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INTRODUCTIN

TO

FERTILIZER INDUSTRIES

BY

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Fertilizer

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An old fertilizer spreader



A large, modern fertilizer spreader

1- Introduction :

Fertilizers are soil amendments applied to promote plant growth; the main nutrients present in fertilizer are nitrogen, phosphorus, and potassium (the 'macronutrients') and other nutrients ('micronutrients') are added in smaller amounts. Fertilizers are usually directly applied to soil, and also sprayed on leaves ('foliar feeding').

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Fertilizers are roughly broken up between *organic* and *inorganic* fertilizer, with the main difference between the two being sourcing, and not necessarily differences in nutrient content.

Organic fertilizers and some mined inorganic fertilizers have been used for centuries, whereas chemically-synthesized inorganic fertilizers were only widely developed during the industrial revolution. Increased understanding and use of fertilizers were important parts of the pre-industrial British Agricultural Revolution and the industrial green revolution of the 20th century.

2 - Plant nutrients supplied by fertilizers



Tennessee Valley Authority: "Results of Fertilizer" demonstration 1942

Fertilizers typically provide, in varying proportions:

- the three primary macronutrients: nitrogen, phosphorus, and potassium.
- the three secondary macronutrients such as calcium (Ca), sulfur (S), magnesium (Mg).
- and the micronutrients or trace minerals: boron (Bo), chlorine (Cl), manganese (Mn), iron (Fe), zinc (Zn), copper (Cu), molybdenum (Mo) and selenium (Se).

The macronutrients are consumed in larger quantities and are present in plant tissue in quantities from 0.2% to 4.0% (on a dry

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matter weight basis). Micronutrients are consumed in smaller quantities and are present in plant tissue in quantities measured in parts per million (ppm), ranging from 5 to 200 ppm, or less than 0.02 % dry weight.

3 - Labeling of fertilizers:

3 – 1 - Macro nutrient fertilizers;

Macronutrient fertilizers are labeled with an *NPK* analysis and also "N-P-K-S" in Australia .

An example of labeling for the fertilizer *potash* is composed of 1:1 potassium to chloride or 52 % potassium and 48% chlorine *by weight* (owing to differences in molecular weight between the elements). Traditional analysis of 100g. of *KCl* would yield 60g. K_2O . The *percentage yield* of K_2O from the original 100g. of fertilizer is the number shown on the label. A potash fertilizer would thus be labeled 0-0-60, *not* 0-0-52.

4 - History of fertilizer

While manure, cinder and iron making slag have been used to improve crops for centuries, use of inorganic artificial fertilizer is one innovations of the 19th century Agricultural Revolution.

5 - Inorganic fertilizer (synthetic fertilizer):

Fertilizers are broadly divided into *organic fertilizers* (composed of enriched organic matter- plant or animal), or *inorganic fertilizers* (composed of synthetic chemicals and / or minerals).

Inorganic fertilizer is often synthesized using the Haber-Bosch process, which produces ammonia as the end product. This ammonia is used as a feedstock for other nitrogen fertilizers, such as anhydrous ammonium nitrate and urea. These concentrated products may be diluted with water to form a concentrated liquid fertilizer (e.g. UAN). Ammonia can be combined with rock phosphate and potassium fertilizer in the Odda Process to produce *compound fertilizer*.

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The use of synthetic nitrogen fertilizers has increased steadily in the last 50 years, rising almost 20-fold to the current rate of 1 billion tonnes of nitrogen per year. The use of phosphate fertilisers has also increased from 9 million tones per year in 1960 to 40 million tonnes per year in 2000. A maize crop yielding 6-9 tones of grain per hectare requires 30 – 50 kg of phosphate fertilizer to be applied, soybean requires 20 - 25kg per hectare.

Top users of nitrogen based fertilizer

Country	Total N use (Mt pa)	Amt. used (feed/pasture)
China	18.7	3.0
U.S.	9.1	4.7
France	2.5	1.3
Germany	2.0	1.2
Brazil	1.7	0.7
Canada	1.6	0.9
Turkey	1.5	0.3
U.K.	1.3	0.9
Mexico	1.3	0.3
Spain	1.2	0.5
Argentina	0.4	0.1

5 – 1 – Application:

Synthetic fertilizers are commonly used to treat fields used for growing maize, followed by barley, sorghum, rapeseed, soy and sunflower . One study has shown that application of nitrogen fertilizer on off - season cover crops can increase the biomass (and subsequent green manure value) of these crops, while having a beneficial effect on soil nitrogen levels for the main crop planted during the summer season.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**5 – 2 - Problems of inorganic fertilizer:****5 – 2 – 1 - Trace mineral depletion;**

Many inorganic fertilizers do not replace trace mineral elements in the soil which become gradually depleted by crops. This depletion has been linked to studies which have shown a marked fall (up to 75 %) in the quantities of such minerals present in fruit and vegetables.

However, a recent review of 55 scientific studies concluded "there is no evidence of a difference in nutrient quality between organically and conventionally produced foodstuffs" ^[9] Conversely, a major long-term study funded by the European Union ^{[10][11] [12]} found that organically - produced milk and produce were significantly higher in antioxidants (such as carotenoids and alpha - linoleic acids) than their conventionally grown counterparts.

In Western Australia deficiencies of zinc, copper, manganese, iron and molybdenum were identified as limiting the growth of broad-acre crops and pastures in the 1940s and 1950s ' Soils in Western Australia are very old, highly weathered and deficient in many of the major nutrients and trace elements ' Since this time these trace elements are routinely added to inorganic fertilizers used in agriculture in this state

5 – 2 – 2 - Over fertilization (Fertilizer burn):

Fertilizer burn

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Over-fertilization of a vital nutrient can be as detrimental as under fertilization. "Fertilizer burn" can occur when too much fertilizer is applied, resulting in a drying out of the roots and damage or even death of the plant.

5 - 2 – 3 - High energy consumption:

The production of *synthetic* ammonia currently consumes about 5% of global natural gas consumption, which is somewhat under 2% of world energy production.

Natural gas is overwhelmingly used for the production of ammonia, but other energy sources, together with a hydrogen source, can be used for the production of nitrogen compounds suitable for fertilizers. The cost of natural gas makes up about 90 % of the cost of producing ammonia. The increase in price of natural gases over the past decade, along with other factors such as increasing demand, have contributed to an increase in fertilizer price.

5 – 2 – 4 - Long - Term Sustainability:

Inorganic fertilizers are now produced in ways which cannot be continued indefinitely. Potassium and phosphorus come from mines (or saline lakes such as the Dead Sea) and such resources are limited. Atmospheric (*unfixed*) nitrogen is effectively unlimited (forming over 70% of the atmospheric gases), but this is not in a form useful to plants. To make nitrogen accessible to plants requires nitrogen fixation (conversion of atmospheric nitrogen to a plant - accessible form).

Artificial nitrogen fertilizers are typically synthesized using fossil fuels such as natural gas and coal, which are limited resources. In lieu of converting natural gas to syngas for use in the Haber process, it is also possible to convert renewable biomass to syngas (or wood gas) to supply the necessary energy for the process, though the amount of land and resources (ironically often including fertilizer) necessary for such a project may be prohibitive (see Energy conservation in the United States).

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6 - Organic fertilizers:



Compost bin for small - scale production of organic fertilizer



A large commercial compost operation

Organic fertilizers include naturally-occurring organic materials, (e.g. manure, worm castings, compost, seaweed), or naturally occurring mineral deposits (e.g. saltpeter, guano).

6 – 1 - Benefits of organic fertilizer;

In addition to increasing yield and fertilizing plants directly, organic fertilizers can improve the biodiversity (soil life) and long-term productivity of soil, and may prove a large depository for excess carbon dioxide.

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Organic nutrients increase the abundance of soil organisms by providing organic matter and micronutrients for organisms such as fungal mycorrhiza, (which aid plants in absorbing nutrients), and can drastically reduce external inputs of pesticides, energy and fertilizer, at the cost of decreased yield.

6 – 2 - Comparison with inorganic fertilizer;

Organic fertilizer nutrient content, solubility, and nutrient release rates are typically all lower than inorganic fertilizers. One study found that over a 140 - day period, after 7 leachings :

- Organic fertilizers had released between 25% and 60 % of their nitrogen content
- Controlled release fertilizers (CRFs) had a relatively constant rate of release
- Soluble fertilizer released most of its nitrogen content at the first leaching

In general, the nutrients in organic fertilizer are both more dilute and also much less readily available to plants. According to UC IPM, all *organic fertilizers* are classified as 'slow - release' fertilizers, and therefore cannot cause nitrogen burn .

Organic fertilizers from composts and other sources can be quite variable from one batch to the next ' without batch testing amounts of applied nutrient cannot be precisely known. Nevertheless they are at least as effective as chemical fertilizers over longer periods of use .

6 – 3 - Organic fertilizer sources:

6 – 3 – 1 - Animal:

Animal - sourced Urea , are suitable for application organic agriculture, while pure synthetic forms of urea are not . The common thread that can be seen through these examples is that *organic* agriculture attempts to define itself through minimal processing (in contrast to the man - made Haber process), as well as being naturally - occurring or via natural biological processes such as composting.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER*Decomposing animal manure, an organic fertilizer source*

Sewage sludge use in organic agricultural operations in the U.S. has been extremely limited and rare due to USDA prohibition of the practice (due to toxic metal accumulation, among other factors). The USDA now requires 3rd - party certification of high-nitrogen liquid organic fertilizers sold in the U.S.

6 - 3 – 2 – Plant:

Cover crops are also grown to enrich soil as a green manure through nitrogen fixation from the atmosphere^[34]; as well as phosphorus (through nutrient mobilization) content of soils.

6 – 3 – 3 - Mineral:

Naturally mined powdered limestone, mined rock phosphate and sodium nitrate, are *inorganic* (in a *chemical* sense), are energetically - intensive to harvest, yet are approved for usage in organic agriculture in *minimal* amounts.

7 - Environmental effects of fertilizer use:**7 – 1 - Water:****7 – 1 – 1 – Eutrophication:**

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The nitrogen - rich compounds found in fertilizer run-off is the primary cause of a serious depletion of oxygen in many parts of the ocean, especially in coastal zones; the resulting lack of dissolved oxygen is greatly reducing the ability of these areas to sustain oceanic fauna . Visually, water may become cloudy and discolored (green, yellow, brown, or red).



*Runoff of soil and **fertilizer** during a rain storm*



An algal bloom causing eutrophication

About half of all the lakes in the United States are now eutrophic, while the number of oceanic dead zones near inhabited coastlines are increasing. As of 2006, the application of nitrogen fertilizer is being increasingly controlled in Britain and the United States. If eutrophication *can* be reversed, it may take decades before the accumulated nitrates in groundwater can be broken down by natural processes.

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High application rates of inorganic nitrogen fertilizers in order to maximize crop yields, combined with the high solubilities of these fertilizers leads to increased runoff into surface water as well as leaching into groundwater. The use of ammonium nitrate in *inorganic* fertilizers is particularly damaging, as plants absorb ammonium ions preferentially over nitrate ions, while excess nitrate ions which are not absorbed dissolve (by rain or irrigation) into runoff or groundwater.

7 -1 – 2 - Blue Baby Syndrome;

Nitrate levels above 10 mg / L (10 ppm) in groundwater can cause 'blue baby syndrome' (acquired methemoglobinemia) , leading to hypoxia (which can lead to coma and death if not treated).

7 – 2 - Soil :

7 - 2 – 1 - Soil acidification:

Nitrogen-containing inorganic and organic fertilizers can cause soil acidification when added . This may lead to decreases in nutrient availability which may be offset by liming.

7 – 2 – 2 - Persistent organic pollutants;

Toxic persistent organic pollutants (" POPs ") , such as Dioxins, polychlorinated di benzo – p - dioxins (PCDDs) , and polychlorinated di benzo furans (PCDFs) have been detected in agricultural fertilizers and soil amendments

7 – 2 – 3 - Heavy metal accumulation;

The concentration of up to 100 mg / kg of cadmium in phosphate minerals (for example, minerals from Nauru and the Christmas islands) increases the contamination of soil with cadmium, for example in New Zealand.

Uranium is another example of a contaminant often found in phosphate fertilizers (at levels from 7 to 100 p Ci / g). Eventually these heavy metals can build up to unacceptable levels and build up in vegetable produce. Average annual intake of uranium by adults is

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estimated to be about 0.5mg (500 μg) from ingestion of food and water and 0.6 μg from breathing air.

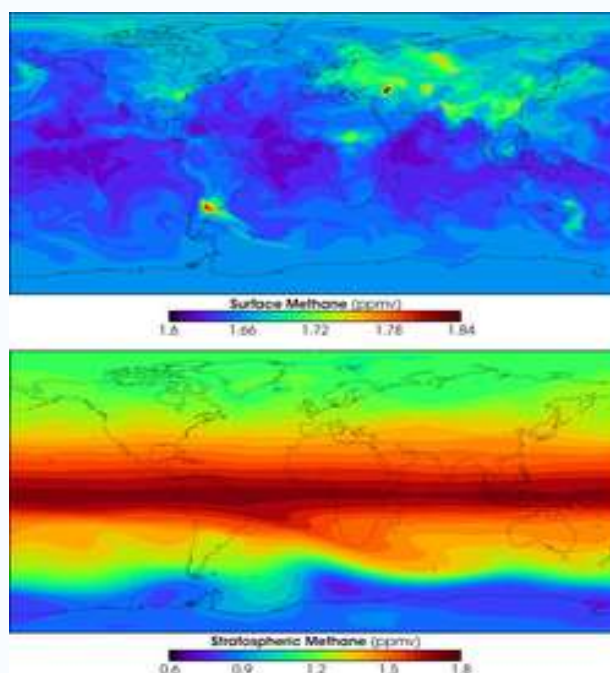
Steel industry wastes, recycled into fertilizers for their high levels of zinc (essential to plant growth) , wastes can include the following toxic metals: lead¹arsenic, cadmium, chromium, and nickel. The most common toxic elements in this type of fertilizer are mercury, lead, and arsenic. Concerns have been raised concerning fish meal mercury content by at least one source in Spain .

Also, highly - radioactive Polonium - 210 contained in phosphate fertilizers is absorbed by the roots of plants and stored in its tissues; tobacco derived from plants fertilized by rock phosphates contains Polonium - 210 which emits alpha radiation estimated to cause about 11,700 lung cancer deaths each year worldwide.

For these reasons, it is recommended that nutrient budgeting, through careful observation and monitoring of crops, take place to mitigate the effects of excess fertilizer application.

7 – 3 - Other problems:

7 – 3 – 1 - Atmospheric effects:



Global methane concentrations (surface and atmospheric) for 2005; note distinct plumes

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Methane emissions from crop fields (notably rice paddy fields) are increased by the application of ammonium-based fertilizers; these emissions contribute greatly to global climate change as methane is a potent greenhouse gas .

Through the increasing use of nitrogen fertilizer, which is added at a rate of 1 billion tons per year presently^[64] to the already existing amount of reactive nitrogen, nitrous oxide (N₂O) has become the third most important greenhouse gas after carbon dioxide and methane. It has a global warming potential 296 times larger than an equal mass of carbon dioxide and it also contributes to stratospheric ozone depletion.

Storage and application of some nitrogen fertilizers in some weather or soil conditions can cause emissions of the potent greenhouse gas - nitrous oxide. Ammonia gas (NH₃) may be emitted following application of 'inorganic' fertilizers and/or manures and slurries .

The use of fertilizers on a global scale emits significant quantities of greenhouse gas into the atmosphere. Emissions come about through the use of :

- animal manures and urea, which release methane, nitrous oxide, ammonia, and carbon dioxide in varying quantities depending on their form (solid or liquid) and management (collection, storage, spreading)
- fertilizers that use nitric acid or ammonium bicarbonate, the production and application of which results in emissions of nitrogen oxides, nitrous oxide, ammonia and carbon dioxide into the atmosphere.

By changing processes and procedures, it is possible to mitigate some, but not all, of these effects on anthropogenic climate change.

7 - 3 – 2 - Increased pest health:

Excessive nitrogen fertilizer applications can also lead to pest problems by increasing the birth rate, longevity and overall fitness of certain agricultural pests.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**NPK rating****1 – Introduction :**

NPK rating (or N-P-K) is used to label fertilizer based on the relative content of the chemicals nitrogen (N), phosphorus(P), and potassium(K) that are commonly used in fertilizers.

Except for the N number, the numbers for P and K do not reflect the amount of elemental phosphorus and potassium in the fertilizer. Rather they represent the amount of oxide in the form of P_2O_5 and K_2O that would form if all the elemental phosphorus and potassium was oxidized into this form.

2 - Method for converting an NPK value to an actual composition

The factors for converting from P_2O_5 and K_2O values to their respective P and K elemental values are as follows:

- P_2O_5 consists of 57.4 % oxygen and 43.6 % elemental phosphorus. The percentage([mass fraction]) of elemental phosphorus is 43.6 % so $P = 0.43 \times P_2O_5$
- K_2O consists of 17 % oxygen and 83 % elemental potassium. The percentage (mass fraction) of elemental potassium is 83 % so $K = 0.83 \times K_2O$
- Nitrogen values represent actual nitrogen content so these numbers do not need to be converted.

Using these conversion factors we can determine that an 18 – 51– 20 fertilizer contains by weight:

- 18 % elemental (N)
- 22 % elemental (P), and
- 16 % elemental (K)

In the U.K., fertilizer labeling regulations allow for reporting the elemental mass fractions of phosphorus and potassium. The

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regulations stipulate that this should be done in parentheses after the standard N-P-K values.

3 - NPK values for commercial fertilizers;

NPK values for various popular synthetic fertilizers include^[3]:

- 82 – 00 - 00 Anhydrous Ammonia
- 21 – 00 - 00 Ammonium Sulfate
- 33 – 00 - 00 Ammonium Nitrate
- 45 – 00 - 00 Urea
- 15 – 00 - 00 Calcium Nitrate
- 13 – 00 - 44 Potassium Nitrate

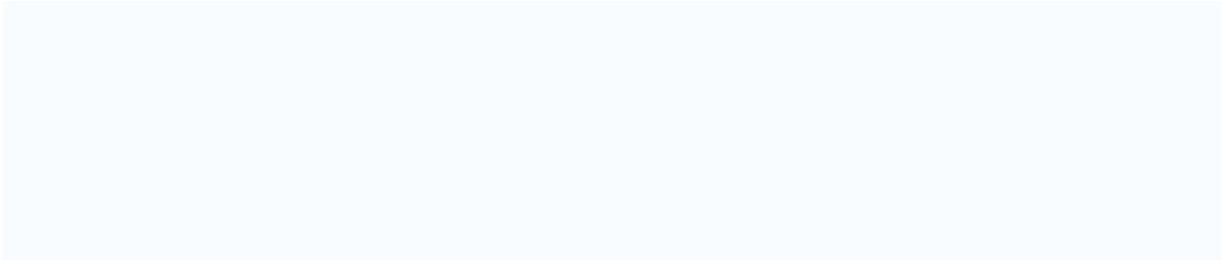
NPK Values for naturally occurring fertilizer minerals:

- 00 – 26 - 00 to 00 – 37 - 00 Phosphate Rock
- 00 - 00 - 60 Potassium Chloride

FERTILIZERS

INORGANIC ACIDS

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Sulfur

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1 – Introduction :

Sulfur or **sulphur** is the chemical element that has the atomic number 16. It is denoted with the symbol **S**. It is an abundant multivalent non-metal. Sulfur, in its native form, is a yellow crystalline solid. In nature, it can be found as the pure element and as sulfide and sulfate minerals. It is an essential element for life and is found in two amino acids, cysteine and methionine. Its commercial uses are primarily in fertilizers, but it is also widely used in black

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gunpowder, matches, insecticides and fungicides. Elemental sulfur crystals are commonly sought after by mineral collectors for their brightly colored polyhedron shapes. In nonscientific context it can also be referred to as *brimstone*.

2 - History

Sulfur was known in ancient times, and is referred to in the Biblical Pentateuch (Genesis).

English translations of the Bible commonly referred to sulfur as "brimstone", giving rise to the name of 'fire and brimstone' sermons, in which listeners are reminded of the fate of eternal damnation that await the unbelieving and unrepentant. It is from this part of the Bible that Hell is implied to "smell of sulfur", although sulfur, in itself, is in fact odorless. The "smell of sulfur" usually refers to either the odor of hydrogen sulfide, e.g. from rotten egg, or of burning sulfur, which produces sulfur dioxide, the smell associated with burnt matches. The smell emanating from raw sulfur originates from a slow oxidation in the presence of air. Hydrogen sulfide is the principal odor of untreated sewage and is one of several smelly sulfur-containing components of flatulence (along with sulfur-containing mercaptans).

Sulfur was known in China since the 6th century BC, in a natural form that the Chinese had called 'brimstone', or *shiliuhuang* that was found in Hanzhong. By the 3rd century, the Chinese discovered that sulfur could be extracted from pyrite. Chinese Daoists were interested in sulfur's flammability and its reactivity with certain metals, yet its earliest practical uses were found in traditional Chinese medicine. A Song Dynasty military treatise of 1044 AD described different formulas for Chinese gun powder, which is a mixture of potassium nitrate (KNO_3), carbon, and sulfur. Early alchemists gave sulfur its own alchemical symbol which was a triangle at the top of a cross.

In 1777 Antoine Lavoisier helped convince the scientific community that sulfur was an element and not a compound. In 1867, sulfur was discovered in underground deposits in Louisiana and Texas. The overlying layer of earth was quicksand, prohibiting

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ordinary mining operations, therefore the Frasch process was developed.

2 – 1 - Spelling and etymology:

The element has traditionally been spelled *sulphur* in the United Kingdom, most of the Commonwealth including India, Malaysia, South Africa and Hong Kong, along with the rest of the Caribbean and Ireland, but *sulfur* in the United States, while both spellings are used in Australia, New Zealand and Canada. IUPAC adopted the spelling “sulfur” in 1990, as did the Royal Society of Chemistry Nomenclature Committee in 1992 and the Qualifications and Curriculum Authority for England and Wales recommended its use in 2000.^[3]

In Latin, the word is variously written *sulpur*, *sulphur*, and *sulfur* (the Oxford Latin Dictionary lists the spellings in this order). It means brimstone. It is an original Latin name and not a Classical Greek loan, so the *ph* variant does not denote the Greek letter φ. Sulfur in Greek is *thion* (θείον), whence comes the prefix thio-. The simplification of the Latin word's p or ph to an f appears to have taken place towards the end of the classical period, with the f spelling becoming dominant in the medieval period.

3 - Characteristics:

At room temperature, sulfur is a soft, bright - yellow solid. Elemental sulfur has only a faint odor, similar to that of matches. The odor associated with rotten eggs is due to hydrogen sulfide (H₂S) and organic sulfur compounds rather than elemental sulfur. Sulfur burns with a blue flame that emits sulfur dioxide, notable for its peculiar suffocating odor due to dissolving in the mucosa to form dilute sulfurous acid. Sulfur itself is insoluble in water, but soluble in carbon disulfide — and to a lesser extent in other non-polar organic solvents such as benzene and toluene. Common oxidation states of sulfur include − 2, + 2, + 4 and + 6. Sulfur forms stable compounds with all elements except the noble gases. Sulfur in the solid state ordinarily exists as cyclic crown-shaped S₈ molecules.

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The crystallography of sulfur is complex. Depending on the specific conditions, the sulfur allotropes form several distinct crystal structures, with rhombic and monoclinic S_8 best known.

A noteworthy property of sulfur is that its viscosity in its molten state, unlike most other liquids, increases above temperatures of 200 °C due to the formation of polymers. The molten sulfur assumes a dark red color above this temperature. At higher temperatures, however, the viscosity is decreased as depolymerization occurs.

Amorphous or "plastic" sulfur can be produced through the rapid cooling of molten sulfur. X - ray crystallography studies show that the amorphous form may have a helical structure with eight atoms per turn. This form is metastable at room temperature and gradually reverts back to crystalline form. This process happens within a matter of hours to days but can be rapidly catalyzed.

3 – 1 – Allotropes of Sulfur:

Sulfur forms more than 30 solid allotropes, more than any other element. Besides S_8 , several other rings are known. Removing one atom from the crown gives S_7 , which is more deeply yellow than S_8 . HPLC analysis of "elemental sulfur" reveals an equilibrium mixture of mainly S_8 , but also S_7 and small amounts of S_6 . Larger rings have been prepared, including S_{12} and S_{18} .^{[9][10]} By contrast, sulfur's lighter neighbor oxygen only exists in two states of allotropic significance: O_2 and O_3 . Selenium, the heavier analogue of sulfur, can form rings but is more often found as a polymer chain.

3 – 2 - Isotopes of Sulfur:

Sulfur has 18 isotopes, four of which are stable : ^{32}S (95.02%) , ^{33}S (0.75%) , ^{34}S (4.21%) , and ^{36}S (0.02%) . Other than ^{35}S , the radioactive isotopes of sulfur are all short lived. ^{35}S is formed from cosmic ray spallation of ^{40}Ar in the atmosphere. It has a half-life of 87 days.

When sulfide minerals are precipitated, isotopic equilibration among solids and liquid may cause small differences in the $\delta S\text{-}34$

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values of co-genetic minerals. The differences between minerals can be used to estimate the temperature of equilibration. The $\delta C - 13$ and $\delta S - 34$ of coexisting carbonates and sulfides can be used to determine the pH and oxygen fugacity of the ore-bearing fluid during ore formation.

In most forest ecosystems, sulfate is derived mostly from the atmosphere; weathering of ore minerals and evaporites also contribute some sulfur. Sulfur with a distinctive isotopic composition has been used to identify pollution sources, and enriched sulfur has been added as a tracer in hydrologic studies. Differences in the natural abundances can also be used in systems where there is sufficient variation in the ^{34}S of ecosystem components. Rocky Mountain lakes thought to be dominated by atmospheric sources of sulfate have been found to have different $\delta S-34$ values from lakes believed to be dominated by watershed sources of sulfate.

3 – 3 - Occurrence

Elemental sulfur can be found near hot springs and volcanic regions in many parts of the world, especially along the Pacific Ring of Fire. Such volcanic deposits are currently mined in Indonesia, Chile, and Japan. Sicily is also famous for its sulfur mines.

Significant deposits of elemental sulfur also exist in salt domes along the coast of the Gulf of Mexico, and in evaporites in eastern Europe and western Asia. The sulfur in these deposits is believed to come from the action of anaerobic bacteria on sulfate minerals, especially gypsum, although apparently native sulfur may be produced by geological processes alone, without the aid of living organisms .

However, fossil - based sulfur deposits from salt domes are the basis for commercial production in the United States, Poland, Russia, Turkmenistan, and Ukraine.

Sulfur production through hydrodesulfurization of oil, gas, and the Athabasca Oil Sands has produced a surplus - huge stockpiles of sulfur now exist throughout Alberta, Canada.

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Common naturally occurring sulfur compounds include the sulfide minerals, such as pyrite (iron sulfide), cinnabar (mercury sulfide), galena (lead sulfide), sphalerite (zinc sulfide) and stibnite (antimony sulfide); and the sulfates, such as gypsum (calcium sulfate), alunite (potassium aluminium sulfate), and barite (barium sulfate). It occurs naturally in volcanic emissions, such as from hydrothermal vents, and from bacterial action on decaying sulfur-containing organic matter.

The distinctive colors of Jupiter's volcanic moon, Io, are from various forms of molten, solid and gaseous sulfur. There is also a dark area near the Lunar crater Aristarchus that may be a sulfur deposit.

Sulfur is present in many types of meteorites. Ordinary chondrites contain on average 2.1 % sulfur, and carbonaceous chondrites may contain as much as 6.6 %. Sulfur in meteorites is normally present entirely as troilite (FeS), but other sulfides are found in some meteorites, and carbonaceous chondrites contain free sulfur, sulfates, and possibly other sulfur compounds.^[11]

4 - Extraction and production:

4 – 1 - Extraction from natural resources:

Sulfur is extracted by mainly two processes: the Sicilian process and the Frasch process. The Sicilian process, which was first used in Sicily, was used in ancient times to get sulfur from rocks present in volcanic regions. In this process, the sulfur deposits are piled and stacked in brick kilns built on sloping hillsides, and with airspaces between them. Then powdered sulfur is put on top of the sulfur deposit and ignited. As the sulfur burns, the heat melts the sulfur deposits, causing the molten sulfur to flow down the sloping hillside. The molten sulfur can then be collected in wooden buckets.

The second process used to obtain sulfur is the Frasch process. In this method, three concentric pipes are used: the outermost pipe contains superheated water, which melts the sulfur, and the innermost pipe is filled with hot compressed air, which serves to create foam and

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pressure. The resulting sulfur foam is then expelled through the middle pipe.

The Frasch process produces sulfur with a 99.5 % purity content, and which needs no further purification. The sulfur produced by the Sicilian process must be purified by distillation.

4 – 2 - Production from hydrogen sulfide:

4- 2 – 1 – Chemically:

The Claus process is used to extract elemental sulfur from hydrogen sulfide produced in hydrodesulfurization of petroleum or from natural gas.

4 – 2 – 2 - Biologically:

In the biological route, hydrogen sulfide (H_2S) from natural gas or refinery gas is absorbed with a slight alkaline solution in a wet scrubber. Or the sulfide is produced by biological sulfate reduction. In the subsequent process step, the dissolved sulfide is biologically converted to elemental sulfur. This solid sulfur is removed from the reactor. This process has been built on commercial scale. The main advantages of this process are :

1. No use of expensive chemicals,
2. The process is safe as the H_2S is directly absorbed in an alkaline solution,
3. No production of a polluted waste stream,
4. Re - usable sulfur is produced, and
5. The process occurs under ambient conditions.

The biosulfur product is different from other processes in which sulfur is produced because the sulfur is hydrophilic. Next to straightforward reuses as source for sulfuric acid production, it can also be applied as sulfur fertilizer.

5 - Chemistry :

5 – 1 - Inorganic compounds :

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Hydrogen sulfide has the characteristic smell of rotten eggs. Dissolved in water, hydrogen sulfide is acidic and will react with metals to form a series of metal sulfides. Natural metal sulfides are common, especially those of iron. Iron sulfide is called pyrite, the so-called *fool's gold*. Pyrite can show semiconductor properties.^[14] Galena, a naturally occurring lead sulfide, was the first semiconductor discovered, and found a use as a signal rectifier in the "cat's whiskers" of early crystal radios.

Many of the unpleasant odors of organic matter are based on sulfur-containing compounds such as methyl and ethyl mercaptan, also used to scent natural gas so that leaks are easily detectable. The odor of garlic and "skunk stink" are also caused by sulfur-containing organic compounds. Not all organic sulfur compounds smell unpleasant; for example, grapefruit mercaptan, a sulfur-containing monoterpenoid is responsible for the characteristic scent of grapefruit.

Polymeric sulfur nitride has metallic properties even though it does not contain any metal atoms. This compound also has unusual electrical and optical properties. This polymer can be made from tetrasulfur tetranitride S_4N_4 .

Phosphorus sulfides are useful in synthesis. For example, P_4S_{10} and its derivatives Lawesson's reagent and naphthalen - 1,8 - diyl 1,3,2,4-dithiadiphosphetane 2,4 - disulfide are used to replace oxygen from some organic molecules with sulfur.

- Sulfides (S^{2-}), a complex family of compounds usually derived from S^{2-} . Cadmium sulfide (CdS) is an example.
- Sulfites (SO_3^{2-}), the salts of sulfurous acid (H_2SO_3) which is generated by dissolving SO_2 in water. Sulfurous acid and the corresponding sulfites are fairly strong reducing agents. Other compounds derived from SO_2 include the pyrosulfite or metabisulfite ion ($S_2O_5^{2-}$).
- Sulfates (SO_4^{2-}), the salts of sulfuric acid. Sulfuric acid also reacts with SO_3 in equimolar ratios to form pyrosulfuric acid ($H_2S_2O_7$).
- Thiosulfates ($S_2O_3^{2-}$). Sometimes referred as thiosulfites or "hyposulfites", Thiosulfates are used in photographic fixing

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(HYPO) as reducing agents. Ammonium thiosulfate is being investigated as a cyanide replacement in leaching gold.

- Sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, is the highly reducing dianion derived from hyposulfurous/dithionous acid.
- Sodium dithionate ($\text{Na}_2\text{S}_2\text{O}_6$).
- Polythionic acids ($\text{H}_2\text{S}_n\text{O}_6$), where n can range from 3 to 80.
- Peroxymonosulfuric acid (H_2SO_5) and peroxydisulfuric acids ($\text{H}_2\text{S}_2\text{O}_8$), made from the action of SO_3 on concentrated H_2O_2 , and H_2SO_4 on concentrated H_2O_2 respectively.
- Sodium polysulfides (Na_2S_x)
- Sulfur hexafluoride, SF_6 , a dense gas at ambient conditions, is used as nonreactive and nontoxic propellant
- Sulfur nitrides are chain and cyclic compounds containing only S and N. Tetrasulfur tetranitride S_4N_4 is an example.
- Thiocyanates contain the SCN^- group. Oxidation of thiocyanate gives thiocyanogen, $(\text{SCN})_2$ with the connectivity NCS-SCN .

5 – 2 - Organic compounds:

(R, R', and R are organic groups such as CH_3):

- Thioethers have the form R-S-R' . These compounds are the sulfur equivalents of ethers.
- Sulfonium ions have the formula RR'S-R'' , i.e. where three groups are attached to the cationic sulfur center. Dimethylsulfoniopropionate (DMSP; $(\text{CH}_3)_2\text{S}^+\text{CH}_2\text{CH}_2\text{COO}^-$) is a sulfonium ion, which is important in the marine organic sulfur cycle.
- Thiols (also known as mercaptans) have the form R-SH . These are the sulfur equivalents of alcohols.
- Thiolates ions have the form R-S^- . Such anions arise upon treatment of thiols with base.
- Sulfoxides have the form R-S(=O)-R' . The simplest sulfoxide, DMSO, is a common solvent.
- Sulfones have the form $\text{R-S(=O)}_2\text{-R'}$. A common sulfone is sulfolane $\text{C}_4\text{H}_8\text{SO}_2$.

6 - Applications:

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One of the direct uses of sulfur is in vulcanization of rubber, where polysulfides crosslink organic polymers. Sulfur is a component of gunpowder. It reacts directly with methane to give carbon disulfide, which is used to manufacture cellophane and rayon.

Elemental sulfur is mainly used as a precursor to other chemicals. Approximately 85 % (1989) is converted to sulfuric acid (H_2SO_4), which is of such prime importance to the world's economies that the production and consumption of sulfuric acid is an indicator of a nation's industrial development . For example, more sulfuric acid is produced in the United States every year than any other industrial chemical . The principal use for the acid is the extraction of phosphate ores for the production of fertilizer manufacturing. Other applications of sulfuric acid include oil refining, wastewater processing, and mineral extraction.

Sulfur compounds are also used in detergents, fungicides, dyestuffs, and agrichemicals. In silver-based photography sodium and ammonium thiosulfate are used as "fixing agents."

Sulfur is an ingredient in some acne treatments.

An increasing application is as fertilizer. Standard sulfur is hydrophobic and therefore has to be covered with a surfactant by bacteria in the ground before it can be oxidized to sulfate. This makes it a slow release fertilizer, which cannot be taken up by the plants instantly, but has to be oxidized to sulfate over the growth season. Sulfur also improves the use efficiency of other essential plant nutrients, particularly nitrogen and phosphorus. Biologically produced sulfur particles are naturally hydrophilic due to a biopolymer coating. This sulfur is therefore easier to disperse over the land (via spraying as a diluted slurry), and results in a faster release.

Sulfites, derived from burning sulfur, are heavily used to bleach paper. They are also used as preservatives in dried fruit.

Magnesium sulfate, better known as Epsom salts, can be used as a laxative, a bath additive, an exfoliant, a magnesium supplement for plants, or a desiccant.

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6 – 1 - Specialized applications:

Sulfur is used as a light - generating medium in the rare lighting fixtures known as sulfur lamps.

6 – 2 - Historical applications:

In the late 18th century, furniture makers used molten sulfur to produce decorative inlays in their craft. Because of the sulfur dioxide produced during the process of melting sulfur, the craft of sulfur inlays was soon abandoned. Molten sulfur is sometimes still used for setting steel bolts into drilled concrete holes where high shock resistance is desired for floor - mounted equipment attachment points. Pure powdered sulfur was also used as a medicinal tonic and laxative. Sulfur was also used in baths for people who had fits.

6 – 3 - Fungicide:

Sulfur is the only fungicide used in organically farmed apple production against the main disease apple scab under colder conditions. Sulfur is also a major fungicide in conventional culture of grapes, strawberry, many vegetables and several other crops. It has a good efficacy against a wide range of powdery mildew diseases as well as black spot. Sulfur is one of the oldest pesticides used in agriculture. In organic production sulfur is the most important fungicide used. Biosulfur (biologically produced elemental sulfur with hydrophilic characteristics) can be used well for these applications.

Wettable sulfur is the commercial name for sulfur which has been altered to be water - soluble. It is used as a fungicide against mildew and other mold related problems with plants and soil. Available in hydroponic and gardening stores.

6 – 4 - Insecticide:

Sulfur is also used as an "organic" (i.e. "green") insecticide, effective against mites.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**7 - Biological role : (*Sulfur assimilation*)**

Sulfur is an essential component of all living cells.

Inorganic sulfur forms a part of iron-sulfur clusters, and sulfur is the bridging ligand in the Cu_A site of cytochrome c oxidase, a basic substance involved in utilization of oxygen by all aerobic life.

Sulfur may also serve as chemical food source for some primitive organisms: some forms of bacteria use hydrogen sulfide (H₂S) in the place of water as the electron donor in a primitive photosynthesis-like process in which oxygen is the electron receptor. The photosynthetic green and purple sulfur bacteria and some chemolithotrophs use elemental oxygen to carry out such oxidation of hydrogen sulfide to produce elemental sulfur (S⁰), oxidation state = 0. Primitive bacteria which live around deep ocean volcanic vents oxidize hydrogen sulfide in this way with oxygen: see giant tube worm for an example of large organisms (via bacteria) making metabolic use of hydrogen sulfide as food to be oxidized.

The so - called sulfur bacteria, by contrast, "breathe sulfate" instead of oxygen. They use sulfur as the electron acceptor, and reduce various oxidized sulfur compounds back into sulfide -- often into hydrogen sulfide. They also can grow on a number of other partially oxidized sulfur compounds (e. g. thiosulfate, thionates, polysulfides, sulfite) . These bacteria are responsible for the rotten egg smell of some intestinal gases and decomposition products.

Sulfur is a part of many bacterial defense molecules. For example, though sulfur is not a part of the lactam ring, it is a part of most beta lactam antibiotics, including the penicillins, cephalosporins, and monobactams.

Sulfur is absorbed by plants via the roots from soil as the sulfate ion and reduced to sulfide before it is incorporated into cysteine and other organic sulfur compounds .

Sulfur is regarded as secondary nutrient although plant requirements for sulfur are equal to and sometimes exceed those for

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phosphorus. However sulfur is recognized as one of the major nutrients essential for plant growth, root nodule formation of legumes and plants protection mechanisms. Sulfur deficiency has become widespread in many countries in Europe . Because atmospheric inputs of sulfur will continue to decrease, the deficit in the sulfur input / output is likely to increase, unless sulfur fertilizers are used.

In plants and animals the amino acids cysteine and methionine contain sulfur, as do all polypeptides, proteins, and enzymes which contain these amino acids. Homo cysteine and taurine are other sulfur-containing acids which are similar in structure, but which are not coded for by DNA, and are not part of the primary structure of proteins. Glutathione is an important sulfur-containing tripeptide which plays a role in cells as a source of chemical reduction potential in the cell, through its sulfhydryl (-SH) moiety. Many important cellular enzymes use prosthetic groups ending with -SH moieties to handle reactions involving acyl - containing biochemicals: two common examples from basic metabolism are coenzyme A and alpha-lipoic acid.

Disulfide bonds (S - S bonds) formed between cysteine residues in peptide chains are very important in protein assembly and structure. These strong covalent bonds between peptide chains give proteins a great deal of extra toughness and resiliency. For example, the high strength of feathers and hair is in part due to their high content of S-S bonds and their high content of cysteine and sulfur (eggs are high in sulfur because large amounts of the element are necessary for feather formation). The high disulfide content of hair and feathers contributes to their indigestibility, and also their odor when burned.

7 – 1 - Traditional medical role for elemental sulfur:

In traditional medical skin treatment which predates modern era of scientific medicine, elemental sulfur has been used mainly as part of creams to alleviate various conditions such as psoriasis, eczema and acne. The mechanism of action is not known, although elemental sulfur does oxidize slowly to sulfurous acid, which in turn (though the action of sulfite) acts as a mild reducing and antibacterial agent.

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8 - Precautions:

Carbon disulfide, carbon oxysulfide, hydrogen sulfide, and sulfur dioxide should all be handled with care.

Although sulfur dioxide is sufficiently safe to be used as a food additive in small amounts, at high concentrations it reacts with moisture to form sulfurous acid which in sufficient quantities may harm the lungs, eyes or other tissues. In organisms without lungs such as insects or plants, it otherwise prevents respiration.

Hydrogen sulfide is toxic. Although very pungent at first, it quickly deadens the sense of smell, so potential victims may be unaware of its presence until death or other symptoms occur.

