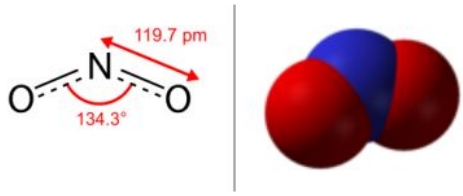
Nitrogen dioxide

Nitrogen dioxide is a chemical compound with the formula NO_2. It is one of several nitrogen oxides. NO_2 is an intermediate in the industrial synthesis of nitric acid, millions of tons of which are produced each year which is used primarily in the production of fertilizers. At higher temperatures it is a reddish-brown.[8]

Nitrogen dioxide is a paramagnetic, bent molecule with C_{2v} point group symmetry.

Nitrogen dioxide



(NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures and reverts to NO_2 at higher temperatures.

Names

IUPAC name

Nitrogen dioxide

Other names

Properties	
Chemical formula	$NO_2^{\bullet}$
Molar mass	46.006 g/mol[2]
Appearance	Brown gas[2]
Odor	Chlorine like

Density	1.880 g/L[2]
Melting point	−9.3 °C (15.3 °F; 263.8 K)[2]
Boiling point	21.15 °C (70.07 °F; 294.30 K)[2]
Solubility in water	Hydrolyses
Solubility	soluble in CCl_4, nitric acid,[3] chloroform
Vapor pressure	98.80 kPa (at 20 °C)
Magnetic susceptibility (χ)	$+150.0 \cdot 10^{-6}$ cm^3/mol[4]
Refractive index (n_D)	1.449 (at 20 °C)
Structure	
Point group	C_{2v}

Molecular shape	Bent
Thermochemistry[5]	
Heat capacity (C)	37.2 J/(mol·K)
Std molar entropy ($S^{\ominus}_{298}$)	240.1 J/(mol·K)
Std enthalpy of formation ($\Delta_f H^{\boxminus}_{298}$)	+33.2 kJ/mol
Hazards	
Main hazards	Poison, oxidizer
Safety data sheet	ICSC 0930
GHS pictograms	
GHS Signal word	**Danger**
GHS hazard statements	H270, H314, H330

294.3 K), and converts to the colorless dinitrogen tetroxide (N_2O_4) below −11.2 °C (11.8 °F; 261.9 K).[6]

The bond length between the nitrogen atom and the oxygen atom is 119.7 pm. This bond length is consistent with a bond order between one and two.

Unlike ozone, O_3, the ground electronic state of nitrogen dioxide is a doublet state, since nitrogen has one unpaired electron,[9] which decreases the alpha effect compared with nitrite and creates a weak bonding interaction with the oxygen

lone pairs. The lone electron in NO_2 also means that this compound is a free radical, so the formula for nitrogen dioxide is often written as $^{\bullet}NO_2$.

The reddish-brown color is a consequence of preferential absorption of light in the blue (400 – 500 nm), although the absorption extends throughout the visible (at shorter wavelengths) and into the infrared (at longer wavelengths). Absorption of light at wavelengths shorter than about 400 nm results in photolysis (to form NO + O, atomic oxygen); in the

Properties

Nitrogen dioxide is a reddish-brown gas above 21.2 °C (70.2 °F; 294.3 K) with a pungent, acrid odor, becomes a yellowish-brown liquid below 21.2 °C (70.2 °F;

atmosphere the addition of O atom so formed to O_2 results in ozone formation.

Preparation and reactions

Nitrogen dioxide typically arises via the oxidation of nitric oxide by oxygen in air:[10]

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

Nitrogen dioxide is formed in most combustion processes using air as the oxidant. At elevated temperatures nitrogen combines with oxygen to form nitric oxide:

$$O_2 + N_2 \rightarrow 2\ NO$$

In the laboratory, NO_2 can be prepared in a two-step procedure where dehydration of nitric acid produces dinitrogen pentoxide, which subsequently undergoes thermal decomposition:

$$2\,HNO_3 \rightarrow N_2O_5 + H_2O$$
$$2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$$

The thermal decomposition of some metal nitrates also affords NO_2:

$$2\,Pb(NO_3)_2 \rightarrow 2\,PbO + 4\,NO_2 + O_2$$

Alternatively, reduction of concentrated nitric acid by metal (such as copper).

$$4\,HNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2\,NO_2 + 2\,H_2O$$

Or finally by adding concentrated nitric acid over tin, hydrated stannic oxide is produced as byproduct.

$$4\,HNO_3 + Sn \rightarrow H_2O + H_2SnO_3 + 4\,NO_2$$

Main reactions

Basic thermal properties

NO_2 exists in equilibrium with the colourless gas dinitrogen tetroxide (N_2O_4):

$$2\,NO_2 \rightleftharpoons N_2O_4$$

The equilibrium is characterized by $\Delta H = -57.23$ kJ/mol, which is exothermic. NO_2 is favored at higher temperatures, while at lower temperatures, dinitrogen tetroxide (N_2O_4) predominates. Dinitrogen tetroxide (N_2O_4) can be obtained as a white solid with melting point −11.2 °C.[10] NO_2 is paramagnetic due to its unpaired electron, while N_2O_4 is diamagnetic.

The chemistry of nitrogen dioxide has been investigated extensively. At 150 °C, NO_2 decomposes with release of oxygen

via an endothermic process
(ΔH = 14 kJ/mol):

$$2\ NO_2 \rightarrow 2\ NO + O_2$$

As an oxidizer

As suggested by the weakness of the N–O bond, NO_2 is a good oxidizer. Consequently, it will combust, sometimes explosively, with many compounds, such as hydrocarbons.

