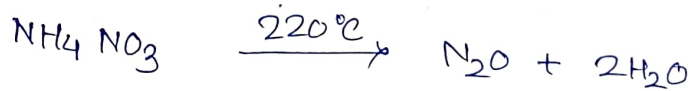


Oxides of Nitrogen

① Nitrous oxide, N₂O

Preparation It may be prepared by reducing NO with moist iron filings or by heating NH₄NO₃.



It may also be prepared by heating a mixture of NaNO₃ and (NH₄)₂SO₄ or NH₄Cl



Properties

- (i) Davy (1799) has called this gas laughing gas as it produces hysterical laughter on inhalation. Continuous inhalation causes insensibility to pain and finally death.
- (ii) It is colourless gas with a faint sweetish odour and taste. (m.p. = -90.8 °C, b.p. = 88.7 °C)
- (iii) It is appreciably soluble in water and more so in alcohol but is insoluble in hot water. The aqueous solution is neutral and does not behave as the anhydride of hyponitrous acid (H₂N₂O₂), although it is formed by its decomposition.



N₂O is a neutral oxide.

(iv) Decomposition When heated, N_2O gets decomposed into N_2 and O_2 .



The gas is also decomposed by electric sparks.

(v) Reduction Burnish pieces of P, C, S etc. burn brilliantly in N_2O gas and free N_2 is evolved, i.e. N_2O is reduced to N_2 .



When passed over hot Cu, N_2O is reduced to N_2 .



② Nitric oxide (NO)

Preparation

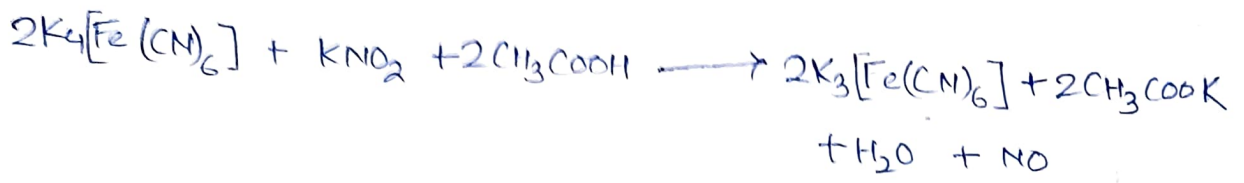
(i) In the laboratory, NO is obtained by the action of cold dil. HNO_3 on Cu.



(ii) Pure NO is obtained by the action of $NaNO_2$ solution on an acidified solution of KI



or by dropping a solution of $K_4[Fe(CN)_6]$ and $NaNO_2$ into dil. (CH_3COOH) .



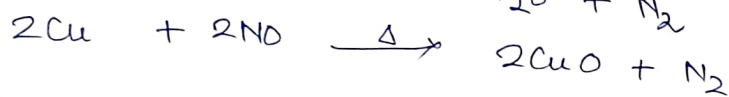
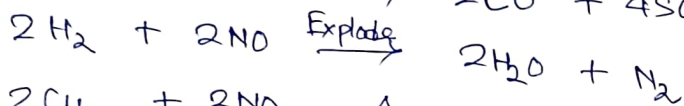
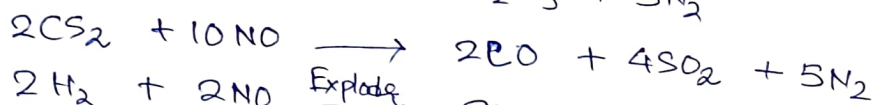
Properties

- (i) NO is colourless gas which is slightly heavier than air.
- (ii) It is only sparingly soluble in water and is neutral oxide like N_2O .
- (iii) Liquid NO is blue in colour and boils at $-151.7^\circ C$. At $-163.6^\circ C$ it freezes to blue solid.
- (iv) Action of solid NO_2 The action of solid NO_2 cooled in liquid air gives N_2O_3 .



