Unit 17 · Modern Chemical Manufactures

STUDY NOTES

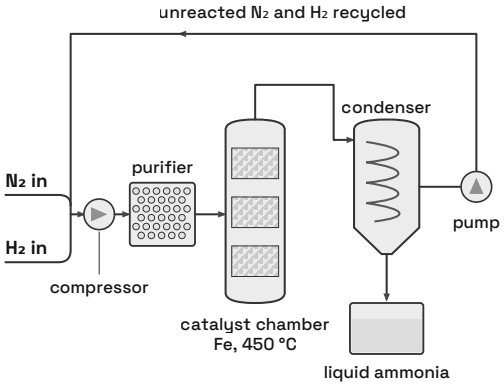
WHAT NEB'S GRADE 11 EXAM ASKS

- **CDC's grid (2077):** Applied Chemistry (Units 16–17 together): 9 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: urea's intermediate, ammonium carbamate; MCQ: the Solvay process reuses CO_2 and NH_3; short: Haber's process with a flow sheet; long: the contact process from iron pyrites in four steps, and H_2SO_4 as a precipitant, a dehydrating agent, an oxidizing agent and in a fertilizer
- **MCQ (1 mark)**: Fe with promoters; label a Haber flow sheet; Ostwald: catalytic oxidation of NH_3; low temperature, high pressure for NH_3; contact chamber equation; oleum $H_2S_2O_7$; carbonation tower; Solvay reuses NH_3 (via CaO, NH_4Cl); NH_4Cl + slaked lime; yellow leaves: nitrogen; carbamate → urea; 46.67% N
- **Short (5 marks, in parts)**
  - conditions for a high yield of NH_3; Haber's process with a flow sheet
  - flow sheets: Ostwald's process; the contact process
  - NaOH by the diaphragm cell; Na_2CO_3 by the Solvay process; identify tower and products (P–T, A–E)
  - fertilizers, four qualities of a good one; N, P, K: fertilizer and function
  - leaving out the washing and drying towers; how oleum and H_2SO_4 form
- **Long (8 marks)**: urea from ammonium carbamate with a flow sheet; the contact process, every step with a diagram, conditions; NPK, two functions each, why fertilizers; principles of the contact and Ostwald processes, the diaphragm cell; its three advantages

Ammonia: Haber's process

$$N_2 + 3\,H_2 \underset{400\text{-}450\ ^\circ C,\ \text{about } 200\ \text{atm}}{\overset{Fe,\ K_2O,\ Al_2O_3}{\rightleftharpoons}} 2\,NH_3,\ \Delta H = -92\ \text{kJ}$$

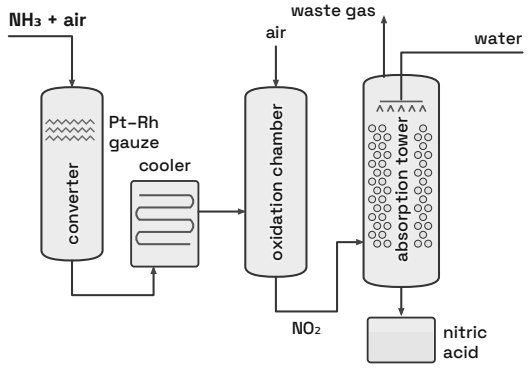
- **conditions** (Le Chatelier): exothermic → fairly **low temperature**, 400–450 °C (below, too slow; above 500, NH_3 splits); 4 volumes → 2: **high pressure**, 150–300 atm (about 200: steel, energy cost); N_2 : H_2 **1 : 3**, NH_3 removed as liquid; **iron catalyst** with promoters (speed, not yield); **pure gases** (CO, CO_2, H_2O, S compounds poison the iron)
- H_2 from natural gas: $CH_4 + H_2O \xrightarrow[800\ ^\circ C]{Ni} CO + 3\,H_2$; N_2 from liquid air
- **steps**: compressor (200 atm) → **purifier** (CO_2 by soda lime: $2\,NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$) → **converter** (catalyst beds; heated to start, then its own heat) → **condenser** (NH_3 liquefies, drawn off) → unreacted gas **recycled** (about 15% per pass)



Haber's process: $N_2 + 3H_2$ compressed, purified, passed over iron in the converter; ammonia liquefied in the condenser; unreacted gas pumped round again.

