fe^{2+} + O_2 + 4\,H_2O \longrightarrow 2\,Fe_2O_3 + 8\,H^+$
  - chemical (acid) theory: $H_2CO_3 \rightarrow Fe(HCO_3)_2 \rightarrow Fe(OH)_3$; fails: iron rusts without CO_2
- prevention: galvanizing (sacrificial Zn), alloying (stainless, ≥ 10.5% Cr), paint, oil, Bower–Barff Fe_3O_4 film, inhibitors

Silver (7.5)

- 47, [Kr] $4d^{10}\ 5s^1$, +1; mp 962 °C, 10.49 g/cm³; best conductor; 95% reflector
- **cyanide (MacArthur–Forrest)**: flotation; 0.4–0.6% NaCN + air: $Ag_2S + 4\,NaCN \rightleftharpoons 2\,Na[Ag(CN)_2] + Na_2S$; air takes Na_2S to Na_2SO_4
- zinc dust: $2\,Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2\,Ag$; refine by cupellation (Pb → PbO) or electrolysis ($AgNO_3$; Au to the mud)
- tarnish: $4\,Ag + 2\,H_2S + O_2 \longrightarrow 2\,Ag_2S + 2\,H_2O$; no H_2 from dil. acids; conc. $HNO_3 \rightarrow NO_2$, dil. → NO; hot conc. $H_2SO_4 \rightarrow Ag_2SO_4 + SO_2$
- not in aqua regia (an AgCl film); uses: contacts, solar cells, sterling (92.5% Ag), mirrors, dressings
- **lunar caustic** $AgNO_3$: Ag in HNO_3; dark bottles; heat: $2\,AgNO_3 \longrightarrow 2\,Ag + 2\,NO_2 + O_2$
  - NaOH or a little NH_3: brown Ag_2O; excess NH_3: $[Ag(NH_3)_2]^+$, **Tollens' reagent**
  - skin, light: black Ag (**indelible ink**, voters' fingers); KCN: AgCN, excess → $K[Ag(CN)_2]$; Cu, Zn, Fe displace Ag
  - AgCl white (dissolves in NH_3), AgBr pale yellow (conc. NH_3 only), AgI yellow (doesn't), Ag_3PO_4 yellow, Ag_2CrO_4 brick red, Ag_2S black
- **horn silver** AgCl: $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$; light: $2\,AgCl \longrightarrow 2\,Ag + Cl_2$ (photochromic lenses); NH_3: $[Ag(NH_3)_2]Cl$, HNO_3 precipitates it again

COMMON MISTAKES

✗ copper matte is Cu_2S only
✓ Cu_2S with some FeS.

✗ zinc reduced in an open furnace
✓ closed retort: Zn boils at 907 °C.

✗ $HgCl_2$ is calomel
✓ calomel is Hg_2Cl_2; $HgCl_2$ corrosive sublimate.

✗ coke reduces Fe_2O_3 in the reduction zone
✓ CO does.

✗ spiegeleisen is pure iron
✓ iron rich in Mn and C.

✗ silver dissolves in aqua regia
✓ an AgCl film stops it.

✗ German silver contains silver
✓ Cu, Zn, Ni.

✗ $2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + H_2O$
✓ $2H_2O$.