(v) Reduction

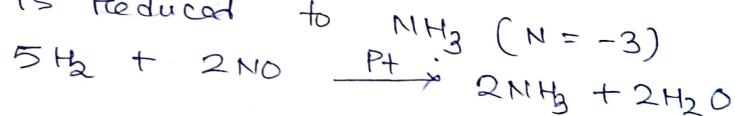
- (a) Burning phosphorus, CS_2 vapour, H_2 and heated metals (eg. Cu, Fe, Ni, Na etc.) reduce NO ($N = +2$) and N_2 ($N = 0$).



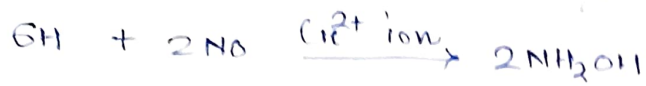
- (b) H_2SO_3 and moist Fe filings reduce NO ($N = +2$) to N_2O ($N = +1$).



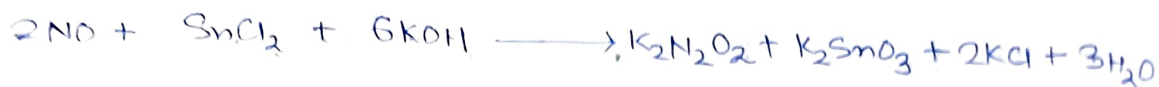
- (c) When heated with H_2 in presence of Pt metal, NO ($N = +2$) is reduced to NH_3 ($N = -3$)



(d) Chromous ion (Cr^{2+}) reduces NO ($N = +2$) to NH_2OH ($N = -1$).

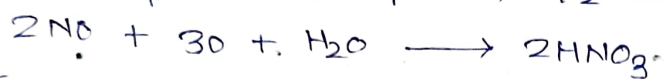
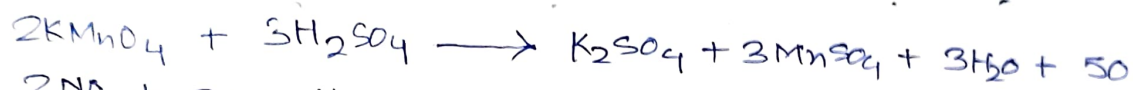


(e) Alkaline solution of SnCl_2 reduces NO to potassium hyponitrite ($\text{K}_2\text{N}_2\text{O}_2$).

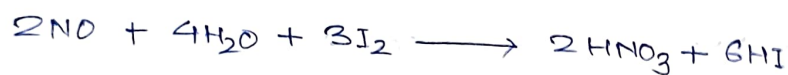


(vi) Oxidation

(a) Acidified solution of KMnO_4 and dil. solution of I_2 oxidise NO ($N = +2$) to HNO_3 ($N = +5$).



This reaction is quantitative and is used for the estimation of NO .



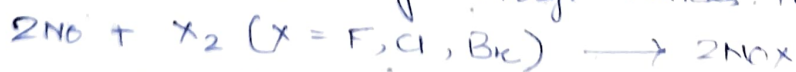
(b) Conc. HNO_3 and O_2 oxidise NO ($N = +2$) to NO_2 ($N = +4$)



(vii) Absorption by FeSO_4 : FeSO_4 solution absorbs NO , forming brown nitrosoferrous sulphate, $(\text{NO})\text{FeSO}_4$



(viii) Action of halogens: Excepting I_2 , F_2 , Cl_2 and Br_2 react with NO and give corresponding nitrosyl halides, NOX .



Nitrogen dioxide (NO₂) and dinitrogen tetroxide (N₂O₄)

Preparation .1) NO₂ is prepared by mixing NO with O₂.



2) By heating dry powdered Pb(NO₃)₂ in hard glass tube.



3) By the action of conc. HNO₃ on Cu or Bi.



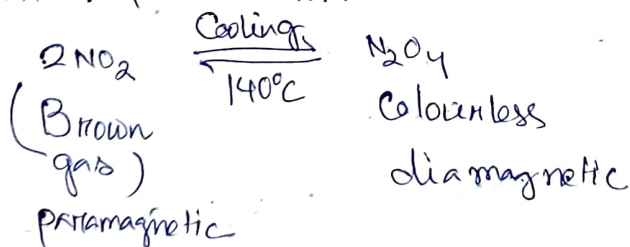
4) By heating nitroso sulphuric acid (NO)HSO₄ with dry KNO₃.



