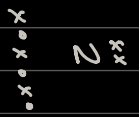
NITROGEN & SULFUR

INORGANIC CHEMISTRY

NITROGEN

- exists as N_2 molecules, where the two atoms are held together by strong triple covalent bonds

$:N \equiv N:$ 180°, linear



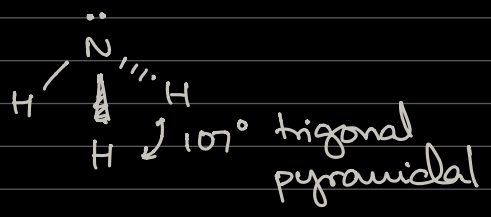
- Makes up about 78% of air
- EC: $1s^2\,2s^2\,2p^3$
  - ↳ 5 valence electrons → gains $3e^-$ for stable EC → N^{3-} : $1s^2 2s^2 2p^6$
  - Nitride

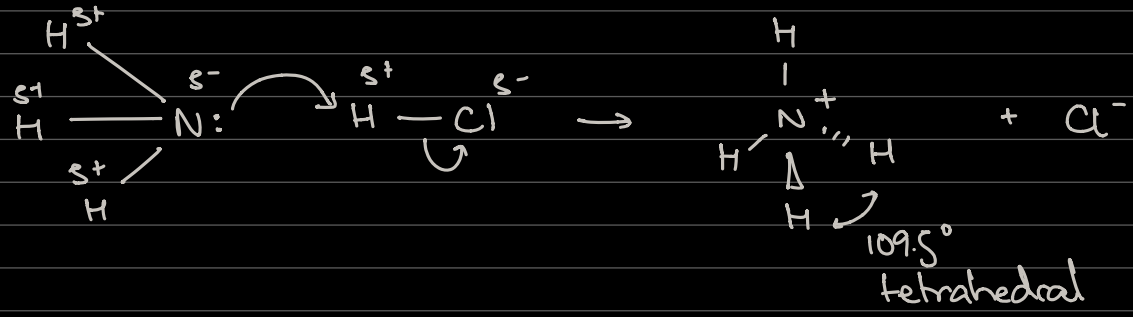
Q. Why is nitrogen inert / unreactive?
A. Because the energy required to break the N≡N bond is very high.

NITROGEN COMPOUNDS

Ammonia (NH_3)

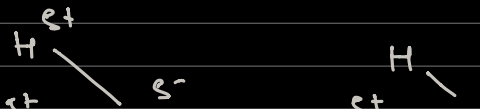
- Alkaline gas
- Accepts proton, hence it is a base
  - ↳ becomes NH_4^+ when it accepts protons
    - ↳ conjugate acid of NH_3

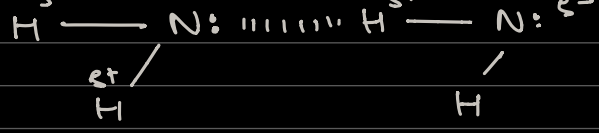




Bonds in NH_3:
- 3 N-H covalent bonds
- 1 N→H dative bond
- 1 $NH_4^+ - Cl^-$ ionic bond

Main intermolecular force in NH_3 is Hydrogen bonding





- NH_3 is soluble in water as it dissociates in water to form $NH_4^+ + OH^-$. It is a weak base → it dissociates partially

- NH_3 reacts with acids to form salts :

$$NH_3 + HCl \longrightarrow NH_4Cl$$
$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$
$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$
$$3NH_3 + H_3PO_4 \longrightarrow (NH_4)_3PO_4$$

Note : Ammonium salts are fertilizers

- Test for NH_4^+ ion

  - NH_4^+ is a conjugate acid, so it reacts with bases, to give $NH_3(g)$ and this is used as a test for the NH_4^+ ion.

$$(NH_4)_2SO_4(aq) + 2NaOH \xrightarrow[\text{gently}]{\text{warm}} Na_2SO_4 + 2NH_3(g) + 2H_2O$$

pungent colorless gas

↓

Also turns damp red litmus paper blue

$$2NH_4Cl + CaO \longrightarrow CaCl_2 + 2NH_3(g) + H_2O$$

USES OF NH_3 :

- Manufacture of fertilizers (ie. $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, NH_4NO_3 ...)
- To make explosives like TNT

EXCESSIVE USE OF FERTILIZERS

1. Excessive fertilizers are washed out (leached) by rain water and collects in streams, lakes, ponds and rivers

Eutrophication

excess fertilizers in the lake (excessive NO_3^-, PO_4^{3-} SO_4^{2-}) leads to an algal bloom as the algae multiply rapidly by feeding on the ions

↳ Sunlight is blocked out

↳ Aquatic plants die + Algae dies

↳ Bacteria starts to decompose the dead plants & algae. This uses up the dissolved O_2

↳ All fish & other aquatic life die

2. If the excessive fertilizers are washed out and they seep into ground water, then groundwater is contaminated by nitrates

↳ NO_3^- ions are toxic, because they can oxidise Fe^{2+} in haemoglobin to Fe^{3+}.

