9701 CHEMISTRY · TOPIC 12 · AS LEVEL

Nitrogen and Sulfur

01 · WHY N_2 IS UNREACTIVE

The N≡N triple bond has a very high bond enthalpy (994 kJ mol^{-1}), so the activation energy for any reaction is large.

N_2 is also non-polar with no permanent dipole, so nothing attacks it readily. This is why 78 % of the air is chemically inert nitrogen.

02 · AMMONIA — SHAPE AND BASICITY

NH_3 is trigonal pyramidal, bond angle 107°, because the lone pair repels the three bonding pairs more strongly.

That **lone pair accepts a proton**, so ammonia is a Brønsted base: $NH_3 + H^+ \rightarrow NH_4^+$. The resulting bond is dative covalent, and NH_4^+ is tetrahedral at 109.5°.

03 · THE HABER PROCESS

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

Conditions ~450 °C, ~200 atm, iron catalyst. High pressure favours the side with fewer gas moles; the temperature is a compromise between yield and rate.

Ammonia is condensed out and unreacted gases recycled, so the overall conversion is far higher than the single-pass yield.

04 · AMMONIUM SALTS AND FERTILISERS

NH_3 + acid → ammonium salt: $NH_3 + HNO_3 \rightarrow NH_4NO_3$, used as fertiliser because it supplies soluble nitrogen for protein synthesis.

Never mix an ammonium fertiliser with lime: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ releases ammonia and wastes the nitrogen. Warming with NaOH and testing with damp red litmus is the test for NH_4^+.

Excess fertiliser leaches into rivers and causes eutrophication.

05 · OXIDES OF NITROGEN

Formed in engines where the temperature is high enough to overcome the N≡N bond: $N_2 + O_2 \rightarrow 2NO$, then $2NO + O_2 \rightarrow 2NO_2$.

NO_2 dissolves to give acid rain and, with unburnt hydrocarbons and sunlight, photochemical smog. NO also catalyses the oxidation of SO_2 to SO_3 in the atmosphere.

06 · CATALYTIC CONVERTERS

$2CO + 2NO \rightarrow 2CO_2 + N_2$
hydrocarbons + $NO \rightarrow CO_2 + H_2O + N_2$

Pt/Rh on a honeycomb ceramic gives a huge surface area. The gases adsorb onto active sites, react and desorb.

07 · THE CONTACT PROCESS

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \Delta H = -196 \text{ kJ mol}^{-1}$$

Conditions ~450 °C, ~2 atm, V_2O_5 catalyst. The yield is already about 96 %, so high pressure is not worth its cost.

SO_3 is absorbed into concentrated H_2SO_4 to give oleum, then diluted — adding SO_3 directly to water is dangerously violent.

08 · THE V_2O_5 CATALYST

$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$
$2V_2O_4 + O_2 \rightarrow 2V_2O_5$

Vanadium cycles between +5 and +4, which is why a transition metal makes a good catalyst: it can lend and take back electrons.

09 · SULFUR DIOXIDE AND ACID RAIN

SO_2 comes from burning sulfur-containing fossil fuels. $SO_2 + H_2O \rightarrow H_2SO_3$, and oxidation gives H_2SO_4, both far stronger than the natural acidity of rain from dissolved CO_2.

Effects: limestone buildings eroded, lakes acidified, trees damaged. Control: flue-gas desulfurisation with CaO or $CaCO_3$, giving $CaSO_3$ which is oxidised to gypsum.

10 · USES OF SULFURIC ACID AND SO_2

H_2SO_4 — fertilisers, detergents, paints, and as the electrolyte in lead–acid batteries. It is the most produced industrial chemical by mass.

SO_2 — food preservative and bleach for paper, in both cases acting as a reducing agent that kills bacteria or destroys coloured compounds.

11 · WORKED EXAMPLE — HABER YIELD

28.0 t of N_2 reacts with excess H_2 and the yield is 15 %. What mass of NH_3 is formed?

$N_2 + 3H_2 \rightarrow 2NH_3$
$n(N_2) = 28.0 \div 28.0 = 1.00$ t-mol
theoretical $n(NH_3) = 2.00$ t-mol → 34.0 t
actual = 34.0 × 0.15 = **5.1 t**

The unreacted gas is recycled, so the process yield is far higher than 15 % overall.

12 · TESTS TO KNOW

Test	Result
NH_4^+ + NaOH, warm	NH_3 turns damp red litmus blue
SO_4^{2-} + $BaCl_2$ / HCl	white precipitate
SO_2 + acidified $Cr_2O_7^{2-}$	orange → green

13 · EQUATIONS TO KNOW

$N_2 + 3H_2 \rightleftharpoons 2NH_3$
$NH_3 + HNO_3 \rightarrow NH_4NO_3$
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

$N_2 + O_2 \rightarrow 2NO$
$2NO + O_2 \rightarrow 2NO_2$
$2CO + 2NO \rightarrow 2CO_2 + N_2$

$S + O_2 \rightarrow SO_2$
$2SO_2 + O_2 \rightleftharpoons 2SO_3$
$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$
$CaO + SO_2 \rightarrow CaSO_3$

14 · WORKED EXAMPLE — AMMONIA IN A FERTILISER

What mass of ammonium sulfate is made from 34.0 kg of ammonia?
$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

$n(NH_3) = 34.0 \div 17.0 = 2.00$ kg-mol
$n((NH_4)_2SO_4) = 1.00$ kg-mol
m = 1.00 × 132.1 = **132 kg**

Nitrogen content = 28.0 ÷ 132.1 × 100 = 21.2 %.

MARKS LOST HERE

— Saying N_2 is unreactive "because it is a gas" instead of quoting the strong triple bond and high E_a.

— Giving the Contact process a high pressure; it runs at about 2 atm.

— Writing $SO_3 + H_2O$ as the industrial step; SO_3 is absorbed in H_2SO_4 first.

— Explaining ammonia's basicity without mentioning the lone pair.