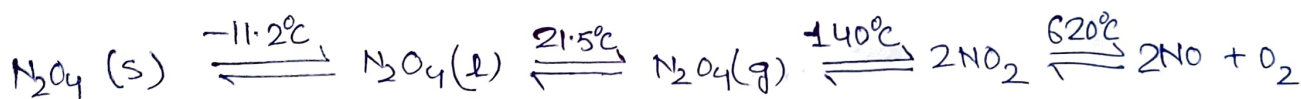
Properties

(i) NO₂ is brown while N₂O₄ is colourless.

(ii) Action of heat: NO₂ and N₂O₄ exist in a temperature dependent equilibrium.



In the solid state, the oxide is entirely N₂O₄ which appears to be colourless. At -11.2°C the solid N₂O₄ melts and is converted into N₂O₄ liquid. At 21.5°C N₂O₄ is present as reddish brown vapour. At 140°C the oxide is present as NO₂. At 620°C NO₂ dissociates into NO and O₂. Reverse changes takes place on cooling.



Colourless

(iii) Action of metals and non-metals: Heated sodium burns in NO_2 while potassium inflames spontaneously in the gas.

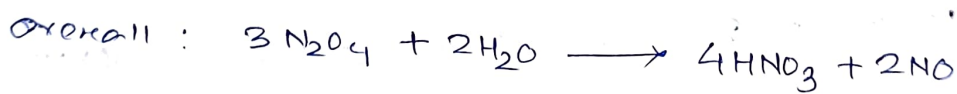
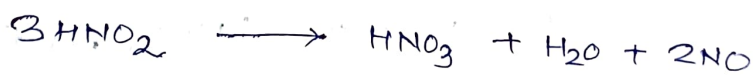


Strongly burning P and C burn in it because at high temperature, NO_2 dissociates into NO and O_2 .

(iv) Acidic nature: N_2O_4 is an acidic oxide, since it dissolves in H_2O and gives a mixture of HNO_2 and HNO_3 . Thus N_2O_4 is called a mixed acid anhydride.



HNO_2 produced as above decomposes into HNO_3 and NO .



N_2O_4 is absorbed by an alkali, forming a mixture of nitrite and nitrate.



(v) Action of conc. H_2SO_4 : Conc. H_2SO_4 absorbs N_2O_4 and forms nitroso sulphuric acid, $(\text{NO})\text{HSO}_4$ and HNO_3

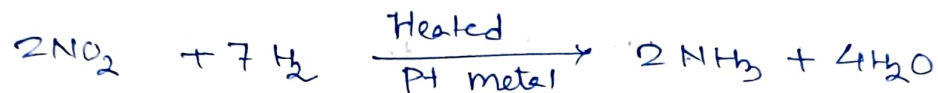


(vi) Oxidising Properties (Reduction).

(a) NO_2 ($\text{N} = +4$) oxidises SO_2 to H_2SO_4 in presence of H_2O , H_2S to S , CO to CO_2 and liberates I_2 from KI solution and itself reduces to NO ($\text{N} = +2$)



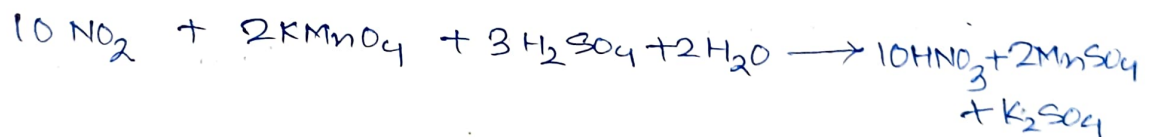
(b) NO_2 (N = +4) oxidises H_2 (H = 0) to H_2O (H = +1) and is reduced to NH_3 (N = -3)



(c) NO_2 (N = +4) oxidises Cu (Cu = 0) heated to bright redness to CuO (Cu = +2) and itself gets reduced to N_2 (N = 0)



(vii) Oxidation: NO_2 (N = +4) is oxidised to HNO_3 (N = +5) by means of acidified KMnO_4 solution.