Nitric acid: Ostwald's process

- $4\,NH_3 + 5\,O_2 \xrightarrow[850\ ^\circ C]{Pt\text{–}Rh\ gauze} 4\,NO + 6\,H_2O,\ \Delta H = -906\ \text{kJ}$
- $2\,NO + O_2 \longrightarrow 2\,NO_2$ (on cooling; faster when cooler)
- $4\,NO_2 + O_2 + 2\,H_2O \longrightarrow 4\,HNO_3$ (absorption tower, water sprayed down; without extra air $3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$)
- NH_3 + 10 volumes of air, through **90% Pt, 10% Rh gauze**; product 50–68%

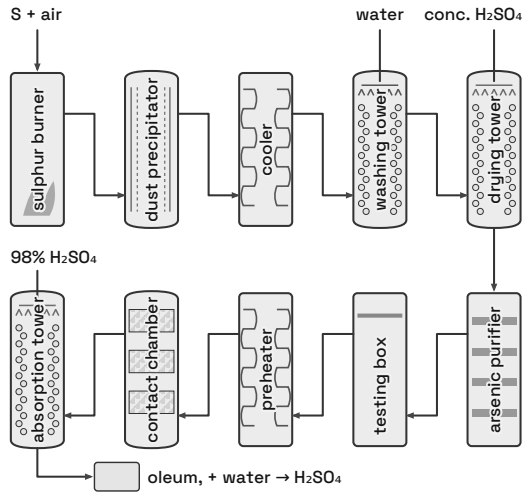


Ostwald's process: ammonia and air over the hot Pt–Rh gauze; NO cooled and oxidized to NO_2; absorbed in water with air to give nitric acid.

Sulphuric acid: contact process

1. **SO_2**: $S + O_2 \longrightarrow SO_2$ or from **iron pyrites** $4\,FeS_2 + 11\,O_2 \longrightarrow 2\,Fe_2O_3 + 8\,SO_2$
2. **oxidation**: $2\,SO_2 + O_2 \underset{450\,^\circ C}{\overset{V_2O_5}{\rightleftharpoons}} 2\,SO_3$, $\Delta H = -198$ kJ
3. **oleum**: $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ (in 98% acid; SO_3 + water gives a mist that escapes)
4. **dilution**: $H_2S_2O_7 + H_2O \longrightarrow 2\,H_2SO_4$

- **plant**: burner → **dust precipitator** (electrostatic) → cooler → **washing tower** (water over quartz) → **drying tower** (conc. H_2SO_4) → **arsenic purifier** (moist $Fe(OH)_3$) → **testing box** (Tyndall beam) → **preheater** (400–450 °C) → **contact chamber** (3–4 beds of V_2O_5 pellets, cooled between) → **absorption tower** (98% H_2SO_4) → oleum → diluted
- without washing and drying: dust, moisture, arsenic **poison** the catalyst; moist SO_3 forms acid mist, corrodes the plant
- **conditions**: 3 volumes → 2, so pressure helps, but conversion is over 99% at **1–2 atm**; **400–450 °C**; **excess O_2**; pure, dry gases; V_2O_5 (cheaper than Pt, hard to poison)

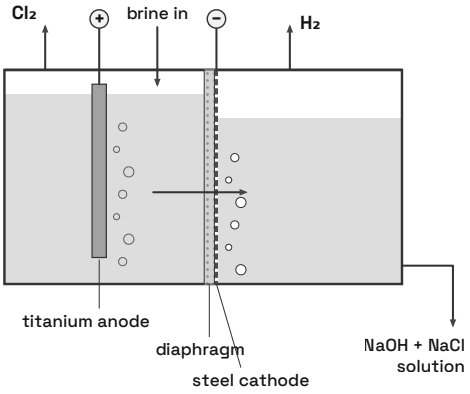


The contact process: SO_2 cleaned, cooled, washed, dried, tested, preheated, passed over V_2O_5 in the contact chamber; SO_3 absorbed in 98% acid as oleum, then diluted.