↳ This reduces the oxygen-carrying capacity of blood.

Note: 2016 onwards: Details of Haber and contact process are no longer in syllabus.

NO_x POLLUTION

Oxides of Nitrogen

- NO_2 — Colorless gas
- NO — Brown gas

How are these oxides prepared in nature?

- During lightning storms
- Lightning strikes heat up the surrounding air to a temperature at which the N≡N can be broken, allowing N to combine with oxygen in the atmosphere

How are they produced by human activities?

Car Engines: work at very high temperatures

↳ Provides the activation energy to break N≡N bond

step 1: $N_2 + O_2 \longrightarrow 2NO$ $\quad \Delta H = (+)$ ie. endothermic

step 2: $NO + \frac{1}{2}O_2 \longrightarrow NO_2$ $\quad \Delta H = (-)$ ie. exothermic

Power Stations: High temperatures due to coal and oil fuels being burned provides enough activation energy for $N \equiv N$ to break and NO_x to form

How does NO_x damage the environment?

1. Acid Rain [Directly]
   NO_x reacts with water (rain) to form a mixture of acids

Step 1: $NO_2 + H_2O \longrightarrow \underset{\text{nitrous}}{HNO_2} + \underset{\text{nitric}}{HNO_3}$

Step 2: $HNO_2 + \frac{1}{2}O_2 \longrightarrow \underset{\text{nitric}}{HNO_3}$

Overall: $NO_2 + \underset{\text{rain}}{H_2O} + \frac{1}{2}O_2 \longrightarrow 2HNO_3(aq)$
↳ part of acid rain

2. Acid Rain [Indirectly]
   - Indirectly, NO_2 acts as the catalyst in the oxidation of SO_2 to SO_3
   - Acid rain is mostly sulfuric acid

a) NO_2 as the catalyst

$SO_2 + NO_2 \longrightarrow SO_3 + NO$

$NO + \frac{1}{2}O_2 \longrightarrow NO_2$
↳ catalyst regenerated

$SO_3 + \underset{\text{rain water}}{H_2O} \longrightarrow \underset{\text{Sulfuric Acid}}{H_2SO_4(aq)}$

b) NO as the catalyst

$NO + \frac{1}{2}O_2 \longrightarrow NO_2$

$NO_2 + SO_2 \longrightarrow SO_3 + NO$
↳ catalyst regenerated

$SO_3 + H_2O \longrightarrow H_2SO_4(aq)$

- SO_3 is a pollutant that is released when fossil fuels like coal containing sulfur as an impurity are burnt in power stations
- SO_3 is a "flue" gas and an acidic oxide

3. NOx also causes problems in the lower atmosphere as it combines with other air pollutants ie. ozone, leading to smog

EFFECTS OF ACID RAIN

- Corrosion of buildings and limestone structures ($CaCO_3$)

$$CaCO_3(s) + \underbrace{H_2SO_4(aq)}_{\text{Acid Rain}} \longrightarrow CuSO_4 + H_2O + CO_2$$

- Corrosion of steel structures ie. bridges, vehicles, cars, etc.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

- Acidification of lakes (reduces the pH of lakewater)
  - All aquatic life is destroyed

- Lowers the pH of soil which reduces crop yield
  - Farmers have to neutralize the acidic soil by applying lime (CaO)

$$CaO + H_2O \rightarrow Ca(OH)_2$$

↳ acts as a base to neutralize the acidic soil

PREVENTION OF ACID RAIN

- Burn less fossil fuels like coal which contains sulfur as an impurity
- Treat exhaust gases from industries and power stations with SO_2-absorbing chemicals ie. heated limestone

$$CaCO_3 \xrightarrow{\text{heat}} CaO + SO_2$$

$$\underbrace{CaO}_{\text{Basic}} + \underbrace{SO_2}_{\text{Acidic}} \longrightarrow \underline{CaSO_3}$$