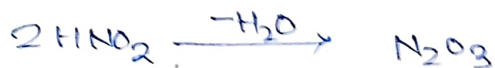


(viii) Action of ozonised O_2 : When ozonised O_2 (ie. O_3) is passed into cooled liquid N_2O_4 , N_2O_5 is obtained.



Dinitrogen trioxide or nitrogen sesquioxide, N_2O_3

It is considered as anhydride of nitrous acid.



Preparation

(i) By the action of copper on 5N nitric acid.



(ii) By cooling (below $-20^\circ C$) a mixture (2:1) of nitric oxide and nitrogen dioxide in a tube.



(iii) By the distillation of a mixture of arsenous oxide (As_4O_6) and 60% HNO_3 by collecting the N_2O_3 vapours in a U-tube, cooled in a freezing mixture.

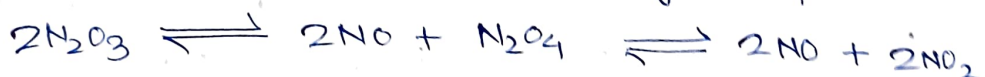


Properties

(i) Solid N_2O_3 forms blue crystals (m.p. = $-120^\circ C$)

(ii) It boils at $3.5^\circ C$ with decomposition.

(iii) It decomposes on melting as follows—



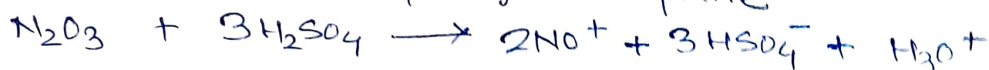
(iv) It dissolves in water to form nitrous acid, HNO_2



(v) It reacts with bases to form nitrites.



(vi) When treated with concentrated sulphuric acid, blue colour of N_2O_3 disappears due to the formation of fully ionised nitrosonium hydrogen sulphate



Dinitrogen Pentoxide N_2O_5

Preparation

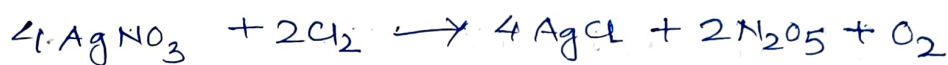
(i) When conc. HNO_3 is distilled with phosphorus pentoxide in a glass retort at $70^\circ C$, we get N_2O_5



(ii) By passing ozone through liquid N_2O_4



(iii) By the action of Cl_2 on heated dry silver nitrate.



Properties

(i) It is a white solid, mp. = $30^\circ C$, b.p. = $47^\circ C$

(ii) It decomposes above $30^\circ C$ and explodes when heated rapidly.



(iii) It is an anhydride of nitric acid because it dissolves in water to form this acid.



(iv) As an oxidant

(a) It oxidises iodine to iodine pentoxide.



(b) It oxidises all organic substances like cork, rubber etc. and destroys them.

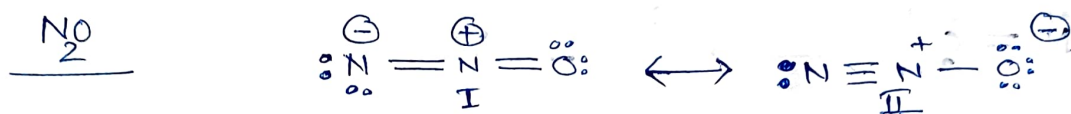
(v) N_2O_5 reacts with alkalis to form nitrates.



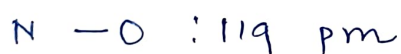
(vi) N_2O_5 ionises, in conc. H_2SO_4 to form nitronium ion, NO_2^+ .