H_2SO_4 in use (properties: Unit 9)

- **precipitant**: $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2\,HCl$ (white)
- **dehydrating agent**: $C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12\,C + 11\,H_2O$; $CuSO_4 \cdot 5\,H_2O \longrightarrow CuSO_4 + 5\,H_2O$; dries gases
- **oxidizing agent** (hot, conc.): $Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\,H_2O$; $C + 2\,H_2SO_4 \longrightarrow CO_2 + 2\,SO_2 + 2\,H_2O$
- **fertilizers**: $Ca_3(PO_4)_2 + 2\,H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\,CaSO_4$ (superphosphate); $2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

Sodium hydroxide: diaphragm cell



The diaphragm cell: Cl_2 at the titanium anode; H_2 and OH^- at the steel cathode; brine seeps through the porous diaphragm, so Cl_2 and NaOH are kept apart.

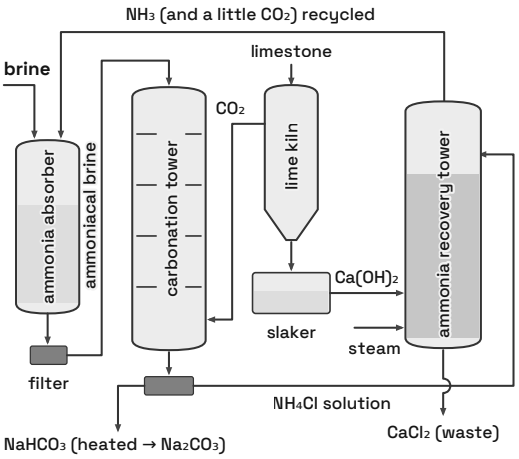
- anode (Ti, coated): $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$; cathode (steel): $2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$; $Na^+ + OH^- \longrightarrow NaOH$
- overall $2\,NaCl + 2\,H_2O \longrightarrow 2\,NaOH + Cl_2 + H_2$
- brine level higher on the anode side, so the flow keeps OH^- from the anode (else $Cl_2 + OH^- \rightarrow NaOCl$)
- cell liquor 10–12% NaOH + 15% NaCl → evaporated to 50%, salt crystallizes out
- **advantages**: no mercury; less electricity than the mercury cell; less pure brine than a membrane cell; cheaper, simple
- **disadvantages**: NaOH has about 1% salt; Cl_2 has some O_2; much steam to evaporate; old asbestos diaphragms
- diaphragm is **porous** (brine, salt and all, seeps through); a membrane cell's ion-exchange membrane passes only Na^+

Sodium carbonate: Solvay process

1. brine purified; **ammonia absorber**: brine saturated with NH_3
2. **carbonation tower** (30–35 °C, cooled): $NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$, $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3\downarrow + NH_4Cl$ ($NaHCO_3$ least soluble, filtered off)
3. **calcination** (180 °C): $2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$ (CO_2 back to the tower)

4. **lime kiln**: $CaCO_3 \longrightarrow CaO + CO_2$;
   $CaO + H_2O \longrightarrow Ca(OH)_2$
5. **ammonia recovery**:
   $2\,NH_4Cl + Ca(OH)_2 \longrightarrow 2\,NH_3 + CaCl_2 + 2\,H_2O$

- overall $CaCO_3 + 2\,NaCl \longrightarrow Na_2CO_3 + CaCl_2$; used up: brine, limestone; **recycled: NH_3 and CO_2**; waste $CaCl_2$



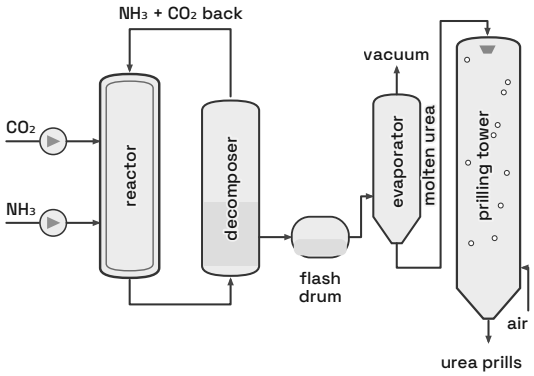
The Solvay process: ammoniacal brine meets CO_2 in the carbonation tower; $NaHCO_3$ filtered and heated to Na_2CO_3; NH_3 recovered from NH_4Cl with slaked lime from the lime kiln.