8 – 1 - Environmental impact:

The burning of coal and / or petroleum by industry and power plants generates sulfur dioxide (SO_2), which reacts with atmospheric water and oxygen to produce sulfuric acid (H_2SO_4). This sulfuric acid is a component of acid rain, which lowers the pH of soil and freshwater bodies, sometimes resulting in substantial damage to the environment and chemical weathering of statues and structures. Fuel standards increasingly require sulfur to be extracted from fossil fuels to prevent the formation of acid rain. This extracted sulfur is then refined and represents a large portion of sulfur production. In coal fired power plants, the flue gases are sometimes purified. In more modern power plants that use syngas the sulfur is extracted before the gas is burned.

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Sulfur dioxide

Contents

- 1 Introduction
- 2 Preparation
- 3 Structure and bonding
- 4 Reactions
- 5 Uses
 - 5.1 As a preservative
 - 5.2 In winemaking
 - 5.3 As a reducing bleach
 - 5.4 Precursor to sulfuric acid
 - 5.5 Biochemical and biomedical roles
 - 5.6 As a refrigerant
 - 5.7 As a reagent and solvent
 - 5.8 Dechlorination
- 6 Emissions
- 7 Temperature dependence of aqueous solubility
- 8 Threats to Health

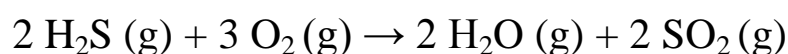
1 – Introduction :

Sulfur Dioxide is the chemical compound with the formula SO_2 . In the gaseous form, this species is a significant pollutant, being the primary agent in acid rain. It is prepared on massive scale as a precursor to sulfuric acid .

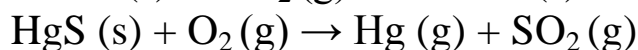
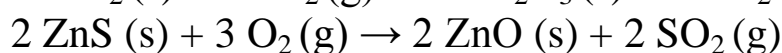
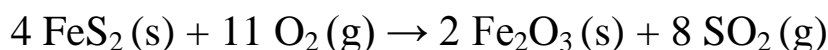
2 - Preparation :

2 - Preparation :

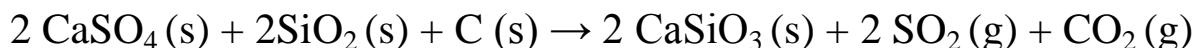
The combustion of hydrogen sulfide and organo sulfur compounds proceeds similarly.



The roasting of sulfide ores such as iron pyrites, sphalerite (zinc blende) and cinnabar (mercury sulfide) also releases SO_2 :

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Sulfur dioxide is a by - product in the manufacture of calcium silicate cement: CaSO_4 is heated with coke and sand in this process:



Action of hot sulfuric acid on copper turnings produces sulfur dioxide:

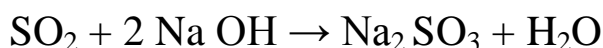
**3 - Structure and bonding**

SO_2 is a bent molecule with C_{2v} symmetry point group. In terms of electron-counting formalisms, the sulfur atom has an oxidation state of +4, a formal charge of 0, and is surrounded by 5 electron pairs and can be described as a hypervalent molecule. From the perspective of molecular orbital theory, most of these valence electrons are engaged in S - O bonding.

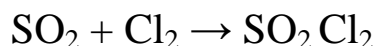
The S - O bonds are shorter in SO_2 (143.1 pm) than in sulfur monoxide, SO (148.1 pm), whereas the O-O bonds are longer in O_3 (127.8 pm) than in dioxygen, O_2 (120.7 pm). The mean bond energy is greater in SO_2 (548 kJ mol^{-1}) than in SO (524 kJ mol^{-1}), whereas it is less in O_3 (297 kJ mol^{-1}) than in O_2 (490 kJ mol^{-1}). These pieces of evidence lead chemists to conclude that the S-O bonds in sulfur dioxide have a bond order of at least 2, unlike the O-O bonds in ozone, which have a bond order of 1.5.

4 - Reactions :

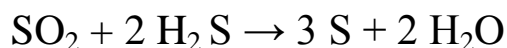
Treatment of basic solutions with sulfur dioxide affords sulfite salts:



Featuring sulfur in the +4 oxidation state, sulfur dioxide is a reducing agent. It is oxidized by halogens such as chlorine to give the sulfuryl halides:

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However, on rare occasions, it can also act as an oxidising agent: in the Claus process, sulfur dioxide is reduced by hydrogen sulfide to give elemental sulfur:



Sulfur dioxide can act as a metal binding ligand, typically where the transition metal is in oxidation state 0 or +1. Up to 9 different bonding modes have been determined which include^[4]:

- S donation - planar and pyramidal η^1
- O donation η^1
- π donation- side on η^2
- S bridging across two metal centres or two ends of a metal - metal bond
- O - S bridging to two metal centres
- bridging- one metal centre π donation- side on, the other metal center O donation
- bridging over three metal centres

5 - Uses

5 – 1 - As a preservative:

Sulfur dioxide is sometimes used as a preservative for dried apricots and other dried fruits due to its antimicrobial properties, it is sometimes called E220 when used in this way. The preservative is used to maintain the appearance of the fruit and prevent rotting. Its presence can give fruit a distinctive chemical taste.

5 – 2 - In winemaking:

Sulfur dioxide is a very important compound in winemaking, and is designated as parts per million in wine, E number: E220. It is present even in so - called unsulphurated wine at concentrations of up to 10 milligrams per litre. It serves as an antibiotic and antioxidant, protecting wine from spoilage by bacteria and oxidation. It also helps to keep volatile acidity at desirable levels. Sulfur dioxide is

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responsible for the words "contains sulfites" found on wine labels. Wines with SO_2 concentrations below 10 ppm do not require "contains sulfites" on the label by US and EU laws. The upper limit of SO_2 allowed in wine is 350ppm in US, in the EU is 160 ppm for red wines and 210 ppm for white and rosé wines. In low concentrations SO_2 is mostly undetectable in wine, but at over 50ppm, SO_2 becomes evident in the nose and taste of wine.

SO_2 is also a very important element in winery sanitation. Wineries and equipment must be kept very clean, and because bleach cannot be used in a winery, a mixture of SO_2 , water, and citric acid is commonly used to clean hoses, tanks, and other equipment to keep it clean and free of bacteria.

5 – 3 - As a reducing bleach:

Sulfur dioxide is also a good reductant. In the presence of water, sulfur dioxide is able to decolorize substances. Specifically it is a useful reducing bleach for papers and delicate materials such as clothes.

5 - 4 - Precursor to sulfuric acid:

Sulfur dioxide is also used to make sulfuric acid, being converted to sulfur trioxide, and then to oleum, which is made into sulfuric acid. Sulfur dioxide for this purpose is made when sulfur combines with oxygen. The method of converting sulfur dioxide to sulfuric acid is called the contact process.

5 – 5 - Biochemical and biomedical roles:

Sulfur dioxide is toxic in large amounts. It or its conjugate base bisulfite is produced biologically as an intermediate in both sulfate-reducing organisms and in sulfur oxidizing bacteria as well. Sulfur dioxide has no role in mammalian biology. Sulfur dioxide blocks nerve signals from the pulmonary stretch receptors (PSR's) and abolishes the Hering - Breuer inflation reflex .

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**5 – 6 - As a refrigerant :**

Being easily condensed and with a high heat of evaporation, sulfur dioxide is a candidate material for refrigerants. Prior to the development of freons, sulfur dioxide was used as a refrigerant in home refrigerators.

5 - 7 - As a reagent and solvent:

Sulfur dioxide is a versatile inert solvent that has been widely used for dissolving highly oxidizing salts. It is also used occasionally as a source of the sulfonyl group in organic synthesis. Treatment of aryl diazonium salts with sulfur dioxide affords the corresponding aryl sulfonyl chloride.

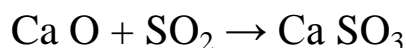
5 – 8 - Dechlorination:

In municipal wastewater treatment sulfur dioxide is used to treat chlorinated wastewater prior to release. Sulfur dioxide reacts with free and combined chlorine to form negatively charged chloride ions. ^[8]

6 - Emissions

According to the U.S. EPA , the following amount of sulfur dioxide was released in the U.S. per year, measured in thousands of short tons:

Due largely to the US EPA's Acid Rain Program, the U.S. has witnessed a 33 percent decrease in emissions between 1983 and 2002. This improvement resulted from flue gas desulfurization, a technology that enables SO₂ to be chemically bound in power plants burning sulfur - containing coal or oil. In particular, calcium oxide (lime) reacts with sulfur dioxide to form calcium sulfite:



Aerobic oxidation converts this Ca SO₃ into CaSO₄, gypsum. Most gypsum sold in Europe comes from flue gas desulfurization.

New fuel additive catalysts, such as ferox, are being used in gasoline and diesel engines in order to lower the emission of sulfur

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oxide gases into the atmosphere. This is also done by forcing the sulfur into stable mineral salts and mixed mineral sulfates as opposed to sulfuric acid and sulfur oxides.

As of 2006, China is the world's largest sulfur dioxide polluter, with 2005 emissions estimated to be 25.49 million tons. This amount represents a 27 % increase since 2000, and is roughly comparable with U.S. emissions in 1980 .

7 - Temperature dependence of aqueous solubility:

22 g / 100 ml (0 °C)	15 g / 100 ml (10 °C)
11 g / 100 ml (20 °C)	9.4 g / 100 ml (25 °C)
8 g / 100 ml (30 °C)	6.5 g / 100 ml (40 °C)
5 g / 100 ml (50 °C)	4 g / 100 ml (60 °C)
3.5 g / 100 ml (70 °C)	3.4 g / 100 ml (80 °C)
3.5 g / 100 ml (90 °C)	3.7 g / 100 ml (100 °C)

- The values are tabulated for 101.3 kPa partial pressure of SO₂. Solubility of gas in a liquid depends on the gas partial pressure according to Henry's law.
- The solubility is given for "pure water", i.e., water that contains only SO₂ in the amount at equilibrium with the gas phase. This "pure water" is going to be acidic. The solubility of SO₂ in neutral (or alkaline) water is generally going to be higher because of the pH - dependent speciation of SO₂ in the solution with the production of bisulfite and some sulfite ions.

8 - Threats to Health :

Sulfur dioxide acts as an acid. Inhalation results in labored breathing, coughing, and / or a sore throat and may cause permanent pulmonary damage. When mixed with water and contacted by skin, frostbite may occur. When it makes contact with eyes, redness and pain will occur.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**Sulfur trioxide****Contents**

- 1 Introduction
- 2 Structure and bonding
- 3 Chemical reactions
- 4 Preparation
- 5 Structure of solid SO₃
- 6 Sources

1 – Introduction:

Sulfur trioxide is the chemical compound with the formula SO₃. In the gaseous form, this species is a significant pollutant, being the primary agent in acid rain. It is prepared on massive scale as a precursor to sulfuric acid.

2 - Structure and bonding

Gaseous SO₃ is a trigonal planar molecule of D_{3h} symmetry, as predicted by VSEPR theory.

In terms of electron - counting formalisms, the sulfur atom has an oxidation state of +6 , a formal charge of 0, and is surrounded by 6 electron pairs. From the perspective of molecular orbital theory, most of these electron pairs are non-bonding in character, as is typical for hypervalent molecules.

Sulfur trioxide also exhibits hybridization.

3 - Chemical reactions

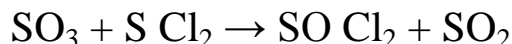
SO₃ is the anhydride of H₂SO₄. Thus, the following reaction occurs :



The reaction occurs both rapidly and exothermically. At or above ~340 °C , sulfuric acid, sulfur trioxide, and water coexist in significant equilibrium concentrations.

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Sulfur trioxide also reacts with sulfur dichloride to yield the useful reagent, thionyl chloride.

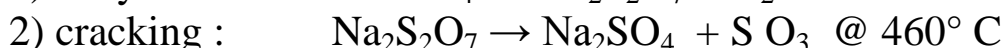
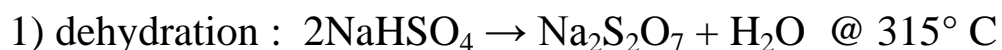


Sulfur Trioxide reacts with water to create sulfuric acid , though the reaction is too violent to be used in large - scale manufacturing.

SO₃ is a strong Lewis acid readily forming crystalline complexes with pyridine , dioxane and trimethylamine which can be used as sulfonating agents .

4 - Preparation:

Sulfur trioxide can be prepared in the laboratory by the two-stage pyrolysis of sodium bisulfate. Sodium pyrosulfate is an intermediate product:



This method will work for other metal bisulfates, the controlling factor being the stability of the intermediate pyrosulfate salt.

Industrially SO₃ is made by the contact process. Sulfur dioxide, generally made by the burning of sulfur or iron pyrite (a sulfide ore of iron), is first purified by electrostatic precipitation. The purified SO₂ is then oxidised by atmospheric oxygen at between 400 and 600 °C over a catalyst consisting of vanadium pentoxide V₂O₅ activated with potassium oxide K₂O on kieselguhr or silica support. Platinum also works very well but is too expensive and is poisoned (rendered ineffective) much more easily by impurities.

The majority of sulphur trioxide made in this way is converted into sulfuric acid not by the direct addition of water, with which it forms a fine mist, but by absorption in concentrated sulfuric acid and dilution with water of the produced oleum.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**5 - Structure of solid SO₃:**

The nature of solid SO₃ is a surprisingly complex area because of structural changes caused by traces of water. Upon condensation of the gas, absolutely pure SO₃ condenses into a trimer, which is often called γ - SO₃. This molecular form is a colorless solid with a melting point of 16.8 °C. It adopts a cyclic structure described as [S(=O)₂(μ -O)]₃.

If SO₃ is condensed above 27 °C, then α - "SO₃" forms, which has a melting point of 62.3°C. α -SO₃ is fibrous in appearance, like asbestos (with which it has no chemical relationship). Structurally, it is the polymer [S(=O)₂(μ -O)]_n. Each end of the polymer is terminated with OH groups (hence α - "SO₃" is not really a form of SO₃). β -SO₃, like the alpha form, is fibrous but of different molecular weight, consisting of an hydroxyl - capped polymer, but melts at 32.5 °C. Both the gamma and the beta forms are metastable, eventually converting to the stable alpha form if left standing for sufficient time. This conversion is caused by traces of water .

Relative vapor pressures of solid SO₃ are $\alpha < \beta < \gamma$ at identical temperatures, indicative of their relative molecular weights. Liquid sulfur trioxide has vapor pressure consistent with the gamma form. Thus heating a crystal of α - SO₃ to its melting point results in a sudden increase in vapor pressure, which can be forceful enough to shatter a glass vessel in which it is heated. This effect is known as the "alpha explosion."

SO₃ is aggressively hygroscopic. In fact, the heat of hydration is sufficient that mixtures of SO₃ and wood or cotton can ignite. In such cases, SO₃ dehydrates these carbohydrates.

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Sulfuric acid

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1 – Introduction :

Sulfuric acid, H_2SO_4 , is a strong mineral acid. It is soluble in water at all concentrations. It was once known as **oil of vitriol**, coined by the 8th - century Muslim alchemist Jabir ibn Hayyan (Geber) after his discovery of the chemical. Sulfuric acid has many applications, and is one of the top products of the chemical industry. World production in 2001 was 165 million tonnes, with an approximate value of US \$ 8 billion. Principal uses include ore processing, fertilizer manufacturing, oil refining, wastewater processing, and chemical synthesis.

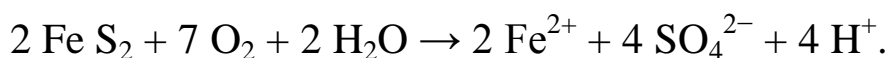
2 – Occurrence:

Pure (undiluted) sulfuric acid is not encountered on Earth, due to sulfuric acid's great affinity for water. Apart from that, sulfuric acid is

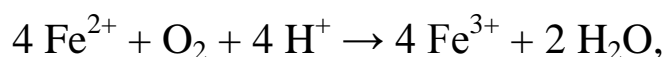
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a constituent of acid rain, which is formed by atmospheric oxidation of sulfur dioxide in the presence of water - i.e., oxidation of sulfurous acid. Sulfur dioxide is the main byproduct produced when sulfur-containing fuels such as coal or oil are burned.

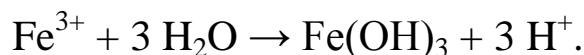
Sulfuric acid is formed naturally by the oxidation of sulfide minerals, such as iron sulfide. The resulting water can be highly acidic and is called Acid Mine Drainage (AMD). This acidic water is capable of dissolving metals present in sulfide ores, which results in brightly-colored, toxic streams. The oxidation of iron sulfide pyrite by molecular oxygen produces iron(II), or Fe^{2+} :



The Fe^{2+} can be further oxidized to Fe^{3+} , according to:



and the Fe^{3+} produced can be precipitated as the hydroxide or hydrous oxide. The equation for the formation of the hydroxide is



The iron (III) ion ("ferric iron", in casual nomenclature) can also oxidize pyrite. When iron (III) oxidation of pyrite occurs, the process can become rapid. pH values below zero have been measured in ARD produced by this process.

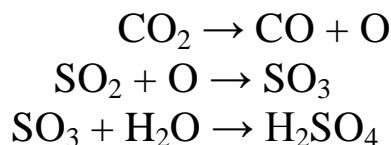
ARD can also produce sulfuric acid at a slower rate, so that the Acid Neutralization Capacity (ANC) of the aquifer can neutralize the produced acid. In such cases, the Total Dissolved solids (TDS) concentration of the water can be increased from the dissolution of minerals from the acid-neutralization reaction with the minerals.

2 – 1 - Extraterrestrial sulfuric acid :

Sulfuric acid is produced in the upper atmosphere of Venus by the sun's photochemical action on carbon dioxide, sulfur dioxide, and water vapor. Ultraviolet photons of wavelengths less than 169 nm can photodissociate carbon dioxide into carbon monoxide and atomic

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oxygen. Atomic oxygen is highly reactive. When it reacts with sulfur dioxide, a trace component of the Venerian atmosphere, the result is sulfur trioxide, which can combine with water vapor, another trace component of Venus's atmosphere, to yield sulfuric acid.



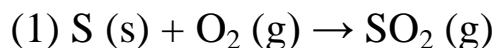
In the upper, cooler portions of Venus's atmosphere, sulfuric acid exists as a liquid, and thick sulfuric acid clouds completely obscure the planet's surface when viewed from above. The main cloud layer extends from 45–70 km above the planet's surface, with thinner hazes extending as low as 30 and as high as 90 km above the surface.

Infrared spectra from NASA's Galileo mission show distinct absorptions on Jupiter's moon Europa that have been attributed to one or more sulfuric acid hydrates. The interpretation of the spectra is somewhat controversial. Some planetary scientists prefer to assign the spectral features to the sulfate ion, perhaps as part of one or more minerals on Europa's surface.^[2]

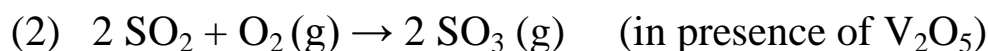
3 - Manufacture (Contact process) :

Sulfuric acid is produced from sulfur, oxygen and water via the contact process.

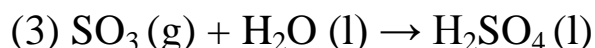
In the first step, sulfur is burned to produce sulfur dioxide.



This is then oxidised to sulfur trioxide using oxygen in the presence of a vanadium(V) oxide catalyst.



Finally the sulfur trioxide is treated with water (usually as 97-98% H_2SO_4 containing 2 - 3 % water) to produce 98 – 99 % sulfuric acid.



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Note that directly dissolving SO_3 in water is not practical due to the highly exothermic nature of the reaction, forming a corrosive mist instead of a liquid. Alternatively, SO_3 can be absorbed into H_2SO_4 to produce oleum ($\text{H}_2\text{S}_2\text{O}_7$), which may then be mixed with water to form sulfuric acid.



Oleum is reacted with water to form concentrated H_2SO_4 .

**4 - Physical properties:****4 – 1 - Forms of sulfuric acid:**

Although nearly 100 % sulfuric acid can be made, this loses SO_3 at the boiling point to produce 98.3 % acid. The 98 % grade is more stable in storage, and is the usual form of what is described as *concentrated sulfuric acid*. Other concentrations are used for different purposes. Some common concentrations are

- 10 % , *dilute sulfuric acid* for laboratory use,
- 33.53 % , *battery acid* (used in lead - acid batteries),
- 62.18 % , *chamber or fertilizer acid*,
- 73.61 % , *tower or Glover acid*,
- 97 % , *concentrated acid* .

Different purities are also available. Technical grade H_2SO_4 is impure and often colored, but is suitable for making fertilizer. Pure grades such as United States Pharmacopoeia (USP) grade are used for making pharmaceuticals and dyestuffs.

When high concentrations of $\text{SO}_3(g)$ are added to sulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$, called *pyrosulfuric acid*, *fuming sulfuric acid* or *oleum* or, less commonly, *Nordhausen acid*, is formed. Concentrations of oleum are either expressed in terms of% SO_3 (called% oleum) or as% H_2SO_4 (the amount made if H_2O were added) ; common concentrations are 40% oleum (109 % H_2SO_4) and 65 % oleum (114.6 % H_2SO_4). Pure $\text{H}_2\text{S}_2\text{O}_7$ is a solid with melting point 36°C .

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**4 – 2 - Polarity and conductivity:**

Anhydrous H_2SO_4 is a very polar liquid, having a dielectric constant of around 100. It has a high electrical conductivity, caused by dissociation through protonating itself, a process known as autoprotolysis: $2 \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{SO}_4^+ + \text{HSO}_4^-$

The equilibrium constant for the autoprotolysis is:

$$K_{\text{ap}} (25^\circ\text{C}) = [\text{H}_3\text{SO}_4^+][\text{HSO}_4^-] = 2.7 \times 10^{-4}.$$

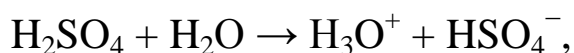
The comparable equilibrium constant for water, K_w is 10^{-14} , a factor of 10^{10} (10 billion) smaller.

In spite of the viscosity of the acid, the effective conductivities of the H_3SO_4^+ and HSO_4^- ions are high due to an intra - molecular proton-switch mechanism (analogous to the Grotthuss mechanism in water), making sulfuric acid a good conductor. It is also an excellent solvent for many reactions.

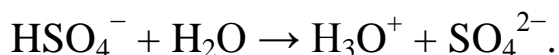
The equilibrium is actually more complex than shown above; 100% H_2SO_4 contains the following species at equilibrium (figures shown as millimol per kg solvent): HSO_4^- (15.0), H_3SO_4^+ (11.3), H_3O^+ (8.0), HS_2O_7^- (4.4), $\text{H}_2\text{S}_2\text{O}_7$ (3.6), H_2O (0.1).

5 - Chemical properties:**5 -1 - Reaction with water:**

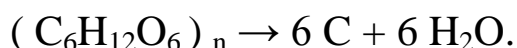
The hydration reaction of sulfuric acid is highly exothermic. If water is added to the concentrated sulfuric acid, it can boil and spit dangerously. One should always add the acid to the water rather than the water to the acid. The necessity for this safety precaution is due to the relative densities of these two liquids. Water is less dense than sulfuric acid, meaning water will tend to float on top of this acid. The reaction is best thought of as forming hydronium ions, by



and then

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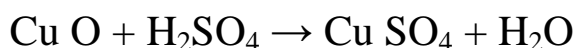
Because the hydration of sulfuric acid is thermo dynamically favorable, sulfuric acid is an excellent dehydrating agent, and is used to prepare many dried fruits. The affinity of sulfuric acid for water is sufficiently strong that it will remove hydrogen and oxygen atoms from other compounds; for example, mixing starch $(\text{C}_6\text{H}_{12}\text{O}_6)_n$ and concentrated sulfuric acid will give elemental carbon and water which is absorbed by the sulfuric acid (which becomes slightly diluted):



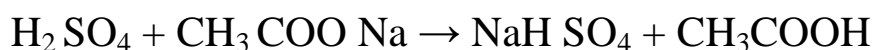
The effect of this can be seen when concentrated sulfuric acid is spilled on paper; the cellulose reacts to give a burned appearance, the carbon appears much as soot would in a fire. A more dramatic reaction occurs when sulfuric acid is added to a table spoon of white sugar; a rigid column of black, porous carbon will quickly emerge. The carbon will smell strongly of caramel.

5 – 2 - Other reactions:

As an acid, sulfuric acid reacts with most bases to give the corresponding sulfate. For example, copper (II) sulfate. This blue salt of copper, commonly used for electroplating and as a fungicide, is prepared by the reaction of copper (II) oxide with sulfuric acid:



Sulfuric acid can also be used to displace weaker acids from their salts. Reaction with sodium acetate, for example, displaces acetic acid:

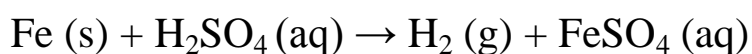


Similarly, reacting sulfuric acid with potassium nitrate can be used to produce nitric acid and a precipitate of potassium bisulfate. When combined with nitric acid, sulfuric acid acts both as an acid and a dehydrating agent, forming the nitronium ion NO_2^+ , which is important in nitration reactions involving electrophilic aromatic substitution. This type of reaction, where protonation occurs on an

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oxygen atom, is important in many organic chemistry reactions, such as Fischer esterification and dehydration of alcohols.

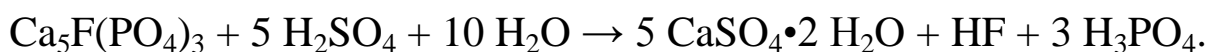
Sulfuric acid reacts with most metals via a single displacement reaction to produce hydrogen gas and the metal sulfate. Dilute H_2SO_4 attacks iron, aluminium, zinc, manganese, magnesium and nickel, but reactions with tin and copper require the acid to be hot and concentrated. Lead and tungsten, however, are resistant to sulfuric acid. The reaction with iron (shown) is typical for most of these metals, but the reaction with tin is unusual in that it produces sulfur dioxide rather than hydrogen.



Sulfuric acid undergoes electrophilic aromatic substitution with aromatic compounds to give the corresponding sulfonic acids:^[4]

6 - Uses :

Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength .The major use (60 % of total production worldwide) for sulfuric acid is in the " wet method " for the production of phosphoric acid, used for manufacture of phosphate fertilizers as well as trisodium phosphate for detergents. In this method, phosphate rock is used, and more than 100 million tonnes are processed annually. This raw material is shown below as fluorapatite, though the exact composition may vary. This is treated with 93 % sulfuric acid to produce calcium sulfate, hydrogen fluoride (HF) and phosphoric acid. The HF is removed as hydrofluoric acid. The overall process can be represented as:



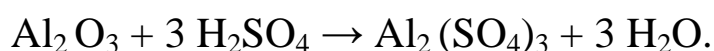
Sulfuric acid is used in large quantities by the iron and steelmaking industry to remove oxidation, rust and scale from rolled sheet and billets prior to sale to the automobile and white-goods industry. Used acid is often recycled using a Spent Acid Regeneration

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(SAR) plant. These plants combust spent acid with natural gas, refinery gas, fuel oil or other fuel sources. This combustion process produces gaseous sulfur dioxide (SO₂) and sulfur trioxide (SO₃) which are then used to manufacture "new" sulfuric acid. SAR plants are common additions to metal smelting plants, oil refineries, and other industries where sulfuric acid is consumed in bulk, as operating a SAR plant is much cheaper than the recurring costs of spent acid disposal and new acid purchases.

Ammonium sulfate, an important nitrogen fertilizer, is most commonly produced as a byproduct from coking plants supplying the iron and steel making plants. Reacting the ammonia produced in the thermal decomposition of coal with waste sulfuric acid allows the ammonia to be crystallized out as a salt (often brown because of iron contamination) and sold into the agro-chemicals industry.

Another important use for sulfuric acid is for the manufacture of aluminum sulfate, also known as paper maker's alum. This can react with small amounts of soap on paper pulp fibers to give gelatinous aluminum carboxylates, which help to coagulate the pulp fibers into a hard paper surface. It is also used for making aluminum hydroxide, which is used at water treatment plants to filter out impurities, as well as to improve the taste of the water. Aluminum sulfate is made by reacting bauxite with sulfuric acid:

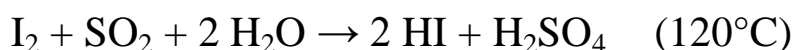
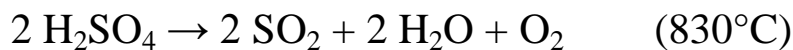


Sulfuric acid is used for a variety of other purposes in the chemical industry. For example, it is the usual acid catalyst for the conversion of cyclohexanoneoxime to caprolactam, used for making nylon. It is used for making hydrochloric acid from salt via the Mannheim process. Much H₂SO₄ is used in petroleum refining, for example as a catalyst for the reaction of isobutane with isobutylene to give isooctane, a compound that raises the octane rating of gasoline (petrol). Sulfuric acid is also important in the manufacture of dyestuffs solutions and is the "acid" in lead - acid (car) batteries.

Sulfuric acid is also used as a general dehydrating agent in its concentrated form. See Reaction with water.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**6 – 1 – Sulfur - iodine cycle:**

The sulfur - iodine cycle is a series of thermo - chemical processes used to obtain hydrogen. It consists of three chemical reactions whose net reactant is water and whose net products are hydrogen and oxygen.



The sulfur and iodine compounds are recovered and reused, hence the consideration of the process as a cycle. This process is endothermic and must occur at high temperatures, so energy in the form of heat has to be supplied.

The sulfur - iodine cycle has been proposed as a way to supply hydrogen for a hydrogen - based economy. It does not require hydrocarbons like current methods of steam reforming.

The sulfur - iodine cycle is currently being researched as a feasible method of obtaining hydrogen, but the concentrated, corrosive acid at high temperatures poses currently insurmountable safety hazards if the process were built on large - scale.

7 - History:

John Dalton's 1808 sulfuric acid molecule shows a central sulfur atom bonded to three oxygen atoms.

The discovery of sulfuric acid is credited to the 8th century Arabian chemist and alchemist, Jabir ibn Hayyan (Geber). The acid was later studied by 9th century Persian physician and alchemist Ibn Zakariya al - Razi (Rhazes), who obtained the substance by dry distillation of minerals including iron(II) sulfate heptahydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and copper(II) sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. When heated, these compounds decompose to iron(II) oxide and copper(II) oxide, respectively, giving off water and sulfur trioxide, which combine to produce a dilute solution of sulfuric acid. This method was popularized in Europe through translations of Arabic and Persian

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treatises, as well as books by European alchemists, such as the 13th-century German Albertus Magnus.

Sulfuric acid was known to medieval European alchemists as *oil of vitriol*, *spirit of vitriol*, or simply *vitriol*, among other names. The word vitriol derives from the Latin vitreus, 'glass', referring to the glassy appearance of the sulfate salts, which also carried the name vitriol. Salts called by this name included copper(II) sulfate (blue vitriol, or rarely Roman vitriol), zinc sulfate (white vitriol), iron (II) sulfate (green vitriol), iron (III) sulfate (vitriol of Mars), and cobalt (II) sulfate (red vitriol).

Vitriol was widely considered the most important alchemical substance, intended to be used as a philosopher's stone. Highly purified vitriol was used as a medium for reacting other substances. This was largely because the acid does not react with gold, production of which was often the final goal of alchemical processes. The importance of vitriol to alchemy is highlighted in the alchemical motto, *Visita Interiora Terrae Rectificando Invenies Occultum Lapidem* which is a backronym meaning ('Visit the interior of the earth and rectifying (i.e. purifying) you will find the hidden/secret stone'), found in *L'Azothe des Philosophes* by the 15th Century alchemist Basilus Valentinus, .

In the 17th century, the German-Dutch chemist Johann Glauber prepared sulfuric acid by burning sulfur together with saltpeter (potassium nitrate, KNO_3), in the presence of steam. As saltpeter decomposes, it oxidizes the sulfur to SO_3 , which combines with water to produce sulfuric acid. In 1736, Joshua Ward, a London pharmacist, used this method to begin the first large - scale production of sulfuric acid.

In 1746 in Birmingham, John Roebuck adapted this method to produce sulfuric acid in lead-lined chambers, which were stronger, less expensive, and could be made larger than the previously used glass containers. This *lead chamber process* allowed the effective industrialization of sulfuric acid production. After several refinements, this method remained the standard for sulfuric acid production for almost two centuries.

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Sulfuric acid created by John Roebuck's process only approached a 35 – 40 % concentration. Later refinements to the lead-chamber process by French chemist Joseph - Louis Gay-Lussac and British chemist John Glover improved the yield to 78 %. However, the manufacture of some dyes and other chemical processes require a more concentrated product. Throughout the 18th century, this could only be made by dry distilling minerals in a technique similar to the original alchemical processes. Pyrite (iron disulfide, FeS_2) was heated in air to yield iron (II) sulfate, FeSO_4 , which was oxidized by further heating in air to form iron (III) sulfate, $\text{Fe}_2(\text{SO}_4)_3$, which, when heated to 480 °C, decomposed to iron (III) oxide and sulfur trioxide, which could be passed through water to yield sulfuric acid in any concentration. However, the expense of this process prevented the large-scale use of concentrated sulfuric acid.

In 1831, British vinegar merchant Peregrine Phillips patented the contact process, which was a far more economical process for producing sulfur trioxide and concentrated sulfuric acid. Today, nearly all of the world's sulfuric acid is produced using this method.

8 - Safety

8 – 1 - Laboratory hazards:

The corrosive properties of sulfuric acid are accentuated by its highly exothermic reaction with water. Hence burns from sulfuric acid are potentially more serious than those of comparable strong acids (e.g. hydrochloric acid) , as there is additional tissue damage due to dehydration and particularly due to the heat liberated by the reaction with water; i.e. secondary thermal damage. The danger is obviously greater with more concentrated preparations of sulfuric acid, but it should be remembered that even the normal laboratory "dilute" grade (approx. 1 M, 10 %) will char paper by dehydration if left in contact for a sufficient time. Solutions equal to or stronger than 1.5 M should be labeled CORROSIVE, while solutions greater than 0.5 M but less than 1.5 M should be labeled IRRITANT. Fuming sulfuric acid (oleum) is not recommended for use in schools due to it being quite hazardous. The standard first aid treatment for acid spills on the skin is, as for other corrosive agents, irrigation with large quantities of

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water: Washing should be continued for at least ten to fifteen minutes in order to cool the tissue surrounding the acid burn and to prevent secondary damage. Contaminated clothing must be removed immediately and the underlying skin washed thoroughly.

Preparation of the diluted acid can also be dangerous due to the heat released in the dilution process. It is essential that the concentrated acid is added to water and not the other way round, to take advantage of the relatively high heat capacity of water. Addition of water to concentrated sulfuric acid leads at best to the dispersal of a sulfuric acid aerosol, at worst to an explosion. Preparation of solutions greater than 6 M (35%) in concentration is the most dangerous, as the heat produced can be sufficient to boil the diluted acid: efficient mechanical stirring and external cooling (e.g. an ice bath) are essential.

8 – 2 - Industrial hazards:

Although sulfuric acid is non-flammable, contact with metals in the event of a spillage can lead to the liberation of hydrogen gas. The dispersal of acid aerosols and gaseous sulfur dioxide is an additional hazard of fires involving sulfuric acid.

Sulfuric acid is not considered toxic besides its obvious corrosive hazard, and the main occupational risks are skin contact leading to burns and the inhalation of aerosols. Exposure to aerosols at high concentrations leads to immediate and severe irritation of the eyes, respiratory tract and mucous membranes: this ceases rapidly after exposure, although there is a risk of subsequent pulmonary edema if tissue damage has been more severe. At lower concentrations, the most commonly reported symptom of chronic exposure to sulfuric acid aerosols is erosion of the teeth, found in virtually all studies: indications of possible chronic damage to the respiratory tract are inconclusive as of 1997. In the United States, the permissible exposure limit (PEL) for sulfuric acid is fixed at 1 mg/m³: limits in other countries are similar. Interestingly there have been reports of sulfuric acid ingestion leading to vitamin B12 deficiency with subacute combined degeneration. The spinal cord is most often affected in such

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cases, but the optic nerves may show demyelination, loss of axons and gliosis.

9 - Legal restrictions:

International commerce of sulfuric acid is controlled under the United Nations Convention Against Illicit Traffic in Narcotic Drugs and Psychotropic Substances, 1988, which lists sulfuric acid under Table II of the convention as a chemical frequently used in the illicit manufacture of narcotic drugs or psychotropic substances.^[6]

In the United States of America, sulfuric acid is included in List II of the list of essential or precursor chemicals established pursuant to the Chemical Diversion and Trafficking Act. Accordingly, transactions of sulfuric acid—such as sales, transfers, exports from and imports to the United States—are subject to regulation and monitoring by the Drug Enforcement Administration.

10 - In fiction:

In several films, cartoons and TV shows, especially sci - fi ones, sulfuric acid is normally depicted as a bubbling green steaming liquid, sometimes capable of dissolving almost anything in an instant. This is purely for visual appeal, since boiling green acid is more dangerous-looking than the actual clear and syrupy form it really is. The use of sulfuric acid as a weapon in crimes of assault, known as "vitriol throwing", has at times been sufficiently common (if sensational) to make its way into novels and short stories. Examples include *The Adventure of the Illustrious Client*, by Arthur Conan Doyle, *The Love of Long Ago*, by Guy de Maupassant and *Brighton Rock* by Graham Greene. A band, My Vitriol, take their name from its use as a weapon in *Brighton Rock*. An episode of *Saturday Night Live* hosted by Mel Gibson included a parody Western sketch about "Sheriff Jeff Acid," who carries a flask of acid instead of a six shooter. The DC Comics villain Two Face was disfigured as a result of a vitriol throw. This crime is also mentioned in *Nineteen Eighty-Four* by George Orwell; the protagonist Winston Smith agrees to throw vitriol into a child's face if that would be "the Brotherhood's" order, and Winston's enemy O'Brien later uses those barbaric words to undermine his logic. The

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novel *Veronika Decides to Die* by Paulo Coelho talks of a girl who has attempted to commit suicide and ends up with vitriol poisoning. The doctor/therapist in this novel also writes a thesis on curing vitriol poisoning. The substance was also used by a young gangster in Season 6B, Episode 5 of *The Sopranos* as a form of torture. Mentioned in Christian metal rock song "Acid Head" on Tourniquet's album "Vanishing Lessons" (1995).

Nitrogen

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- 8 Safety

1 – Introduction :

Nitrogen is a chemical element that has the symbol **N**, atomic number of 7 and atomic mass 14.00674 u. Elemental nitrogen is a colorless, odorless, tasteless and mostly inert diatomic gas at standard conditions, constituting 78 % by volume of Earth's atmosphere.

Many industrially important compounds, such as ammonia, nitric acid, organic nitrates (propellants and explosives), and cyanides, contain nitrogen. The extremely strong bond in elemental nitrogen dominates nitrogen chemistry, causing difficulty for both organisms and industry in converting the N_2 into useful compounds, and releasing large amounts of energy when these compounds burn or decay back into nitrogen gas.

The element nitrogen was discovered by a Scottish physician Daniel Rutherford in 1772. Nitrogen occurs in all living organisms. It is a constituent element of amino acids and thus of proteins, and of nucleic acids (DNA and RNA). It resides in the chemical structure of

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almost all neurotransmitters, and is a defining component of alkaloids, biological molecules produced by many organisms.

General properties

Name, symbol, number	Nitrogen , N , 7
Element category	Non metal
Group, period, block	15, 2, p
Standard atomic weight	14 g·mol ⁻¹
Electron configuration	1s ² 2s ² 2p ³
Electrons per shell	2, 5

Physical properties

Phase	gas
Density	(0 °C, 101.325 kPa) 1.251 g / L
Melting point	63.153 K , -210.00 °C, - 346.00 °F
Boiling point	77.36 K , -195.79 °C , -320 °F
Triple point	63.1526 K (-210°C), 12.53 kPa
Critical point	126.19 K, 3.3978 MPa
Heat of fusion	(N ₂) 0.72 kJ·mol ⁻¹
Heat of vaporization	(N ₂) 5.56 kJ·mol ⁻¹
Specific heat capacity	(25 °C) (N ₂) 29.124 J·mol ⁻¹ ·K ⁻¹

Atomic properties

Oxidation states	5, 4, 3, 2, 1, -1, -2, -3 (strongly acidic oxide)
Electronegativity	3.04 (Pauling scale)
Ionization energies (more)	1st : 1402.3 kJ·mol ⁻¹ 2nd : 2856 kJ·mol ⁻¹ 3rd : 4578.1 kJ·mol ⁻¹
Covalent radius	71±1 pm
Van der Waals radius	155 pm

Miscellanea

Thermal conductivity	(300 K) $25.83 \times 10^{-3} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$
Speed of sound	(gas, 27 °C) 353 m/s

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**2 – History:**

Nitrogen (Latin *nitrogenium*, where *nitrum* (from Greek *nitron* νιτρον) means "saltpetre" (see nitre), and *genes* γενης means "forming") is formally considered to have been discovered by Daniel Rutherford in 1772, who called it *noxious air* or *fixed air*.^[1] That there was a fraction of air that did not support combustion was well known to the late 18th century chemist. Nitrogen was also studied at about the same time by Carl Wilhelm Scheele, Henry Cavendish, and Joseph Priestley, who referred to it as *burnt air* or *phlogisticated air*. Nitrogen gas was inert enough that Antoine Lavoisier referred to it as "mephitic air" or *azote*, from the Greek word *ἄζωτος* (*azotos*) meaning "lifeless".^[2] Animals died in it, and it was the principal component of air in which animals had suffocated and flames had burned to extinction. Lavoisier's name for nitrogen is used in many languages (French, Russian, etc.) and still remains in English in the common names of many compounds, such as hydrazine and compounds of the azide ion. Compounds of nitrogen were known in the Middle Ages. The alchemists knew nitric acid as *aqua fortis* (strong water). The mixture of nitric and hydrochloric acids was known as *aqua regia* (royal water), celebrated for its ability to dissolve gold (the *king* of metals). The earliest military, industrial and agricultural applications of nitrogen compounds involved uses of saltpeter (sodium nitrate or potassium nitrate), notably in gunpowder, and much later, as fertilizer. In 1910, Lord Rayleigh discovered that an electrical discharge in nitrogen gas produced "active nitrogen", an allotrope considered to be monatomic. The "whirling cloud of brilliant yellow light" produced by his apparatus reacted with quicksilver to produce explosive mercury nitride.