Structure



This molecule is linear and unsymmetrical having a small dipole moment. It is explained by considering it as a resonance hybrid of structure I and II. The bond lengths are



In N_2O , both nitrogen and oxygen atoms are considered to use sp -hybrid orbitals. The molecule is, thus, considered to have two sigma bonds. The two pairs of delocalised π -electrons extend over three atoms (N, N, and O)

NO

Valence bond theory

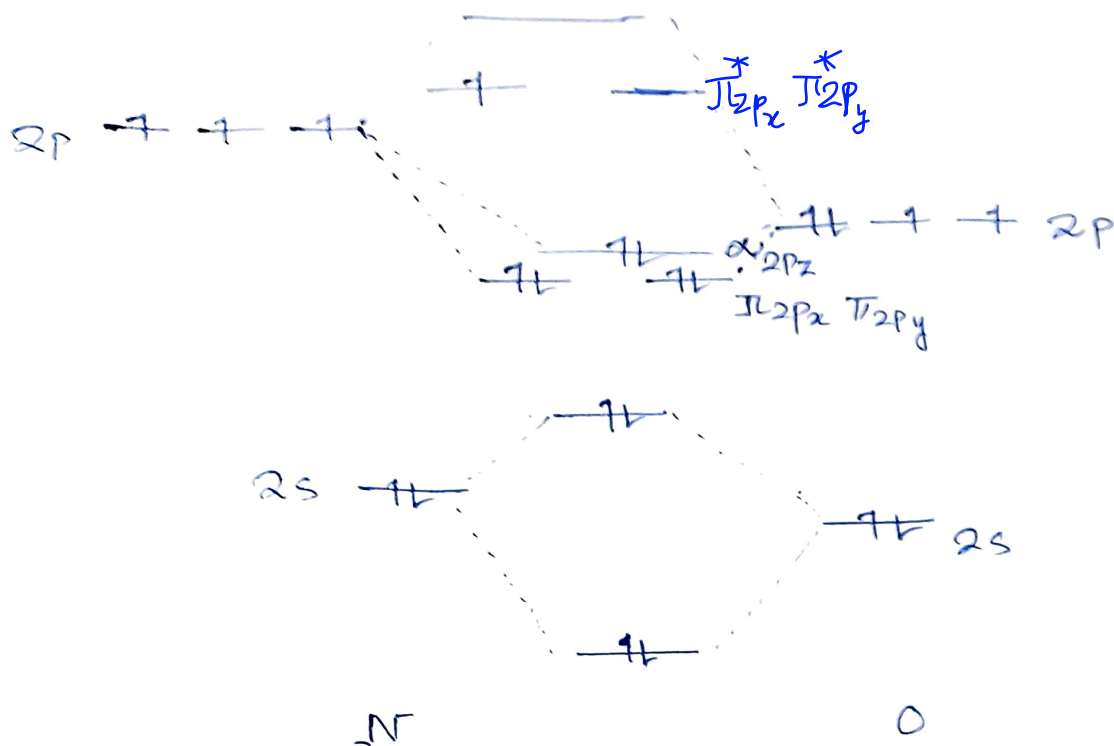
One N atom ($1s^2 2s^2 2p^3$) and one O atom ($1s^2, 2s^2, 2p^4$) have total 11 valence electrons.

The unpaired electrons of NO is spread over the whole molecule. It is represented as the average of the following structures.

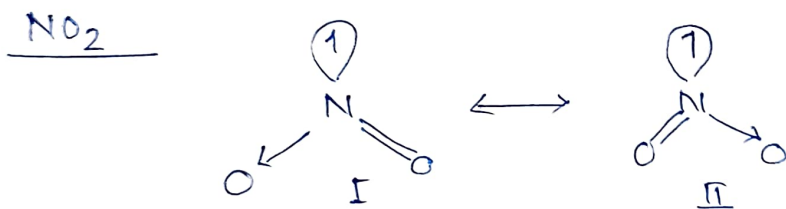


The N-O bond length is 1.10 \AA .

Molecular Orbital theory



$$\text{Bond order} = \frac{8 - 3}{2} = 2.5$$



The electron diffraction studies have revealed that monomeric dioxide, NO₂ is angular with bond angle ONO equal to 134°. It is considered as a resonance hybrid of the structure I and II.