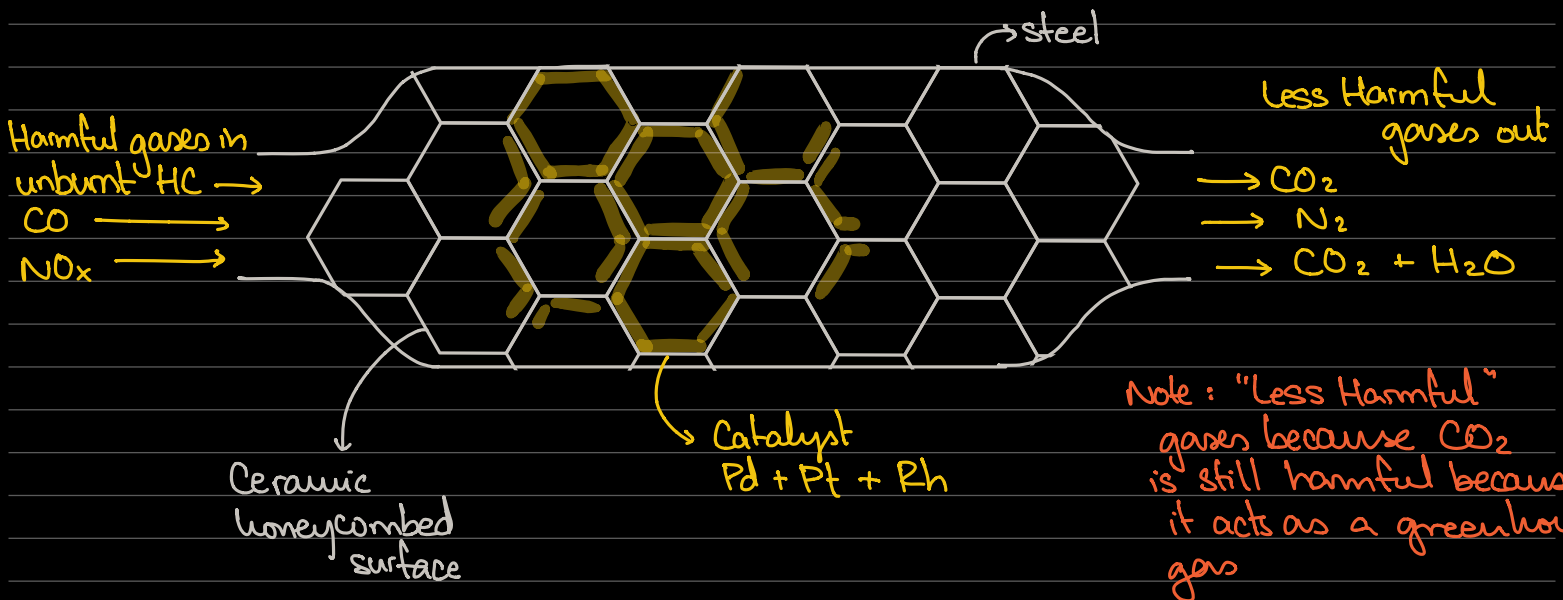
Calcium Sulfite

Further Oxid: $CaSO_3 + \frac{1}{2}O_2 \longrightarrow CaSO_4$

Calcium Sulfate

- Preventing NOx pollution
  i) By fitting cars / vehicles with a catalytic converter in the exhaust system

  - Steel structure with a honeycomb ceramic surface
  - The ceramic surface is coated with a mixture of catalysts over which the rxn. occurs
  - The honeycomb pattern increases the surface area over which the reaction takes place / surface area of the catalyst



Note: "Less Harmful" gases because CO_2 is still harmful because it acts as a greenhouse gas

CREATION OF HARMFUL GASES

CO → incomplete combustion of petrol
NOx → at high temperatures, $N_2 + O_2$ in the atmosphere react together
↓
inside the car engine

DEALING W/ THESE HARMFUL GASES

NO:

$$2NO + 2CO \xrightarrow[200^\circ C]{Pt/Pd/Rh} 2CO_2 + N_2$$

CO:

$$2CO + O_2 \xrightarrow[200^\circ C]{Pt/Pd/Rh} 2CO_2$$

Unburnt HC:

$$2C_8H_{18} + 25O_2 \xrightarrow[200^\circ C]{Pt/Pd/Rh} 16CO_2 + 18H_2O$$

- Catalytic converter has to be at approximately 200°C to work effectively
- It is <u>not</u> very efficient when the car is first started

ii) We should run/operate power stations that burn any fuel at a lower temperature

↳ so that N_2 in the atmosphere is not oxidised to NOx

USES

✓ = just remembering these should be enough

Sulfuric Acid (H_2SO_4):

i) Manufacture of fertilizers ✓
ii) Manufacture of paint
iii) Tanning of leather
iv) Used as the electrolyte in car batteries ✓
v) Used to remove rust from iron and steel objects before they're painted
↳ aka "pickling"
vi) Manufacture of organic chemicals such as dyes, drugs and explosives

vii) Used in food preservation

Sulfur Dioxide (SO_2):

i) Used as a food preservative as it inhibits the growth of bacteria and fungi, hence preventing food from spoiling

ii) SO_2 is a reducing agent, it prevents the oxidation of food and is used to prevent fruit from over-ripening

iii) SO_2 is used to preserve wines

↳ Keeps them at a pH < 4

x ——————————— x

End of syllabus - Finally