3 – Properties:

Nitrogen is a nonmetal, with an electro negativity of 3.04. It has five electrons in its outer shell and is therefore trivalent in most compounds. The triple bond in molecular nitrogen (N_2) is the strongest in nature. The resulting difficulty of converting N_2 into other compounds, and the ease (and associated high energy release) of

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converting nitrogen compounds into elemental N_2 , have dominated the role of nitrogen in both nature and human economic activities.

At atmospheric pressure molecular nitrogen condenses (liquefies) at 77 K ($-195.8\text{ }^\circ\text{C}$) and freezes at 63 K ($-210.0\text{ }^\circ\text{C}$) into the beta hexagonal close-packed crystal allotropic form. Below 35.4 K ($-237.6\text{ }^\circ\text{C}$) nitrogen assumes the alpha cubic crystal allotropic form. Liquid nitrogen, a fluid resembling water in appearance, but with 80.8% of the density (the density of liquid nitrogen at its boiling point is 0.808 g/mL), is a common cryogen.

Unstable allotropes of nitrogen consisting of more than two nitrogen atoms have been produced in the laboratory, like N_3 and N_4 .^[4] Under extremely high pressures (1.1 million atm) and high temperatures (2000 K), as produced using a diamond anvil cell, nitrogen polymerizes into the single-bonded cubic gauche crystal structure. This structure is similar to that of diamond, and both have extremely strong covalent bonds. N_4 is nicknamed "nitrogen diamond."

3 – 1 – Isotopes:

There are two stable isotopes of nitrogen: ^{14}N and ^{15}N . By far the most common is ^{14}N (99.634 %), which is produced in the CNO cycle in stars. Of the ten isotopes produced synthetically, ^{13}N has a half-life of ten minutes and the remaining isotopes have half-lives on the order of seconds or less. Biologically-mediated reactions (e.g., assimilation, nitrification, and denitrification) strongly control nitrogen dynamics in the soil. These reactions typically result in ^{15}N enrichment of the substrate and depletion of the product.

A small part (0.73 %) of the molecular nitrogen in Earth's atmosphere is the isotopologue $^{14}\text{N}^{15}\text{N}$, and almost all the rest is $^{14}\text{N}_2$.

Radioisotope ^{16}N is the dominant radionuclide in the coolant of pressurized water reactors during normal operation. It is produced from ^{16}O (in water) via (n,p) reaction. It has a short half-life of about 7.1 s, but during its decay back to ^{16}O produces high-energy gamma radiation (5 to 7 MeV). Because of this, the access to the primary

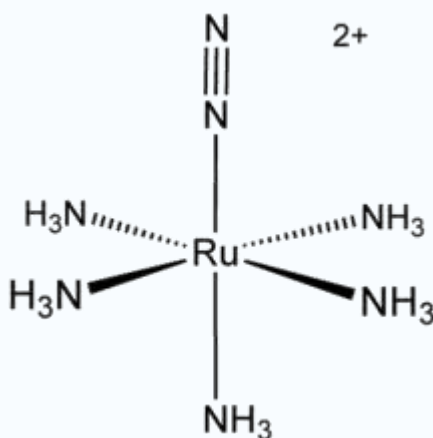
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coolant piping must be restricted during reactor power operation^[6]. ^{16}N is one of the main means used to immediately detect even small leaks from the primary coolant to the secondary steam cycle.

3 – 2 - Electro magnetic spectrum;

Molecular nitrogen ($^{14}\text{N}_2$) is largely transparent to infrared and visible radiation because it is a homonuclear molecule and thus has no dipole moment to couple to electromagnetic radiation at these wavelengths. Significant absorption occurs at extreme ultraviolet wavelengths, beginning around 100 nanometers. This is associated with electronic transitions in the molecule to states in which charge is not distributed evenly between nitrogen atoms. Nitrogen absorption leads to significant absorption of ultraviolet radiation in the Earth's upper atmosphere as well as in the atmospheres of other planetary bodies. For similar reasons, pure molecular nitrogen lasers typically emit light in the ultraviolet range.

Nitrogen also makes a contribution to visible air glow from the Earth's upper atmosphere, through electron impact excitation followed by emission. This visible blue air glow (seen in the polar aurora and in the re-entry glow of returning spacecraft) typically results not from molecular nitrogen, but rather from free nitrogen atoms combining with oxygen to form nitric oxide (NO).

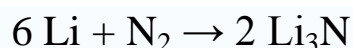
3 – 3 – Reactions:

Structure of $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$.

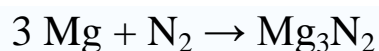
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Nitrogen is generally unreactive at standard temperature and pressure. N₂ reacts spontaneously with few reagents, being resilient to acids and bases as well as oxidants and most reductants. When nitrogen reacts spontaneously with a reagent, the net transformation is often called nitrogen fixation.

Nitrogen reacts with elemental lithium.^[7] Lithium burns in an atmosphere of N₂ to give lithium nitride:



Magnesium also burns in nitrogen, forming magnesium nitride.



N₂ forms a variety of adducts with transition metals. The first example of a dinitrogen complex is [Ru(NH₃)₅(N₂)]²⁺ (see figure at right). Such compounds are now numerous, other examples include IrCl(N₂)(PPh₃)₂, W(N₂)₂(Ph₂CH₂CH₂PPh₂)₂, and [(η⁵-C₅Me₄H)₂Zr]₂(μ₂, η², η²-N₂). These complexes illustrate how N₂ might bind to the metal(s) in nitrogenase and the catalyst for the Haber process.^[8] A catalytic process to reduce N₂ to ammonia with the use of a molybdenum complex in the presence of a proton source was published in 2005.

The starting point for industrial production of nitrogen compounds is the Haber process, in which nitrogen is fixed by reacting N₂ and H₂ over an iron (III) oxide (Fe₃O₄) catalyst at about 500 °C and 200 atmospheres pressure. Biological nitrogen fixation in free-living cyanobacteria and in the root nodules of plants also produces ammonia from molecular nitrogen. The reaction, which is the source of the bulk of nitrogen in the biosphere, is catalyzed by the nitrogenase enzyme complex which contains Fe and Mo atoms, using energy derived from hydrolysis of adenosine triphosphate (ATP) into adenosine diphosphate and inorganic phosphate (−20.5 kJ / mol).

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**4 – Occurrence;**

Nitrogen is the largest single constituent of the Earth's atmosphere (78.082 % by volume of dry air, 75.3 % by weight in dry air). It is created by fusion processes in stars, and is estimated to be the 7th most abundant chemical element by mass in the universe.^[9]

Molecular nitrogen and nitrogen compounds have been detected in interstellar space by astronomers using the Far Ultraviolet Spectroscopic Explorer.^[10] Molecular nitrogen is a major constituent of the Saturnian moon Titan's thick atmosphere, and occurs in trace amounts in other planetary atmospheres.

Nitrogen is present in all living organisms, in proteins, nucleic acids and other molecules. It typically makes up around 4% of the dry weight of plant matter, and around 3% of the weight of the human body. It is a large component of animal waste (for example, guano), usually in the form of urea, uric acid, ammonium compounds and derivatives of these nitrogenous products, which are essential nutrients for all plants that are unable to fix atmospheric nitrogen.

Nitrogen occurs naturally in a number of minerals, such as saltpetre (potassium nitrate), Chile saltpetre (sodium nitrate) and sal ammoniac (ammonium chloride). Most of these are relatively uncommon, partly because of the minerals' ready solubility in water. See also Nitrate minerals and Ammonium minerals.

5 - Nitrogen compounds

The main neutral hydride of nitrogen is ammonia (NH₃), although hydrazine (N₂H₄) is also commonly used. Ammonia is more basic than water by 6 orders of magnitude. In solution ammonia forms the ammonium ion (NH₄⁺). Liquid ammonia (boiling point 240 K) is amphiprotic (displaying either Brønsted-Lowry acidic or basic character) and forms ammonium and the less common amide ions (NH₂⁻); both amides and nitride (N³⁻) salts are known, but decompose in water. Singly, doubly, triply and quadruply substituted alkyl compounds of ammonia are called amines (four substitutions, to form commercially and biologically important quaternary amines,

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results in a positively charged nitrogen, and thus a water-soluble, or at least amphiphilic, compound). Larger chains, rings and structures of nitrogen hydrides are also known, but are generally unstable. N_2^{+2} is another polyatomic cation as in hydrazine.

Other classes of nitrogen anions (negatively charged ions) are the poisonous azides (N^{3-}), which are linear and isoelectronic to carbon dioxide, but which bind to important iron-containing enzymes in the body in a manner more resembling cyanide. Another molecule of the same structure is the colorless and relatively inert anesthetic gas Nitrous oxide (dinitrogen monoxide, N_2O), also known as laughing gas. This is one of a variety of nitrogen oxides that form a family often abbreviated as **NO_x**. Nitric oxide (nitrogen monoxide, NO), is a natural free radical used in signal transduction in both plants and animals, for example in vasodilation by causing the smooth muscle of blood vessels to relax. The reddish and poisonous nitrogen dioxide NO_2 contains an unpaired electron and is an important component of smog. Nitrogen molecules containing unpaired electrons show an understandable tendency to dimerize (thus pairing the electrons), and are generally highly reactive. The corresponding acids are nitrous HNO_2 and nitric acid HNO_3 , with the corresponding salts called nitrites and nitrates.

The higher oxides dinitrogen trioxide N_2O_3 , dinitrogen tetroxide N_2O_4 and dinitrogen pentoxide N_2O_5 , are fairly unstable and explosive, a consequence of the chemical stability of N_2 . Nearly every hypergolic rocket engine uses N_2O_4 as the oxidizer; their fuels, various forms of hydrazine, are also nitrogen compounds. These engines are extensively used on spacecraft such as the space shuttle and those of the Apollo Program because their propellants are liquids at room temperature and ignition occurs on contact without an ignition system, allowing many precisely controlled burns. Some launch vehicles, such as the Titan II and Ariane 1 through 4 also use hypergolic fuels, although the trend is away from such engines for cost and safety reasons. N_2O_4 is an intermediate in the manufacture of nitric acid HNO_3 , one of the few acids stronger than hydronium and a fairly strong oxidizing agent.

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Nitrogen is notable for the range of explosively unstable compounds that it can produce. Nitrogen triiodide NI_3 is an extremely sensitive contact explosive. Nitrocellulose, produced by nitration of cellulose with nitric acid, is also known as guncotton. Nitroglycerin, made by nitration of glycerin, is the dangerously unstable explosive ingredient of dynamite. The comparatively stable, but more powerful explosive trinitrotoluene (TNT) is the standard explosive against which the power of nuclear explosions are measured.

Nitrogen can also be found in organic compounds. Common nitrogen functional groups include: amines, amides, nitro groups, imines, and enamines. The amount of nitrogen in a chemical substance can be determined by the Kjeldahl method.

6 – Applications:

Nitrogen gas is an industrial gas produced by the fractional distillation of liquid air, or by mechanical means using gaseous air (i.e. pressurized reverse osmosis membrane or Pressure swing adsorption). Commercial nitrogen is often a byproduct of air-processing for industrial concentration of oxygen for steelmaking and other purposes. When supplied compressed in cylinders it is often referred to as OFN (oxygen-free nitrogen).

Nitrogen gas has a wide variety of applications, including serving as an inert replacement for air where oxidation is undesirable;

- To preserve the freshness of packaged or bulk foods (by delaying rancidity and other forms of oxidative damage)
- In ordinary incandescent light bulbs as an inexpensive alternative to argon.
- On top of liquid explosives as a safety measure
- The production of electronic parts such as transistors, diodes, and integrated circuits
- Dried and pressurized, as a dielectric gas for high voltage equipment
- The manufacturing of stainless steel
- Use in military aircraft fuel systems to reduce fire hazard.

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- Filling automotive and aircraft tires^[15] due to its inertness and lack of moisture or oxidative qualities, as opposed to air, though this is not necessary for consumer automobiles.
- Nitrogen is commonly used during sample preparation procedures for chemical analysis. Specifically, it is used as a means of concentrating and reducing the volume of liquid samples. Directing a pressurized stream of nitrogen gas perpendicular to the surface of the liquid allows the solvent to evaporate while leaving the solute(s) and un-evaporated solvent behind.

Nitrogen tanks are also replacing carbon dioxide as the main power source for paintball guns. The downside is that nitrogen must be kept at higher pressure than CO₂, making N₂ tanks heavier and more expensive.

6 – 1 - Nitrogenated beer:

A further example of its versatility is its use as a preferred alternative to carbon dioxide to pressurize kegs of some beers, particularly stouts and British ales, due to the smaller bubbles it produces, which make the dispensed beer smoother and headier. A modern application of a pressure sensitive nitrogen capsule known commonly as a "widget" now allows nitrogen charged beers to be packaged in cans and bottles.

6 – 2 - Liquid nitrogen:

Liquid nitrogen is a cryogenic liquid. At atmospheric pressure, it boils at -195.8 °C. When insulated in proper containers such as Dewar flasks, it can be transported without much evaporative loss.

Like dry ice, the main use of liquid nitrogen is as a refrigerant. Among other things, it is used in the cryopreservation of blood, reproductive cells (sperm and egg), and other biological samples and materials. It is used in cold traps for certain laboratory equipment and to cool X-ray detectors. It has also been used to cool central processing units and other devices in computers which are over clocked, and which produce more heat than during normal operation.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**6 – 3 - Applications of nitrogen compounds :**

Molecular nitrogen (N_2) in the atmosphere is relatively non-reactive due to its strong bond, and N_2 plays an inert role in the human body, being neither produced nor destroyed. In nature, nitrogen is converted into biologically (and industrially) useful compounds by lightning, and by some living organisms, notably certain bacteria (i.e. nitrogen fixing bacteria). Molecular nitrogen is released into the atmosphere in the process of decay, in dead plant and animal tissues.

The ability to combine or **fix** molecular nitrogen is a key feature of modern industrial chemistry, where nitrogen and natural gas are converted into ammonia via the Haber process. Ammonia, in turn, can be used directly (primarily as a fertilizer, and in the synthesis of nitrated fertilizers), or as a precursor of many other important materials including explosives, largely via the production of nitric acid by the Ostwald process.

The organic and inorganic salts of nitric acid have been important historically as convenient stores of chemical energy. They include important compounds such as potassium nitrate (or saltpeter used in gunpowder) and ammonium nitrate, an important fertilizer and explosive . Various other nitrated organic compounds, such as nitroglycerin and trinitrotoluene, and nitrocellulose, are used as explosives and propellants for modern firearms. Nitric acid is used as an oxidizing agent in liquid fueled rockets. Hydrazine and hydrazine derivatives find use as rocket fuels and monopropellants. In most of these compounds, the basic instability and tendency to burn or explode is derived from the fact that nitrogen is present as an oxide, and not as the far more stable nitrogen molecule (N_2) which is a product of the compounds' thermal decomposition. When nitrates burn or explode, the formation of the powerful triple bond in the N_2 produces most of the energy of the reaction.

Nitrogen is a constituent of molecules in every major drug class in pharmacology and medicine. Nitrous oxide (N_2O) was discovered early in the 19th century to be a partial anesthetic, though it was not used as a surgical anesthetic until later. Called "laughing gas", it was found capable of inducing a state of social disinhibition resembling

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drunkenness. Other notable nitrogen-containing drugs are drugs derived from plant alkaloids, such as morphine (there exist many alkaloids known to have pharmacological effects; in some cases they appear natural chemical defenses of plants against predation). Nitrogen containing drugs include all of the major classes of antibiotics, and organic nitrate drugs like nitroglycerin and nitroprusside which regulate blood pressure and heart action by mimicking the action of nitric oxide.

7 - Biological role:

Nitrogen is an essential building block of amino and nucleic acids, essential to life on Earth.

Elemental nitrogen in the atmosphere cannot be used directly by either plants or animals, and must be converted to a reduced (or 'fixed') state in order to be useful for higher plants and animals. Precipitation often contains substantial quantities of ammonium and nitrate, thought to result from nitrogen fixation by lightning and other atmospheric electric phenomena . This was first proposed by Liebig in 1827 and later confirmed . However, because ammonium is preferentially retained by the forest canopy relative to atmospheric nitrate, most fixed nitrogen reaches the soil surface under trees as nitrate. Soil nitrate is preferentially assimilated by these tree roots relative to soil ammonium.

Specific bacteria (e.g. *Rhizobium trifolium*) possess nitrogenase enzymes which can fix atmospheric nitrogen (see nitrogen fixation) into a form (ammonium ion) that is chemically useful to higher organisms. This process requires a large amount of energy and anoxic conditions. Such bacteria may live freely in soil (e.g. *Azotobacter*) but normally exist in a symbiotic relationship in the root nodules of leguminous plants (e.g. clover, *Trifolium*, or soybean plant, *Glycine max*). Nitrogen-fixing bacteria are also symbiotic with a number of unrelated plant species such as alders (*Alnus*) spp., lichens (*Casuarina*), *Myrica*, liverworts, and *Gunnera*.

As part of the symbiotic relationship, the plant converts the 'fixed' ammonium ion to nitrogen oxides and amino acids to form

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proteins and other molecules, (e.g. alkaloids). In return for the 'fixed' nitrogen, the plant secretes sugars to the symbiotic bacteria.

Plants are able to assimilate nitrogen directly in the form of nitrates which may be present in soil from natural mineral deposits, artificial fertilizers, animal waste, or organic decay (as the product of bacteria, but not bacteria specifically associated with the plant). Nitrates absorbed in this fashion are converted to nitrites by the enzyme *nitrate* reductase, and then converted to ammonia by another enzyme called *nitrite* reductase.

Nitrogen compounds are basic building blocks in animal biology as well. Animals use nitrogen-containing amino acids from plant sources, as starting materials for all nitrogen-compound animal biochemistry, including the manufacture of proteins and nucleic acids. Plant-feeding insects are dependent on nitrogen in their diet, such that varying the amount of nitrogen fertilizer applied to a plant can affect the reproduction rate of insects feeding on fertilized plants.

Soluble nitrate is an important limiting factor in the growth of certain bacteria in ocean waters. In many places in the world, artificial fertilizers applied to crop - lands to increase yields result in run-off delivery of soluble nitrogen to oceans at river mouths. This process can result in eutrophication of the water, as nitrogen-driven bacterial growth depletes water oxygen to the point that all higher organisms die. Well - known "dead zone" areas in the U.S. Gulf Coast and the Black Sea are due to this important polluting process.

Many saltwater fish manufacture large amounts of tri methyl amine oxide to protect them from the high osmotic effects of their environment (conversion of this compound to dimethylamine is responsible for the early odor in not fresh saltwater fish. In animals, free radical nitric oxide (*NO*) (derived from an amino acid), serves as an important regulatory molecule for circulation.

Animal metabolism of *NO* results in production of nitrite. Animal metabolism of nitrogen in proteins generally results in excretion of urea, while animal metabolism of nucleic acids results in excretion of urea and uric acid. The characteristic odor of animal flesh

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decay is caused by the creation of long-chain, nitrogen-containing amines, such as putrescine and cadaverine.

Decay of organisms and their waste products may produce small amounts of nitrate, but most decay eventually returns nitrogen content to the atmosphere, as molecular nitrogen. The circulation of nitrogen from atmosphere to organic compounds and back is referred to as the nitrogen cycle.

8 – Safety:

Rapid release of nitrogen gas into an enclosed space can displace oxygen, and therefore represents an asphyxiation hazard. This may happen with few warning symptoms, since the human carotid body is a relatively slow and a poor low - oxygen (hypoxia) sensing system.^[28] An example occurred shortly before the launch of the first Space Shuttle mission in 1981, when two technicians lost consciousness and died after they walked into a space located in the Shuttle's Mobile Launcher Platform that was pressurized with pure nitrogen as a precaution against fire. The technicians would have been able to exit the room if they had experienced early symptoms from nitrogen-breathing.

When inhaled at high partial pressures (more than about 4 bar, encountered at depths below about 30 m in scuba diving) nitrogen begins to act as an anesthetic agent. It can cause nitrogen narcosis, a temporary semi-anesthetized state of mental impairment similar to that caused by nitrous oxide.

Nitrogen also dissolves in the bloodstream and body fats. Rapid decompression (particularly in the case of divers ascending too quickly, or astronauts decompressing too quickly from cabin pressure to spacesuit pressure) can lead to a potentially fatal condition called decompression sickness (formerly known as caisson sickness or more commonly, the "bends"), when nitrogen bubbles form in the bloodstream, nerves, joints, and other sensitive or vital areas.^{[31][32]} Other "inert" gases (those gases other than carbon dioxide and oxygen) cause the same effects from bubbles composed of them, so

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replacement of nitrogen in breathing gases may prevent nitrogen narcosis, but does not prevent decompression sickness.

Direct skin contact with liquid nitrogen will eventually cause severe frostbite (cryogenic burns). This may happen almost instantly on contact, depending on the form of liquid nitrogen. Bulk liquid nitrogen causes less rapid freezing than a spray of nitrogen mist (such as is used to freeze certain skin growths in the practice of dermatology). The extra surface area provided by nitrogen - soaked materials is also important, with soaked clothing or cotton causing far more rapid damage than a spill of direct liquid to skin. Full "contact" between naked skin and large droplets or pools of undisturbed liquid nitrogen may be prevented for a few seconds by a layer of insulating gas from the Leidenfrost effect. However, liquid nitrogen applied to skin in mists, and on fabrics, bypasses this effect.

Liquid nitrogen

1 –Introduction :

Liquid nitrogen is nitrogen in a liquid state at a very low temperature. It is produced industrially by fractional distillation of liquid air. Liquid nitrogen is a colourless clear liquid with density at its boiling point of 0.807 g / mL and a dielectric constant of 1.4.^[1] Liquid nitrogen is often referred to by the abbreviation, **LN₂** and has the UN number 1977.

At atmospheric pressure, liquid nitrogen boils at 77 K (−196 °C; −321 °F) and is a cryogenic fluid which can cause rapid freezing on contact with living tissue, which may lead to frostbite. When appropriately insulated from ambient heat, liquid nitrogen can be stored and transported, for example in vacuum flasks. Here, the very low temperature is held constant at 77 K by slow boiling of the liquid, resulting in the evolution of nitrogen gas. Depending on the size and design, the holding time of vacuum flasks ranges from a few hours to a few weeks.

To liquify nitrogen at room temperature (approximately 300 K (27 °C; 80 °F)) would require a pressure of approximately 700 million atmospheres or 10 billion PSI. These enormous pressures are why liquid nitrogen is always stored at cryogenic temperature.

Liquid nitrogen can easily be converted to the solid by placing it in a vacuum chamber pumped by a rotary vacuum pump.^[2] Liquid nitrogen freezes at 63 K (−210 °C; −346 °F). Despite its reputation, liquid nitrogen's efficiency as a coolant is limited by the fact that it boils immediately on contact with a warmer object, enveloping the object in insulating nitrogen gas. This effect, known as the Leidenfrost effect, applies to any liquid in contact with an object significantly hotter than its boiling point. More rapid cooling may be obtained by plunging an object into a slush of liquid and solid nitrogen than into liquid nitrogen alone.

Nitrogen was first liquefied 15 April 1883 by Polish physicists, Zygmunt Wróblewski and Karol Olszewski.

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Liquid nitrogen is a compact and readily transported source of nitrogen gas without pressurization. Further, its ability to maintain temperatures far below the freezing point of water makes it extremely useful in a wide range of applications, primarily as an open-cycle refrigerant, including:

- used to store cells at low temperature for laboratory work
- in cryogenics
- as a source of very dry nitrogen gas
- the immersion freezing and transportation of food products
- the cryopreservation of blood, reproductive cells (sperm and egg), and other biological samples and materials
- as a coolant for overclocking a central processing unit, a graphics processing unit, or another type of computer hardware
- as a method of freezing water pipes in order to work on them in situations where a valve is not available to block water flow to the work area.
- in cryotherapy for removing unsightly or potentially malignant skin lesions such as warts and actinic keratosis.
- in the process of promession, a way to dispose of the dead.
- cooling a high-temperature superconductor to a temperature sufficient to achieve superconductivity.
- the cryonic preservation of humans and pets in the hope of future reanimation.
- as a coolant for vacuum pump traps and in controlled-evaporation processes in chemistry.
- as a coolant to increase the sensitivity of infrared homing seeker heads of missiles such as the Strela 3.
- as a coolant to temporarily “shrink” mechanical components during machine assembly and allow improved interference fits.
- as a coolant for super computers
- in food preparation, such as for making ultra-smooth ice cream.

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3 - Safety:



Filling a liquid nitrogen Dewar from a storage tank

Since the liquid to gas expansion ratio of this substance is 1:694, a tremendous amount of force can be generated if liquid nitrogen is rapidly vaporized. In an incident in 2006 at Texas A&M University, the pressure-relief devices of a tank of liquid nitrogen were sealed with brass plugs. As a result, the tank failed catastrophically, and exploded. The force of the explosion was sufficient to propel the tank through the ceiling immediately above it.

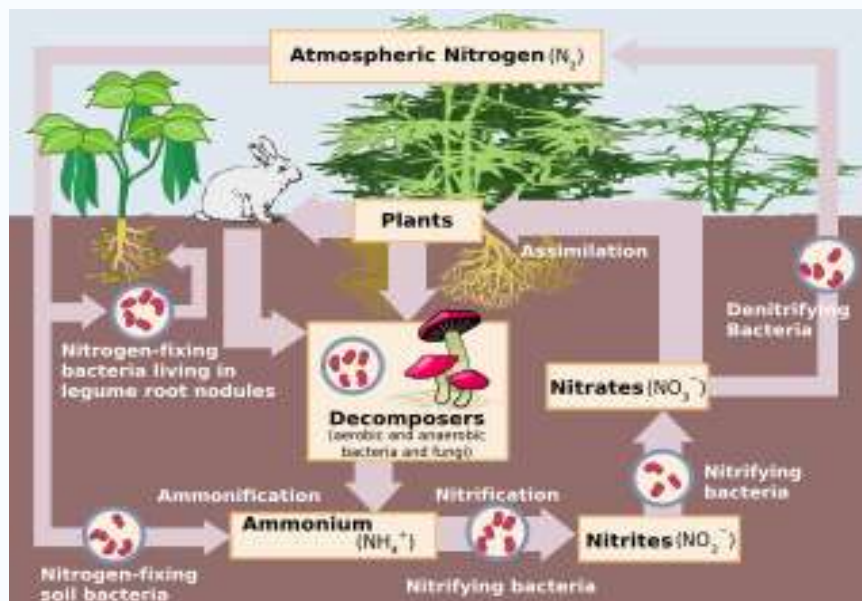
Because of its extremely low temperature, careless handling of liquid nitrogen may result in cold burns.

As liquid nitrogen evaporates it will reduce the oxygen concentration in the air and might act as an asphyxiant, especially in confined spaces. Nitrogen is odourless, colourless and tasteless, and may produce asphyxia without any sensation or prior warning.^[6] A laboratory assistant died in Scotland in 1999, apparently from asphyxiation, after liquid nitrogen spilled in a basement storage room.

Uninsulated vessels containing liquid nitrogen can condense oxygen from air. The liquid in such a vessel becomes increasingly enriched in oxygen (boiling point = 90 K) as the nitrogen evaporates, and can cause violent oxidation of organic material.

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Nitrogen cycle



Schematic representation of the flow of Nitrogen through the environment. The importance of bacteria in the cycle is immediately recognized as being a key element in the cycle, providing different forms of nitrogen compounds assimilable by higher organisms

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 - 5.1 Wastewater treatment
 - 5.1.1 Environmental Damage

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1- Introduction :

The **nitrogen cycle** is the process by which nitrogen in all its forms, cycles through the earth, much in the same way the water cycle occurs. The majority of Earth's atmosphere (approximately 78 – 80 %) is nitrogen, making it the largest pool of nitrogen.

2 - Ecological function

Nitrogen is essential for many processes; it is crucial for any life on Earth. It is in all amino acids, is incorporated into proteins, and is present in the bases that make up nucleic acids, such as DNA and RNA. In plants, much of the nitrogen is used in chlorophyll molecules, which are essential for photosynthesis and further growth.

Although earth's atmosphere is an abundant source of nitrogen, most is relatively unusable by plants^[3]. Chemical processing, or natural fixation (through processes such as bacterial conversion--see rhizobium), are necessary to convert gaseous nitrogen into forms usable by living organisms. This makes nitrogen a crucial part of food production. The abundance or scarcity of this "fixed" form of nitrogen, (also known as reactive nitrogen), dictates how much food can be grown on a piece of land.

2 – 1 - Toxicit:

Increased use of nitrogen fertilizers is causing dramatic environmental changes, including surface and groundwater pollution, ocean dead zones and boosting global warming.

Ammonia is highly toxic to fish and the water discharge level of ammonia from wastewater treatment plants must often be closely monitored. To prevent loss of fish, nitrification prior to discharge is often desirable. Land application can be an attractive alternative to the mechanical [aeration] needed for nitrification.

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During anaerobic (low oxygen) conditions, *denitrification* by bacteria occurs. This results in nitrate solids being converted to nitrogen gases (NO, N₂O, N₂) thus being returned to the atmosphere.

Nitrate can also be reduced to nitrite and subsequently combine with ammonium in the anammox process, which also results in the production of dinitrogen gas.

4 - The Processes of the nitrogen cycle:**4 – 1 - Nitrogen fixation:**

Atmospheric nitrogen must be processed, or "fixed" (see page on nitrogen fixation), in order to be used by plants. Some fixation occurs in lightning strikes, but most fixation is done by free-living or symbiotic bacteria. These bacteria have the nitrogenase enzyme that combines gaseous nitrogen with hydrogen to produce ammonia, which is then further converted by the bacteria to make their own organic compounds. Some nitrogen fixing bacteria, such as *Rhizobium*, live in the root nodules of legumes (such as peas or beans). Here they form a mutualistic relationship with the plant, producing ammonia in exchange for carbohydrates. Nutrient-poor soils can be planted with legumes to enrich them with nitrogen. A few other plants can form such symbioses. Today, a very considerable portion of nitrogen is fixated in ammonia chemical plants.

4 – 1 – 1 - Conversion of N₂:

The conversion of nitrogen (N₂) from the atmosphere into a form readily available to plants and hence to animals and humans is an important step in the nitrogen cycle, which distributes the supply of this essential nutrient. There are four ways to convert N₂ (atmospheric nitrogen gas) into more chemically reactive forms:

1. Biological fixation: some symbiotic bacteria (most often associated with leguminous plants) and some free - living bacteria are able to fix nitrogen as organic nitrogen. An example

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of mutualistic nitrogen fixing bacteria are the *Rhizobium* bacteria, which live in legume root nodules. These species are diazotrophs. An example of the free-living bacteria is *Azotobacter*.

2. Industrial N-fixation : Under great pressure, at a temperature of 600 C, and with the use of a catalyst, atmospheric nitrogen and hydrogen (usually derived from natural gas or petroleum) can be combined to form ammonia (NH₃). In the Haber-Bosch process, N₂ is converted together with hydrogen gas (H₂) into ammonia (NH₃), which is used to make fertilizer and explosives.

3. Combustion of fossil fuels : automobile engines and thermal power plants, which release various nitrogen oxides (NO_x).

4. Other processes : In addition, the formation of NO from N₂ and O₂ due to photons and especially lightning, are important for atmospheric chemistry, but not for terrestrial or aquatic nitrogen turnover.

4 – 2 – Assimilation:

Some plants get nitrogen from the soil, and by absorption of their roots in the form of either nitrate ions or ammonium ions. All nitrogen obtained by animals can be traced back to the eating of plants at some stage of the food chain.

Plants can absorb nitrate or ammonium ions from the soil via their root hairs. If nitrate is absorbed, it is first reduced to nitrite ions and then ammonium ions for incorporation into amino acids, intense nucleic acids, and chlorophyll. In plants that have a mutualistic relationship with rhizobia, some nitrogen is assimilated in the form of ammonium ions directly from the nodules. Animals, fungi, and other heterotrophic organisms absorb nitrogen as amino acids, nucleotides and other small organic molecules.

4 – 3 - Ammonification

When a plant dies, an animal dies, or an animal expels waste, the initial form of nitrogen is organic. Bacteria, or in some cases, fungi,

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convert the organic nitrogen within the remains back into ammonium (NH_4^+), a process called ammonification or mineralization. Enzymes Involved:

- GS: Gln Synthetase (Cytosolic & PLastid)
- GOGAT: Glu 2 - oxoglutarate amino transferase (Ferredoxin & NADH dependent)
- GDH: Glu Dehydrogenase:
 - Minor Role in ammonium assimilation.
 - Important in amino acid catabolism.

4 – 4 – Nitrification:

The conversion of ammonia to nitrates is performed primarily by soil-living bacteria and other nitrifying bacteria. The primary stage of nitrification, the oxidation of ammonia (NH_3) is performed by bacteria such as the *Nitrosomonas* species, which converts ammonia to nitrites (NO_2^-). Other bacterial species, such as the *Nitrobacter*, are responsible for the oxidation of the nitrites into nitrates (NO_3^-).^[2] It is important for the nitrites to be converted to nitrates because accumulated nitrites are toxic to plant life.

Due to their very high solubility, nitrates can enter groundwater. Elevated nitrate in groundwater is a concern for drinking water use because nitrate can interfere with blood - oxygen levels in infants and cause methemoglobinemia or blue - baby syndrome.^[4] Where groundwater recharges stream flow, nitrate - enriched groundwater can contribute to eutrophication, a process leading to high algal, especially blue-green algal populations and the death of aquatic life due to excessive demand for oxygen. While not directly toxic to fish life like ammonia, nitrate can have indirect effects on fish if it contributes to this eutrophication. Nitrogen has contributed to severe eutrophication problems in some water bodies. As of 2006, the application of nitrogen fertilizer is being increasingly controlled in Britain and the United States. This is occurring along the same lines as control of phosphorus fertilizer, restriction of which is normally considered essential to the recovery of eutrophied water bodies.

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Denitrification is the reduction of nitrates back into the largely inert nitrogen gas (N_2), completing the nitrogen cycle. This process is performed by bacterial species such as *Pseudomonas* and *Clostridium* in anaerobic conditions. They use the nitrate as an electron acceptor in the place of oxygen during respiration. These facultatively anaerobic bacteria can also live in aerobic conditions.

4 – 6 - Anaerobic ammonium oxidation:

In this biological process, nitrite and ammonium are converted directly into dinitrogen gas. This process makes up a major proportion of dinitrogen conversion in the oceans.

5 - Human influences on the nitrogen cycle:

As a result of extensive cultivation of legumes (particularly soy, alfalfa, and clover), growing use of the Haber - Bosch process in the creation of chemical fertilizers, and pollution emitted by vehicles and industrial plants, human beings have more than doubled the annual transfer of nitrogen into biologically available forms.^[4] In addition, humans have significantly contributed to the transfer of nitrogen trace gases from Earth to the atmosphere, and from the land to aquatic systems. Human alterations to the global nitrogen cycle are most intense in developed countries and in Asia, where vehicle emissions and industrial agriculture are highest.

N_2O (nitrous oxide) has risen in the atmosphere as a result of agricultural fertilization, biomass burning, cattle and feedlots, and other industrial sources.^[6] N_2O has deleterious effects in the stratosphere, where it breaks down and acts as a catalyst in the destruction of atmospheric ozone. N_2O in the atmosphere is a greenhouse gas, currently the third largest contributor to global warming, after carbon dioxide and methane. While not as abundant in the atmosphere as carbon dioxide, for an equivalent mass, nitrous oxide is nearly 300 times more potent in its ability to warm the planet.

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Ammonia (NH_3) in the atmosphere has tripled as the result of human activities. It is a reactant in the atmosphere, where it acts as an aerosol, decreasing air quality and clinging on to water droplets, eventually resulting in acid rain. Fossil fuel combustion has contributed to a 6 or 7 fold increase in NO_x flux to the atmosphere. NO_2 actively alters atmospheric chemistry, and is a precursor of tropospheric (lower atmosphere) ozone production, which contributes to smog, acid rain, damages plants and increases nitrogen inputs to ecosystems.^[2] Ecosystem processes can increase with nitrogen fertilization, but anthropogenic input can also result in nitrogen saturation, which weakens productivity and can kill plants.^[4] Decreases in biodiversity can also result if higher nitrogen availability increases nitrogen-demanding grasses, causing a degradation of nitrogen-poor, species diverse heathlands.

5 – 1 - Waste water treatment:

Onsite sewage facilities such as septic tanks and holding tanks release large amounts of nitrogen into the environment by discharging through a drainfield into the ground. Microbial activity consumes the nitrogen and other contaminants in the wastewater.

However, in certain areas, the soil is unsuitable to handle some or all of the wastewater, and, as a result, the wastewater with the contaminants enters the aquifers. These contaminants accumulate and eventually end up in drinking water. One of the contaminants concerned about the most is nitrogen in the form of nitrates. A nitrate concentration of 10 ppm or 10 milligrams per liter is the current EPA limit for drinking water and typical household wastewater can produce a range of 20 - 85 ppm.

The health risk associated with drinking water (with >10 ppm nitrate) is the development of methemoglobinemia and has been found to cause blue baby syndrome. Several states have now started programs to introduce advanced wastewater treatment systems to the typical onsite sewage facilities. The result of these systems is an overall reduction of nitrogen, as well as other contaminants in the waste water.

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5 – 1 – 1 - Environmental Damage :

Additional risks posed by increases in fixed nitrogen in aquatic systems include spurring the creation and growth of eutrophic lakes and oceanic dead zones through algal bloom-induced hypoxia.^{[9][10]}

The extent and effects of the anthropogenically-induced doubling of biologically available nitrogen in the soils, waters, and air of the earth during the past century are still poorly understood.

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Nitrogen oxide

Introduction to Nitrogen Oxides :

Nitrogen oxide is typically any binary compound of oxygen and nitrogen, or a mixture of such compounds:

- Nitric oxide (NO) , nitrogen (II) oxide
- Nitrogen dioxide (NO₂) , nitrogen (IV) oxide
- Nitrous oxide (N₂O) , nitrogen (I) oxide
- Dinitrogen trioxide (N₂O₃) , nitrogen (II,IV) oxide
- Dinitrogen tetroxide (N₂O₄) , nitrogen (IV) oxide
- Dinitrogen pentoxide (N₂O₅) , nitrogen (V) oxide

(Note that the last three are unstable.)

Chemical reactions that produce nitrogen oxides often produce several different compounds, the proportions of which depend on the specific reaction and conditions. For this reason, secondary production of N₂O is undesirable, as NO and NO₂ — which are extremely toxic — are liable to be produced as well.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**Nitric oxide (NO_x)****Contents :**

- 1 NO_x
 - 1.1 In atmospheric chemistry
 - 1.2 Natural sources
 - 1.3 Industrial sources
 - 1.3.1 Thermal
 - 1.3.2 Fuel
 - 1.3.3 Prompt
 - 1.4 Health effects
- 2 Regulation and emission control technologies
- 3 Biogenic sources
- 4 Derivatives

1 - NO_x :

NO_x is a generic term for mono - nitrogen oxides (NO and NO₂). These oxides are produced during combustion, especially at high temperatures.

At ambient temperatures, the oxygen and nitrogen gases in air will not react with each other. In an internal combustion engine, combustion of a mixture of air and fuel produces combustion temperatures high enough to drive endothermic reactions between atmospheric nitrogen and oxygen in the flame, yielding various oxides of nitrogen. In areas of high motor vehicle traffic, such as in large cities, the amount of nitrogen oxides emitted into the atmosphere can be quite significant.

In the presence of excess oxygen (O₂), nitric oxide (NO) will be converted to nitrogen dioxide (NO₂), with the time required dependent on the concentration in air as shown below:

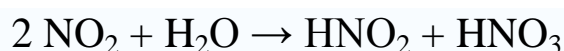
NO concentration in air (ppm)	Time required for half NO to be oxidized to NO ₂ (min)
20,000	0.175
10,000	0.35

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1,000	3.5
100	35
10	350
1	3500

When NO_x and volatile organic compounds (VOCs) react in the presence of sunlight, they form photochemical smog, a significant form of air pollution, especially in the summer. Children, people with lung diseases such as asthma, and people who work or exercise outside are susceptible to adverse effects of smog such as damage to lung tissue and reduction in lung function.

Mono - nitrogen oxides eventually form nitric acid when dissolved in atmospheric moisture, forming a component of acid rain. The following chemical reaction occurs when nitrogen dioxide reacts with water:



Nitrous acid then decomposes as follows:



where nitric oxide will oxidize to form nitrogen dioxide that again reacts with water, ultimately forming nitric acid:



Mono - nitrogen oxides are also involved in tropospheric production of ozone.