Fertilizers

- supply nutrients the soil lacks; **primary** N, P, K; secondary Ca, Mg, S; micronutrients Fe, Mn, Zn, Cu, B, Mo, Cl, Ni
- **nitrogenous**: $NaNO_3$, $(NH_4)_2SO_4$ (21% N), NH_4NO_3, CAN, DAP, **urea (46.67% N)**
- **phosphatic**: SSP ($Ca(H_2PO_4)_2$ + gypsum), TSP $Ca_3(PO_4)_2 + 4\,H_3PO_4 \longrightarrow 3\,Ca(H_2PO_4)_2$, DAP $(NH_4)_2HPO_4$; **potassic**: KCl (muriate of potash), K_2SO_4, KNO_3
- **NPK** (e.g. 20 : 20 : 10): % N, P as P_2O_5, K as K_2O
- **N** (urea, $(NH_4)_2SO_4$): growth, green leaves, chlorophyll, proteins; lack → older leaves yellow
- **P** (superphosphate, DAP): roots; flowers, fruits, seeds; ripening; ATP, DNA
- **K** (KCl, KNO_3): stomata; resist drought, disease; strong stems
- **good fertilizer**: cheap; soluble; enough nutrient; safe for roots; stable in storage; doesn't make soil acidic; easily absorbed
- **harm**: **eutrophication** (nitrate, phosphate feed algae; bacteria decaying them use up O_2); acidic soil (lime it); nitrate in wells → **blue baby** (limit 50 mg/L); N_2O (greenhouse gas, ozone); Cd, F, U from phosphate rock

Urea

- $2\,NH_3 + CO_2 \rightleftharpoons NH_2COONH_4$ (ammonium carbamate; fast, exothermic, 180–200 °C, 140–200 atm, NH_3 in excess)
- $NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O$ (slow, slightly endothermic; about two thirds per pass)
- overall $2\,NH_3 + CO_2 \longrightarrow NH_2CONH_2 + H_2O$; too hot or slow: $2\,NH_2CONH_2 \longrightarrow NH_2CONHCONH_2 + NH_3$ (**biuret**, harms seedlings, $\leq 1\%$)
- **plant**: NH_3 pumped and CO_2 compressed → **reactor** (lined with stainless steel, Ti or Zr) → **decomposer** (130 °C, low pressure; carbamate → $NH_3 + CO_2$, recycled) → flash drum → **vacuum evaporator** (99% melt) → **prilling tower** (sprayed down against air → prills)
- 46.67% N: $\frac{28}{60} \times 100$; 1 t NH_3 → at most 1.76 t urea
- **advantages**: most N of any solid fertilizer; cheap per kg N; easy to store, can't explode; no residue; **disadvantages**: hygroscopic (cakes); NH_3 lost on moist soil; biuret



A urea plant: NH_3 and CO_2 into the reactor; unreacted carbamate split in the decomposer and recycled; the solution evaporated and prilled.

COMMON MISTAKES

✗ Haber at 450–500 °C, 200–900 atm, used from 1930
✓ **400–450 °C, 150–300 atm** (about 200); made at BASF from **1913**.

✗ V_2O_5 coated on the chamber wall
✓ held in **beds** of pellets; plants run at **1–2 atm**, not high pressure.

✗ the diaphragm lets only Na^+ through
✓ it is **porous**; only a membrane cell's membrane is selective.

✗ $NaHCO_3$ dissolves in the carbonation tower
✓ it **precipitates** (least soluble); CO_2 comes from the lime kiln and the calciner.