Hydrolysis

It hydrolyses to give nitric acid and nitrous acid:

$$2\ NO_2\ (N_2O_4) + H_2O \rightarrow HNO_2 + HNO_3$$

This reaction is one step in the Ostwald process for the industrial production of nitric acid from ammonia.[11] This reaction is negligibly slow at low concentrations of NO_2 characteristic of the ambient atmosphere, although it does proceed upon NO_2 uptake to surfaces. Such surface reaction is thought to produce gaseous HNO_2 (often written as HONO) in outdoor and indoor environments.[12]

Formation from decomposition of nitric acid

Nitric acid decomposes slowly to nitrogen dioxide by the overall reaction:

$$4\,HNO_3 \rightarrow 4\,NO_2 + 2\,H_2O + O_2$$

The nitrogen dioxide so formed confers the characteristic yellow color often exhibited by this acid.

Conversion to nitrates

NO_2 is used to generate anhydrous metal nitrates from the oxides:[10]

$$MO + 3\ NO_2 \rightarrow M(NO_3)_2 + NO$$

Conversion to nitrites

Alkyl and metal iodides give the corresponding nitrites:

$$2\ CH_3I + 2\ NO_2 \rightarrow 2\ CH_3NO_2 + I_2$$
$$TiI_4 + 4\ NO_2 \rightarrow Ti(NO_2)_4 + 2\ I_2$$

Ecology

NO_2 is introduced into the environment by natural causes, including entry from the stratosphere, bacterial respiration, volcanos, and lightning. These sources make NO_2 a trace gas in the atmosphere

of Earth, where it plays a role in absorbing sunlight and regulating the chemistry of the troposphere, especially in determining ozone concentrations.[13]

Uses

NO_2 is used as an intermediate in the manufacturing of nitric acid, as a nitrating agent in manufacturing of chemical explosives, as a polymerization inhibitor for acrylates, as a flour bleaching agent.,[14]:223 and as a room temperature sterilization agent.[15] It is also used as an oxidizer in rocket fuel, for example in red

fuming nitric acid; it was used in the Titan rockets, to launch Project Gemini, in the maneuvering thrusters of the Space Shuttle, and in unmanned space probes sent to various planets.[16]

Nitrogen dioxide NO_2 and dinitrogen tetroxide N_2O_4

NO_2 is a red–brown poisonous gas and is produced on a large scale by oxidizing NO in the Ostwald process for the manufacture of nitric acid. In the laboratory it is prepared by heating lead nitrate:

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

The gaseous products O_2 and NO_2 are passed through a U-tube cooled in ice. The NO_2 (b.p. 21 °C) condenses. The $Pb(NO_3)_2$ must be carefully dried, since NO_2 reacts with water. The NO_2 is obtained as a brown liquid which turns paler on cooling, and eventually becomes a colourless solid. This is because NO_2 dimerizes into colourless N_2O_4. NO_2 is an odd electron molecule, and is paramagnetic and very reactive. It dimerizes to N_2O_4, pairing the previously unpaired electrons. N_2O_4 has no unpaired electrons and is diamagnetic.

$$\underset{\text{paramagnetic}\\\text{brown}}{2NO_2} \rightleftharpoons \underset{\text{diamagnetic}\\\text{colourless}}{N_2O_4}$$

N_2O_4 is a mixed anhydride, because it reacts with water to give a mixture of nitric and nitrous acids:

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$$

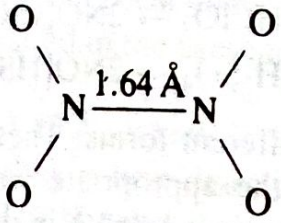
The HNO_2 formed decomposes to give NO.

$$2HNO_2 \rightarrow NO_2 + NO + H_2O$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

Thus moist NO_2 or N_2O_4 gases are strongly acidic.

The NO_2 molecule is angular with an O—N—O angle of 132°. The bond length O—N of 1.20 Å is intermediate between a single and a double bond. X-ray diffraction on solid N_2O_4 shows the structure to be planar.



The N—N bond is very long (1.64 Å), and is therefore weak. It is much longer than the single bond N-N distance of 1.47 Å in N_2H_4, but there is no satisfactory explanation of why it is long.

Liquid N_2O_4 is useful as a non-aqueous solvent. It self-ionizes:

$$N_2O_4 \rightleftharpoons \underset{\text{acid}}{NO^+} + \underset{\text{base}}{NO_3^-}$$

In N_2O_4 substances containing NO^+ are acids and those containing NO_3^- are bases. A typical acid–base reaction is:

$$\underset{\text{acid}}{NOCl} + \underset{\text{base}}{NH_4NO_3} \rightarrow \underset{\text{salt}}{NH_4Cl} + \underset{\text{solvent}}{N_2O_4}$$

Liquid N_2O_4 is particularly useful as a solvent for preparing anhydrous metal nitrates and also nitrato complexes.

$$ZnCl_2 + N_2O_4 \rightarrow Zn(NO_3)_2 + 2NOCl$$

$$TiBr_4 + N_2O_4 \rightarrow Ti(NO_3)_4 + 4NO + 2I_2$$

The NO_2–N_2O_4 system is a strong oxidizing agent. NO_2 reacts with fluorine and chlorine, forming nitryl fluoride NO_2F and nitryl chloride NO_2Cl. It oxidizes HCl to Cl_2 and CO to CO_2.

$$2NO_2 + F_2 \rightarrow 2NO_2F$$

$$2NO_2 + Cl_2 \rightarrow 2NO_2Cl$$

$$2NO_2 + 4HCl \rightarrow 2NOCl + Cl_2 + 2H_2O$$

$$NO_2 + CO \rightarrow CO_2 + NO$$