NO_x should not be confused with nitrous oxide (N_2O) which has many uses as an oxidizer, an anesthesia, and a food additive.

1 – 1 - In atmospheric chemistry:

In atmospheric chemistry the term NO_x is used to mean the total concentration of NO plus NO_2 . During daylight NO and NO_2 are in equilibrium with the ratio NO/NO_2 determined by the intensity of sunshine (which converts NO_2 to NO) and the concentration of ozone

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(which reacts with NO to give back NO₂). NO and NO₂ are also central to the formation of tropospheric ozone. This definition excludes other oxides of nitrogen such as nitrous oxide (N₂O). NO_y (reactive odd nitrogen) is defined as the sum of NO_x plus the compounds produced from the oxidation of NO_x which include nitric acid.

1 – 2 - Natural sources:

Nitrous oxide is produced during thunderstorms due to the extreme heat of lightning,^[4] and is caused by the splitting of nitrogen molecules. This can result in the production of acid rain, if nitrous oxide forms compounds with the water molecules in precipitation, thus creating acid rain.

1 – 3 - Industrial sources:

The three primary sources of NO_x in combustion processes:

- thermal NO_x
- fuel NO_x
- prompt NO_x

Thermal NO_x formation, which is highly temperature dependent, is recognized as the most relevant source when combusting natural gas. Fuel NO_x tends to dominate during the combustion of fuels, such as coal, which have a significant nitrogen content, particularly when burned in combustors designed to minimise thermal NO_x. The contribution of prompt NO_x is normally considered negligible. A fourth source, called *feed NO_x* is associated with the combustion of nitrogen present in the feed material of cement rotary kilns, at between 300° and 800°C, where it is also a minor contributor.

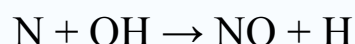
1 – 3 – 1 – Thermal :

Thermal NO_x refers to NO_x formed through high temperature oxidation of the diatomic nitrogen found in combustion air. The formation rate is primarily a function of temperature and the residence time of nitrogen at that temperature. At high temperatures, usually

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above 1600°C , molecular nitrogen (N₂) and oxygen (O₂) in the combustion air disassociate into their atomic states and participate in a series of reactions.

The three principal reactions (the extended Zeldovich mechanism) producing thermal NO_x are:



All 3 reactions are reversible. Zeldovich was the first to suggest the importance of the first two reactions. The last reaction of atomic nitrogen with the hydroxyl radical, OH, was added by Lavoie, Heywood and Keck to the mechanism and makes a significant contribution to the formation of thermal NO_x.

1 – 3 – 2 – Fuel :

The major source of NO_x production from nitrogen-bearing fuels such as certain coals and oil, is the conversion of fuel bound nitrogen to NO_x during combustion. During combustion, the nitrogen bound in the fuel is released as a free radical and ultimately forms free N₂, or NO. Fuel NO_x can contribute as much as 50 % of total emissions when combusting oil and as much as 80 % when combusting coal.

Although the complete mechanism is not fully understood, there are two primary paths of formation. The first involves the oxidation of volatile nitrogen species during the initial stages of combustion. During the release and prior to the oxidation of the volatiles, nitrogen reacts to form several intermediaries which are then oxidized into NO. If the volatiles evolve into a reducing atmosphere, the nitrogen evolved can readily be made to form nitrogen gas, rather than NO_x. The second path involves the combustion of nitrogen contained in the char matrix during the combustion of the char portion of the fuels. This reaction occurs much more slowly than the volatile phase. Only around 20 % of the char nitrogen is ultimately emitted as NO_x, since

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much of the NO_x that forms during this process is reduced to nitrogen by the char, which is nearly pure carbon.

3 – 1 – 3 - Prompt :

This third source is attributed to the reaction of atmospheric nitrogen, N_2 , with radicals such as C, CH, and CH_2 fragments derived from fuel, where this cannot be explained by either the aforementioned thermal or fuel processes. Occurring in the earliest stage of combustion, this results in the formation of fixed species of nitrogen such as NH (nitrogen monohydride), HCN (hydrogen cyanide), H_2CN (dihydrogen cyanide) and CN - (cyano radical) which can oxidize to NO. In fuels that contain nitrogen, the incidence of prompt NO_x is especially minimal and it is generally only of interest for the most exacting emission targets.

1 – 4 - Health effects:

NO_x react with ammonia, moisture, and other compounds to form nitric acid vapor and related particles. Small particles can penetrate deeply into sensitive lung tissue and damage it, causing premature death in extreme cases. Inhalation of such particles may cause or worsen respiratory diseases such as emphysema, bronchitis it may also aggravate existing heart disease.^[5]

NO_x react with volatile organic compounds in the presence of heat and sunlight to form Ozone. Ozone can cause adverse effects such as damage to lung tissue and reduction in lung function mostly in susceptible populations (children, elderly, asthmatics). Ozone can be transported by wind currents and cause health impacts far from the original sources. The American Lung Association estimates that nearly 50 percent of United States inhabitants live in counties that are not in ozone compliance.

NO_x (especially N_2O) destroys ozone layer.^[7] This layer absorbs ultraviolet light, which is potentially damaging to life on earth.

NO_x also readily react with common organic chemicals, and even ozone, to form a wide variety of toxic products: nitroarenes,

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nitrosamines and also the nitrate radical some of which may cause biological mutations. Recently another pathway, via NO_x, to ozone has been found that predominantly occurs in coastal areas but of note is that not only is ozone produced directly from NO_x but the much more insidious Chlorine radical pathway as well.

2 - Regulation and emission control technologies

The Kyoto Protocol, ratified by 54 nations in 1997, classifies N₂O as a greenhouse gas, and calls for substantial worldwide reductions in its emission.

As discussed above, atmospheric NO_x eventually forms nitric acid, which contributes to acid rain. NO_x emissions are regulated in the United States by the Environmental Protection Agency, and in the UK by the Department for Environment, Food and Rural Affairs.

Technologies such as flameless oxidation (FLOX) and staged combustion significantly reduce thermal NO_x in industrial processes. Bowin low NO_x technology is a hybrid of staged – premixed - radiant combustion technology with a major surface combustion preceded by a minor radiant combustion. In the Bowin burner, air and fuel gas are premixed at a ratio greater than or equal to the stoichiometric combustion requirement . Water Injection technology, whereby water is introduced into the combustion chamber, is also becoming an important means of NO_x reduction through increased efficiency in the overall combustion process. Alternatively, the water (e.g. 10 to 50%) is emulsified into the fuel oil prior to the injection and combustion. This emulsification can either be made in-line (unstabilized) just before the injection or as a drop-in fuel with chemical additives for long term emulsion stability (stabilized). Other technologies, such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) reduce post combustion NO_x.

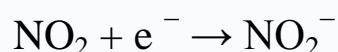
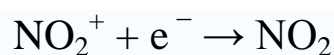
The use of exhaust gas recirculation and catalytic converters in motor vehicle engines have significantly reduced emissions.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**3 - Biogenic sources:**

Agricultural fertilization and the use of nitrogen fixing plants also contribute to atmospheric NO_x , by promoting nitrogen fixation by microorganisms.

4 - Derivatives:

Oxidized (cationic) and reduced (anionic) derivatives of many of these oxides exist: nitrite (NO^{-2}), nitrate (NO^{-3}), nitronium (NO^{+2}), and nitrosonium (NO^{+}). NO_2 is intermediate between nitrite and nitronium:



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Nitrogen dioxide

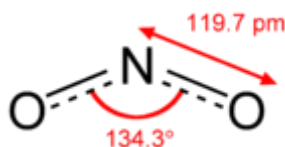
Contents:

- 1 Introduction
- 2 Preparation and reactions
 - 2.1 Monomer-dimer equilibrium
 - 2.2 Main reactions
- 3 Safety and pollution considerations

1 – Introduction :

Nitrogen dioxide is the chemical compound with the formula NO_2 . 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. This reddish-brown toxic gas has a characteristic sharp, biting odor and is a prominent air pollutant. Nitrogen dioxide is a paramagnetic bent molecule with C_{2v} point group symmetry.

Nitrogen dioxide



Properties

Molecular formula	NO_2
Molar mass	46 g / mol
Appearance	brown gas
Density	1449 kg / m ³ (liquid, 20 °C) 3.4 kg / m ³ (gas, 22 °C)
Melting point	-11.2 °C, 262 K, 12 °F
Boiling point	21.1 °C, 294 K, 70 °F

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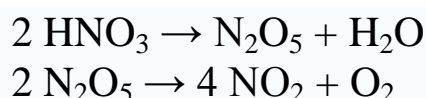
Solubility in water	reacts
Refractive index (n_D)	1.449 (20 °C)
EU classification	Highly toxic (T+) Corrosive (C)
Flash point	Non - flammable

2 - Preparation and reactions:

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



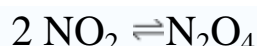
In the laboratory, NO_2 can be prepared in a two step procedure by thermal decomposition of dinitrogen pentoxide, which is obtained by dehydration of nitric acid:



The thermal decomposition of some metal nitrates also affords NO_2 :

**2 – 1 - Monomer - dimer equilibrium:**

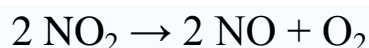
NO_2 exists in equilibrium with N_2O_4 :



The equilibrium is characterized by $\Delta H = -57.23 \text{ kJ/mol}$, which is exothermic. Resulting from an endergonic reaction at higher temperatures, the paramagnetic monomer is favored. Colourless diamagnetic N_2O_4 can be obtained as a solid melting at m.p. $-11.2 \text{ }^\circ\text{C}$

2 – 2 - Main reactions:

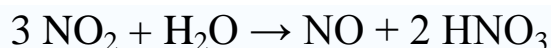
The chemistry of nitrogen dioxide has been investigated extensively. At $150 \text{ }^\circ\text{C}$, NO_2 decomposes with release of oxygen via an endothermic process ($\Delta H = 114 \text{ kJ / mol}$) :



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As suggested by the weakness of the N–O bond, NO₂ is a good oxidizer and will sustain the combustion, sometimes explosively, with many compounds, such as hydrocarbons.

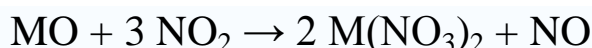
It hydrolyzes with disproportionation to give nitric acid:



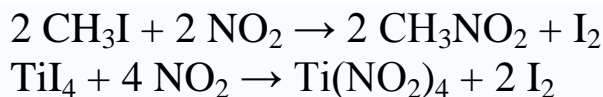
This reaction is one step in the Ostwald process for the industrial production of nitric acid from ammonia.^[2] Nitric acid decomposes slowly to nitrogen dioxide, which confers the characteristic yellow color of most samples of this acid:



NO₂ is used to generate anhydrous metal nitrates from the oxides:



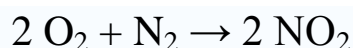
Alkyl and metal iodides give the corresponding nitrites:

**3 - Safety and pollution considerations:**

Nitrogen dioxide is toxic by inhalation, but this could be avoided as the material is acrid and easily detected by our sense of smell. One potential source of exposure is fuming nitric acid, which spontaneously produces NO₂ above 0 °C. Symptoms of poisoning (lung edema) tend to appear several hours after one has inhaled a low but potentially fatal dose. Also, low concentrations (4 ppm) will anesthetize the nose, thus creating a potential for over exposure.

Long - term exposure to NO₂ at concentrations above 40–100 µg / m³ causes adverse health effects.

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

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The most important sources of NO_2 are internal combustion engines,^[4] thermal power stations and, to a lesser extent, pulp mills. Butane gas heaters and stoves are also sources. The excess air required for complete combustion of fuels in these processes introduces nitrogen into the combustion reactions at high temperatures and produces nitrogen oxides (NO_x). Limiting NO_x production demands the precise control of the amount of air used in combustion.

Nitrogen dioxide is also produced by atmospheric nuclear tests, and is responsible for the reddish colour of mushroom clouds.^[5]

Nitrogen dioxide is a large scale pollutant, with rural background ground level concentrations in some areas around $30 \mu\text{g}/\text{m}^3$, not far below unhealthy levels. Nitrogen dioxide plays a role in atmospheric chemistry, including the formation of tropospheric ozone. A 2005 study by researchers at the University of California, San Diego, suggests a link between NO_2 levels and Sudden Infant Death Syndrome.

Nitrous oxide

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- 2 "Laughing gas" (name)
- 3 Manufacture
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 - 4.2 Internal combustion engine
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 - 6.1 Chemical/physical
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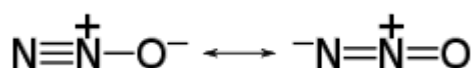
1 – Introduction :

Nitrous oxide, commonly known as **happy gas** or **laughing gas**, is a chemical compound with the chemical formula N_2O . At room temperature, it is a colorless non-flammable gas, with a pleasant, slightly sweet odor and taste. It is used in surgery and dentistry for its anesthetic and analgesic effects. It is known as "laughing gas" due to the euphoric effects of inhaling it, a property that has led to its recreational use as a dissociative drug. It is also used as an oxidizer in rocketry and in motor racing to increase the power output of engines. At elevated temperatures, nitrous oxide is a powerful oxidizer similar to molecular oxygen. For example, nitrous oxide in a test tube will re-ignite a smoldering splint.

Nitrous oxide reacts with ozone and is the main naturally occurring regulator of stratospheric ozone. Nitrous oxide is also a

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major greenhouse gas and air pollutant. Considered over a 100 year period, it has 298 times more impact per unit weight than carbon dioxide.

Nitrous oxide

IUPAC name : Dinitrogen monoxide

other names : Laughing gas

Properties

Molecular formula	N ₂ O
Molar mass	44.013 g/mol
Appearance	colorless gas
Density	1.977 g / L (gas)
Melting point	−90.86 °C (182.29 K)
Boiling point	−88.48 °C (184.67 K)
Solubility in water	0.15 g / 100 ml (15 °C)
Solubility	soluble in alcohol, ether, sulfuric acid
log P	0.35
Vapor pressure	5150 kPa (20 °C)
Refractive index (n _D)	1.330

2 - Laughing gas:

Scientist Humphrey Davy introduced nitrous oxide to the public (primarily the British upper class) as a recreational drug at "laughing gas parties" in 1799, 36 years before it was used medically. The effects of the gas can make the user feel stuporous, dreamy and sedated. While some people, in a state of induced euphoria by the gas, can sometimes "get the giggles" and erupt in laughter and overall amusement. At his parties, the audience was amused by watching the user's "nitrous oxide capers," which included stumbling around, slurred speech and falling down.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**3 - Manufacture:**

Nitrous oxide is most commonly prepared by careful heating of ammonium nitrate, which decomposes into nitrous oxide and water vapor.^[3] The addition of various phosphates favors formation of a purer gas at slightly lower temperatures. One of the earliest commercial producers was George Poe in Trenton, New Jersey.



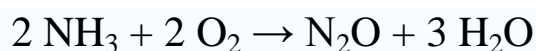
This reaction occurs between 170 - 240°C, temperatures where ammonium nitrate is a moderately sensitive explosive and a very powerful oxidizer. Above 240 °C the exothermic reaction may accelerate to the point of detonation, so the mixture must be cooled to avoid such a disaster. Superheated steam is used to reach reaction temperature in some turnkey production plants.

Down stream, the hot, corrosive mixture of gases must be cooled to condense the steam, and filtered to remove higher oxides of nitrogen. Ammonium nitrate smoke, as an extremely persistent colloid, will also have to be removed. The cleanup is often done in a train of 3 gas washes; namely base, acid and base again. Any significant amounts of nitric oxide (NO) may not necessarily be absorbed directly by the base (sodium hydroxide) washes.

The nitric oxide impurity is sometimes chelated out with ferrous sulfate, reduced with iron metal, or oxidised and absorbed in base as a higher oxide. The first base wash may (or may not) react out much of the ammonium nitrate smoke, however this reaction generates ammonia gas, which may have to be absorbed in the acid wash.

3 – 1 - Other routes:

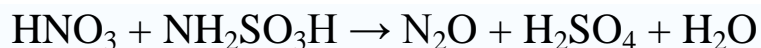
The direct oxidation of ammonia may someday rival the ammonium nitrate pyrolysis synthesis of nitrous oxide mentioned above. This capital-intensive process, which originates in Japan, uses a manganese dioxide-bismuth oxide catalyst:



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Higher oxides of nitrogen are formed as impurities. In comparison, uncatalyzed ammonia oxidation (i.e. combustion or explosion) goes primarily to N₂ and H₂O.

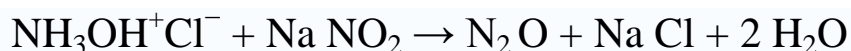
Nitrous oxide can be made by heating a solution of sulfamic acid and nitric acid. Many gases are made this way in Bulgaria.



There is no explosive hazard in this reaction if the mixing rate is controlled. However, as usual, toxic higher oxides of nitrogen form.

Nitrous oxide is produced in large volumes as a by-product in the synthesis of adipic acid; one of the two reactants used in nylon manufacture. This might become a major commercial source, but will require the removal of higher oxides of nitrogen and organic impurities. Currently much of the gas is decomposed before release for environmental protection. Greener processes may prevail that substitute hydrogen peroxide for nitric acid oxidation; hence no generation of oxide of nitrogen by-products.

Hydroxylammonium chloride can react with sodium nitrite to produce N₂O as well:



If the nitrite is added to the hydroxylamine solution, the only remaining byproduct is salt water. However, if the hydroxylamine solution is added to the nitrite solution (nitrite is in excess), then toxic higher oxides of nitrogen are also formed.

4 – Uses:

4 – 1 - Rocket motors:

Nitrous oxide can be used as an oxidizer in a rocket motor. This has the advantages over other oxidizers that it is non-toxic and, due to its stability at room temperature, easy to store and relatively safe to carry on a flight. As a secondary benefit it can be readily decomposed

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to form breathing air. Its high density and low storage pressure enable it to be highly competitive with stored high - pressure gas systems.

In a 1914 patent, American rocket pioneer Robert Goddard suggested nitrous oxide and gasoline as possible propellants for a liquid - fueled rocket . Nitrous oxide has been the oxidizer of choice in several hybrid rocket designs (using solid fuel with a liquid or gaseous oxidizer). The combination of nitrous oxide with hydroxyl-terminated polybutadiene fuel has been used by SpaceShipOne and others. It is also notably used in amateur and high power rocketry with various plastics as the fuel.

Nitrous oxide can also be used in a monopropellant rocket. In the presence of a heated catalyst, N_2O will decompose exothermically into nitrogen and oxygen, at a temperature of approximately 1300 °C. Because of the large release the catalytic action rapidly becomes secondary as thermal autodecomposition becomes dominant. In a vacuum thruster, this can provide a monopropellant specific impulse (I_{sp}) of as much as 180s. While noticeably less than the I_{sp} available from hydrazine thrusters (monopropellant or bipropellant with nitrogen tetroxide), the decreased toxicity makes nitrous oxide an option worth investigating.

Specific impulse (I_{sp}) can be improved by blending a hydrocarbon fuel with the nitrous oxide inside the same storage tank, becoming a Nitrous Oxide Fuel Blend (NOFB) monopropellant. This storage mixture does not incur the danger of spontaneous ignition, since N_2O is chemically stable. When the nitrous oxide decomposes by a heated catalyst, high temperature oxygen is released and rapidly ignites the hydrocarbon fuel - blend. NOFB monopropellants are capable of I_{sp} greater than 300 seconds , while avoiding the toxicity associated with hypergolic propulsion systems. The low freezing point of NOFB eases thermal management compared to hydrazine and dinitrogen tetroxide—a valuable property on a spacecraft which may contain quantities of cryogenic propellant.

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4 – 2 - Internal combustion engine :

In vehicle racing, nitrous oxide (often referred to as just "nitrous" or as NOS after the name of the brand Nitrous Oxide Systems) allows the engine to burn more fuel and air, resulting in a more powerful combustion. The gas itself is not flammable, but it delivers more oxygen than atmospheric air by breaking down at elevated temperatures.

Nitrous oxide is stored as a compressed liquid; the evaporation and expansion of liquid nitrous oxide in the intake manifold causes a large drop in intake charge temperature, resulting in a denser charge, further allowing more air/fuel mixture to enter the cylinder. Nitrous oxide is sometimes injected into (or prior to) the intake manifold, whereas other systems directly inject right before the cylinder (direct port injection) to increase power.

The technique was used during World War II by *Luftwaffe* aircraft with the GM - 1 system to boost the power output of aircraft engines. Originally meant to provide the *Luftwaffe* standard aircraft with superior high-altitude performance, technological considerations limited its use to extremely high altitudes. Accordingly, it was only used by specialized planes like high - altitude reconnaissance aircraft, high-speed bombers, and high - altitude interceptor aircraft.

One of the major problems of using nitrous oxide in a reciprocating engine is that it can produce enough power to damage or destroy the engine. Very large power increases are possible, and if the mechanical structure of the engine is not properly reinforced, the engine may be severely damaged or destroyed during this kind of operation. It is very important with nitrous oxide augmentation of internal combustion engines to maintain proper operating temperatures and fuel levels to prevent "preignition", or "detonation" (sometimes referred to as "knocking" or "pinging"). Most problems that are associated with nitrous do not come from mechanical failure due to the power increases. Since nitrous allows a much denser charge into the cylinder it dramatically increases cylinder pressures. The increased pressure results in heat , and heat will cause many problems

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from melting the piston, valves or warping the head/cracking or predetonation.

4 – 3 - Aerosol propellant:

An 8g canister of nitrous oxide intended for use as a whipped cream aerating agent

The gas is approved for use as a food additive (also known as E942), specifically as an aerosol spray propellant. Its most common uses in this context are in aerosol whipped cream canisters, cooking sprays, and as an inert gas used to displace oxygen, to inhibit bacterial growth, when filling packages of potato chips and other similar snack foods.

The gas is extremely soluble in fatty compounds. In aerosol whipped cream, it is dissolved in the fatty cream until it leaves the can, when it becomes gaseous and thus creates foam. Used in this way, it produces whipped cream four times the volume of the liquid, whereas whipping air into cream only produces twice the volume. If air were used as a propellant, oxygen would accelerate rancidification of the butterfat; nitrous oxide inhibits such degradation. Carbon dioxide cannot be used for whipped cream because it is acidic in water, which would curdle the cream and give it a seltzer-like 'sparkling' sensation.

However, the whipped cream produced with nitrous oxide is unstable and will return to a more or less liquid state within half an

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hour to one hour. Thus, the method is not suitable for decorating food that will not be immediately served.

Similarly, cooking spray, which is made from various types of oils combined with lecithin (an emulsifier), may use nitrous oxide as a propellant; other propellants used in cooking spray include food-grade alcohol and propane.

Users of nitrous oxide often obtain it from whipped cream dispensers that use nitrous oxide as a propellant (see above section), for recreational use as a euphoria-inducing inhalant drug. It is not harmful in small doses, but risks due to lack of oxygen do exist .

4 – 4 - In medicine:

Nitrous oxide has been used for anesthesia in dentistry since the 1840s. The most common use is as a 50:50 mix with oxygen (commonly known as Entonox or Nitronox) delivered through a demand valve; it is frequently used to relieve pain associated with childbirth, trauma, oral surgery, and heart attacks.

Professional use can involve constant-supply flowmeters, which allow the proportion of nitrous oxide and the combined gas flow rate to be individually adjusted. Nitrous oxide is typically administered by dentists through a demand-valve inhaler over the nose that only releases gas when the patient inhales through the nose.

Because nitrous oxide is minimally metabolized, it retains its potency when exhaled into the room by the patient and can pose an intoxicating and prolonged - exposure hazard to the clinic staff if the room is poorly ventilated. Where nitrous oxide is administered, a continuous - flow fresh - air ventilation system or nitrous-scavenging system is used to prevent waste - gas buildup.

Nitrous oxide is a weak general anesthetic, and so is generally not used alone in general anesthesia. In general anesthesia it is used as a carrier gas in a 2:1 ratio with oxygen for more powerful general anesthetic agents such as sevoflurane or desflurane. It has a MAC

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(minimum alveolar concentration) of 105% and a blood:gas partition coefficient of 0.46. Less than 0.004% is metabolised in humans.

4 – 5 - Recreational use:*Whippits*

Nitrous oxide (N_2O) is a dissociative drug that can cause analgesia, depersonalization, derealization, dizziness, euphoria, and some sound distortion. Research has also found that it increases suggestibility and imagination.

Since the earliest uses of nitrous oxide for medical or dental purposes, it has also been used recreationally as an inhalant, because it causes euphoria and slight hallucinations. Only a small number of recreational users (such as dental office workers or medical gas technicians) have legal access to pure nitrous oxide canisters that are intended for medical or dental use. Most recreational users obtain nitrous oxide from compressed gas containers which use nitrous oxide as a propellant for whipped cream or from automotive nitrous systems. Recreational users should be aware that inhaling nitrous oxide from tanks used in automotive systems is unsafe because Sulfur Dioxide, a toxic gas, is mixed in around 100 ppm specifically to discourage substance abuse.

Users typically inflate a balloon or a plastic bag with nitrous oxide from a tank or a one-use 'charger', and then inhale the gas for its

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effects. Highly compressed liquid expelled from a tank or canister is extremely cold, and is thus dangerous to inhale directly. Thus, for medical and recreational use, nitrous oxide is first decompressed into some receptacle, such as a balloon. Mis-cracked canisters can cause skin damage due to freezing temperatures. Users may also inhale nitrous oxide directly from pre - packaged whipped cream canisters, where it is used as propellant .

Recreational users typically do not mix it with air or oxygen and thus may risk injury or death from anoxia if they tie plastic bags around their heads or otherwise obstruct their breathing .

Nitrous oxide can be habit - forming because of its short-lived effect (generally from 0.1 – 1 minutes in recreational doses). Long-term use in excessive quantities has been associated with vitamin B₁₂ deficiency anemia due to reduced hemopoiesis, neuropathy, tinnitus, and numbness in extremities, unless vitamin B₁₂ supplements are taken to counteract this. Pregnant women should not use nitrous oxide as chronic use is teratogenic and foetotoxic. One study in mice found that long term exposure to high doses of nitrous oxide may lead to Olney's lesions that may become persistent.

5 - Neuropharmacology:

Nitrous oxide shares many pharmacological similarities with other inhaled anesthetics, but there are a number of differences. Nitrous oxide is relatively non-polar, has a low molecular weight, and high lipid solubility. As a result, it can quickly diffuse into phospholipid cell membranes

Like many other classical anesthetics, nitrous oxide's exact mechanism of action is still open to some conjecture. It acts as an NMDA receptor antagonist at partial pressures similar to those used in general anaesthesia. The evidence on the effect of N₂O on GABA_A receptor currently is mixed, but tends to show a lower potency potentiation via acting as a positive allosteric modulator of the receptor.^[16] N₂O, like other volatile anesthetics, activates twin-pore potassium channels, albeit weakly. These channels are largely responsible for keeping neurons at the resting (unexcited) potential.^[17]

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Unlike many anesthetics, however, N₂O does not seem to affect calcium channels.

Unlike most general anesthetics, N₂O appears to affect the GABA receptor. In many behavioral tests of anxiety, a low dose of N₂O is a successful anxiolytic. This anti-anxiety effect is partially reversed by benzodiazepine receptor antagonists. Mirroring this, animals which have developed tolerance to the anxiolytic effects of benzodiazepines are partially tolerant to nitrous oxide.^[18] Indeed, in humans given 30 % N₂O, benzodiazepine receptor antagonists reduced the subjective reports of feeling “high”, but did not alter psycho-motor performance.

The effects of N₂O seem linked to the interaction between the endogenous opioid system and the descending noradrenergic system. When animals are given morphine chronically they develop tolerance to its analgesic (pain killing) effects; this also renders the animals tolerant to the analgesic effects of N₂O. Administration of antibodies which bind and block the activity of some endogenous opioids (not beta - endorphin), also block the antinociceptive effects of N₂O. Drugs which inhibit the breakdown of endogenous opioids also potentiate the antinociceptive effects of N₂O. Several experiments have shown that opioid receptor antagonists applied directly to the brain block the antinociceptive effects of N₂O, but these drugs have no effect when injected into the spinal cord.

Conversely, alpha-adrenoreceptor antagonists block the antinociceptive effects of N₂O when given directly to the spinal cord, but not when applied directly to the brain. Indeed, alpha 2B – adrenoceptor knockout mice or animals depleted in noradrenaline are nearly completely resistant to the antinociceptive effects of N₂O. It seems N₂O - induced release of endogenous opioids causes disinhibition of brain stem noradrenergic neurons, which release norepinephrine into the spinal cord and inhibit pain signaling (Maze, M. and M. Fujinaga, 2000). Exactly how N₂O causes the release of opioids is still uncertain .

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**6 – Safety :**

The major safety hazards of nitrous oxide come from the fact that it is a compressed liquefied gas, an asphyxiation risk, and a dissociative anaesthetic. Exposure to nitrous oxide causes short-term decreases in mental performance, audiovisual ability, and manual dexterity.

A study of workers and several experimental animal studies indicate that adverse reproductive effects for pregnant females may also result from chronic exposure to nitrous oxide.

The National Institute for Occupational Safety and Health recommends that workers' exposure to nitrous oxide should be controlled during the administration of anesthetic gas in medical, dental, and veterinary operators.

6 – 1 – Chemical / physical :

At room temperature (20°C) the saturated vapor pressure is 58.5 bar, rising up to 72.45 bar at 36.4°C — the critical temperature. The pressure curve is thus unusually sensitive to temperature.^[31] Liquid nitrous oxide acts as a good solvent for many organic compounds; liquid mixtures may form shock sensitive explosives.^[citation needed]

As with many strong oxidizers, contamination of parts with fuels have been implicated in rocketry accidents, where small quantities of nitrous / fuel mixtures explode due to 'water hammer' like effects (sometimes called 'dieseling' - heating due to adiabatic compression of gases can reach decomposition temperatures). Some common building materials such as stainless steel and aluminium can act as fuels with strong oxidisers such as nitrous oxide, as can contaminants, which can ignite due to adiabatic compression.

6 – 2 – Biological:

Nitrous oxide inactivates the cobalamin form of vitamin B₁₂ by oxidation. Symptoms of vitamin B₁₂ deficiency, including sensory neuropathy, myelopathy, and encephalopathy, can occur within days

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or weeks of exposure to nitrous oxide anesthesia in people with subclinical vitamin B₁₂ deficiency¹ Symptoms are treated with high doses of vitamin B₁₂, but recovery can be slow and incomplete.^[35] People with normal vitamin B₁₂ levels have stores to make the effects of nitrous oxide insignificant, unless exposure is repeated and prolonged (nitrous oxide abuse). Vitamin B₁₂ levels should be checked in people with risk factors for vitamin B₁₂ deficiency prior to using nitrous oxide anesthesia.

Nitrous oxide has also been shown to induce early stages of Olney's lesions in the brains of rats. However none of the lesions found were irreversible.

6 – 3 – Environmental:

Nitrous oxide is a greenhouse gas, accounting for around 6% of the heating effect of greenhouse gases in the atmosphere.^[36] According to 2006 data from the United States Environmental Protection Agency, industrial sources make up only about 20 % of all anthropogenic sources, and include the production of nylon, and the burning of fossil fuel in internal combustion engines. Human activity is thought to account for 30 % ; tropical soils and oceanic release account for 70 %. However, a 2008 study by Nobel Laureate Paul Crutzen suggests that the amount of nitrous oxide release attributable to agricultural nitrate fertilizers has been seriously underestimated, most of which would presumably come under soil and oceanic release in the Environmental Protection Agency data. Atmospheric levels have risen by more than 15% since 1750. Nitrous oxide also causes ozone depletion. A new study suggests that N₂O emission currently is the single most important ozone - depleting substance (ODS) emission and is expected to remain the largest throughout the 21st century.

7 - Legality :

In the United States, possession of nitrous oxide is legal under federal law and is not subject to DEA purview.^[42] It is, however, regulated by the Food and Drug Administration under the Food Drug and Cosmetics Act; prosecution is possible under its "misbranding"

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clauses, prohibiting the sale or distribution of nitrous oxide for the purpose of human consumption.

Many states have laws regulating the possession, sale, and distribution of nitrous oxide. Such laws usually ban distribution to minors or limit the amount of nitrous oxide that may be sold without special license. In some countries, it is illegal to have nitrous oxide systems plumbed into an engine's intake manifold. These laws are ostensibly used to prevent street racing and to meet emission standards.

Nitrous oxide is entirely legal to possess and inhale in the United Kingdom, although supplying it to others to inhale, especially minors, is more likely to end up with a prosecution under the Medicines Act.

In New Zealand, the Ministry of Health has warned that nitrous oxide is a prescription medicine, and its sale or possession without a prescription is an offense under the Medicines Act.^[43] This statement would seemingly prohibit all non-medicinal uses of the chemical, though it is implied that only recreational use will be legally targeted.

In India, for general anaesthesia purposes, nitrous oxide is available as Nitrous Oxide IP. India's gas cylinder rules (1985) permit the transfer of gas from one cylinder to another for breathing purposes. This law benefits remote hospitals, which would otherwise suffer as a result of India's geographic immensity. Nitrous Oxide IP is transferred from bulk cylinders (17,000 liters capacity gas) to smaller pin-indexed valve cylinders (1,800 liters of gas), which are then connected to the yoke assembly of Boyle's machines. Because India's Food & Drug Authority (FDA - India) rules state that transferring a drug from one container to another (refilling) is equivalent to manufacturing, anyone found doing so must possess a drug manufacturing license.

8 – History:

The gas was first synthesized by English chemist and natural philosopher Joseph Priestley in 1775, who called it *phlogisticated nitrous air*. Priestley describes the preparation of "nitrous air

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diminished" by heating iron filings dampened with nitric acid in *Experiments and Observations on Different Kinds of Air* (1775).

Humphry Davy in the 1790s tested the gas on himself and some of his friends, including the poet Samuel Taylor Coleridge. They realized that nitrous oxide considerably dulled the sensation of pain, even if the inhaler were still semi - conscious. After it was publicized extensively by Gardner Quincy Colton in the United States in the 1840s, it came into use as an anaesthetic, particularly by such dentists as Horace Wells, who was one of the first dentists to use it on his patients. This was because dentists did not typically have access to the services of anesthesiologists and might benefit from patients who could respond to verbal commands.

Nitric oxide

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 - 1.1 Preparation
 - 1.2 Coordination chemistry
 - 1.3 Measurement of nitric oxide concentration
- 2 Production environmental effects
- 3 Technical applications
 - 3.1 Miscellaneous applications
- 4 Biological functions
 - 4.1 Mechanism of action
 - 4.2 Use in pediatric intensive care
 - 4.3 Pharmacology

1 – Introduction :

Nitric oxide (common name) or **nitrogen monoxide** (systematic name) is a chemical compound with chemical formula NO. This gas is an important signaling molecule in the body of mammals, including humans, and is an extremely important intermediate in the chemical industry. It is also an air pollutant produced by cigarette smoke, automobile engines and power plants.

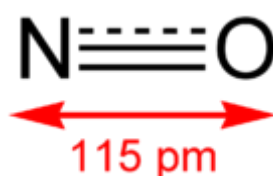
NO is an important messenger molecule involved in many physiological and pathological processes within the mammalian body both beneficial and detrimental. Appropriate levels of NO production are important in protecting an organ such as the liver from ischemic damage. However sustained levels of NO production result in direct tissue toxicity and contribute to the vascular collapse associated with septic shock, whereas chronic expression of NO is associated with various carcinomas and inflammatory conditions including juvenile diabetes, multiple sclerosis, arthritis and ulcerative colitis.

Nitric oxide should not be confused with nitrous oxide (N₂O), an anesthetic and greenhouse gas, or with nitrogen dioxide (NO₂), a brown toxic gas and one of major air pollutants. The nitric oxide

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molecule is a free radical, which is relevant to understanding its high reactivity.

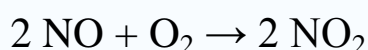
Despite being a simple molecule, NO is a fundamental player in the fields of neuroscience, physiology, and immunology, and was proclaimed “Molecule of the Year” in 1992.



Properties	
Molecular formula	NO
Molar mass	30 g / mol
Appearance	Colour less gas paramagnetic
Density	1.269 g / cm ³ (liquid) 1.3402 g / l (gas)
Melting point	−163.6 °C, 110 K, -262 °F
Boiling point	−150.8 °C, 122 K, -239 °F
Solubility in water	7.4 ml/100 ml (STP)
Solubility	soluble in alcohol, CS ₂
Refractive index (<i>n_D</i>)	1.0002697
Structure	
Molecular shape	linear, <i>C</i> _{∞v}
Pharmacology	
Bioavailability	good
Routes of administration	Inhalation
Elimination half - life	2 – 6 seconds

2 - Reactions:

- When exposed to oxygen, NO is converted into nitrogen dioxide.

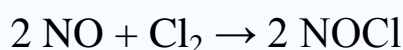


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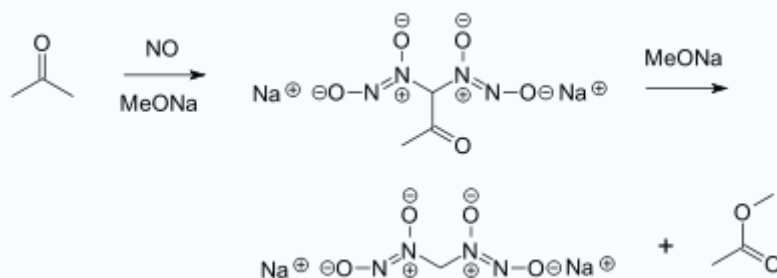
This conversion has been speculated as occurring via the ONOONO intermediate. In water, NO reacts with oxygen and water to form HNO₂ or nitrous acid. The reaction is thought to proceed via the following stoichiometry:



- NO will react with fluorine, chlorine, and bromine to form the XNO species, known as the nitrosyl halides, such as nitrosyl chloride. Nitrosyl iodide can form but is an extremely short lived species and tends to reform I₂.



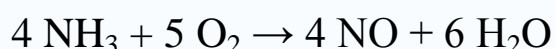
- Nitroxyl (HNO) is the reduced form of nitric oxide.
- Nitric oxide reacts with acetone and an alkoxide to a *diazoniumdiolate* or *nitrosohydroxylamine* and methyl acetate:



This is a very old reaction (1898) but of interest today in NO prodrug research. Nitric oxide can also react directly with sodium methoxide, forming sodium formate and nitrous oxide.

2 – 1 – Preparation:

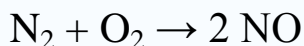
- Commercially, NO is produced by the oxidation of ammonia at 750°C to 900°C (normally at 850°C) in the presence of platinum as catalyst:



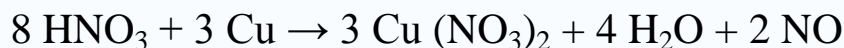
The uncatalyzed endothermic reaction of O₂ and N₂, which is performed at high temperature (>2000°C) by lightning has not

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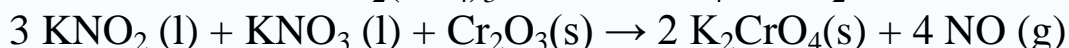
been developed into a practical commercial synthesis (see Birkeland – Eyde process):



- In the laboratory, it is conveniently generated by reduction of nitric acid with copper:



- or by the reduction of nitrous acid in the form of sodium nitrite or potassium nitrite:



The iron (II) sulfate route is simple and has been used in undergraduate laboratory experiments.

- So - called NO NO ate compounds are also used for NO generation.

2 – 2 - Coordination chemistry:

NO forms complexes with all transition metals to give complexes called metal nitrosyls. The most common bonding mode of NO is the terminal linear type (M – NO). The angle of the M - N - O group can vary from 160° to 180° but are still termed as "linear". In this case, the NO group is considered a 3-electron donor under the covalent (neutral) method of electron counting, or a 2-electron donor under the ionic method.^[6] In the case of a bent M - N - O conformation, the NO group can be considered a one-electron donor using neutral counting, or a 2-electron donor using ionic counting.^[7] One can view such complexes as derived from NO⁺, which is isoelectronic with CO.

Nitric oxide can serve as a one-electron pseudohalide. In such complexes, the M - N - O group is characterized by an angle between 120° and 140°.

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The NO group can also bridge between metal centers through the nitrogen atom in a variety of geometries.

2 - 3 - Measurement of nitric oxide concentration:

Nitric oxide (white) in conifer cells, visualized using DAF-2 DA (diamino fluorescein diacetate)

The concentration of nitric oxide can be determined using a simple chemiluminescent reaction involving ozone.^[8] A sample containing nitric oxide is mixed with a large quantity of ozone. The nitric oxide reacts with the ozone to produce oxygen and nitrogen dioxide. This reaction also produces light (chemiluminescence), which can be measured with a photodetector. The amount of light produced is proportional to the amount of nitric oxide in the sample.



Other methods of testing include electroanalysis (amperometric approach), where NO reacts with an electrode to induce a current or voltage change. The detection of NO radicals in biological tissues is particularly difficult due to the short lifetime and concentration of these radicals in tissues. One of the few practical methods is spin trapping of nitric oxide with iron-dithiocarbamate complexes and subsequent detection of the mono-nitrosyl-iron complex with Electron Paramagnetic Resonance (EPR).

A group of fluorescent dye indicators that are also available in acetylated form for intracellular measurements exist. The most common compound is 4 , 5 – di amino fluorescein (DAF - 2) .

3 - Production environmental effects:

From a thermodynamic perspective, NO is unstable with respect to O₂ and N₂, although this conversion is very slow at ambient temperatures in the absence of a catalyst. Because the heat of formation of NO is endothermic, its synthesis from molecular nitrogen and oxygen requires elevated temperatures, >1000°C. A major natural source is lightning. The use of internal combustion engines has

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drastically increased the presence of nitric oxide in the environment. One purpose of catalytic converters in cars is to minimize NO emission by catalytic reversion to O₂ and N₂.

Nitric oxide in the air may convert to nitric acid, which has been implicated in acid rain. Furthermore, both NO and NO₂ participate in ozone layer depletion. Nitric oxide is a small highly diffusible gas and a ubiquitous bioactive molecule.

4 - Technical applications:

Although NO has relatively few direct uses, it is produced on a massive scale as an intermediate in the Ostwald process for the synthesis of nitric acid from ammonia. In 2005, the US alone produced 6M metric tons of nitric acid. It finds use in the semiconductor industry for various processes. In one of its applications it is used along with nitrous oxide to form oxynitride gates in CMOS devices.

4 – 1 - Miscellaneous applications

Nitric oxide can be used for detecting surface radicals on polymers. Quenching of surface radicals with nitric oxide results in incorporation of nitrogen, which can be quantified by means of X-ray photo electron spectroscopy.

5 - Biological functions of nitric oxide:

NO is one of the few gaseous signaling molecules known. It is a key vertebrate biological messenger, playing a role in a variety of biological processes. Nitric oxide, known as the 'endothelium-derived relaxing factor', or 'EDRF', is biosynthesized endogenously from arginine and oxygen by various nitric oxide synthase (NOS) enzymes and by reduction of inorganic nitrate. The endothelium (inner lining) of blood vessels uses nitric oxide to signal the surrounding smooth muscle to relax, thus resulting in vasodilation and increasing blood flow. Nitric oxide is highly reactive (having a lifetime of a few seconds), yet diffuses freely across membranes. These attributes make nitric oxide ideal for a transient paracrine (between adjacent cells) and

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autocrine (within a single cell) signaling molecule.^[12] The production of nitric oxide is elevated in populations living at high-altitudes, which helps these people avoid hypoxia by aiding in pulmonary vasculature vasodilation. Effects include vasodilatation, neuro - transmission , modulation of the hair cycle, production of reactive nitrogen intermediates and penile erections (through its ability to vasodilate). Nitroglycerin and amyl nitrite serve as vasodilators because they are converted to nitric oxide in the body. Sildenafil citrate, popularly known by the trade name *Viagra*, stimulates erections primarily by enhancing signaling through the nitric oxide pathway in the penis.

Nitric oxide (NO) contributes to vessel homeostasis by inhibiting vascular smooth muscle contraction and growth, platelet aggregation, and leukocyte adhesion to the endothelium. Humans with atherosclerosis, diabetes, or hypertension often show impaired NO pathways. A high - salt intake was demonstrated to attenuate NO production, although bioavailability remains unregulated.

Nitric oxide is also generated by phagocytes (monocytes, macrophages, and neutrophils) as part of the human immune response. Phagocytes are armed with inducible nitric oxide synthase (iNOS), which is activated by interferon - gamma (IFN - γ) as a single signal or by tumor necrosis factor (TNF) along with a second signal. On the converse, transforming growth factor-beta (TGF- β) provides a strong inhibitory signal to iNOS, whereas interleukin-4 (IL-4) and IL-10 provide weak inhibitory signals. In this way the immune system may regulate the armamentarium of phagocytes that play a role in inflammation and immune responses. Nitric oxide secreted as an immune response is as free radicals and is toxic to bacteria; the mechanism for this includes DNA damage^{[16][17][18]} and degradation of iron sulfur centers into iron ions and iron-nitrosyl compounds.^[19] In response , however, many bacterial pathogens have evolved mechanisms for nitric oxide resistance. Because nitric oxide might serve as an *inflammometer* in conditions like asthma, there has been increasing interest in the use of exhaled nitric oxide as a breath test in diseases with airway inflammation.

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Nitric oxide can contribute to reperfusion injury when an excessive amount produced during reperfusion (following a period of ischemia) reacts with superoxide to produce the damaging oxidant peroxynitrite. In contrast, inhaled nitric oxide has been shown to help survival and recovery from paraquat poisoning, which produces lung tissue-damaging superoxide and hinders NOS metabolism.

In plants, nitric oxide can be produced by any of four routes :

(i) L – arginine - dependent nitric oxide synthase, (although the existence of animal NOS homologs in plants is debated).

(ii) by plasma membrane - bound nitrate reductase .

(iii) by mitochondrial electron transport chain .

or (iv) by non - enzymatic reactions. It is a signaling molecule, acts mainly against oxidative stress and also plays a role in plant pathogen interactions. Treating cut flowers and other plants with nitric oxide has been shown to lengthen the time before wilting.

An important biological reaction of nitric oxide is S-nitrosylation, the conversion of thiol groups, including cysteine residues in proteins, to form S - nitrosothiols (RSNOs). S - Nitrosylation is a mechanism for dynamic, post - translational regulation of most or all major classes of protein.

5 – 1 - Mechanism of action:

There are several mechanisms by which NO has been demonstrated to affect the biology of living cells. These include oxidation of iron - containing proteins such as ribonucleotide reductase and aconitase, activation of the soluble guanylate cyclase, ADP ribosylation of proteins, protein sulfhydryl group nitrosylation, and iron regulatory factor activation. NO has been demonstrated to activate NF - κ B in peripheral blood mononuclear cells, an important transcription factor in iNOS gene expression in response to inflammation. It was found that NO acts through the stimulation of the soluble guanylate cyclase, which is a heterodimeric enzyme with subsequent formation of cyclic GMP. Cyclic GMP activates protein kinase G, which caused phosphorylation of myosin light chain phosphatase (and therefore inactivation) of myosin light-chain kinase

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and leads ultimately to the dephosphorylation of the myosin light chain, causing smooth muscle relaxation.

5 – 2 - Use in pediatric intensive care:

Nitric oxide / oxygen blends are used in critical care to promote capillary and pulmonary dilation to treat primary pulmonary hypertension in neonatal patients post meconium aspiration and related to birth defects. These are often a last-resort gas mixture before the use of extracorporeal membrane oxygenation (ECMO). Nitric oxide therapy has the potential to significantly increase the quality of life and, in some cases, save the lives of infants at risk for pulmonary vascular disease.

5 – 3 - Pharmacology:

Nitric oxide is considered an anti-anginal drug: it causes vasodilation, which can help with ischemic pain known as angina by decreasing the cardiac workload. By dilating the veins there is less blood returned to the heart per cycle. This decreases the amount of volume that the heart has to pump. Nitroglycerin pills, taken sublingually (under the tongue), are used to prevent or treat acute chest pain (ACS). The nitroglycerin reacts with a sulfhydryl group (–SH) to produce nitric oxide, which eases the pain by causing vasodilation. Contrary to popular belief, nitrates do not increase the diameter of the coronary arteries and increase flow to the myocardium, rather they decrease the heart muscle's oxygen consumption by decreasing the workload.

Dinitrogen Pentoxide

Contents :

- 1 Introduction
- 2 Syntheses and properties
- 3 Structure
- 4 Reactions and applications
- 5 $\text{NO}_2 \text{BF}_4$
- 6 Hazards

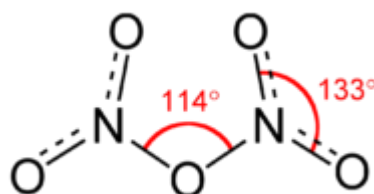
1 – Introduction :

Dinitrogen pentoxide is the chemical compound with the formula N_2O_5 . Also known as nitrogen pentoxide, N_2O_5 is one of the binary nitrogen oxides, a family of compounds that only contain nitrogen and oxygen. It is an unstable and potentially dangerous oxidizer that once was used as a reagent when dissolved in chloroform for nitrations but has largely been superseded by NO_2BF_4 (nitronium tetrafluoroborate).

N_2O_5 is a rare example of a compound that adopts two structures depending on the conditions: most commonly it is a salt, but under some conditions it is a nonpolar molecule:



Dinitrogen pentoxide



IUPAC Name: Dinitrogen penta oxide

other Names : Nitric anhydride

: dnpo

Properties

Molecular Formula N_2O_5

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Molar mass	108.01 g /mol
Appearance	white solid
Density	1.642 g/cm ³ (18 °C)
Melting point	30
Boiling point	47 °C subl.
Solubility in water	reacts to give HNO ₃
Solubility	soluble in chloroform

Structure

Molecular shape	planar, C _{2v} (approx. D _{2h}) N–O–N ≈ 180°
-----------------	--

Thermochemistry

Std enthalpy of formation $\Delta_f H^\ominus_{298}$	–43.1 kJ/mol (s) +11.3 kJ/mol (g)
Standard molar entropy S^\ominus_{298}	178.2 J K ^{–1} mol ^{–1} (s) 355.6 J K ^{–1} mol ^{–1} (g)

Hazards

EU Index	Not listed
Main hazards	strong oxidizer, forms strong acid in contact with water
Flash point	Non - flammable

2 - Syntheses and properties:

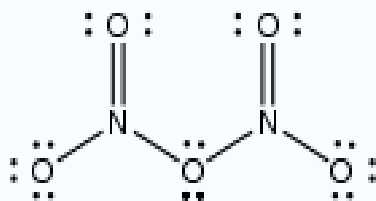
N₂O₅ was first reported by Deville in 1840, who prepared it by treating AgNO₃ with Cl₂.^[1] A recommended laboratory synthesis entails dehydrating nitric acid (HNO₃) with phosphorus(V) oxide:^[2]



In the reverse process, N₂O₅ reacts with water (hydrolyses) to produce nitric acid. Thus, nitrogen pentoxide is the anhydride of nitric acid:



N₂O₅ exists as colourless crystals that sublime slightly above room temperature. The salt eventually decomposes at room temperature into NO₂ and O₂.

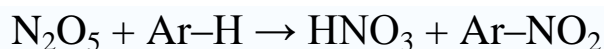
ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**3 - Structure:***Lewis structure of gas - phase N₂O₅*

Solid N₂O₅ is a salt, consisting of separated anions and cations. The cation is the linear nitronium ion NO₂⁺ and the anion is the planar NO₃[−] ion. Thus, the solid could be called *nitronium nitrate*. Both nitrogen centers have oxidation state +5.

The intact molecule O₂N – O – NO₂ exists in the gas phase (obtained by subliming N₂O₅) and when the solid is extracted into nonpolar solvents such as CCl₄. In the gas phase, the O–N–O angle is 133° and the N– O – N angle is 114°. When gaseous N₂O₅ is cooled rapidly ("quenched"), one can obtain the metastable molecular form, which exothermically converts to the ionic form above −70 °C.^[2]

4 - Reactions and applications:

Dinitrogen pentoxide, for example as a solution in chloroform, has been used as a reagent to introduce the NO₂ functionality. This nitration reaction is represented as follows:



where Ar represents an arene moiety.

N₂O₅ is of interest for the preparation of explosives.

5 - NO₂ BF₄:

Replacement of the NO₃[−] portion of N₂O₅ with BF₄[−] gives NO₂BF₄ (CAS#13826-86-3). This salt retains the high reactivity of NO₂⁺, but it is thermally stable, decomposing at ca. 180°C (into NO₂F and BF₃). NO₂BF₄ has been used to nitrate a variety of organic compounds, especially arenes and heterocycles. Interestingly, the

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reactivity of the NO_2^+ can be further enhanced with strong acids that generate the "super-electrophile" HNO_2^{2+} .

6 - Hazards:

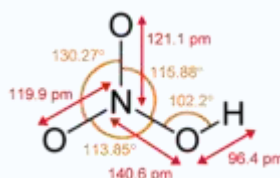
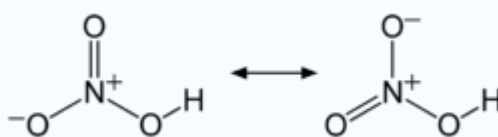
N_2O_5 is a strong oxidizer that forms explosive mixtures with organic compounds and ammonium salts. The decomposition of dinitrogen pentoxide produces the highly toxic nitrogen dioxide gas.

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Nitric acid

Contents

- 1 Introduction :
- 2 Properties
 - 2.1 Acidic properties
 - 2.2 Oxidizing properties
 - 2.2.1 Reactions with metals
 - 2.2.2 Passivation
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 - 2.3 Xanthoproteic test
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- 5 Laboratory synthesis
- 6 Uses
 - 6.1 Elemental Analysis
 - 6.2 Woodworking
 - 6.3 Other uses
- 7 Safety



ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**1 – Introduction :**

Nitric acid (HNO_3), also known as *aqua fortis* and **spirit of nitre**, is a highly corrosive and toxic strong acid.

Colorless when pure, older samples tend to acquire a yellow cast due to the accumulation of oxides of nitrogen. If the solution contains more than 86% nitric acid, it is referred to as **fuming nitric acid**. Fuming nitric acid is characterized as white fuming nitric acid and red fuming nitric acid, depending on the amount of nitrogen dioxide present. At concentrations above 95% at room temperature, it tends to rapidly develop a yellow color due to slow decomposition.

IUPAC Name : Nitric acid

Other Names : Aqua fortis

Spirit of nitre

Salpetre acid

Hydrogen Nitrate

Azotic acid

Properties	
Molecular formula	HNO_3
Molar mass	63 g / mol
Appearance	Clear, colorless liquid
Density	1.5129 g / cm ³
Melting point	- 42 °C, 231 K, - 44 °F
Boiling point	83 °C, 356 K, 181 °F (bp of pure acid. 68 % solution boils at 120.5 °C)
Solubility in water	completely miscible
Acidity ($\text{p}K_a$)	-1.4
Refractive index (n_D)	1.397 (16.5 °C)
Dipole moment	$2.17 \pm 0.02 \text{ D}$

Hazards	
EU classification	Oxidant (O) Corrosive (C)
Flash point	Non - flammable

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**2 - Properties:**

Pure anhydrous nitric acid (100 %) is a colorless mobile liquid with a density of 1.522 g / cm^3 which solidifies at $-42 \text{ }^\circ\text{C}$ to form white crystals and boils at $83 \text{ }^\circ\text{C}$. When boiling in light, even at room temperature, there is a partial decomposition with the formation of nitrogen dioxide following the reaction:



which means that anhydrous nitric acid should be stored below $0 \text{ }^\circ\text{C}$ to avoid decomposition. The nitrogen dioxide (NO_2) remains dissolved in the nitric acid coloring it yellow, or red at higher temperatures. While the pure acid tends to give off white fumes when exposed to air, acid with dissolved nitrogen dioxide gives off reddish-brown vapors, leading to the common name "red fuming acid" or "fuming nitric acid". Fuming nitric acid is also referred to as 16 molar nitric acid. It is the most concentrated form of nitric acid at Standard Temperature and Pressure (STP).

Nitric acid is miscible with water and distillation gives a maximum-boiling azeotrope with a concentration of 68% HNO_3 and a boiling temperature of $120.5 \text{ }^\circ\text{C}$ at 1 atm, which is the ordinary concentrated nitric acid of commerce. Two solid hydrates are known; the monohydrate ($\text{HNO}_3 \cdot \text{H}_2\text{O}$) and the trihydrate ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$).

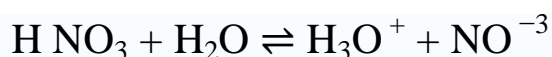
Nitrogen oxides (NO_x) are soluble in nitric acid and this property influences more or less all the physical characteristics depending on the concentration of the oxides. These mainly include the vapor pressure above the liquid and the boiling temperature, as well as the color mentioned above.

Nitric acid is subject to thermal or light decomposition with increasing concentration and this may give rise to some non-negligible variations in the vapor pressure above the liquid because the nitrogen oxides produced dissolve partly or completely in the acid.

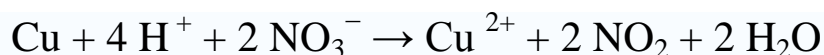
ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**2 - 1 - Acidic properties**

Being a typical strong acid, nitric acid reacts with alkalis, basic oxides, and carbonates to form salts, such as ammonium nitrate. Due to its oxidizing nature, nitric acid generally does not donate its proton (that is, it does not liberate hydrogen) on reaction with metals and the resulting salts are usually in the higher oxidized states. For this reason, heavy corrosion can be expected and should be guarded against by the appropriate use of corrosion resistant metals or alloys.

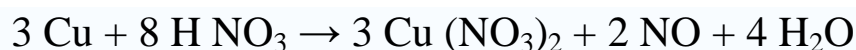
Nitric acid has an acid dissociation constant (pK_a) of -1.4 . In aqueous solution, it almost completely (93 % at 0.1 mol / L) ionizes into the nitrate ion NO_3^- and a hydrated proton, known as a hydronium ion, H_3O^+ .

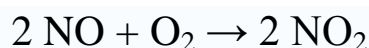
**2 – 2 - Oxidizing properties:****2 – 2 – 1 - Reactions with metals:**

Being a powerful oxidizing agent, nitric acid reacts violently with many organic materials and the reactions may be explosive. Depending on the acid concentration, temperature and the reducing agent involved, the end products can be variable. Reaction takes place with all metals except a few of the precious metal series and certain alloys. This characteristic has made it a common agent to be used in acid tests. As a general rule, oxidizing reactions occur primarily with the concentrated acid, favoring the formation of nitrogen dioxide (NO_2).

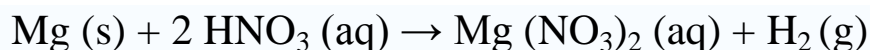


The acidic properties tend to dominate with dilute acid, coupled with the preferential formation of nitric oxide (NO). However, when the reaction is carried out in the presence of atmospheric oxygen, the nitric oxide rapidly reacts to form brown nitrogen dioxide (NO_2):



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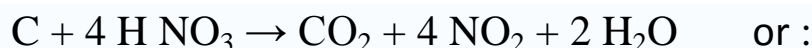
Since nitric acid is an oxidizing agent, hydrogen (H_2) is rarely formed. Only magnesium (Mg), manganese (Mn) and calcium (Ca) react with *cold, dilute* nitric acid to give hydrogen:

**2 – 2 – 2 - Passivation:**

Although chromium (Cr), iron (Fe) and aluminium (Al) readily dissolve in dilute nitric acid, the concentrated acid forms a metal oxide layer that protects the metal from further oxidation, which is called passivation. Typical passivation concentrations range from 18 % to 22 % by weight.

2 – 2 – 3 - Reactions with non – metals:

Reaction with non - metallic elements, with the exceptions of nitrogen, oxygen, noble gases, silicon and halogens, usually oxidizes them to their highest oxidation states as acids with the formation of nitrogen dioxide for concentrated acid and nitric oxide for dilute acid.

**2 – 3 - Xanthoproteic test:**

Nitric acid reacts with proteins to form yellow nitrated products. This reaction is known as the xanthoproteic reaction. This test is carried out by adding concentrated nitric acid to the substance being tested, and then heating the mixture. If proteins are present that contains amino acids with aromatic rings, the mixture turns yellow. Upon adding a strong base such as liquid ammonia, the color turns orange. These color changes are caused by nitrated aromatic rings in the protein. Xanthoproteins are formed when the acid contacts epithelial cells and are indicative of inadequate safety precautions when handling nitric acid.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**3 - Grades:**

The concentrated nitric acid of commerce consists of the maximum boiling azeotrope of nitric acid and water. Technical grades are normally 68 % HNO_3 , (approx 15 molar), while reagent grades are specified at 70 % HNO_3 . The density of concentrated nitric acid is 1.42 g / mL. An older density scale is occasionally seen, with concentrated nitric acid specified as 42° Baumé.

White fuming nitric acid, also called 100 % nitric acid or WFNA, is very close to anhydrous nitric acid. One specification for white fuming nitric acid is that it has a maximum of 2% water and a maximum of 0.5% dissolved NO_2 . Anhydrous nitric acid has a density of 1.513 g / mL and has the approximate concentration of 24 molar.

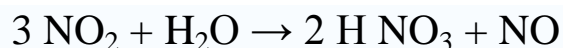
A commercial grade of fuming nitric acid, referred to in the trade as "strong nitric acid" contains 90 % HNO_3 and has a density of 1.50 g/mL. This grade is much used in the explosives industry. It is not as volatile nor as corrosive as the anhydrous acid and has the approximate concentration of 21.4 molar.

Red fuming nitric acid, or RFNA, contains substantial quantities of dissolved nitrogen dioxide (NO_2) leaving the solution with a reddish-brown color. One formulation of RFNA specifies a minimum of 17 % NO_2 , another specifies 13 % NO_2 . Because of the dissolved nitrogen dioxide, the density of red fuming nitric acid is lower at 1.490 g / mL.

An *inhibited* fuming nitric acid (either IWFNA, or IRFNA) can be made by the addition of 0.6 to 0.7% hydrogen fluoride (HF). This fluoride is added for corrosion resistance in metal tanks. The fluoride creates a metal fluoride layer that protects the metal.

4 - Industrial production:

Nitric acid is made by reacting nitrogen dioxide (NO_2) with water.



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Normally, the nitric oxide produced by the reaction is reoxidized by the oxygen in air to produce additional nitrogen dioxide.

Dilute nitric acid may be concentrated by distillation up to 68% acid, which is a maximum boiling azeotrope containing 32 % water. In the laboratory, further concentration involves distillation with either sulfuric acid or magnesium nitrate which act as dehydrating agents. Such distillations must be done with all - glass apparatus at reduced pressure, to prevent decomposition of the acid. Industrially, strong nitric acid is produced by dissolving additional nitrogen dioxide in 68% nitric acid in an absorption tower. Dissolved nitrogen oxides are either stripped in the case of white fuming nitric acid, or remain in solution to form red fuming nitric acid. More recently, electrochemical means have been developed to produce anhydrous acid from concentrated nitric acid feed stock .

Commercial grade nitric acid solutions are usually between 52% and 68% nitric acid. Production of nitric acid is via the Ostwald process, named after German chemist Wilhelm Ostwald. In this process, anhydrous ammonia is oxidized to nitric oxide, which is then reacted with oxygen in air to form nitrogen dioxide. This is subsequently absorbed in water to form nitric acid and nitric oxide. The nitric oxide is cycled back for reoxidation. By using ammonia derived from the Haber process, the final product can be produced from nitrogen, hydrogen, and oxygen which are derived from air and natural gas as the sole feed stocks.

Prior to the introduction of the Haber process for the production of ammonia in 1923, nitric acid was produced using the Birkeland–Eyde process, also known as the arc process. This process is based upon the oxidation of atmospheric nitrogen by atmospheric oxygen to nitric oxide at very high temperatures. An electric arc was used to provide the high temperatures, and yields of up to 4% nitric oxide were obtained. The nitric oxide was cooled and oxidized by the remaining atmospheric oxygen to nitrogen dioxide, and this was subsequently absorbed in dilute nitric acid. The process was very energy intensive and was rapidly displaced by the Ostwald process once cheap ammonia became available.

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In laboratory, nitric acid can be made from copper (II) nitrate or by reacting approximately equal masses of a nitrate salt with 96 % sulfuric acid (H₂SO₄), and distilling this mixture at nitric acid's boiling point of 83 °C until only a white crystalline mass, a metal sulfate, remains in the reaction vessel. The red fuming nitric acid obtained may be converted to the white nitric acid.



The dissolved NO_x are readily removed using reduced pressure at room temperature (10-30 min at 200 mmHg or 27 kPa) to give white fuming nitric acid. This procedure can also be performed under reduced pressure and temperature in one step in order to produce less nitrogen dioxide gas.

6 – Uses:

The main use of nitric acid is for the production of fertilizers; other important uses include the production of explosives, etching and dissolution of metals, especially as a component of aqua regia for the purification and extraction of gold, and in chemical synthesis.

6 - 1 - Elemental Analysis:

In elemental analysis by ICP - MS, ICP-AES, GFAA, and Flame AA, dilute nitric acid (0.5 to 5.0 %) is used as a matrix compound for determining metal traces in solutions.^[7] Ultrapure trace metal grade acid is required for such determination, because small amounts of metal ions could affect the result of the analysis.

It is also typically used in the digestion process of turbid water samples, sludge samples, solid samples as well as other types of unique samples which require elemental analysis via ICP-MS, ICP-OES, ICP-AES, GFAA and FAA. Typically these digestions use a 50 % solution of the purchased HNO₃ mixed with Type 1 DI Water.

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In a low concentration (approximately 10 %), nitric acid is often used to artificially age pine and maple. The color produced is a grey-gold very much like very old wax or oil finished wood (wood finishing).

6 – 3 - Other uses :

IWFNA may be used as the oxidizer in liquid fuel rockets.^[10] IRFNA was one of 3 liquid fuel components for the BOMARC missile.

A solution of nitric acid and alcohol, Nital, is used for etching of metals to reveal the microstructure.

Commercially available aqueous blends of 5 - 30 % nitric acid and 15 - 40 % phosphoric acid are commonly used for cleaning food and dairy equipment primarily to remove precipitated calcium and magnesium compounds (either deposited from the process stream or resulting from the use of hard water during production and cleaning).

Alone, it is useful in metallurgy and refining as it reacts with most metals, and in organic syntheses.

A mixture of concentrated nitric and sulfuric acids causes the nitration of aromatic compounds, such as benzene. Examination of the infrared spectrum of the acid mixture using a corrosive resistant diamond cell shows infrared peaks close to that expected for carbon dioxide. The species responsible for the peaks is the nitronium ion, NO^{+2} , which like CO_2 , is a linear molecule. The nitronium ion is the species responsible for nitration: being positive, it is attacked by electron-rich benzene rings. This is described more fully in organic chemistry books.

7 – Safety:

Nitric acid is a powerful oxidizing agent, and the reactions of nitric acid with compounds such as cyanides, carbides, and metallic powders can be explosive. Reactions of nitric acid with many organic

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compounds, such as turpentine, are violent and hypergolic (i.e., self – igniting) . Due to its properties it is stored away from bases and organics.

Concentrated nitric acid dyes human skin yellow due to a reaction with the keratin. These yellow stains turn orange when neutralized.

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Phosphate minerals

1 – Introduction :

Phosphate minerals are those minerals that contain the tetrahedrally coordinated phosphate (PO_4^{3-}) anion along with the freely substituting arsenate (AsO_4^{3-}) and vanadate (VO_4^{3-}). Chlorine (Cl^-), fluorine (F^-), and hydroxide (OH^-) anions also fit into the crystal structure.

The phosphate class of minerals is a large and diverse group, however, only a few species are relatively common.

Phosphate minerals include :

- triphylite Li(Fe,Mn)PO_4
- monazite $(\text{Ce,La,Y,Th})\text{PO}_4$
- Apatite group $\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$
 - hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$
 - fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$
 - chlorapatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$
- hinsdalite $\text{PbAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$
- pyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$
- vanadinite $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$
- erythrite $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$
- amblygonite LiAlPO_4F
- lazulite $(\text{Mg,Fe})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$
- wavellite $\text{Al}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$
- turquoise $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 5\text{H}_2\text{O}$
- autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}$
- carnotite $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$
- phosphophyllite $\text{Zn}_2(\text{Fe,Mn})(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$
- struvite $(\text{NH}_4)\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$

2 - Applications

Phosphate rock is a general term that refers to rock with high concentration of phosphate minerals, most commonly of the apatite group. It is the major resource mined to produce phosphate fertilisers

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for the agriculture sector. Phosphate is also used in animal feed supplements, food preservatives, anti-corrosion agents, cosmetics, fungicides, ceramics, water treatment and metallurgy.

The largest use of minerals mined for their phosphate content is the production of fertilizer.

Phosphate minerals are often used for control of rust and prevention of corrosion on ferrous materials applied with electrochemical conversion coatings.

Phosphorite

1- Introduction :

Phosphorite , phosphate rock or rock phosphate is a non - detrital sedimentary rock which contains high amounts of phosphate bearing minerals. The phosphate content of phosphorite is at least 20% which is a large enrichment over the typical sedimentary rock content of less than 0.2 % . The phosphate is present as fluorapatite typically in cryptocrystalline masses (grain sizes < 1 μm) referred to as collophane.^[1] The dark brown to black beds range from a few centimetres to several metres in thickness. The layers contain the same textures and structures as fine grained limestones and may represent diagenetic replacements of carbonate minerals by phosphates .

Phosphorites are known from Proterozoic banded iron formations in Australia, but are more common from Paleozoic and Cenozoic sediments. The Permian Phosphoria Formation of the western United States represents some 15 million years of sedimentation reaches a thickness of 420 metres and covers an area of 350 000 km^2 . Commercially mined phosphorites occur in France, Belgium, Spain, Morocco, Tunisia and Algeria. In the United States phosphorites have been mined in Florida, Tennessee, Wyoming and Idaho .

2 - Production and use :

Deposits which contain phosphate in quantity and concentration which are economic to mine as ore for their phosphate content are not particularly common. The two main sources for phosphate are guano, formed from bird droppings, and rocks containing concentrations of the calcium phosphate mineral, apatite.

Phosphate rock is mined, beneficiated, and either solubilized to produce wet-process phosphoric acid, or smelted to produce elemental phosphorus. Phosphoric acid is reacted with phosphate rock to produce the fertilizer triple superphosphate or with anhydrous ammonia to produce the ammonium phosphate fertilizers. Elemental phosphorus is the base for furnace - grade phosphoric acid,

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phosphorus pentasulfide, phosphorus pentoxide, and phosphorus trichloride. Approximately 90 % of phosphate rock production is used for fertilizer and animal feed supplements and the balance for industrial chemicals.

For general use in the fertilizer industry, phosphate rock or its concentrates preferably have levels of 30% phosphorus pentoxide (P_2O_5), reasonable amounts of calcium carbonate (5 %), and < 4 % combined iron and aluminium oxides. Worldwide, the resources of high-grade ore are declining, and the beneficiation of lower grade ores by washing, flotation and calcining is becoming more widespread.

In addition to phosphate fertilisers for agriculture, phosphorus from rock phosphate is also used in animal feed supplements, food preservatives, anti-corrosion agents, cosmetics, fungicides, ceramics, water treatment and metallurgy.

In the world, the United States is the leading producer and exporter of phosphate fertilizers, accounting for about 37% of world P_2O_5 exports. The world's total economic demonstrated resource of rock phosphate is 18 Gt, which occurs principally as sedimentary marine phosphorites.

China, the United States and Morocco are the world's largest miners of phosphate rock, each producing about a quarter of the total world production. Other countries with significant production include Brazil, Russia, Jordan and Tunisia. Historically, large amounts of phosphates were obtained from guano deposits on small islands such as Christmas Island and Nauru, but these sources are now largely depleted.

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Phosphorus



waxy white (yellow cut), red, violet and black phosphorus

Contents

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- 2 Physical properties
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1 – Introduction :

Phosphorus is the chemical element that has the symbol **P** and atomic number **15**. A multivalent nonmetal of the nitrogen group, phosphorus is commonly found in inorganic phosphate rocks. Elemental phosphorus exists in two major forms - white phosphorus and red phosphorus. Although the term "phosphorescence", meaning

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glow after illumination, derives from phosphorus, glow of phosphorus originates from oxidation of the white (but not red) phosphorus and should be called chemiluminescence.

Due to its high reactivity, phosphorus is never found as a free element in nature on Earth. The first form of phosphorus to be discovered (white phosphorus, in 1669) emits a faint glow upon exposure to oxygen — hence its name given from Greek mythology, Φωσφόρος meaning "light-bearer" (Latin *Lucifer*), referring to the "Morning Star", the planet Venus.

Phosphorus is a component of DNA, RNA, ATP, and also the phospholipids that form all cell membranes. It is, thus, an essential element for all living cells. The most important commercial use of phosphorus-based chemicals is the production of fertilizers.

Phosphorus compounds are also widely used in explosives, nerve agents, friction matches, fireworks, pesticides, toothpaste, and detergents.

Appearance

Colorless , waxy white , yellow , scarlet , red , violet , black

General properties

Name, symbol , number	phosphorus, P, 15
Element category	non metal
Group, period, block	15, 3, p
Standard atomic weight	31 g · mol ⁻¹
Electrons per shell	2, 8, 5

Physical properties

Density (near r.t.)	(white) 1.823, (red) $\approx 2.2 - 2.34$, (violet) 2.36, (black) 2.69 g·cm ⁻³
Melting point	(white) 44.2 °C, (black) 610 °C
Sublimation point	(red) $\approx 416 - 590$ °C, (violet) 620 °C
Boiling point	(white) 280.5 °C
Heat of fusion	(white) 0.66 kJ·mol ⁻¹
Heat of vaporization	(white) 12.4 kJ·mol ⁻¹

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTERSpecific heat capacity (25 °C) (white) $23.824 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ **Vapor pressure (white)**

<i>P</i> /Pa	1	10	100	1 k	10 k	100 k
at <i>T</i> /K	279	307	342	388	453	549

Vapor pressure (red, bp. 431 °C)

<i>P</i> /Pa	1	10	100	1 k	10 k	100 k
at <i>T</i> /K	455	489	529	576	635	704

Atomic properties

Oxidation states	5, 4, 3, 2, 1, -1, -2, -3 (mildly acidic oxide)
Electronegativity	2.19 (Pauling scale)
Ionization energies	1st : $1011.8 \text{ kJ} \cdot \text{mol}^{-1}$ 2nd : $1907 \text{ kJ} \cdot \text{mol}^{-1}$ 3rd : $2914.1 \text{ kJ} \cdot \text{mol}^{-1}$
Covalent radius	$107 \pm 3 \text{ pm}$
Van der Waals radius	180 pm

Miscellanea

Magnetic ordering	(white,red,violet,black) diamagnetic
Thermal conductivity	(300 K) (white) 0.236, (black) $12.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$
Bulk modulus	(white) 5, (red) 11 GPa

Most stable isotopes

Main article: Isotopes of phosphorus

iso	NA	half - life	DM	DE (MeV)	DP
^{31}P	100 %	^{31}P is stable with 16 neutrons			
^{32}P	syn	14.28 d	β^-	1.709	^{32}S
^{33}P	syn	25.3 d	β^-	0.249	^{33}S

2 - Physical properties:**2 – 1 - Glow from white phosphorus:**

In 1669, German alchemist Hennig Brand attempted to create the philosophers stone from his urine, and in the process he produced a

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white material that glowed in the dark. The phosphorus had been produced from inorganic phosphate, which is a significant component of dissolved urine solids. White phosphorus is highly reactive and gives off a faint greenish glow upon uniting with oxygen. The glow observed by Brand was caused by the very slow burning of the phosphorus, but as he neither saw flame nor felt any heat he did not recognize it as burning.

It was known from early times that the glow would persist for a time in a stoppered jar but then cease. Robert Boyle in the 1680s ascribed it to "debilitation" of the air; in fact, it is oxygen being consumed. By the 18th century, it was known that in pure oxygen, phosphorus does not glow at all ; there is only a range of partial pressure at which it does. Heat can be applied to drive the reaction at higher pressures.

In 1974, the glow was explained by R. J. van Zee and A. U. Khan.^[7] A reaction with oxygen takes place at the surface of the solid (or liquid) phosphorus, forming the short-lived molecules HPO and P₂O₂ that both emit visible light. The reaction is slow and only very little of the intermediates are required to produce the luminescence, hence the extended time the glow continues in a stoppered jar.

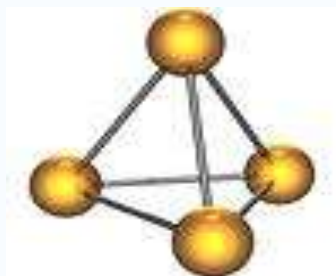
Although the term phosphorescence is derived from phosphorus, the reaction that gives phosphorus its glow is properly called chemiluminescence (glowing due to a cold chemical reaction), not phosphorescence (re - emitting light that previously fell onto a substance and excited it).

Phosphorescence is the slow decay of a metastable electronic state to a lower energy state through emission of light. The decay is slow because the transition from the excited to the lower state requires a spin flip, making it classically forbidden. Often it involves a transition from an excited triplet state to a singlet ground state. The metastable excited state may have been populated by thermal excitations or some light source. Since phosphorescence is slow, it persists for some time after the exciting source is removed. In contrast, chemiluminescence occurs when the product molecules of a chemical reaction (HPO and P₂O₂ in this case) leave the reaction in an

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electronically excited state. These excited molecules then release their excess energy in the form of light. The frequency (colour) of the light emitted is proportional to the energy difference of the two electronic states involved.

2 – 2 – Allotropes of phosphorus:



P₄ molecule

Phosphorus has several forms (allotropes) that have strikingly different properties. The two most common allotropes are **white phosphorus** and **red phosphorus**. Red phosphorus is an intermediate phase between white and violet phosphorus. Another form, scarlet phosphorus, is obtained by allowing a solution of white phosphorus in carbon disulfide to evaporate in sunlight. Black phosphorus is obtained by heating white phosphorus under high pressures (about 12,000 atmospheres). In appearance, properties, and structure, it resembles graphite, being black and flaky, a conductor of electricity, and has puckered sheets of linked atoms. Another allotrope is diphosphorus; it contains a phosphorus dimer as a structural unit and is highly reactive.

White phosphorus has two forms, low-temperature β form and high-temperature α form. They both contain a phosphorus P₄ tetrahedron as a structural unit, in which each atom is bound to the other three atoms by a single bond. This P₄ tetrahedron is also present in liquid and gaseous phosphorus up to the temperature of 800 °C when it starts decomposing to P₂ molecules. White phosphorus is the least stable, the most reactive, more volatile, less dense, and more toxic than the other allotropes. The toxicity of white phosphorus led to its discontinued use in matches. White phosphorus is thermodynamically unstable at normal condition and will gradually change to

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red phosphorus. This transformation, which is accelerated by light and heat, makes white phosphorus almost always contain some red phosphorus and therefore appear yellow. For this reason, it is also called yellow phosphorus. It glows greenish in the dark (when exposed to oxygen), is highly flammable and pyrophoric (self-igniting) upon contact with air as well as toxic (causing severe liver damage on ingestion). Because of pyrophoricity, white phosphorus is used as an additive in napalm. The odour of combustion of this form has a characteristic garlic smell, and samples are commonly coated with white "(di)phosphorus pentoxide", which consists of P_4O_{10} tetrahedra with oxygen inserted between the phosphorus atoms and at their vertices. White phosphorus is insoluble in water but soluble in carbon disulfide.

The white allotrope can be produced using several different methods. In one process, calcium phosphate, which is derived from phosphate rock, is heated in an electric or fuel - fired furnace in the presence of carbon and silica. Elemental phosphorus is then liberated as a vapour and can be collected under phosphoric acid. This process is similar to the first synthesis of phosphorus from calcium phosphate in urine.

In the **red phosphorus**, one of the P_4 bonds is broken, and one additional bond is formed with a neighbouring tetrahedron resulting in a more chain-like structure. Red phosphorus may be formed by heating white phosphorus to $250\text{ }^{\circ}\text{C}$ or by exposing white phosphorus to sunlight. Phosphorus after this treatment exists as an amorphous network of atoms that reduces strain and gives greater stability; further heating results in the red phosphorus becoming crystalline. Therefore red phosphorus is not a certain allotrope, but rather an intermediate phase between the white and violet phosphorus, and most of its properties have a range of values. Red phosphorus does not catch fire in air at temperatures below $260\text{ }^{\circ}\text{C}$, whereas white phosphorus ignites at about $30\text{ }^{\circ}\text{C}$.

Violet phosphorus is a thermodynamic stable form of phosphorus that can be produced by day - long temper of red phosphorus above $550\text{ }^{\circ}\text{C}$. In 1865, Hittorf discovered that when

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phosphorus was recrystallized from molten lead, a red/purple form is obtained. Therefore this form is sometimes known as "Hittorf's phosphorus" (or violet or α -metallic phosphorus).^[10]

Black phosphorus is the least reactive allotrope and the thermodynamic stable form below 550 °C. It is also known as β -metallic phosphorus and has a structure somewhat resembling that of graphite.^{[15][16]} High pressures are usually required to produce black phosphorus, but it can also be produced at ambient conditions using metal salts as catalysts.^[17]

The **diphosphorus** allotrope, P_2 , is stable only at high temperatures. The dimeric unit contains a triple bond and is analogous to N_2 . The diphosphorus allotrope (P_2) can be obtained normally only under extreme conditions (for example, from P_4 at 1100 kelvin). Nevertheless, some advancements were obtained in generating the diatomic molecule in homogeneous solution, under normal conditions with the use by some transitional metal complexes (based on, for example, tungsten and niobium).

Properties of some allotropes of phosphorus:

Form	white(α)	white(β)	violet	black
Symmetry	Body-centred cubic	Triclinic	Monoclinic	Orthorhombic
Pearson symbol		aP24	mP84	oS8
Space group	I43m	P1 No.2	P2/c No.13	Cmca No.64
Density (g/cm ³)	1.828	1.88	2.36	2.69
Bandgap (eV)	2.1		1.5	0.34
Refractive index	1.8244		2.6	2.4

2 – 3 - Isotopes of phosphorus :

Although twenty - three isotopes of phosphorus are known (all possibilities from ^{24}P up to ^{46}P), only ^{31}P , with spin 1/2, is stable and is therefore present at 100 % abundance. The half-integer spin and high abundance of ^{31}P make it useful for nuclear magnetic resonance studies of biomolecules, particularly DNA.

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Two radioactive isotopes of phosphorus have half-lives that make them useful for scientific experiments. ^{32}P has a half-life of 14.262 days and ^{33}P has a half-life of 25.34 days. Biomolecules can be "tagged" with a radioisotope to allow for the study of very dilute samples.

Radioactive isotopes of phosphorus include :

- ^{32}P , a beta-emitter (1.71 MeV) with a half-life of 14.3 days, which is used routinely in life-science laboratories, primarily to produce radiolabeled DNA and RNA probes, *e.g.* for use in Northern blots or Southern blots. Because the high energy beta particles produced penetrate skin and corneas, and because any ^{32}P ingested, inhaled, or absorbed is readily incorporated into bone and nucleic acids, Occupational Safety and Health Administration in the United States, and similar institutions in other developed countries require that a lab coat, disposable gloves, and safety glasses or goggles be worn when working with ^{32}P , and that working directly over an open container be avoided in order to protect the eyes. Monitoring personal, clothing, and surface contamination is also required. In addition, due to the high energy of the beta particles, shielding this radiation with the normally used dense materials (*e.g.* lead), gives rise to secondary emission of X- rays via a process known as Bremsstrahlung, meaning braking radiation. Therefore shielding must be accomplished with low density materials, *e.g.* Plexiglas, Lucite, plastic, wood, or water.

- ^{33}P , a beta-emitter (0.25 MeV) with a half-life of 25.4 days. It is used in life-science laboratories in applications in which lower energy beta emissions are advantageous such as DNA sequencing.

3 - Chemical properties

- Hydrides: PH_3 , P_2H_4
- Halides: PBr_5 , PBr_3 , PCl_3 , PI_3
- Oxides: P_4O_6 , P_4O_{10}
- Sulfides: P_4S_6 , P_4S_{10}
- Acids: H_3PO_2 , H_3PO_4

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- Phosphates: $(\text{NH}_4)_3\text{PO}_4$, $\text{Ca}_3(\text{PO}_4)_2$, FePO_4 , $\text{Fe}_3(\text{PO}_4)_2$, Na_3PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, KH_2PO_4
- Phosphides: Ca_3P_2 , GaP , Zn_3P_2 , Cu_3P

3 – 1 - Chemical bonding:

Because phosphorus is just below nitrogen in the periodic table, the two elements share many of their bonding characteristics. For instance, phosphine, PH_3 , is an analogue of ammonia, NH_3 . Phosphorus, like nitrogen, is trivalent in this molecule.

The "trivalent" or simple 3-bond view is the pre-quantum mechanical Lewis structure, which although somewhat of a simplification from a quantum chemical point of view, illustrates some of the distinguishing chemistry of the element. In quantum chemical valence bond theory, the valence electrons are seen to be in mixtures of four *s* and *p* atomic orbitals, so-called hybrids. In this view, the three unpaired electrons in the three *3p* orbitals combine with the two electrons in the *3s* orbital to form three electron pairs of opposite spin, available for the formation of three bonds. The remaining hybrid orbital contains two paired non - bonding electrons, which show as a lone pair in the Lewis structure.

The phosphorus cation is very similar to the nitrogen cation. In the same way that nitrogen forms the tetravalent ammonium ion, phosphorus can form the tetravalent phosphonium ion, and form salts such as phosphonium iodide $[\text{PH}_4]^+ [\text{I}^-]$.

Like other elements in the third or lower rows of the periodic table, phosphorus atoms can expand their valence to make penta- and hexavalent compounds. The phosphorus chloride molecule is an example. When the phosphorus ligands are not identical, the more electronegative ligands are located in the apical positions and the least electronegative ligands are located in the axial positions.

With strongly electronegative ions, in particular fluorine, hexavalency as in PF_6^- occurs as well. This octahedral ion is isoelectronic with SF_6 . In the bonding the six octahedral sp^3d^2 hybrid atomic orbitals play an important role.

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Before extensive computer calculations were feasible, it was generally assumed that the nearby *d* orbitals in the $n = 3$ shell were the obvious cause of the difference in binding between nitrogen and phosphorus (i.e., phosphorus had 3*d* orbitals available for 3*s* and 3*p* shell bonding electron hybridisation, but nitrogen did not). However, in the early eighties the German theoretical chemist Werner Kutzelnigg^[21] found from an analysis of computer calculations that the difference in binding is more likely due to differences in character between the valence 2*p* and valence 3*p* orbitals of nitrogen and phosphorus, respectively. The 2*s* and 2*p* orbitals of first row atoms are localized in roughly the same region of space, while the 3*p* orbitals of phosphorus are much more extended in space. The violation of the octet rule observed in compounds of phosphorus is then due to the size of the phosphorus atom, and the corresponding reduction of steric hindrance between its ligands. In modern theoretical chemistry, Kutzelnigg's analysis is generally accepted.

The simple Lewis structure for the trigonal bipyramidal PCl_5 molecule contains five covalent bonds, implying a hypervalent molecule with ten valence electrons contrary to the octet rule.

An alternate description of the bonding, however, respects the octet rule by using 3 - centre - 4 - electron (3c - 4e) bonds. In this model, the octet on the P atom corresponds to six electrons, which form three Lewis (2c - 2e) bonds to the three equatorial Cl atoms, plus the two electrons in the 3-centre Cl - P - Cl bonding molecular orbital for the two axial Cl electrons. The two electrons in the corresponding nonbonding molecular orbital are not included because this orbital is localized on the two Cl atoms and does not contribute to the electron density on the phosphorus atom. (However, it should always be remembered that the octet rule is not some universal rule of chemical bonding, and while many compounds obey it, there are many elements to which it does not apply).

3 – 2 - Phosphine , diphosphine and phosphonium salts:

Phosphine (PH_3) and arsine (AsH_3) are structural analogues with ammonia (NH_3) and form pyramidal structures with the phosphorus or arsenic atom in the centre bound to three hydrogen atoms and one lone

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electron pair. Both are colourless, ill-smelling, toxic compounds. Phosphine is produced in a manner similar to the production of ammonia. Hydrolysis of calcium phosphide, Ca_3P_2 , or calcium nitride, Ca_3N_2 produces phosphine or ammonia, respectively. Unlike ammonia, phosphine is unstable and it reacts instantly with air giving off phosphoric acid clouds. Arsine is even less stable. Although phosphine is less basic than ammonia, it can form some phosphonium salts (like PH_4I), analogues of ammonium salts, but these salts immediately decompose in water and do not yield phosphonium (PH_4^+) ions. Diphosphine (P_2H_4 or $\text{H}_2\text{P} - \text{PH}_2$) is an analogue of hydrazine (N_2H_4) that is a colourless liquid that spontaneously ignites in air and can disproportionate into phosphine and complex hydrides.

3 – 3 - Halides:

The tri halides PF_3 , PCl_3 , PBr_3 and PI_3 and the pentahalides, PCl_5 and PBr_5 are all known and mixed halides can also be formed. The trihalides can be formed simply by mixing the appropriate stoichiometric amounts of phosphorus and a halogen. For safety reasons, however, PF_3 is typically made by reacting PCl_3 with AsF_5 and fractional distillation because the direct reaction of phosphorus with fluorine can be explosive. The pentahalides, PX_5 , are synthesized by reacting excess halogen with either elemental phosphorus or with the corresponding trihalide. Mixed phosphorus halides are unstable and decompose to form simple halides. Thus $5\text{PF}_3\text{Br}_2$ decomposes into 3PF_5 and 2PBr_5 .

3 - 4 - Oxides and oxyacids:

Phosphorus (III) oxide, P_4O_6 (also called tetra phosphorus hexoxide) and phosphorus (IV) oxide, P_4O_{10} (or tetra phosphorus decoxide) are acid anhydrides of phosphorus oxyacids and hence readily react with water. P_4O_{10} is a particularly good dehydrating agent that can even remove water from nitric acid, HNO_3 . The structure of P_4O_6 is like that of P_4 with an oxygen atom inserted between each of the P-P bonds. The structure of P_4O_{10} is like that of P_4O_6 with the addition of one oxygen bond to each phosphorus atom via a double bond and protruding away from the tetrahedral structure.

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Phosphorous oxyacids can have acidic protons bound to oxygen atoms and nonacidic protons that are bonded directly to the phosphorus atom. Although many oxyacids of phosphorus are formed, only six are important (see table), and three of them, hypophosphorous acid, phosphorous acid and phosphoric acid are particularly important ones.

Oxidation state	Formula	Name	Acidic protons	Compounds
+1	H ₃ PO ₂	hypophosphorous acid	1	acid, salts
+3	H ₃ PO ₃	(ortho)phosphorous acid	2	acid, salts
+5	(HPO ₃) _n	metaphosphoric acids	n	salts (n=3,4)
+5	H ₅ P ₃ O ₁₀	triphosphoric acid	3	salts
+5	H ₄ P ₂ O ₇	pyrophosphoric acid	4	acid, salts
+5	H ₃ PO ₄	(ortho)phosphoric acid	3	acid, salts

4 - Spelling and etymology;

The name *Phosphorus* in Ancient Greece was the name for the planet Venus and is derived from the Greek words (φως = light, φορέω = carry), which roughly translates as light-bringer or light carrier.^[4] (In Greek mythology, Hesperus (evening star) and Eosphorus (dawnbearer) are close homologues, and also associated with Phosphorus - the - planet).

According to the Oxford English Dictionary, the correct spelling of the element is **phosphorus**. The word **phosphorous** is the adjectival form of the P³⁺ valence: so, just as sulfur forms **sulfurous** and **sulfuric** compounds, **phosphorus** forms **phosphorous** compounds and P⁵⁺ valency **phosphoric** compounds .

5 - History and discovery:

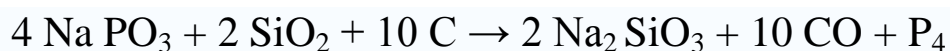
The discovery of phosphorus is credited to the German alchemist Hennig Brand in 1669, although other chemists might have discovered phosphorus around the same time. Brand experimented with urine, which contains considerable quantities of dissolved phosphates from normal metabolism. Working in Hamburg, Brand attempted to create the fabled philosopher's stone through the distillation of some salts by evaporating urine, and in the process produced a white material that

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glowed in the dark and burned brilliantly. His process originally involved letting urine stand for days until it gave off a terrible smell. Then he boiled it down to a paste, heated this paste to a high temperature, and led the vapours through water, where he hoped they would condense to gold. Instead, he obtained a white, waxy substance that glowed in the dark. Brand had discovered phosphorus, the first element discovered since antiquity. We now know that Brand produced ammonium sodium hydrogen phosphate, $(\text{NH}_4)\text{NaHPO}_4$. While the quantities were essentially correct (it took about 1,100 L of urine to make about 60 g of phosphorus), it was unnecessary to allow the urine to rot. Later scientists would discover that fresh urine yielded the same amount of phosphorus.

Since that time, *phosphors* and *phosphorescence* were used loosely to describe substances that shine in the dark without burning. However, as mentioned above, even though the term phosphorescence was originally coined as a term by analogy with the glow from oxidation of elemental phosphorus, is now reserved for another fundamentally different process - re - emission of light after illumination.

Brand at first tried to keep the method secret,^[23] but later sold the recipe for 200 thaler to D Krafft from Dresden,^[4] who could now make it as well, and toured much of Europe with it, including England, where he met with Robert Boyle. The secret that it was made from urine leaked out and first Johann Kunckel (1630–1703) in Sweden (1678) and later Boyle in London (1680) also managed to make phosphorus. Boyle states that Krafft gave him no information as to the preparation of phosphorus other than that it was derived from "somewhat that belonged to the body of man". This gave Boyle a valuable clue, however, so that he, too, managed to make phosphorus, and published the method of its manufacture. Later he improved Brand's process by using sand in the reaction (still using urine as base material),



Robert Boyle was the first to use phosphorus to ignite sulfur-tipped wooden splints, forerunners of our modern matches, in 1680.

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In 1769 Johan Gottlieb Gahn and Carl Wilhelm Scheele showed that calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) is found in bones, and they obtained phosphorus from bone ash. Antoine Lavoisier recognized phosphorus as an element in 1777. Bone ash was the major source of phosphorus until the 1840s. Phosphate rock, a mineral containing calcium phosphate, was first used in 1850 and following the introduction of the electric arc furnace in 1890, this became the only source of phosphorus. Phosphorus, phosphates and phosphoric acid are still obtained from phosphate rock. Phosphate rock is a major feedstock in the fertilizer industry.

Early matches used white phosphorus in their composition, which was dangerous due to its toxicity. Murders, suicides and accidental poisonings resulted from its use. (An apocryphal tale tells of a woman attempting to murder her husband with white phosphorus in his food, which was detected by the stew giving off luminous steam).^[7] In addition, exposure to the vapours gave match workers a severe necrosis of the bones of the jaw, the infamous "phossy jaw". When a safe process for manufacturing red phosphorus was discovered, with its far lower flammability and toxicity, laws were enacted, under the Berne Convention (1906), requiring its adoption as a safer alternative for match manufacture.

6 - Occurrence:

Due to its reactivity with air and many other oxygen - containing substances, phosphorus is not found free in nature but it is widely distributed in many different minerals.

Phosphate rock, which is partially made of apatite (an impure tricalcium phosphate mineral), is an important commercial source of this element. About 50 percent of the global phosphorus reserves are in the Arab nations.^[25] Large deposits of apatite are located in China, Russia, Morocco, Florida, Idaho, Tennessee, Utah, and elsewhere. Albright and Wilson in the United Kingdom and their Niagara Falls plant, for instance, were using phosphate rock in the 1890s and 1900s from Connetable, Tennessee and Florida; by 1950 they were using phosphate rock mainly from Tennessee and North Africa.^[13] In the early 1990s Albright and Wilson's purified wet phosphoric acid

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business was being adversely affected by phosphate rock sales by China and the entry of their long-standing Moroccan phosphate suppliers into the purified wet phosphoric acid business.

In 2007, at the current rate of consumption, the supply of phosphorus was estimated to run out in 345 years. However, scientists are now claiming that a "Peak Phosphorus" will occur in 30 years and that "At current rates, reserves will be depleted in the next 50 to 100 years."

7 - Production:

White phosphorus was first made commercially, for the match industry in the 19th century, by distilling off phosphorus vapour from precipitated phosphates, mixed with ground coal or charcoal, which was heated in an iron pot, in retort. The precipitated phosphates were made from ground-up bones that had been de - greased and treated with strong acids. Carbon monoxide and other flammable gases produced during the reduction process were burnt off in a flare stack.

This process became obsolete when the submerged - arc furnace for phosphorus production was introduced to reduce phosphate rock. Calcium phosphate (phosphate rock), mostly mined in Florida and North Africa, can be heated to 1,200–1,500 °C with sand, which is mostly SiO_2 , and coke (impure carbon) to produce vaporized tetraphosphorus, P_4 , (melting point 44.2 °C), which is subsequently condensed into a white powder under water to prevent oxidation. Even under water, white phosphorus is slowly converted to the more stable red phosphorus allotrope (melting point 597 °C). Both the white and red allotropes of phosphorus are insoluble in water.

The electric furnace method allowed production to increase to the point where phosphorus could be used in weapons of war.^{[7][13]} In World War I it was used in incendiaries, smoke screens and tracer bullets. A special incendiary bullet was developed to shoot at hydrogen-filled Zeppelins over Britain (hydrogen being highly inflammable if it can be ignited). During World War II, Molotov cocktails of benzene and phosphorus were distributed in Britain to specially selected civilians within the British resistance operation, for

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defence; and phosphorus incendiary bombs were used in war on a large scale. Burning phosphorus is difficult to extinguish and if it splashes onto human skin it has horrific effects .

Today phosphorus production is larger than ever. It is used as a precursor for various chemicals, in particular the herbicide glyphosate sold under the brand name Roundup. Production of white phosphorus takes place at large facilities and it is transported heated in liquid form. Some major accidents have occurred during transportation, train derailments at Brownston, Nebraska and Miamisburg, Ohio led to large fires. The worst accident in recent times was an environmental one in 1968 when phosphorus spilled into the sea from a plant at Placentia Bay, Newfoundland.

8 - Applications

Widely used compounds	Use
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	Baking powder & fertilizers
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	Animal food additive, tooth powder
H_3PO_4	Manufacture of phosphate fertilizers
PCl_3	Manufacture of POCl_3 and pesticides
POCl_3	Manufacturing plasticizer
P_4S_{10}	Manufacturing of additives and pesticides
$\text{Na}_5\text{P}_3\text{O}_{10}$	Detergents

Phosphorus, being an essential plant nutrient, finds its major use as a constituent of fertilizers for agriculture and farm production in the form of concentrated phosphoric acids, which can consist of 70 % to 75 % P_2O_5 . Global demand for fertilizers led to large increase in phosphate (PO_4^{3-}) production in the second half of the 20th century. Due to the essential nature of phosphorus to living organisms, the low solubility of natural phosphorus-containing compounds, and the slow natural cycle of phosphorus, the agricultural industry is heavily reliant on fertilizers that contain phosphate, mostly in the form of superphosphate of lime. Superphosphate of lime is a mixture of two phosphate salts, calcium dihydrogen phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and

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calcium sulfate dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced by the reaction of sulfuric acid and water with calcium phosphate.

- Phosphorus is widely used to make organo phosphorus compounds, through the intermediates phosphorus chlorides and two phosphorus sulfides: phosphorus pentasulfide, and phosphorus sesquisulfide. Organophosphorus compounds have many applications, including in plasticizers, flame retardants, pesticides, extraction agents, and water treatment.
- Phosphorus is also an important component in steel production, in the making of phosphor bronze, and in many other related products.
- Phosphates are utilized in the making of special glasses that are used for sodium lamps.
- Bone - ash, calcium phosphate, is used in the production of fine china.
- Sodium tripolyphosphate made from phosphoric acid is used in laundry detergents in some countries, but banned for this use in others.
- Phosphoric acid made from elemental phosphorus is used in food applications such as some soda beverages. The acid is also a starting point to make food grade phosphates. These include mono - calcium phosphate that is employed in baking powder and sodium tripoly phosphate and other sodium phosphates. Among other uses these are used to improve the characteristics of processed meat and cheese. Others are used in toothpaste. Trisodium phosphate is used in cleaning agents to soften water and for preventing pipe/boiler tube corrosion.
 - White phosphorus, called "WP" (slang term "Willie Peter") is used in military applications as incendiary bombs, for smoke - screening as smoke pots and smoke bombs, and in tracer ammunition. It is also a part of an obsolete M34 White Phosphorus US hand grenade. This multi purpose grenade was mostly used for signalling, smoke screens and inflammation; it could also cause severe burns and had a psychological impact on the enemy.

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- Red phosphorus is essential for manufacturing matchbook strikers, flares, safety matches, pharmaceutical grade and street methamphetamine, and is used in cap gun caps.
- Phosphorus sesquisulfide is used in heads of strike-anywhere matches.
- In trace amounts, phosphorus is used as a dopant for n-type semiconductors.
- ^{32}P and ^{33}P are used as radioactive tracers in biochemical laboratories .

9 - Biological role:

Phosphorus is a key element in all known forms of life. Inorganic phosphorus in the form of the phosphate PO_4^{3-} plays a major role in biological molecules such as DNA and RNA where it forms part of the structural framework of these molecules. Living cells also use phosphate to transport cellular energy in the form of adenosine triphosphate (ATP). Nearly every cellular process that uses energy obtains it in the form of ATP. ATP is also important for phosphorylation, a key regulatory event in cells. Phospholipids are the main structural components of all cellular membranes. Calcium phosphate salts assist in stiffening bones.

Every cell has a membrane that separates it from its surrounding environment. Biological membranes are made from a phospholipid matrix and proteins, typically in the form of a bilayer. Phospholipids are derived from glycerol, such that two of the glycerol hydroxyl (OH) protons have been replaced with fatty acids as an ester, and the third hydroxyl proton has been replaced with phosphate bonded to another alcohol.

An average adult human contains about 0.7 kg of phosphorus, about 85 - 90 % of which is present in bones and teeth in the form of apatite, and the remainder in soft tissues and extra cellular fluids (~ 1 %) . The phosphorus content increases from about 0.5 weight % in infancy to 0.65 - 1.1 weight % in adults. Average phosphorus concentration in the blood is about 0.4 g / L, about 70 % of that is organic and 30 % inorganic phosphates. A well - fed adult in the industrialized world consumes and excretes about 1 - 3 g of

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phosphorus per day, with consumption in the form of inorganic phosphate and phosphorus-containing biomolecules such as nucleic acids and phospholipids; and excretion almost exclusively in the form of urine phosphate ion. Only about 0.1 % of body phosphate circulates in the blood, but this amount reflects the amount of phosphate available to soft tissue cells.

In medicine, low - phosphate syndromes are caused by malnutrition, by failure to absorb phosphate, and by metabolic syndromes that draw phosphate from the blood (such as re-feeding after malnutrition) or pass too much of it into the urine. All are characterized by hypophosphatemia (see article for medical details), which is a condition of low levels of soluble phosphate levels in the blood serum, and therefore inside cells. Symptoms of hypophosphatemia include muscle and neurological dysfunction, and disruption of muscle and blood cells due to lack of ATP. Too much phosphate can lead to diarrhoea and calcification (hardening) of organs and soft tissue, and can interfere with the body's ability to use iron, calcium, magnesium, and zinc.

Phosphorus is an essential macromineral for plants, which is studied extensively in edaphology in order to understand plant uptake from soil systems. In ecological terms, phosphorus is often a limiting factor in many environments; i.e. the availability of phosphorus governs the rate of growth of many organisms. In ecosystems an excess of phosphorus can be problematic, especially in aquatic systems, see eutrophication and algal blooms.

10 - Precautions:

Organic compounds of phosphorus form a wide class of materials, some of which are extremely toxic. Fluoro phosphate esters are among the most potent neurotoxins known. A wide range of organo phosphorus compounds are used for their toxicity to certain organisms as pesticides (herbicides, insecticides, fungicides, etc.) and weaponised as nerve agents. Most inorganic phosphates are relatively nontoxic and essential nutrients. For environmentally adverse effects of phosphates see eutrophication and algal blooms.

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The white phosphorus allotrope should be kept under water at all times as it presents a significant fire hazard due to its extreme reactivity with atmospheric oxygen, and it should only be manipulated with forceps since contact with skin can cause severe burns. Chronic white phosphorus poisoning leads to necrosis of the jaw called "phossy jaw". Ingestion of white phosphorus may cause a medical condition known as "Smoking Stool Syndrome".

When the white form is exposed to sunlight or when it is heated in its own vapour to 250 °C, it is transmuted to the red form, which does not chemoluminesce in air. The red allotrope does not spontaneously ignite in air and is not as dangerous as the white form. Nevertheless, it should be handled with care because it reverts to white phosphorus in some temperature ranges and it also emits highly toxic fumes that consist of phosphorus oxides when it is heated.^[12]

Upon exposure to elemental phosphorus, in the past it was suggested to wash the affected area with 2 % copper sulfate solution to form harmless compounds that can be washed away. According to the recent *US Navy's Treatment of Chemical Agent Casualties and Conventional Military Chemical Injuries: FM8-285: Part 2 Conventional Military Chemical Injuries*, "Cupric (copper (II)) sulfate has been used by U.S. personnel in the past and is still being used by some nations. However, copper sulfate is toxic and its use will be discontinued. Copper sulfate may produce kidney and cerebral toxicity as well as intravascular hemolysis."

The manual suggests instead "a bicarbonate solution to neutralize phosphoric acid, which will then allow removal of visible white phosphorus. Particles often can be located by their emission of smoke when air strikes them, or by their phosphorescence in the dark. In dark surroundings, fragments are seen as luminescent spots." Then, "Promptly debride the burn if the patient's condition will permit removal of bits of WP (white phosphorus) that might be absorbed later and possibly produce systemic poisoning . DO NOT apply oily-based ointments until it is certain that all WP has been removed. Following complete removal of the particles, treat the lesions as thermal burns." As white phosphorus readily mixes with oils, any oily substances or

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ointments are not recommended until the area is thoroughly cleaned and all white phosphorus removed.

10 – 1 - US DEA List I status :

Phosphorus can reduce elemental iodine to hydroiodic acid, which is a reagent effective for reducing ephedrine or pseudo ephedrine to methamphetamine. For this reason, two allotropes of elemental phosphorus - red phosphorus and white phosphorus - were designated by the United States Drug Enforcement Administration as List I precursor chemicals under

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Phosphorus oxide

Phosphorus oxide can refer to :

- Phosphorus pentoxide (phosphorus (V) oxide, phosphoric anhydride), P_2O_5
- Phosphorus trioxide (phosphorus (III) oxide, phosphorous anhydride), P_2O_3
- Several other , less common , oxides of phosphorus , including P_4O_7 , P_4O_8 , P_4O_9 , PO and P_2O_6

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Phosphorus Tri Oxide

1 – Introduction :

Phosphorus trioxide is the chemical compound with the molecular formula P_4O_6 . Although it should properly be named tetraphosphorus hexoxide, the name phosphorus trioxide preceded the knowledge of the compound's molecular structure, and its usage continues today. This colorless solid is structurally related to adamantane. It is formally the anhydride of phosphorous acid, H_3PO_3 , but cannot be obtained by the dehydration of the acid. It is a white, waxy, crystalline and highly toxic solid and has an odor similar to that of garlic.

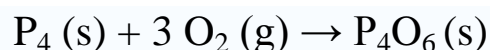
other names : Phosphorus (III) oxide,
Phosphorus sesquioxide,
Phosphorous oxide,
Phosphorous anhydride

Properties

Molecular formula	$P_4 O_6$
Molar mass	110 g mol^{-1}
Appearance	colourless monoclinic crystals or liquid
Density	2.135 g / cm^3
Melting point	$23.8 \text{ }^\circ\text{C}$
Boiling point	$173.1 \text{ }^\circ\text{C}$
Solubility in water	reacts
Acidity (pK_a)	9.2

2 - Preparation:

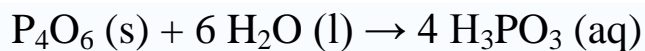
It is obtained by the combustion of phosphorus in a limited supply of air at low temperature.



By - products include red phosphorus suboxide.

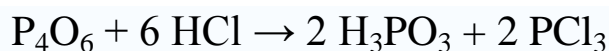
ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**3 - Chemical Properties:**

Phosphorus trioxide reacts with cold water to form phosphorous acid:



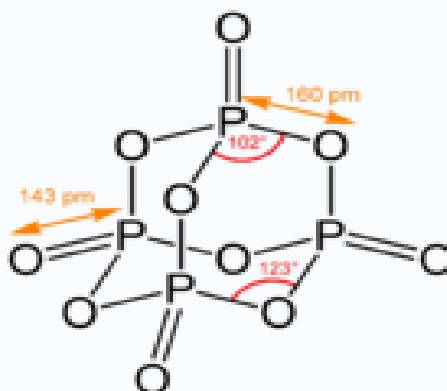
It reacts vigorously with hot water, via a complex set of reactions, to form red phosphorus, phosphines, H_3PO_3 and H_3PO_4 .

P_4O_6 reacts with hydrogen chloride to form H_3PO_3 and phosphorus tri chloride.



With chlorine or bromine it forms the corresponding phosphoryl halide, and it reacts with iodine in a sealed tube to form diphosphorus tetra iodide.

Phosphorus Pentoxide



Contents

- 1 Introduction
- 2 Structure
- 3 Preparation
- 4 Applications
- 5 Related phosphorus oxides
- 6 Hazards
- 7 Fiction

1 – Introduction :

Phosphorus pentoxide is a chemical compound with molecular formula P_4O_{10} . This white crystalline solid is the anhydride of phosphoric acid. It is a powerful desiccant.

Other names : Phosphorus (V) oxide
Phosphoric anhydride

Properties

Molecular formula	$O_{10} P_4$
Molar mass	284 g mol^{-1}
Appearance	white powder very deliquescent pungent odour
Density	2.39 g / cm^3
Melting point	$340 \text{ }^\circ\text{C}$, 613 K , $644 \text{ }^\circ\text{F}$

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Boiling point	360 °C (sublimes)
Solubility in water	exothermic hydrolysis
Vapor pressure	1 mmHg @ 384 °C

Hazards

EU classification	Not listed
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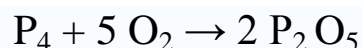
2 - Structure:

Phosphorus pentoxide crystallizes in at least four forms or polymorphs. The most familiar one, shown in the figure, comprises molecules of P_4O_{10} . Weak van der Waals forces hold these molecules together in a hexagonal lattice (However, in spite of the high symmetry of the molecules, the crystal packing is not a close packing) The structure of the P_4O_{10} cage is reminiscent of adamantane with T_d symmetry point group. It is closely related to the corresponding anhydride of phosphorous acid, P_4O_6 . The latter lacks terminal oxo groups. Its density is 2.30 g / cm³. It boils at 423 °C under atmospheric pressure; if heated more rapidly it can sublime.

The other polymorphs are polymeric, but in each case the phosphorus atoms are bound by a tetrahedron of oxygen atoms, one of which forms a terminal $P = O$ bond. The O - form (density 3.05 g/cm³, m.p. 580 °C), adopts a layered structure consisting of interconnected P_6O_6 rings, not unlike the structure adopted by certain polysilicates. A lower density phase, the so-called O' form, consists of a 3-dimensional framework is also known, density 2.72 g/cm³. The remaining polymorph is a glass or amorphous form; it can be made by fusing any of the others.

3 – Preparation:

P_2O_5 is prepared by burning elemental phosphorus with sufficient supply of air :



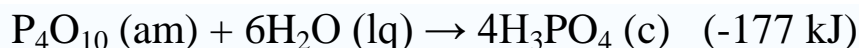
For most of the 20th century, phosphorus pentoxide was used to provide a supply of concentrated pure phosphoric acid. In the thermal process, the phosphorus pentoxide obtained by burning white

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phosphorus was dissolved in dilute phosphoric acid to produce concentrated acid. Improvements in filter technology is leading to the "wet phosphoric acid process" taking over from the thermal process, obviating the need to produce white phosphorus as a starting material. The dehydration of phosphoric acid to give phosphorus pentoxide is not practicable; on heating, metaphosphoric acid will decompose before it loses water.

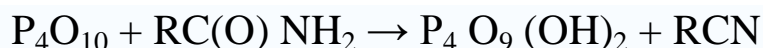
4 - Applications:

Phosphorus pentoxide is a potent dehydrating agent as indicated by the exothermic nature of its hydrolysis:



However, its utility for drying is limited somewhat by its tendency to form a protective viscous coating that inhibits further dehydration by unspent material. A granular form of P_4O_{10} is used in desiccators.

Consistent with its strong desiccating power, P_4O_{10} is used in organic synthesis for dehydration. The most important application is for the conversion of amides into nitriles:



The indicated coproduct $\text{P}_4\text{O}_9(\text{OH})_2$ is an idealized formula for undefined products resulting from the hydration of P_4O_{10} .

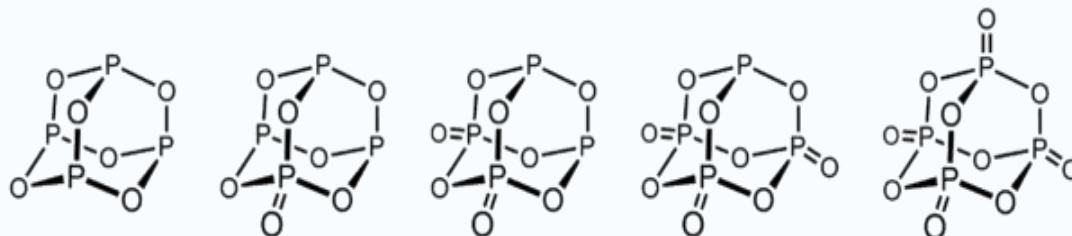
Supposedly, when combined with a carboxylic acid, the result is the corresponding anhydride :



The "Onodera reagent", a solution of P_4O_{10} in DMSO, is employed for the oxidation of alcohols. This reaction is reminiscent of the Swern oxidation. The desiccating power of P_4O_{10} is strong enough to convert many mineral acids to their anhydrides. Examples: HNO_3 is converted to N_2O_5 ; H_2SO_4 is converted to SO_3 ; HClO_4 is converted to Cl_2O_7 .

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**5 - Related phosphorus oxides**

Between the commercially important P_4O_6 and P_4O_{10} , phosphorus oxides are known with intermediate structures:

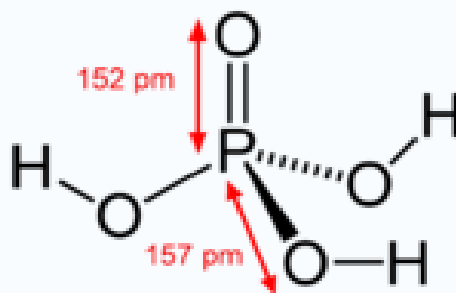
**6 - Hazards:**

Non - flammable. Reacts vigorously with water and water - containing substances like wood or cotton, liberates much heat and may even cause fire. Corrosive to metal. Very irritating. May cause severe burn to the eye, skin, mucous membrane, and respiratory tract even at as low as $1\text{mg} / \text{cm}^3$.

Fire fighting measures: Wear full protective gear. Do NOT use water directly on fire. Use dry chemical, carbon dioxide, or alcohol-resistant foam.

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Phosphoric acid



Contents :

- 1 Introduction
- 2 Ortho phosphoric acid chemistry
 - 2.1 pH and composition of a phosphoric acid aqueous solution
- 3 Chemical reagent
 - 3.1 Preparation of hydrogen halides
 - 3.2 Rust removal
 - 3.3 Processed food use
 - 3.3.1 Biological effects on bone calcium and kidney health
 - 3.4 Medical use
- 4 Preparation
 - 4.1 Thermal phosphoric acid
 - 4.2 Wet phosphoric acid
 - 4.3 Kiln Phosphoric Acid
- 5 Other applications

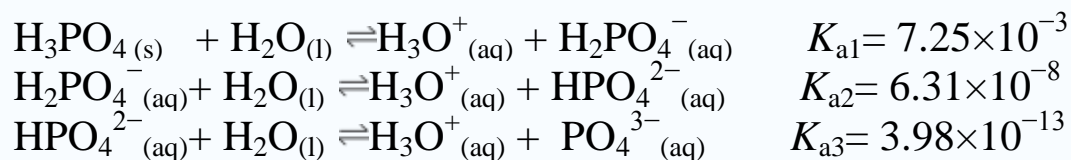
1 –Introduction :

Phosphoric acid, also known as **orthophosphoric acid** or **phosphoric(V) acid**, is a mineral (inorganic) acid having the chemical formula H_3PO_4 . Orthophosphoric acid molecules can combine with themselves to form a variety of compounds which are also referred to as **phosphoric acids**, but in a more general way. The term *phosphoric acid* can also refer to a chemical or reagent consisting of phosphoric acids, usually orthophosphoric acid.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**2 - Ortho phosphoric acid chemistry:**

Pure anhydrous phosphoric acid is a white solid that melts at 42.35 °C to form a colorless, viscous liquid.

Most people and even chemists refer to orthophosphoric acid as *phosphoric acid*, which is the IUPAC name for this compound. The prefix *ortho* is used to distinguish the acid from other phosphoric acids, called polyphosphoric acids. Orthophosphoric acid is a non-toxic, inorganic, rather weak triprotic acid, which, when pure, is a solid at room temperature and pressure. The chemical structure of ortho phosphoric acid is shown above in the data table. Ortho phosphoric acid is a very polar molecule; therefore it is highly soluble in water. The oxidation state of phosphorus (P) in ortho - and other phosphoric acids is +5; the oxidation state of all the oxygen atoms (O) is -2 and all the hydrogen atoms (H) is +1. Triprotic means that an orthophosphoric acid molecule can dissociate up to three times, giving up an H⁺ each time, which typically combines with a water molecule, H₂O, as shown in these reactions:



The anion after the first dissociation, H₂PO₄⁻, is the *dihydrogen phosphate* anion. The anion after the second dissociation, HPO₄²⁻, is the *hydrogen phosphate* anion. The anion after the third dissociation, PO₄³⁻, is the **phosphate** or **ortho phosphate** anion. For each of the dissociation reactions shown above, there is a separate acid dissociation constant, called K_{a1}, K_{a2}, and K_{a3} given at 25 °C. Associated with these three dissociation constants are corresponding pK_{a1}=2.12 , pK_{a2}=7.21 , and pK_{a3}=12.67 values at 25 °C. Even though all three hydrogen (H) atoms are equivalent on an orthophosphoric acid molecule, the successive K_a values differ since it is energetically less favorable to lose another H⁺ if one (or more) has already been lost and the molecule/ion is more negatively - charged.

Because the triprotic dissociation of orthophosphoric acid, the fact that its conjugate bases (the phosphates mentioned above) cover a

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wide pH range, and, because phosphoric acid/phosphate solutions are, in general, non - toxic, mixtures of these types of phosphates are often used as buffering agents or to make buffer solutions, where the desired pH depends on the proportions of the phosphates in the mixtures. Similarly, the non-toxic, anion salts of triprotic organic citric acid are also often used to make buffers. Phosphates are found pervasively in biology, especially in the compounds derived from phosphorylated sugars, such as DNA, RNA, and adenosine triphosphate (ATP). There is a separate article on phosphate as an anion or its salts.

Upon heating orthophosphoric acid, condensation of the phosphoric units can be induced by driving off the water formed from condensation. When one molecule of water has been removed for each two molecules of phosphoric acid, the result is pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$). When an average of one molecule of water per phosphoric unit has been driven off, the resulting substance is a glassy solid having an empirical formula of **HPO_3** and is called **meta phosphoric acid**.^[1] Metaphosphoric acid is a singly anhydrous version of orthophosphoric acid and is sometimes used as a water- or moisture-absorbing reagent. Further dehydrating is very difficult, and can be accomplished only by means of an extremely strong desiccant (and not by heating alone). It produces *phosphoric anhydride*, which has an empirical formula P_2O_5 , although an actual molecule has a chemical formula of P_4O_{10} . Phosphoric anhydride is a solid, which is very strongly moisture - absorbing and is used as a desiccant.

2 – 1 - pH and composition of a phosphoric acid aqueous solution:

For a given total acid concentration $[\text{A}] = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$ ($[\text{A}]$ is the total number of moles of pure H_3PO_4 which have been used to prepare 1 liter of solution), the composition of an aqueous solution of phosphoric acid can be calculated using the equilibrium equations associated with the three reactions described above together with the $[\text{H}^+][\text{OH}^-] = 10^{-14}$ relation and the electrical neutrality equation. Possible concentrations of polyphosphoric molecules and ions is neglected. The system may be reduced to a fifth degree equation for $[\text{H}^+]$ which can be solved numerically, yielding:

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[A] (mol/L)	pH	[H ₃ PO ₄]/[A] (%)	[H ₂ PO ₄ ⁻]/[A] (%)	[HPO ₄ ²⁻]/[A] (%)	[PO ₄ ³⁻]/[A] (%)
1	1.08	91.7	8.29	6.20×10 ⁻⁶	1.60×10 ⁻¹⁷
10 ⁻¹	1.62	76.1	23.9	6.20×10 ⁻⁵	5.55×10 ⁻¹⁶
10 ⁻²	2.25	43.1	56.9	6.20×10 ⁻⁴	2.33×10 ⁻¹⁴
10 ⁻³	3.05	10.6	89.3	6.20×10 ⁻³	1.48×10 ⁻¹²
10 ⁻⁴	4.01	1.30	98.6	6.19×10 ⁻²	1.34×10 ⁻¹⁰
10 ⁻⁵	5.00	0.133	99.3	0.612	1.30×10 ⁻⁸
10 ⁻⁶	5.97	1.34×10 ⁻²	94.5	5.50	1.11×10 ⁻⁶
10 ⁻⁷	6.74	1.80×10 ⁻³	74.5	25.5	3.02×10 ⁻⁵
10 ⁻¹⁰	7.00	8.24×10 ⁻⁴	61.7	38.3	8.18×10 ⁻⁵

For large acid concentrations, the solution is mainly composed of H₃PO₄. For [A] = 10⁻², the pH is closed to pK_{a1}, giving an equimolar mixture of H₃PO₄ and H₂PO₄⁻. For [A] below 10⁻³, the solution is mainly composed of H₂PO₄⁻ with [HPO₄²⁻] becoming non negligible for very dilute solutions. [PO₄³⁻] is always negligible.

3 - Chemical reagent:

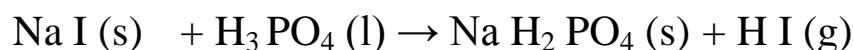
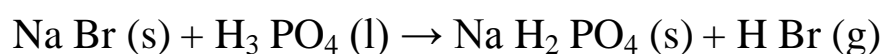
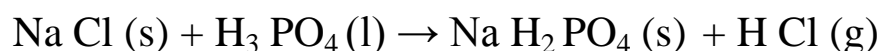
Pure 75 – 85 % aqueous solutions (the most common) are clear, colourless, odourless, non - volatile, rather viscous, syrupy liquids, but still pourable. Phosphoric acid is very commonly used as an aqueous solution of 85 % phosphoric acid or H₃PO₄. Because it is a concentrated acid, an 85 % solution can be corrosive, although nontoxic when diluted. Because of the high percentage of phosphoric acid in this reagent, at least some of the orthophosphoric acid is condensed into polyphosphoric acids in a temperature-dependent equilibrium, but, for the sake of labeling and simplicity, the 85% represents H₃PO₄ as if it were all orthophosphoric acid. Other percentages are possible too, even above 100 %, where the phosphoric acids and water would be in an unspecified equilibrium, but the overall elemental mole content would be considered specified. When aqueous solutions of phosphoric acid and / or phosphate are dilute,

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they are in or will reach an equilibrium after a while where practically all the phosphoric / phosphate units are in the ortho - form.

3 – 1 - Preparation of hydrogen halides :

Phosphoric acid reacts with halides to form the corresponding hydrogen halide gas (steamy fumes are observed on warming the reaction mixture). This is a common practice for the laboratory preparation of hydrogen halides.

**3 – 2 - Rust removal:**

Phosphoric acid may be used as a "rust converter", by direct application to rusted iron, steel tools, or surfaces. The phosphoric acid converts reddish - brown iron (III) oxide (rust) to black ferric phosphate , Fe PO_4 .

"Rust converter" is sometimes a greenish liquid suitable for dipping (in the same sort of acid bath as is used for pickling metal), but it is more often formulated as a gel, commonly called **naval jelly**. It is sometimes sold under other names, such as "rust remover" or "rust killer". As a thick gel, it may be applied to sloping, vertical, or even overhead surfaces.

After treatment, the black ferric - phosphate coating can be scrubbed off, leaving a fresh metal surface. Multiple applications of phosphoric acid may be required to remove all rust. The black phosphate coating can also be left in place, where it will provide moderate further corrosion resistance. (Such protection is also provided by the superficially similar Parkerizing and blued electrochemical conversion coating processes.)

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Food - grade phosphoric acid (additive E338) is used to acidify foods and beverages such as various colas, but not without controversy regarding its health effects. It provides a tangy or sour taste and, being a mass - produced chemical, is available cheaply and in large quantities. The low cost and bulk availability is unlike more expensive seasonings that give comparable flavors, such as citric acid which is obtainable from lemons and limes. (However most citric acid in the food industry is not extracted from citrus fruit, but fermented by *Aspergillus niger* mold from scrap molasses, waste starch hydrolysates and phosphoric acid).

3 - 3 - 1 - Biological effects on bone calcium and kidney health:

Phosphoric acid, used in many soft drinks (primarily cola), has been linked to lower bone density in epidemiological studies. For example, a study using dual - energy X - ray absorptiometry rather than a questionnaire about breakage, provides reasonable evidence to support the theory that drinking cola results in lower bone density. This study was published in the American Journal of Clinical Nutrition. A total of 1672 women and 1148 men were studied between 1996 and 2001. Dietary information was collected using a food frequency questionnaire that had specific questions about the number of servings of cola and other carbonated beverages and that also made a differentiation between regular, caffeine-free, and diet drinks. The paper cites significant statistical evidence to show that women who consume cola daily have lower bone density. Total phosphorus intake was not significantly higher in daily cola consumers than in nonconsumers; however, the calcium - to - phosphorus ratios were lower. The study also suggests that further research is needed to confirm the findings.

On the other hand, a study funded by Pepsi suggests that insufficient intake of phosphorus leads to lower bone density. The study does not examine the effect of phosphoric acid, which binds with magnesium and calcium in the digestive tract to form salts that are not absorbed, but rather studies general phosphorus intake. However, a well - controlled clinical study by Heaney and Rafferty

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using calcium - balance methods found no impact of carbonated soft drinks containing phosphoric acid on calcium excretion. The study compared the impact of water, milk, and various soft drinks (two with caffeine and two without; two with phosphoric acid and two with citric acid) on the calcium balance of 20 - to 40 - year - old women who customarily consumed ~3 or more cups (680 ml) of a carbonated soft drink per day. They found that, relative to water, only milk and the two caffeine - containing soft drinks increased urinary calcium, and that the calcium loss associated with the caffeinated soft drink consumption was about equal to that previously found for caffeine alone. Phosphoric acid without caffeine had no impact on urine calcium, nor did it augment the urinary calcium loss related to caffeine. Because studies have shown that the effect of caffeine is compensated for by reduced calcium losses later in the day,^[5] Heaney and Rafferty concluded that the net effect of carbonated beverages—including those with caffeine and phosphoric acid - is negligible, and that the skeletal effects of carbonated soft drink consumption are likely due primarily to milk displacement.

Other chemicals such as caffeine (also a significant component of popular common cola drinks) were also suspected as possible contributors to low bone density, due to the known effect of caffeine on calciuria. One other study, involving 30 women over the course of a week, suggests that phosphoric acid in colas has no such effect, and postulates that caffeine has only a temporary effect, which is later reversed. The authors of this study conclude that the skeletal effects of carbonated beverage consumption are likely due primarily to milk displacement. (Another possible confounding factor may be an association between high soft drink consumption and sedentary lifestyle.)

Cola consumption has also been associated with chronic kidney disease and kidney stones through medical research.^[6] The preliminary results suggest that cola consumption may increase the risk of chronic kidney disease.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**3 – 4 - Medical use:**

Phosphoric acid is used in dentistry and orthodontics as an etching solution, to clean and roughen the surfaces of teeth where dental appliances or fillings will be placed. Phosphoric acid is also an ingredient in over-the-counter anti-nausea medications that also contain high levels of sugar (glucose and fructose). This acid is also used in many teeth whiteners to eliminate plaque that may be on the teeth before application.

4 – Preparation:

Phosphoric acid can be prepared by three routes - the Thermal Process, the Wet Process and the dry Kiln Process.

4 – 1 - Thermal phosphoric acid:

This very pure phosphoric acid is obtained by burning elemental phosphorus to produce phosphorus pentoxide and dissolving the product in dilute phosphoric acid. This produces a very pure phosphoric acid, since most impurities present in the rock have been removed when extracting phosphorus from the rock in a furnace. The end result is food-grade, thermal phosphoric acid; however, for critical applications, additional processing to remove arsenic compounds may be needed.

4 – 2 - Wet phosphoric acid:

Wet process phosphoric acid is prepared by adding sulfuric acid to tricalcium phosphate rock.

The simplified reaction is:



Wet-process acid can be purified by removing fluorine to produce animal-grade phosphoric acid, or by solvent extraction and arsenic removal to produce food-grade phosphoric acid.

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Kiln phosphoric acid (KPA) process technology is the most recent technology. Called the “Improved Hard Process”, this technology will both make low grade phosphate rock reserves commercially viable and will increase the P_2O_5 recovery from existing phosphate reserves. This may significantly extend the commercial viability of phosphate reserves.

5 - Other applications

- Phosphoric acid is used as the electrolyte in phosphoric-acid fuel cells. It is also used as an external standard for phosphorus - 31 Nuclear magnetic resonance (NMR).
- Phosphoric acid is used as a cleaner by construction trades to remove mineral deposits, cementitious smears, and hard water stains. It is also used as a chelant in some household cleaners aimed at similar cleaning tasks.
- Hot phosphoric acid is used in microfabrication to etch silicon nitride (Si_3N_4). It is highly selective in etching Si_3N_4 instead of SiO_2 , silicon dioxide.
- Phosphoric acid is used as a flux by hobbyists (such as model railroaders) as an aid to soldering.
- Phosphoric acid is also used in hydroponics pH solutions to lower the pH of nutrient solutions. While other types of acids can be used, phosphorus is a nutrient used by plants, especially during flowering, making phosphoric acid particularly desirable. General Hydroponics pH Down liquid solution contains phosphoric acid in addition to citric acid and ammonium bisulfate with buffers to maintain a stable pH in the nutrient reservoir.
- Phosphoric acid is used as an electrolyte in copper electropolishing for burr removal and circuit board planarization.
- Phosphoric acid is used as a pH adjuster in cosmetics and skin-care products.
- Phosphoric acid is used as a chemical oxidizing agent for activated carbon production.

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- Phosphoric acid is also used for High Performance Liquid Chromatography.
- Phosphoric acid can be used as an additive to stabilize acidic aqueous solutions within a wanted and specified pH range
- Phosphoric acid is the key ingredient that gives the bite taste in widely consumed Coca - Cola and Pepsi sodas.

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Phospho Gypsum

1 – Introduction :

Phospho Gypsum refers to the gypsum formed as a by - product of processing phosphate ore into fertilizer with sulfuric acid.

Phosphogypsum is produced from the fabrication of phosphoric acid by reacting phosphate (apatite) with sulfuric acid according to the following reaction :



Phospho gypsum is radioactive due to the presence of naturally occurring uranium and radium in the phosphate ore.

Marine - deposited phosphate typically has a higher level of radioactivity than igneous phosphate deposits, because uranium is present in seawater.^[1]

2 - In the United States:



Phospho gypsum stack located near Fort Meade, Florida. These contain the waste by - products of the phosphate fertilizer industry.

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The United States Environmental Protection Agency has banned most applications of phospho gypsum with a radium - 226 concentration of greater than 10 picocuries / gram (pCi / g) . As a result, phosphogypsum which exceeds this limit is stored in large stacks.

Florida has a large quantity of phosphate deposits, particularly in Bone Valley region. However, the marine-deposited phosphate ore from central Florida is highly radioactive, and as such, the phospho gypsum by - product is too radioactive to be used for most applications. As a result, there are about 1 billion tons of phospho gypsum stacked in 25 stacks in Florida (22 are in central Florida) and about 30 million new tons are generated each year.

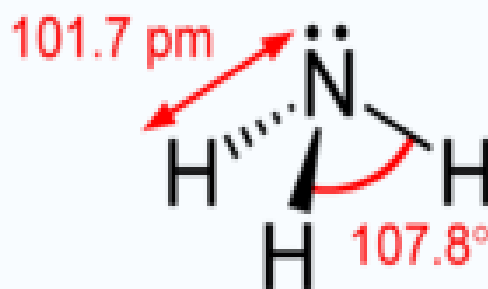
Various applications have been proposed for using phospho gypsum, including using it as material for:

- Road pavement
- Soil conditioner
- Cover for landfills
- Roof tiles
- Artificial reefs & oyster beds

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FERTILIZERS ALKALIZER

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ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**Ammonia****Contents:**

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1- Introduction :

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3 . It is normally encountered as a gas with a characteristic pungent odour. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to foodstuffs and fertilizers. Ammonia, either directly or indirectly, is also a building block for the synthesis of many pharmaceuticals. Although in wide use, ammonia is both caustic and hazardous. In 2006, worldwide production was estimated at 146.5 million tons. It is used in commercial cleaning products.

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Ammonia, as used commercially, is often called *anhydrous ammonia*. This term emphasizes the absence of water in the material. Because NH_3 boils at $-33.34\text{ }^\circ\text{C}$, the liquid must be stored under high pressure or at low temperature. Its heat of vapourization is, however, sufficiently high so that NH_3 can be readily handled in ordinary beakers, in a fume hood (i.e., if it is already a liquid it will not boil readily). "Household ammonia" or "ammonium hydroxide" is a solution of NH_3 in water. The strength of such solutions is measured in units of baume (density), with 26 degrees baume (about 30 weight percent ammonia at $15.5\text{ }^\circ\text{C}$) being the typical high concentration commercial product. Household ammonia ranges in concentration from 5 to 10 weight percent ammonia.

IUPAC Name : Ammonia , Azane

Other Names : Ammonia,

Hydrogen nitride ,

Spirit of Hartshorn ,

Nitro – Sil

Properties	
Molecular formula	NH_3
Molar mass	17 g / mol
Appearance	Colorless gas with strong pungent odour
	0.86 kg / m^3 (1.013 bar at boiling point)
	0.73 kg / m^3 (1.013 bar at $15\text{ }^\circ\text{C}$)
Density	681.9 kg / m^3 at $-33.3\text{ }^\circ\text{C}$ (liquid)
	817 kg / m^3 at $-80\text{ }^\circ\text{C}$ (trans parent solid)
Melting point	$-77.73\text{ }^\circ\text{C}$
Boiling point	$-33.34\text{ }^\circ\text{C}$
	47 % (0 $^\circ\text{C}$)
Solubility in water	31 % (25 $^\circ\text{C}$)
	28 % (50 $^\circ\text{C}$) ^[3]
	Toxic (T)
EU classification	Corrosive (C)
	Dangerous for the environment (N)

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**2 - Structure and basic chemical properties:**

The ammonia molecule has a trigonal pyramidal shape with a bond angle of 107.8° as shown above, as predicted by the valence shell electron pair repulsion theory (VSEPR). The central nitrogen atom has five outer electrons with an additional electron from each hydrogen atom. This gives a total of eight electrons, or four electron pairs which are arranged tetrahedrally. Three of these electron pairs are used as bond pairs, which leaves one lone pair of electrons. The lone pair of electrons repel more strongly than bond pairs, therefore the bond angle is not 109.5° as expected for a regular tetrahedral arrangement, but is measured at 107.8° . The nitrogen atom in the molecule has a lone electron pair, which make ammonia a base, a proton acceptor. This shape gives the molecule a dipole moment and makes it polar. The molecule's polarity and, especially, its ability to form hydrogen bonds, makes ammonia highly miscible with water. Ammonia is moderately basic, a 1.0 M aqueous solution has a pH of 11.6 and if a strong acid is added to such a solution until the solution is neutral (pH = 7), 99.4 % of the ammonia molecules are protonated. Temperature and salinity also affect the proportion of NH_4^+ . NH_4^+ has the shape of a regular tetrahedron and is isoelectronic with methane.

2 – 1 - Natural occurrence:

Ammonia is found in trace quantities in the atmosphere, being produced from the putrefaction of nitrogenous animal and vegetable matter. Ammonia and ammonium salts are also found in small quantities in rainwater, whereas ammonium chloride (sal-ammoniac), and ammonium sulfate are found in volcanic districts; crystals of ammonium bicarbonate have been found in Patagonian guano. The kidneys secrete NH_3 to neutralize excess acid. Ammonium salts also are found distributed through all fertile soil and in seawater. Substances containing ammonia, or those that are similar to it, are called *ammoniacal*.

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The Romans called the ammonium chloride deposits they collected from near the Temple of Jupiter Amun (Greek *Ammon*) in ancient Libya 'sal ammoniacus' (salt of Amun) because of proximity to the nearby temple. Salts of ammonia have been known from very early times; thus the term *Hammoniacus sal* appears in the writings of Pliny, although it is not known whether the term is identical with the more modern *sal - ammoniac*.

In the form of sal-ammoniac (nushadir), ammonia was known to the Muslim alchemists as early as the 8th century, first mentioned by Geber (Jabir ibn Hayyan) iranian chemist , and to the European alchemists since the 13th century, being mentioned by Albertus Magnus. It was also used by dyers in the Middle Ages in the form of fermented urine to alter the colour of vegetable dyes. In the 15th century, Basilius Valentinus showed that ammonia could be obtained by the action of alkalis on sal - ammoniac. At a later period, when sal-ammoniac was obtained by distilling the hooves and horns of oxen and neutralizing the resulting carbonate with hydrochloric acid, the name "spirit of hartshorn" was applied to ammonia.

Gaseous ammonia was first isolated by Joseph Priestley in 1774 and was termed by him *alkaline air*; however it was acquired by the alchemist Basil Valentine. Eleven years later in 1785, Claude Louis Berthollet ascertained its composition.

The Haber process to produce ammonia from the nitrogen in the air was developed by Fritz Haber and Carl Bosch in 1909 and patented in 1910. It was first used on an industrial scale by the Germans during World War I , following the allied blockade that cut off the supply of nitrates from Chile. The ammonia was used to produce explosives to sustain their war effort.

Prior to the advent of cheap natural gas, hydrogen as a precursor to ammonia production was produced via the electrolysis of water or using the chloralkali process. The Vemork 60 MW hydroelectric plant in Norway, constructed in 1911, was used purely for plants using the Birkeland - Eyde process .

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**4 - Synthesis and production:**

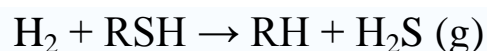
Production trend of ammonia between 1947 and 2007

Because of its many uses, ammonia is one of the most highly produced inorganic chemicals. Dozens of chemical plants worldwide produce ammonia. The worldwide ammonia production in 2004 was 109 million metric tonnes. The People's Republic of China produced 28.4 % of the worldwide production (increasingly from coal as part of urea synthesis)^[14] followed by India with 8.6 %, Russia with 8.4 %, and the United States with 8.2 %. About 80 % or more of the ammonia produced is used for fertilizing agricultural crops.

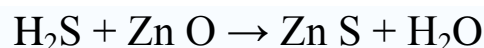
Before the start of World War I, most ammonia was obtained by the dry distillation of nitrogenous vegetable and animal waste products, including camel dung, where it was distilled by the reduction of nitrous acid and nitrites with hydrogen; in addition, it was produced by the distillation of coal, and also by the decomposition of ammonium salts by alkaline hydroxides such as quicklime, the salt most generally used being the chloride (samarmoniac) thus:



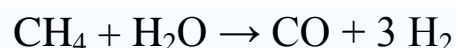
Today, the typical modern ammonia-producing plant first converts natural gas (i.e., methane) or liquefied petroleum gas (such gases are propane and butane) or petroleum naphtha into gaseous hydrogen. The process used in producing the hydrogen begins with removal of sulfur compounds from the natural gas (because sulfur deactivates the catalysts used in subsequent steps). Catalytic hydrogenation converts organosulfur compounds into gaseous hydrogen sulfide:

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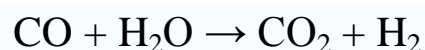
The hydrogen sulfide is then removed by passing the gas through beds of zinc oxide where it is adsorbed and converted to solid zinc sulfide :



Catalytic steam reforming of the sulfur-free feedstock is then used to form hydrogen plus carbon monoxide:

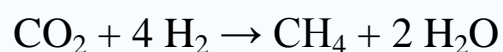


In the next step, the water gas shift reaction is used to convert the carbon monoxide into carbon dioxide and more hydrogen:

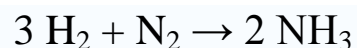


The carbon dioxide is then removed either by absorption in aqueous ethanolamine solutions or by adsorption in pressure swing adsorbers (PSA) using proprietary solid adsorption media.

The final step in producing the hydrogen is to use catalytic methanation to remove any small residual amounts of carbon monoxide or carbon dioxide from the hydrogen:



To produce the desired end - product ammonia, the hydrogen is then catalytically reacted with nitrogen (derived from process air) to form anhydrous liquid ammonia. This step is known as the ammonia synthesis loop (also referred to as the Haber-Bosch process):



Hydrogen required for ammonia synthesis could also be produced economically using other sources like coal or coke gasification, less economically from the electrolysis of water into

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oxygen + hydrogen and other alternatives which are presently impractical for large scale. At one time, most of Europe's ammonia was produced from the Hydro plant at Vemork, via the electrolysis route. Various renewable energy electricity sources are also potentially applicable.

5 - Biosynthesis:

In certain organisms, ammonia is produced from atmospheric N_2 by enzymes called nitrogenases. The overall process is called nitrogen fixation. Although it is unlikely that biomimetic methods will be developed that are competitive with the Haber process, intense effort has been directed toward understanding the mechanism of biological nitrogen fixation. The scientific interest in this problem is motivated by the unusual structure of the active site of the enzyme, which consists of an $Fe_7 Mo S_9$ ensemble.

Ammonia is also a metabolic product of amino acid deamination. Ammonia excretion is common in aquatic animals. In humans, it is quickly converted to urea, which is much less toxic. This urea is a major component of the dry weight of urine. Most reptiles, birds, as well as insects and snails solely excrete uric acid as nitrogenous waste.

6 – Properties:

Ammonia is a colourless gas with a characteristic pungent smell. It is lighter than air, its density being 0.589 times that of air. It is easily liquefied due to the strong hydrogen bonding between molecules; the liquid boils at $-33.3\text{ }^{\circ}\text{C}$, and solidifies at $-77.7\text{ }^{\circ}\text{C}$ to white crystals. The crystal symmetry is cubic, Pearson symbol cP16, space group $P2_13$ No.198, lattice constant 0.5125 nm .^[17] Liquid ammonia possesses strong ionizing powers reflecting its high ϵ of 22. Liquid ammonia has a very high standard enthalpy change of vapourization (23.35 kJ / mol , cf. water 40.65 kJ / mol , methane 8.19 kJ / mol , phosphine 14.6 kJ / mol) and can therefore be used in laboratories in non-insulated vessels without additional refrigeration.

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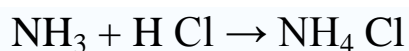
It is miscible with water. Ammonia in an aqueous solution can be expelled by boiling. The aqueous solution of ammonia is basic. The maximum concentration of ammonia in water (a saturated solution) has a density of 0.880 g / cm^3 and is often known as '880 Ammonia'. Ammonia does not burn readily or sustain combustion, except under narrow fuel - to - air mixtures of 15 - 25 % air. When mixed with oxygen, it burns with a pale yellowish-green flame. At high temperature and in the presence of a suitable catalyst, ammonia is decomposed into its constituent elements. Ignition occurs when chlorine is passed into ammonia, forming nitrogen and hydrogen chloride; if ammonia is present in excess, then the highly explosive nitrogen trichloride (N Cl_3) is also formed.

The ammonia molecule readily undergoes nitrogen inversion at room temperature; a useful analogy is an umbrella turning itself inside out in a strong wind. The energy barrier to this inversion is 24.7 kJ/mol , and the resonance frequency is 23.79 GHz , corresponding to microwave radiation of a wavelength of 1.260 cm . The absorption at this frequency was the first microwave spectrum to be observed .

Ammonia may be conveniently deodorized by reacting it with either sodium bicarbonate or acetic acid. Both of these reactions form an odorless ammonium salt.

6 – 1 - Basicity:

One of the most characteristic properties of ammonia is its basicity. It combines with acids to form salts; thus with hydrochloric acid it forms ammonium chloride (sal-ammoniac); with nitric acid, ammonium nitrate, etc. However, perfectly dry ammonia will not combine with perfectly dry hydrogen chloride: moisture is necessary to bring about the reaction.



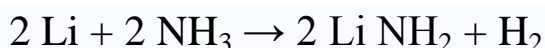
The salts produced by the action of ammonia on acids are known as the ammonium salts and all contain the ammonium ion (NH_4^+). Anhydrous ammonia is often used for the production of methamphetamine. Dilute aqueous ammonia can be applied on the

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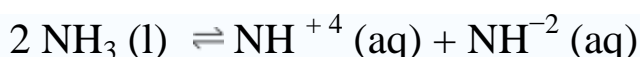
skin to lessen the effects of acidic animal poisons, such as from insects and jelly fish.

6 – 2 - Acidit:

Although ammonia is well-known as a base, it can also act as an extremely weak acid. It is a protic substance and is capable of formation of amides (which contain the NH_2^- ion), for example lithium and ammonia react to give a solution of lithium amide:

**6 – 3 - Self – dissociation:**

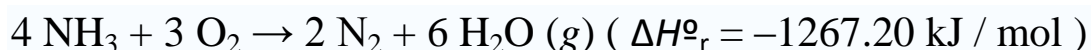
Like water, ammonia is amphoteric as it reacts with itself to form its acid and base conjugates:



At standard pressure and temperature, $[\text{NH}_4^+][\text{NH}_2^-] = 10^{-30} \text{ M}^2$.

6 – 4 - Combustion:

The combustion of ammonia to nitrogen and water is exothermic :



The standard enthalpy change of combustion, ΔH°_c , expressed per mole of ammonia and with condensation of the water formed, is – 382.81 kJ/mol. Dinitrogen is the thermodynamic product of combustion: all nitrogen oxides are unstable with respect to nitrogen and oxygen, which is the principle behind the catalytic converter. However, nitrogen oxides can be formed as kinetic products in the presence of appropriate catalysts, a reaction of great industrial importance in the production of nitric acid:



The combustion of ammonia in air is very difficult in the absence of a catalyst (such as platinum gauze), as the temperature of

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the flame is usually lower than the ignition temperature of the ammonia-air mixture. The flammable range of ammonia in air is 16 – 25 % .

6 – 5 - Formation of other compounds:

In organic chemistry, ammonia can act as a nucleophile in substitution reactions. Amines can be formed by the reaction of ammonia with alkyl halides, although the resulting – NH₂ group is also nucleophilic and secondary and tertiary amines are often formed as by - products. An excess of ammonia helps minimise multiple substitution, and neutralises the hydrogen halide formed. Methylamine is prepared commercially by the reaction of ammonia with chloromethane, and the reaction of ammonia with 2 –bromo propanoic acid has been used to prepare racemic alanine in 70 % yield. Ethanolamine is prepared by a ring - opening reaction with ethylene oxide: the reaction is sometimes allowed to go further to produce diethanolamine and triethanolamine.

Amides can be prepared by the reaction of ammonia with a number of carboxylic acid derivatives. Acyl chlorides are the most reactive, but the ammonia must be present in at least a twofold excess to neutralise the hydrogen chloride formed. Esters and anhydrides also react with ammonia to form amides. Ammonium salts of carboxylic acids can be dehydrated to amides so long as there are no thermally sensitive groups present: temperatures of 150 - 200 °C are required.

The hydrogen in ammonia is capable of replacement by metals, thus magnesium burns in the gas with the formation of magnesium nitride Mg₃ N₂ , and when the gas is passed over heated sodium or potassium, sodamide, NaNH₂, and potassamide, KNH₂ , are formed. Where necessary in substitutive nomenclature, IUPAC recommendations prefer the name **azane** to ammonia: hence chloramine would be named *chloroazane* in substitutive nomenclature, not *chloroammonia*.

Pentavalent ammonia is known as λ⁵- amine, or more commonly, ammonium hydride. This crystalline solid is only stable

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under high pressure, and decomposes back into trivalent ammonia and hydrogen gas at normal conditions. This substance was once investigated as a possible solid rocket fuel in 1966.

6 – 6 - Ammonia as a ligand:

Ammonia can act as a ligand in transition metal complexes. It is a pure σ - donor, in the middle of the spectrochemical series, and shows intermediate hard - soft behaviour. For historical reasons, ammonia is named **ammine** in the nomenclature of coordination compounds. Some notable ammine complexes include:

- **Tetra amine diaqua copper (II)** , $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, a characteristic dark blue complex formed by adding ammonia to solution of copper(II) salts. Known as Schweizer's reagent.
- **Di amine silver (I)**, $[\text{Ag}(\text{NH}_3)_2]^+$, the active species in Tollens' reagent. Formation of this complex can also help to distinguish between precipitates of the different silver halides: silver chloride (AgCl) is soluble in dilute (2M) ammonia solution, silver bromide (AgBr) is only soluble in concentrated ammonia solution while silver iodide (AgI) is insoluble in aqueous solution of ammonia.

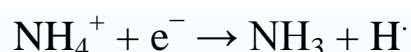
Ammine complexes of chromium (III) were known in the late 19th century, and formed the basis of Alfred Werner's theory of coordination compounds. Werner noted that only two isomers (*fac*- and *mer*-) of the complex $[\text{CrCl}_3(\text{NH}_3)_3]$ could be formed, and concluded that the ligands must be arranged around the metal ion at the vertices of an octahedron. This proposal has since been confirmed by X-ray crystallography.

An ammine ligand bound to a metal ion is markedly more acidic than a free ammonia molecule, although deprotonation in aqueous solution is still rare. One example is the Calomel reaction, where the resulting amidomercury(II) compound is highly insoluble.



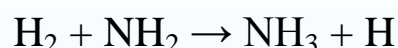
ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**7 - Inter stellar formation and destruction:****7 – 1 - Formation mechanisms:**

The interstellar abundance for ammonia has been measured for a variety of environments. The $[\text{NH}_3] / [\text{H}_2]$ ratio has been estimated to range from 10^{-7} in small dark clouds up to 10^{-5} in the dense core of the Orion Molecular Cloud Complex. Although a total of 18 total production routes have been proposed,^[24] the principal formation mechanism for interstellar NH_3 is the reaction:



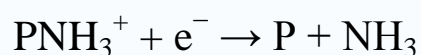
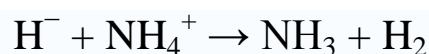
The rate constant, k , of this reaction depends on the temperature of the environment, with a value of 5.2×10^{-6} at 10 K. The rate constant was calculated from the formula $k = a(T/300)^B$. For the primary formation reaction, $a = 1.05 \times 10^{-6}$ and $B = -0.47$. Assuming an NH_4^+ abundance of 3×10^{-7} and an electron abundance of 10^{-7} typical of molecular clouds, the formation will proceed at a rate of $1.6 \times 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$ in a molecular cloud of total density 10^5 cm^{-3} .

All other proposed formation reactions have rate constants of between 2 and 13 orders of magnitude smaller, making their contribution to the abundance of ammonia relatively insignificant.^[27] As an example of the minor contribution other formation reactions play, the reaction:



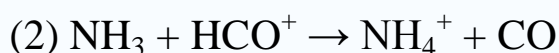
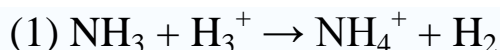
has a rate constant of 2.2×10^{-15} . Assuming H_2 densities of 10^5 and NH_2/H_2 ratio of 10^{-7} , this reaction proceeds at a rate of 2.2×10^{-12} , more than 3 orders of magnitude slower than the primary reaction above.

Some of the other possible formation reactions are:



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There are 113 total proposed reactions leading to the destruction of NH_3 . Of these, 39 were tabulated in extensive tables of the chemistry among C, N, and O compounds. A review of interstellar ammonia cites the following reactions as the principal dissociation mechanisms:



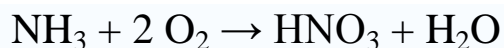
with rate constants of 4.39×10^{-9} [30] and 2.2×10^{-9} , respectively. The above equations (1,2) run at a rate of 8.8×10^{-9} and 4.4×10^{-13} , respectively. These calculations assumed the given rate constants and abundances of $[\text{NH}_3] / [\text{H}_2] = 10^{-5}$, $[\text{H}_3^+] / [\text{H}_2] = 2 \times 10^{-5}$, $[\text{HCO}^+] / [\text{H}_2] = 2 \times 10^{-9}$, and total densities of $n = 10^5$, typical of cold, dense, molecular clouds. Clearly, between these two primary reactions, equation (1) is the dominant destruction reaction, with a rate ~10,000 times faster than equation (2). This is due to the relatively high abundance of H_3^+ .

8 - Uses:**8 – 1 - Fertilizer:**

Approximately 83 % (as of 2003) of ammonia is used as fertilizers either as its salts or as solutions. Consuming more than 1% of all man-made power, the production of ammonia is a significant component of the world energy budget.

8 – 2 - Precursor to nitrogenous compounds:

Ammonia is directly or indirectly the precursor to most nitrogen-containing compounds. Virtually all synthetic nitrogen compounds are derived from ammonia. An important derivative is nitric acid. This key material is generated via the Ostwald process by oxidation of ammonia with air over a platinum catalyst at 700 - 850 °C, ~9 atm. Nitric oxide is an intermediate in this conversion:

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Nitric acid is used for the production of fertilizers, explosives, and many organonitrogen compounds.

8 – 3 - Cleaner:

House hold ammonia is a solution of NH_3 in water (i.e., ammonium hydroxide) used as a general purpose cleaner for many surfaces. Because ammonia results in a relatively streak-free shine, one of its most common uses is to clean glass, porcelain and stainless steel. It is also frequently used for cleaning ovens and soaking items to loosen baked-on or caked - on grime. Household ammonia ranges in concentration from 5 to 10 weight percent ammonia.

8 – 4 - Minor and emerging uses:***8 – 4 -1- Refrigeration - R717:***

Because of its favorable vaporization properties, ammonia is an attractive refrigerant. It was commonly used prior to the popularization of chlorofluorocarbons (Freons). Anhydrous ammonia is widely used in industrial refrigeration applications because of its high energy efficiency and low cost. Ammonia is used less frequently in commercial applications, such as in grocery store freezer cases and refrigerated displays due to its toxicity.

8 – 4 - 2 - For remediation of gaseous emissions

Ammonia is used to scrub SO_2 from the burning of fossil fuels, and the resulting product is converted to ammonium sulfate for use as fertilizer. Ammonia neutralizes the nitrogen oxides (NO_x) pollutants emitted by diesel engines. This technology, called SCR (selective catalytic reduction), relies on a vanadia-based catalyst.

8 – 4 - 3 - As a fuel

Ammonia was used during World War II to power buses in Belgium, and in engine and solar energy applications prior to 1900.

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Liquid ammonia was used as the fuel of the rocket airplane, the X-15. Although not as powerful as other fuels, it left no soot in the reusable rocket engine and its density approximately matches the density of the oxidizer, liquid oxygen, which simplified the aircraft's design.

8 – 4 - 4- Anti microbial agent for food products

As early as in 1895 it was known that ammonia was "strongly antiseptic it requires 1.4 grams per litre to preserve beef tea." Anhydrous ammonia has been shown effective as an antimicrobial agent for animal feed and is currently used commercially to reduce or eliminate microbial contamination of beef. The New York Times reported in October, 2009 on an American company, Beef Products Inc., which turns fatty beef trimmings, averaging between 50 and 70 percent fat, into seven million pounds per week of lean finely textured beef by removing the fat using heat and centrifugation, then disinfecting the lean product with ammonia; the process was rated by the US Department of Agriculture as effective and safe on the basis of a study (financed by Beef Products) which found that the treatment reduces E. coli to undetectable levels. Further investigation by The New York Times published in December, 2009 revealed safety concerns about the process as well as consumer complaints about the taste and smell of beef treated at optimal levels of ammonia.

8 – 4 – 5 - As a Sports Stimulant:

Ammonia has found significant use in various sports - particularly the strength sports of Powerlifting and Olympic Weightlifting as a respiratory stimulant.

8 - 5 - As a vehicle fuel;

Ammonia has been proposed as a practical alternative to fossil fuel for internal combustion engines. The calorific value of ammonia is 22.5 MJ / kg which is about half that of diesel. In a normal engine, in which the water vapour is not condensed, the calorific value of ammonia will be about 21 % less than this figure. It can be used in existing engines with only minor modifications to carburettors / injectors.

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To meet these demands, significant capital would be required to increase present production levels. Although the second most produced chemical, the scale of ammonia production is a small fraction of world petroleum usage. It could be manufactured from renewable energy sources, as well as coal or nuclear power. It is however significantly less efficient than batteries. The 60 MW Rjukan dam in Telemark, Norway produced ammonia via electrolysis of water for many years from 1913 producing fertilizer for much of Europe. If produced from coal, the CO₂ can be readily sequestered. (the combustion products are nitrogen and water). In 1981 a Canadian company converted a 1981 Chevrolet Impala to operate using ammonia as fuel.

8 – 5 – 1 – Textile :

Liquid ammonia is used for treatment of cotton materials, give a properties like mercerisation using alkalies. In particula, it is used for pre-washing of wool.

8 – 5 – 2 - Lifting gas:

At standard temperature and pressure ammonia is lighter than air, and has approximately 60 % of the lifting power of hydrogen or helium. Ammonia has sometimes been used to fill weather balloons as a lifting gas. Due to its relatively high boiling point (compared to helium and hydrogen), ammonia could potentially be refrigerated and liquefied aboard an airship to reduce lift and add ballast (and returned to a gas to add lift and reduce ballast).

8 -5 – 3 - Wood working:

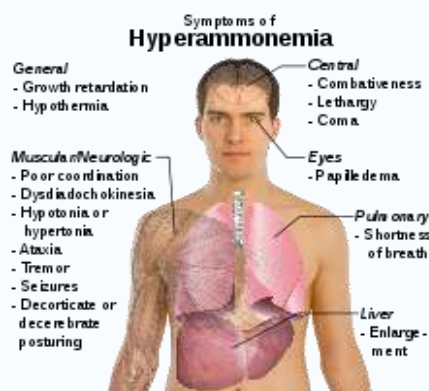
Ammonia was historically used to darken quarter sawn white oak in Arts & Crafts and Mission style furniture. Ammonia fumes react with the natural tannins in the wood and cause it to change colors.

9 - Ammonia's role in biological systems and human disease

Ammonia is an important source of nitrogen for living systems. Although atmospheric nitrogen abounds, few living creatures are

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capable of using this nitrogen. Nitrogen is required for the synthesis of amino acids, which are the building blocks of protein. Some plants rely on ammonia and other nitrogenous wastes incorporated into the soil by decaying matter. Others, such as nitrogen - fixing legumes, benefit from symbiotic relationships with rhizobia which create ammonia from atmospheric nitrogen.



Main symptoms of hyper ammonemia (ammonia reaching toxic concentrations).

Ammonia also plays a role in both normal and abnormal animal physiology. Ammonia is biosynthesised through normal amino acid metabolism and is toxic in high concentrations.^[50] The liver converts ammonia to urea through a series of reactions known as the urea cycle. Liver dysfunction, such as that seen in cirrhosis, may lead to elevated amounts of ammonia in the blood (hyper ammonemia). Likewise, defects in the enzymes responsible for the urea cycle, such as ornithine trans carbamylase, lead to hyper ammonemia. Hyper ammonemia contributes to the confusion and coma of hepatic encephalopathy as well as the neurologic disease common in people with urea cycle defects and organic acidurias.

Ammonia is important for normal animal acid/base balance. After formation of ammonium from glutamine, α - ketoglutarate may be degraded to produce two molecules of bicarbonate, which are then available as buffers for dietary acids. Ammonium is excreted in the urine, resulting in net acid loss. Ammonia may itself diffuse across

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the renal tubules, combine with a hydrogen ion, and thus allow for further acid excretion.

9 – 1 - Excretion:

Ammonium ions are a toxic waste product of the metabolism in animals. In fish and aquatic invertebrates, it is excreted directly into the water. In mammals, sharks, and amphibians, it is converted in the urea cycle to urea, because it is less toxic and can be stored more efficiently. In birds, reptiles, and terrestrial snails, metabolic ammonium is converted into uric acid, which is solid, and can therefore be excreted with minimal water loss.

10 - Liquid ammonia as a solvent:

Liquid ammonia is the best-known and most widely studied non-aqueous ionising solvent. Its most conspicuous property is its ability to dissolve alkali metals to form highly coloured, electrically conducting solutions containing solvated electrons. Apart from these remarkable solutions, much of the chemistry in liquid ammonia can be classified by analogy with related reactions in aqueous solutions. Comparison of the physical properties of NH_3 with those of water shows that NH_3 has the lower melting point, boiling point, density, viscosity, dielectric constant and electrical conductivity; this is due at least in part to the weaker H bonding in NH_3 and the fact that such bonding cannot form cross - linked networks since each NH_3 molecule has only 1 lone - pair of electrons compared with 2 for each H_2O molecule. The ionic self-dissociation constant of liquid NH_3 at $-50\text{ }^\circ\text{C}$ is about $10^{-33}\text{ mol}^2\cdot\text{L}^{-2}$.

10 – 1 - Solubility of salts:

	Solubility (g of salt per 100 g liquid NH_3)
Ammonium acetate	253.2
Ammonium nitrate	389.6
Lithium nitrate	243.7
Sodium nitrate	97.6
Potassium nitrate	10.4

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Sodium fluoride	0.35
Sodium chloride	3.0
Sodium bromide	138.0
Sodium iodide	161.9
Sodium thiocyanate	205.5

Liquid ammonia is an ionising solvent, although less so than water, and dissolves a range of ionic compounds including many nitrates, nitrites, cyanides and thiocyanates. Most ammonium salts are soluble, and these salts act as acids in liquid ammonia solutions. The solubility of halide salts increases from fluoride to iodide. A saturated solution of ammonium nitrate contains 0.83 mol solute per mole of ammonia, and has a vapour pressure of less than 1 bar even at 25 °C .

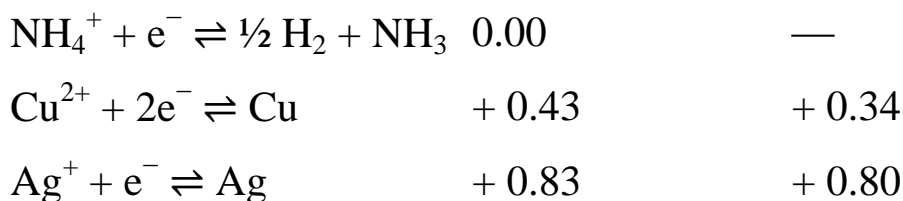
10 – 2 - Solutions of metals:

Liquid ammonia will dissolve the alkali metals and other electro positive metals such as calcium, strontium, barium, europium and ytterbium. At low concentrations (< 0.06 mol / L), deep blue solutions are formed: these contain metal cations and solvated electrons, free electrons which are surrounded by a cage of ammonia molecules.

These solutions are very useful as strong reducing agents. At higher concentrations, the solutions are metallic in appearance and in electrical conductivity. At low temperatures, the two types of solution can coexist as immiscible phases.

10 – 3 - Redox properties of liquid ammonia:

	E° (V, ammonia)	E° (V, water)
$\text{Li}^{+} + \text{e}^{-} \rightleftharpoons \text{Li}$	-2.24	-3.04
$\text{K}^{+} + \text{e}^{-} \rightleftharpoons \text{K}$	-1.98	-2.93
$\text{Na}^{+} + \text{e}^{-} \rightleftharpoons \text{Na}$	-1.85	-2.71
$\text{Zn}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Zn}$	-0.53	-0.76

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The range of thermodynamic stability of liquid ammonia solutions is very narrow, as the potential for oxidation to dinitrogen, $E^\circ (\text{N}_2 + 6\text{NH}_4^+ + 6\text{e}^- \rightleftharpoons 8\text{NH}_3)$, is only +0.04 V. In practice, both oxidation to dinitrogen and reduction to dihydrogen are slow. This is particularly true of reducing solutions: the solutions of the alkali metals mentioned above are stable for several days, slowly decomposing to the metal amide and dihydrogen. Most studies involving liquid ammonia solutions are done in reducing conditions: although oxidation of liquid ammonia is usually slow, there is still a risk of explosion, particularly if transition metal ions are present as possible catalysts.

11 - Detection and determination:

Ammonia and ammonium salts can be readily detected, in very minute traces, by the addition of Nessler's solution, which gives a distinct yellow coloration in the presence of the least trace of ammonia or ammonium salts. Sulfur sticks are burnt to detect small leaks in industrial ammonia refrigeration systems. Larger quantities can be detected by warming the salts with a caustic alkali or with quicklime, when the characteristic smell of ammonia will be at once apparent. The amount of ammonia in ammonium salts can be estimated quantitatively by distillation of the salts with sodium or potassium hydroxide, the ammonia evolved being absorbed in a known volume of standard sulfuric acid and the excess of acid then determined volumetrically; or the ammonia may be absorbed in hydrochloric acid and the ammonium chloride so formed precipitated as ammonium hexachloroplatinate, $(\text{NH}_4)_2 \text{Pt Cl}_6$.

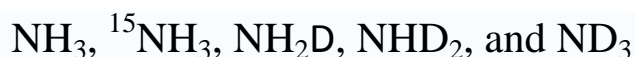
11 – 1 - Inter stellar space:

Ammonia was first detected in interstellar space in 1968, based on microwave emissions from the direction of the galactic core.^[54]

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This was the first polyatomic molecule to be so detected. The sensitivity of the molecule to a broad range of excitations and the ease with which it can be observed in a number of regions has made ammonia one of the most important molecules for studies of molecular clouds.^[29] The relative intensity of the ammonia lines can be used to measure the temperature of the emitting medium.

The following isotopic species of ammonia have been detected:



The detection of triply - deuterated ammonia was considered a surprise as deuterium is relatively scarce. It is thought that the low-temperature conditions allow this molecule to survive and accumulate. The ammonia molecule has also been detected in the atmospheres of the gas giant planets, including Jupiter, along with other gases like methane, hydrogen, and helium. The interior of Saturn may include frozen crystals of ammonia.

Since its interstellar discovery, NH_3 has proved to be an invaluable spectroscopic tool in the study of the interstellar medium. With a large number of transitions sensitive to a wide range of excitation conditions, NH_3 has been widely astronomically detected - its detection has been reported in hundreds of journal articles. Listed below is a sample of journal articles that highlights the range of detectors that have been used to identify ammonia.

11 -1 – 1 - Single antenna detection:

Radio observations of NH_3 from the 100 m Effelsberg Telescope reveal that the ammonia line is separated into two components - a background ridge and an unresolved core. The background corresponds well with the locations previously - detected CO. The 25 m Chilbolton telescope in England detected radio signatures of ammonia in HII regions, HNH_2O MASERS, H - H objects, and other objects associated with star formation. A comparison of emission line widths indicates that turbulent or systematic velocities do not increase in the central cores of molecular clouds.

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Microwave radiation from ammonia was observed in several galactic objects including W3 (OH), Orion A, W43, W51, and five sources in the galactic centre. The high detection rate indicates that this is a common molecule in the interstellar medium and that high density regions are common in the galaxy.

11 – 1 – 2 - Inter ferometric studies:

VLA observations of NH₃ in seven regions with high-velocity gaseous outflows reveal condensations of less than 0.1 pc in L1551, S140, and Cepheus A. Three individual condensations were detected in Cepheus A, one of them with a highly elongated shape. They may play an important role in creating the bipolar outflow in the region.

Extragalactic ammonia was imaged using the VLA in IC 342. The hot gas has temperatures above 70 K inferred from ammonia line ratios and appears to be closely associated with the innermost portions of the nuclear bar seen in CO. NH₃ was also monitored by VLA towards a sample of four galactic ultra compact HII regions: G9.62 + 0.19, G 10.47 + 0.03, G 29.96 - 0.02, and G 31.41+ 0.31. Based upon temperature and density diagnostics, it is concluded that in general such clumps are likely to be the sites of massive star formation in an early evolutionary phase prior to the development of an ultracompact HII region.

11 – 1 – 3 - Infrared detections:

Absorption at 2.97 micrometres due to solid ammonia was recorded from interstellar grains in the Becklin-Neugebauer object and probably in NG C 2264 - IR as well. This detection helped explaining the physical shape of previously poorly-understood related ice absorption lines.

A spectrum of the disk of Jupiter was obtained from the Kuiper Airborne Observatory, covering the 100 to 300 cm⁻¹ spectral range. Analysis of the spectrum provides information on global mean properties of ammonia gas and an ammonia ice haze.

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A total of 149 dark cloud positions were surveyed for evidence of 'dense cores' by using the $(J,K) = (1,1)$ rotating inversion line of NH_3 . The cores are not generally spherically shaped, with aspect ratios ranging from 1.1 to 4.4. It is also found that cores with stars have broader lines than cores without stars.

NH_3 has been detected in the Draco Nebula and in one or possibly two molecular clouds, which are associated with the high latitude galactic infrared cirrus. The finding is significant because they may represent the birthplaces for the Population I metallicity B - type stars in the galactic halo which could have been borne in the galactic disk.

12 - Astronomical observations and research applications:

The study of interstellar ammonia has been important to a number of areas of research in the last few decades. Some of these are delineated below and primarily involve using ammonia as an interstellar thermometer.

12 – 1 - Observations of nearby dark clouds:

By balancing and stimulated emission with spontaneous emission, it is possible to construct a relation between excitation temperature and density. Moreover, since the transitional levels of ammonia can be approximated by a 2 - level system at low temperatures, this calculation is fairly simple. This premise can be applied to dark clouds, regions suspected of having extremely low temperatures and possible sites for future star formation. Detections of ammonia in dark clouds show very narrow lines - indicative not only of low temperatures, but also of a low level of inner-cloud turbulence. Line ratio calculations provide a measurement of cloud temperature that is independent of previously - done CO observations. The ammonia observations were consistent with CO measurements of rotation temperatures of ~ 10 K. With this, densities can be determined, and have been calculated to range between 10^4 and 10^5 cm^{-3} in dark clouds. Mapping of NH_3 gives typical clouds sizes of 0.1 pc and masses near 1 solar mass. These cold, dense cores are the sites of future star formation.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**12 – 2 - UC HII regions:**

Ultra - compact HII regions are among the best tracers of high-mass star formation. The dense material surrounding UC HII regions is likely primarily molecular. Since a complete study of massive star formation necessarily involves the cloud from which the star formed, ammonia is an invaluable tool in understanding this surrounding molecular material. Since this molecular material can be spatially resolved, it is possible to constrain the heating/ionising sources, temperatures, masses, and sizes of the regions. Doppler - shifted velocity components allow for the separation of distinct regions of molecular gas which can trace out flows and hot cores originating from forming stars.

12 – 3 - Extragalactic detection:

NH₃ has been detected in external galaxies, and by simultaneously measuring several lines, it is possible to directly measure the gas temperature in these galaxies. Line ratios imply that gas temperatures are warm (~ 50 K), originating from dense clouds with sizes of tens of pc. This picture is consistent with the picture within our Milky Way galaxy - hot dense molecular cores form around newly - forming stars embedded in larger clouds of molecular material on the scale of several hundred pc (giant molecular clouds; GMCs) .

13 - Safety precautions :

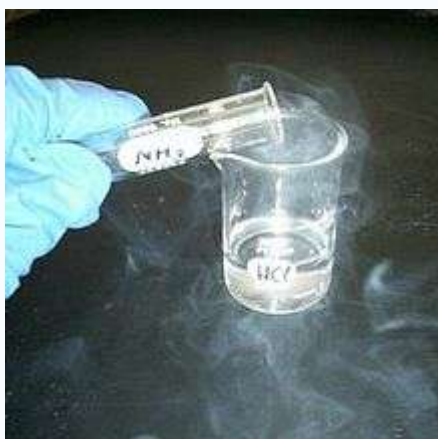
The U. S. Occupational Safety and Health Administration (OSHA) has set a 15 - minute exposure limit for gaseous ammonia of 35 ppm by volume in the environmental air and an 8 - hour exposure limit of 25 ppm by volume. NIOSH recently reduced the IDLH from 500 to 300 based on recent more conservative interpretations of original research in 1943. IDLH (Immediately Dangerous to Life and Health) is the level to which a healthy worker can be exposed for 30 minutes without suffering irreversible health effects. Other organizations have varying exposure levels. U.S. Navy Standards [U.S. Bureau of Ships 1962] Maximum allowable concentrations (MACs): Continuous exposure (60 days): 25 ppm / 1 hour: 400 ppm

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[68] Ammonia vapour has a sharp, irritating, pungent odour that acts as a warning of potentially dangerous exposure. The average odour threshold is 5 ppm, well below any danger or damage. Exposure to very high concentrations of gaseous ammonia can result in lung damage and death. Although ammonia is regulated in the United States as a non-flammable gas, it still meets the definition of a material that is toxic by inhalation and requires a hazardous safety permit when transported in quantities greater than 13,248 L .



The world's longest ammonia pipe line, running from the TogliattiAzot plant in Russia to Odessa in Ukraine.

13 – 1 - Toxicity and storage information:

Hydro chloric acid sample releasing HCl fumes, which are reacting with ammonia fumes to produce a white smoke of ammoniumchloride.

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The toxicity of ammonia solutions does not usually cause problems for humans and other mammals, as a specific mechanism exists to prevent its build - up in the bloodstream. Ammonia is converted to carbamoyl phosphate by the enzyme carbamoyl phosphate synthetase, and then enters the urea cycle to be either incorporated into amino acids or excreted in the urine. However, fish and amphibians lack this mechanism, as they can usually eliminate ammonia from their bodies by direct excretion. Ammonia even at dilute concentrations is highly toxic to aquatic animals, and for this reason it is classified as *dangerous for the environment*. Ammonium compounds should never be allowed to come in contact with bases (unless in an intended and contained reaction), as dangerous quantities of ammonia gas could be released.

13 – 2 - House hold use;

Solutions of ammonia (5 – 10 % by weight) are used as household cleaners, particularly for glass. These solutions are irritating to the eyes and mucous membranes (respiratory and digestive tracts), and to a lesser extent the skin. Caution should be used that the chemical is never mixed into any liquid containing bleach, or a poisonous gas may result. Mixing with chlorine-containing products or strong oxidants, for example household bleach can lead to hazardous compounds such as chloramines.

13 – 3 - Laboratory use of ammonia solutions:

The hazards of ammonia solutions depend on the concentration: " dilute " ammonia solutions are usually 5 – 10 % by weight ($< 5.62 \text{ mol / L}$) ; " concentrated " solutions are usually prepared at $> 25 \%$ by weight. A 25 % (by weight) solution has a density of 0.907 g/cm^3 , and a solution which has a lower density will be more concentrated. The European Union classification of ammonia solutions is given in the table .

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Concentration by weight (w / w)	Molarity	Concentration mass/volume (w / v)	Classification
5 – 10 %	2.87 - 5.62 mol / L	48.9 – 95.7 g / L	Irritant (Xi)
10 – 25 %	5.62–13.29 mol / L	95.7 – 226.3 g / L	Corrosive (C)
			Corrosive (C)
> 25 %	> 13.29 mol / L	> 226.3 g / L	Dangerous for the environment (N)

The ammonia vapour from concentrated ammonia solutions is severely irritating to the eyes and the respiratory tract, and these solutions should only be handled in a fume hood. Saturated ("0.880") solutions can develop a significant pressure inside a closed bottle in warm weather, and the bottle should be opened with care: this is not usually a problem for 25 % ("0.900") solutions.

Ammonia solutions should not be mixed with halogens, as toxic and/or explosive products are formed. Prolonged contact of ammonia solutions with silver, mercury or iodide salts can also lead to explosive products: such mixtures are often formed in qualitative chemical analysis, and should be lightly acidified but not concentrated ($< 6\%$ w / v) before disposal once the test is completed.

13 – 4 - Laboratory use of anhydrous ammonia (gas or liquid)

Anhydrous ammonia is classified as toxic (T) and dangerous for the environment (N). The gas is flammable (autoignition temperature: 651 °C) and can form explosive mixtures with air (16 – 25 %). The permissible exposure limit (PEL) in the United States is 50 ppm (35 mg/m³), while the IDLH concentration is estimated at 300 ppm. Repeated exposure to ammonia lowers the sensitivity to the smell of the gas: normally the odour is detectable at concentrations of less than 50 ppm, but desensitised individuals may not detect it even at concentrations of 100 ppm. Anhydrous ammonia corrodes copper- and zinc-containing alloys, and so brass fittings should not be used for handling the gas. Liquid ammonia can also attack rubber and certain plastics.

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Ammonia reacts violently with the halogens. Nitrogen triiodide, a primary high explosive, is formed when ammonia comes in contact with iodine. Ammonia causes the explosive polymerisation of ethylene oxide. It also forms explosive fulminating compounds with compounds of gold, silver, mercury, germanium or tellurium, and with stibine. Violent reactions have also been reported with acetaldehyde, hypochlorite solutions, potassium ferricyanide and peroxides.

Ammonia Production

Contents

- 1 Introduction ;
- 25 History
- 3 Modern ammonia-producing plants
- 4 Sustainable ammonia production

1 –Introduction :

Because of its many uses, ammonia is one of the most highly - produced inorganic chemicals. There are numerous large - scale **ammonia production** plants worldwide, producing a total of 109,000,000 metric tons of ammonia in 2004. China produced 28.4% of the worldwide production, followed by India with 8.6%, Russia with 8.4 %, and the United States with 8.2%. 80% or more of the ammonia produced is used for fertilizing agricultural crops. Ammonia is also used for the production of plastics, fibers, explosives, and intermediates for dyes and pharmaceuticals.

2 – History :

Before the start of World War I, most ammonia was obtained by the dry distillation of nitrogenous vegetable and animal products; by the reduction of nitrous acid and nitrites with hydrogen; and also by the decomposition of ammonium salts by alkaline hydroxides or by quicklime, the salt most generally used being the chloride (sal-ammoniac).

The Haber process, which is the production of ammonia by combining hydrogen and nitrogen, was first patented by Fritz Haber in 1908. In 1910 Carl Bosch, while working for the German chemical company BASF, successfully commercialized the process and secured further patents. It was first used on an industrial scale by the Germans during World War I. Since then, the process has often been referred to as the Haber - Bosch process.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**3 - Modern ammonia - producing plant :**

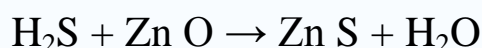
A typical modern ammonia-producing plant first converts natural gas (i.e., methane) or LPG (liquified petroleum gases such as propane and butane) or petroleum naphtha into gaseous hydrogen. The method for producing hydrogen from hydrocarbons is referred to as "Steam Reforming". The hydrogen is then combined with nitrogen to produce ammonia.

Starting with a natural gas feedstock, the processes used in producing the hydrogen are:

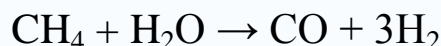
- The first step in the process is to remove sulfur compounds from the feedstock because sulfur deactivates the catalysts used in subsequent steps. Sulfur removal requires catalytic hydrogenation to convert sulfur compounds in the feedstocks to gaseous hydrogen sulfide :



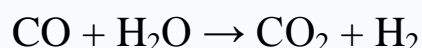
- The gaseous hydrogen sulfide is then absorbed and removed by passing it through beds of zinc oxide where it is converted to solid zinc sulfide:



- Catalytic steam reforming of the sulfur-free feedstock is then used to form hydrogen plus carbon monoxide:

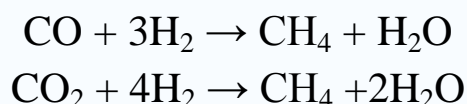


- The next step then uses catalytic shift conversion to convert the carbon monoxide to carbon dioxide and more hydrogen:

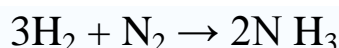


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- The carbon dioxide is then removed either by absorption in aqueous ethanolamine solutions or by adsorption in pressure swing adsorbers (PSA) using proprietary solid adsorption media.
- The final step in producing the hydrogen is to use catalytic methanation to remove any small residual amounts of carbon monoxide or carbon dioxide from the hydrogen:



To produce the desired end-product ammonia, the hydrogen is then catalytically reacted with nitrogen (derived from process air) to form anhydrous liquid ammonia. This step is known as the ammonia synthesis loop (also referred to as the Haber-Bosch process):



The steam reforming, shift conversion, carbon dioxide removal and methanation steps each operate at absolute pressures of about 25 to 35 bar, and the ammonia synthesis loop operates at absolute pressures ranging from 60 to 180 bar depending upon which proprietary design is used. There are many engineering and construction companies that offer proprietary designs for ammonia synthesis plants. Haldor Topsoe of Denmark, Uhde GmbH of Germany, and Kellogg Brown & Root of the United States are among the most experienced companies in that field.

4 - Sustainable ammonia production:

Ammonia production depends on plentiful supplies of natural gas, a finite resource, to provide the hydrogen. Due to ammonia's critical role in intensive agriculture and other processes, sustainable production is desirable. This is possible by using renewable energy to generate hydrogen by electrolysis of water. This would be straightforward in a hydrogen economy by diverting some hydrogen production from fuel to feedstock use. For example, in 2002, Iceland produced 2,000 tons of hydrogen gas by electrolysis, using excess electricity production from its hydroelectric plants, primarily for the

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production of ammonia for fertilizer. The Vemork hydroelectric plant in Norway used its surplus electricity output to generate renewable ammonia from 1911 to 1971 . In practice, natural gas will remain the major source of hydrogen for ammonia production as long as it is cheapest.

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Amine gas treating

Amine gas treating, also known as **gas sweetening** and **acid gas removal**, refers to a group of processes that use aqueous solutions of various alkanolamines (commonly referred to simply as amines) to remove hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from gases. It is a common unit process used in refineries, petrochemical plants, natural gas processing plants and other industries.

Processes within oil refineries or natural gas processing plants that remove hydrogen sulfide and/or mercaptans are commonly referred to as **sweetening** processes because they result in products which no longer have the sour, foul odors of mercaptans and hydrogen sulfide.

There are many different amines used in gas treating:

- Mono ethanol amine (MEA)
- Di ethanol amine (DEA)
- Methyl di ethanol amine (MDEA)
- Di iso propyl amine (DIPA)
- Amino ethoxy ethanol (di glycol amine) (DGA)

The most commonly used amines in industrial plants are the alkanolamines MEA, DEA, and MDEA.

Amines are also used in many oil refineries to remove sour gases from liquid hydrocarbons such as liquified petroleum gas (LPG).

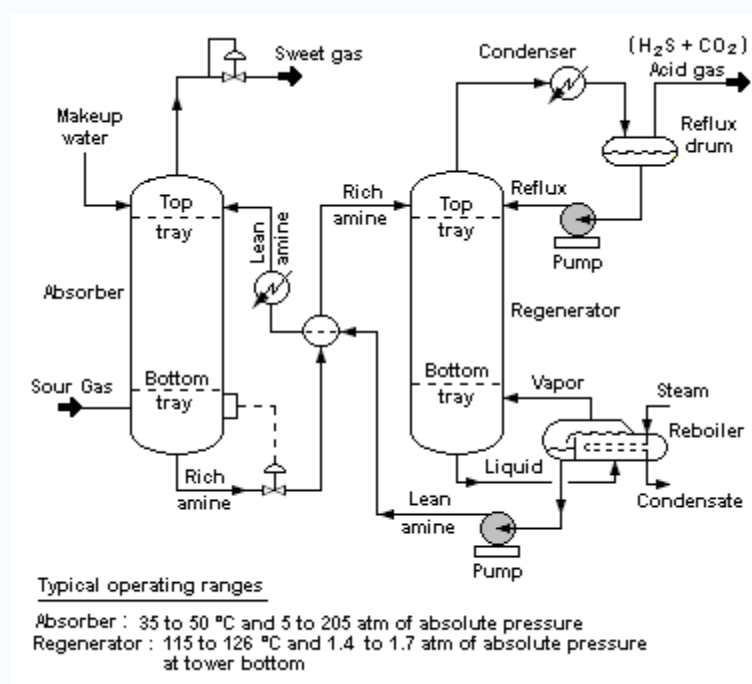
Description of a typical amine treater

Gases containing H_2S or both H_2S and CO_2 are commonly referred to as *sour gases* or *acid gases* in the hydrocarbon processing industries.

A typical amine gas treating process (as shown in the flow diagram below) includes an **absorber** unit and a **regenerator** unit as well as accessory equipment. In the absorber, the downflowing amine solution absorbs H_2S and CO_2 from the upflowing sour gas to produce a sweetened gas stream (i.e., an H_2S - free gas) as a product and an

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amine solution rich in the absorbed acid gases. The resultant "rich" amine is then routed into the regenerator (a stripper with a reboiler) to produce regenerated or "lean" amine that is recycled for reuse in the absorber. The stripped overhead gas from the regenerator is concentrated H_2S and CO_2 . In oil refineries, that stripped gas is mostly H_2S , much of which often comes from a sulfur-removing process called hydro desulfurization. This H_2S - rich stripped gas stream is then usually routed into a Claus process to convert it into elemental sulfur. In fact, the vast majority of the 64,000,000 metric tons of sulfur produced worldwide in 2005 was byproduct sulfur from refineries and other hydrocarbon processing plants. ^{[1][2]} Another sulphur-removing process is the WSA Process which recovers sulphur in any form as concentrated sulphuric acid. In some plants, more than one amine absorber unit may share a common regenerator unit.



Process flow diagram of a typical amine treating process used in industrial plants

In the steam reforming process of hydrocarbons to produce gaseous hydrogen for subsequent use in the industrial synthesis of ammonia, amine treating is one of the commonly used processes for removing excess carbon dioxide in the final purification of the gaseous hydrogen.

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Ammonium hydroxide

Contents

- 1 Introduction
- 2 Basicity of ammonia in water
- 3 Saturated Solutions
- 4 Applications
- 5 Laboratory use

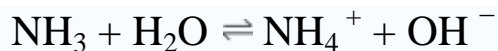
1 – Introduction ;

Ammonium hydroxide ($\text{NH}_3[\text{aq}]$), also known as **ammonia water**, **ammonical liquor**, **ammonia liquor**, **aqua ammonia**, or **aqueous ammonia**, is a solution of ammonia in water. Although its name suggests a salt of the formula NH_4OH , it is not actually possible to generate samples of NH_4OH - it exists only in dilute aqueous solutions.

Properties	
Molecular formula	NH_4OH
Molar mass	35 g / mol
Appearance	very volatile solution , colorless, bitter smell
Density	0.91 g / cm^3 (25 %)
	0.88 g / cm^3 (32 %)
Melting point	-57.5 °C (25%)
	-91.5 °C (32%)
Boiling point	37.7 °C (25%)
	24.7 °C (32%)
Solubility in water	Miscible
Hazards	
EU classification	Corrosive (C)
	Dangerous to the environment (N)

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**2 - Basicity of ammonia in water**

In aqueous solution, ammonia deprotonates a small fraction of the water to give ammonium and hydroxide according to the following equilibrium:



In a 1M ammonia solution, about 0.42 % of the ammonia is converted to ammonium, equivalent to a pH of 11.63. The base ionization constant is

$$K_b = [\text{NH}_4^+] [\text{OH}^-] / [\text{NH}_3] = 1.8 \times 10^{-5}$$

3 - Saturated Solutions

Like other gases, ammonia exhibits decreasing solubility in solvent liquids as the temperature of the solvent increases. "Ammonium hydroxide" solutions decrease in density as the concentration of dissolved ammonia increases. At 15.5556 °C, the density of a saturated solution is 0.88 g/mL and contain 35% ammonia by mass, 308g / L w / v , (308 grams of ammonia per litre of solution) and have a molarity of approximately 18 mole / L. At higher temperatures, the molarity of the saturated solution decreases and the density increases.

When solutions that are saturated at cold temperatures are sealed in containers and subsequently warmed, the concentration of the solution decreases and the vapor pressure of ammonia gas increases. Unsealing such containers can lead to a burst of ammonia gas. In extreme cases, the containers could rupture.

From a laboratory perspective, one should be aware that the concentration of a saturated solution is continually dropping as the container is handled in a warmer environment. Thus, old samples of ammonium hydroxide will deviate from 18 M, as can be verified by titration.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**3 - Applications:**

Household ammonia is dilute ammonium hydroxide, which is also an ingredient of numerous other cleaning agents.

Prepare paintwork for newly painting an already painted surface by cleaning the painted surface with household ammonia or ammonium hydroxide.

In industry, ammonium hydroxide is used as a precursor to some alkyl amines, although anhydrous ammonia is usually preferred. Hexamethylenetetramine forms readily from aqueous ammonia and formaldehyde. Ethylenediamine forms from 1,2-dichloroethane and aqueous ammonia.

Ammonium hydroxide is used in the meat packing industry. Some companies add ammonium hydroxide to their beef.^[5]

5 - Laboratory use;

Aqueous ammonia is used in traditional qualitative inorganic analysis as a complexant and base. Like many amines, it gives a deep blue coloration with copper(II) solutions. Ammonia solution can dissolve silver residues, such as that formed from Tollens' reagent.

When ammonium hydroxide is mixed with dilute hydrogen peroxide in the presence of a metal ion, such as Cu^{2+} , the peroxide will undergo rapid decomposition.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**Category : Ammonium Compounds****A**

- Ammonium chlorate
- Ammonium di hydrogen phosphate
- Ammonium ferric citrate
- Ammonium permanganate
- Ammonium acetate
- Ammonium aluminium sulfate
- Ammonium benzoate
- Ammonium bi carbonate
- Ammonium bi fluoride
- Ammonium bi sulfate
- Ammonium bromide
- Ammonium carbonate
- Ammonium chloride
- Ammonium cyanide
- Ammonium di chromate

- Ammonium fluoro silicate
- Ammonium formate
- Ammonium hepta molybdate
- Ammonium hexa chloro platinate
- Ammonium hexa fluoro phosphate
- Ammonium hydro sulfide
- Ammonium hydroxide
- Ammonium iodide
- Ammonium iron (II) sulfate
- Ammonium iron (III) sulfate
- Ammonium lauryl sulfate
- Ammonium nitrate
- Ammonium nitrite
- Ammonium per chlorate
- Ammonium per sulfate
- Ammonium phosphate

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- Ammonium sulfate
- Ammonium sulfide
- Ammonium tetra thio molybdate
- Ammonium thio cyanate

B

- Brutulf / Ferric Ammonium Sulfate

D

- Di ammonium phosphate

E

- Ethyl ammonium nitrate

M

- Mono ammonium glutamate

Z

- * Zinc ammonium chloride

Potassium

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- 3 History of the free element
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1 –Introduction :

Potassium is the chemical element with the symbol **K** (Latin: *kalium*, from Arabic : القلّية *al - qalyah* "plant ashes", cf. Alkali from the same root) , atomic number 19, and atomic mass 39 . Potassium was first isolated from potash. Elemental potassium is a soft silvery-white metallic alkali metal that oxidizes rapidly in air and is very reactive with water, generating sufficient heat to ignite the evolved hydrogen.

Potassium in nature occurs only as ionic salt. As such, it is found dissolved in seawater, and as part of many minerals. Potassium ion is

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necessary for the function of all living cells, and is thus present in all plant and animal tissues. It is found in especially high concentrations in plant cells, and in a mixed diet, it is most highly concentrated in fruits.

Potassium and sodium are chemically similar, since both are alkali metals. However, their functions in organisms are quite different, especially in animal cells.

General properties

Name , symbol , number	Potassium , K , 19
Element category	alkali metal
Group, period, block	1, 4 , s
Standard atomic weight	39 g · mol ⁻¹
Electrons per shell	2, 8, 8, 1

Physical properties

Phase	solid
Density (near r.t.)	0.89 g·cm ⁻³
Liquid density at m.p.	0.828 g·cm ⁻³
Melting point	336.53 K , 63.38 °C , 146.08 °F
Boiling point	1032 K , 759 °C , 1398 °F
Triple point	336.35 K (63°C), kPa
Heat of fusion	2.33 kJ·mol ⁻¹
Heat of vaporization	76.9 kJ·mol ⁻¹
Specific heat capacity	(25 °C) 29.6 J·mol ⁻¹ ·K ⁻¹

Atomic properties

Oxidation states	1 (strongly basic oxide)
Electronegativity	0.82 (Pauling scale)
Ionization energies	1st : 418.8 kJ·mol ⁻¹
	2 nd : 3052 kJ·mol ⁻¹
	3 rd : 4420 kJ·mol ⁻¹

Miscellanea

Crystal structure	Body - centered cubic
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Magnetic ordering	paramagnetic
Electrical resistivity	(20 °C) 72 nΩ·m
Thermal conductivity	(300 K) 102.5 W·m ⁻¹ ·K ⁻¹
Thermal expansion	(25 °C) 83.3 μm·m ⁻¹ ·K ⁻¹
Speed of sound (thin rod)	(20 °C) 2000 m / s
Mohs hardness	0.4
Brinell hardness	0.363 MPa

2 – Occurrence:*Potassium in feldspar*

Elemental potassium does not occur in nature because it reacts violently with water. As various compounds, potassium makes up about 1.5% of the weight of the Earth's crust and is the seventh most abundant element. As it is very electropositive and highly reactive potassium metal is difficult to obtain from its minerals.

3 - History of the free element:

Elemental potassium was not known in Roman times, and its names are not Classical Latin but rather neo-Latin. The name **kalium** was taken from the word "alkali", which came from Arabic *al qalīy* = "the calcined ashes". The name **potassium** was made from the word "potash", which is English, and originally meant an alkali extracted in a *pot* from the *ash* of burnt wood or tree leaves. The structure of

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potash was not then known , but is now understood to be mostly potassium carbonate. By heating, the carbonate could be freed of carbon dioxide , leaving "caustic potash" , so called because it caused chemical burns in contact with human tissue.

Potassium metal was discovered in 1807 in England by Sir Humphry Davy, who derived it from caustic potash (KOH) , by the use of electrolysis of the molten salt with the newly discovered voltaic pile. Before the 18th century, no distinction was made between potassium and sodium. Potassium was the first metal that was isolated by electrolysis . Davy extracted sodium by a similar technique, demonstrating the elements to be different .

4 - Commercial Production:

Pure potassium metal may be isolated by electrolysis of its hydroxide in a process that has changed little since Davy. Thermal methods also are employed in potassium production, using potassium chloride

Potassium salts such as carnallite, langbeinite, polyhalite, and sylvite form extensive deposits in ancient lake and seabeds, making extraction of potassium salts in these environments commercially viable. The principal source of potassium, potash, is mined in Saskatchewan, California, Germany, New Mexico, Utah, and in other places around the world. It is also found abundantly in the Dead Sea. Three thousand feet below the surface of Saskatchewan are large deposits of potash which are important sources of this element and its salts, with several large mines in operation since the 1960s. Saskatchewan pioneered the use of freezing of wet sands (the Blairmore formation) in order to drive mine shafts through them. The main mining company is the Potash Corporation of Saskatchewan. The oceans are another source of potassium, but the quantity present in a given volume of seawater is much lower than that of sodium.^{[4][5]}

Potassium metal in reagent - grade sells for about \$ 22 / kg in 2010 when purchased in tonage quantities. Lower purity metal sells for considerably less. The market in this metal is volatile due to the difficulty in its long term storage. It must be stored under a dry inert

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gas atmosphere or anhydrous mineral oil to prevent the formation of a surface layer of potassium superoxide. This superoxide is a pressure sensitive explosive which will detonate when scratched. The resulting explosion will usually start a fire which is difficult to extinguish.

5 - isotopes of potassium:

There are 24 known isotopes of potassium. Three isotopes occur naturally: ^{39}K (93.3 %) , ^{40}K (0.0117 %) and ^{41}K (6.7 %) . Naturally occurring ^{40}K decays to stable ^{40}Ar (11.2 % of decays) by electron capture or positron emission, or decays to stable ^{40}Ca (88.8 % of decays) by beta decay; ^{40}K has a half - life of 1.250×10^9 years. The decay of ^{40}K to ^{40}Ar enables a commonly used method for dating rocks. The conventional K - Ar dating method depends on the assumption that the rocks contained no argon at the time of formation and that all the subsequent radiogenic argon (i.e., ^{40}Ar) was quantitatively retained. Minerals are dated by measurement of the concentration of potassium and the amount of radiogenic ^{40}Ar that has accumulated. The minerals that are best suited for dating include biotite, muscovite, plutonic/high grade metamorphic hornblende, and volcanic feldspar; whole rock samples from volcanic flows and shallow intrusives can also be dated if they are unaltered.

Outside of dating, potassium isotopes have been used extensively as tracers in studies of weathering. They have also been used for nutrient cycling studies because potassium is a macronutrient required for life.

^{40}K occurs in natural potassium (and thus in some commercial salt substitutes) in sufficient quantity that large bags of those substitutes can be used as a radioactive source for class room demonstrations. In healthy animals and people, ^{40}K represents the largest source of radioactivity, greater even than ^{14}C . In a human body of 70 kg mass, about 4,400 nuclei of ^{40}K decay per second.^[8] The activity of natural potassium is 31 Bq / g.

6 - Properties :

6 – 1 – Physical :

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The flame - test color for potassium

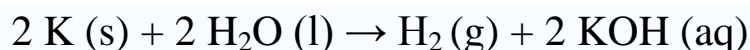
Potassium is the second least dense metal; only lithium is less dense. It is a soft, low - melting solid that can easily be cut with a knife. Freshly cut potassium is silvery in appearance, but in air it begins to tarnish toward grey immediately .

In a flame test, potassium and its compounds emit a pale violet color, which may be masked by the strong yellow emission of sodium if it is also present. Cobalt glass can be used to filter out the yellow sodium color. Potassium concentration in solution is commonly determined by flame photometry, atomic absorption spectro photometry, inductively coupled plasma, or ion selective electrodes.

6 – 2 – Chemical :

Potassium must be protected from air for storage to prevent disintegration of the metal from oxide and hydroxide corrosion. Often samples are maintained under a hydrocarbon medium which does not react with alkali metals, such as mineral oil or kerosene.

Like the other alkali metals, potassium reacts violently with water, producing hydrogen. The reaction is notably more violent than that of lithium or sodium with water, and is sufficiently exothermic that the evolved hydrogen gas ignites.

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Because potassium reacts quickly with even traces of water, and its reaction products are nonvolatile, it is sometimes used alone, or as NaK (an alloy with sodium which is liquid at room temperature) to dry solvents prior to distillation. In this role, it serves as a potent desiccant.

Potassium hydroxide reacts strongly with carbon dioxide to produce potassium carbonate, and is used to remove traces of CO₂ from air. Potassium compounds generally have excellent water solubility, due to the high hydration energy of the K⁺ ion. The potassium ion is colorless in water.

Methods of separating potassium by precipitation, some times used for gravimetric analysis, include the use of sodium tetra phenyl borate, hexa chloro platinic acid, and sodium cobalti nitrite

7 - Potassium cations in the body:

7 – 1 - Bio chemical function (Action potential) :

Potassium cations are important in neuron (brain and nerve) function, and in influencing osmotic balance between cells and the interstitial fluid, with their distribution mediated in all animals (but not in all plants) by the so - called Na⁺ / K⁺ -ATPase pump. This ion pump uses ATP to pump 3 sodium ions out of the cell and 2 potassium ions into the cell, thus creating an electrochemical gradient over the cell membrane. In addition, the highly selective potassium ion channels (which are tetramers) are crucial for the hyperpolarisation, in for example neurons, after an action potential is fired. The most recently resolved potassium ion channel is KirBac3.1, which gives a total of five potassium ion channels (KcsA, KirBac1.1, KirBac3.1, KvAP, MthK) with a determined structure. All five are from prokaryotic species.

Potassium may be detected by taste because it triggers three of the five types of taste sensations, according to concentration. Dilute solutions of potassium ion taste sweet (allowing moderate

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concentrations in milk and juices) , while higher concentrations become increasingly bitter/alkaline, and finally also salty to the taste. The combined bitterness and saltiness of high potassium content solutions makes high - dose potassium supplementation by liquid drinks a palatability challenge.

7 – 2 - Membrane polarization :

Potassium is also important in preventing muscle contraction and the sending of all nerve impulses in animals through action potentials. By nature of their electrostatic and chemical properties, K^+ ions are larger than Na^+ ions, and ion channels and pumps in cell membranes can distinguish between the two types of ions, actively pumping or passively allowing one of the two ions to pass, while blocking the other.

A shortage of potassium in body fluids may cause a potentially fatal condition known as hypokalemia, typically resulting from vomiting, diarrhea, and / or increased diuresis. Deficiency symptoms include muscle weakness, paralytic ileus, ECG abnormalities, decreased reflex response and in severe cases respiratory paralysis, alkalosis and cardiac arrhythmia .

7 – 3 - Filtration and excretion :

Potassium is an essential mineral micronutrient in human nutrition; it is the major cation (positive ion) inside animal cells, and it is thus important in maintaining fluid and electrolyte balance in the body. Sodium makes up most of the cations of blood plasma at a reference range of about 145 milliequivalents per liter (3.345 grams) and potassium makes up most of the cell fluid cations at about 150 milliequivalents per liter (4.8 grams) . Plasma is filtered through the glomerulus of the kidneys in enormous amounts, about 180 liters per day.^[14] Thus 602 grams of sodium and 33 grams of potassium are filtered each day. All but the 1-10 grams of sodium and the 1-4 grams of potassium likely to be in the diet must be reabsorbed. Sodium must be reabsorbed in such a way as to keep the blood volume exactly right and the osmotic pressure correct; potassium must be reabsorbed in such a way as to keep serum concentration as close as possible to 4.8

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milli equivalents (about 0.190 grams) per liter. Sodium pumps in the kidneys must always operate to conserve sodium. Potassium must sometimes be conserved also, but as the amount of potassium in the blood plasma is very small and the pool of potassium in the cells is about thirty times as large, the situation is not so critical for potassium. Since potassium is moved passively^{[16][17]} in counter flow to sodium in response to an apparent (but not actual) Donnan equilibrium,^[18] the urine can never sink below the concentration of potassium in serum except sometimes by actively excreting water at the end of the processing. Potassium is secreted twice and reabsorbed three times before the urine reaches the collecting tubules. At that point, it usually has about the same potassium concentration as plasma. If potassium were removed from the diet, there would remain a minimum obligatory kidney excretion of about 200 mg per day when the serum declines to 3.0-3.5 milliequivalents per liter in about one week, and can never be cut off completely. Because it cannot be cut off completely, death will result when the whole body potassium declines to the vicinity of one - half full capacity. At the end of the processing, potassium is secreted one more time if the serum levels are too high.

The potassium moves passively through pores in the cell wall. When ions move through pumps there is a gate in the pumps on either side of the cell wall and only one gate can be open at once. As a result, 100 ions are forced through per second. Pores have only one gate, and there only one kind of ion can stream through, at 10 million to 100 million ions per second. The pores require calcium in order to open although it is thought that the calcium works in reverse by blocking at least one of the pores. Carbonyl groups inside the pore on the amino acids mimics the water hydration that takes place in water solution by the nature of the electrostatic charges on four carbonyl groups inside the pore.

7 – 4 - Potassium in the diet and by supplement :

7 – 4 – 1 - Adequate intake :

A potassium intake sufficient to support life can generally be guaranteed by eating a variety of foods, especially plant foods. Clear

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cases of potassium deficiency (as defined by symptoms, signs and a below-normal blood level of the element) are rare in healthy individuals eating a balanced diet. Foods rich in potassium include orange juice, potatoes, bananas, avocados, tomatoes, broccoli, soybeans, brown rice, garlic and apricots, although it is also abundant in most fruits, vegetables and meats.

7 – 4 – 2 - Optimal intake:

Epidemiological studies and studies in animals subject to hypertension indicate that diets high in potassium can reduce the risk of hypertension and possibly stroke (by a mechanism independent of blood pressure), and a potassium deficiency combined with an inadequate thiamine intake has produced heart disease in rats.^[27] With these findings, the question of what is the intake of potassium consistent with optimal health, is debated. For example, the 2004 guidelines of the Institute of Medicine specify a DRI of 4,000 mg of potassium (100 mEq), though most Americans consume only half that amount per day, which would make them formally deficient as regards this particular recommendation. Similarly, in the European Union, particularly in Germany and Italy, insufficient potassium intake is somewhat common.

7 – 4 – 3 - Medical supplementation and disease :

Supplements of potassium in medicine are most widely used in conjunction with loop diuretics and thiazides, classes of diuretics which rid the body of sodium and water, but have the side effect of also causing potassium loss in urine. A variety of medical and non-medical supplements are available. Potassium salts such as potassium chloride may be dissolved in water, but the salty / bitter taste of high concentrations of potassium ion make palatable high concentration liquid supplements difficult to formulate. Typical medical supplemental doses range from 10 milli equivalents (400 mg, about equal to a cup of milk or 6 oz. of orange juice) to 20 milliequivalents (800 mg) per dose. Potassium salts are also available in tablets or capsules, which for therapeutic purposes are formulated to allow potassium to leach slowly out of a matrix, as very high concentrations of potassium ion (which might occur next to a solid tablet of

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potassium chloride) can kill tissue, and cause injury to the gastric or intestinal mucosa. For this reason, non - prescription supplement potassium pills are limited by law in the U.S. to only 99 mg of potassium.

Individuals suffering from kidney diseases may suffer adverse health effects from consuming large quantities of dietary potassium. End stage renal failure patients undergoing therapy by renal dialysis must observe strict dietary limits on potassium intake, as the kidneys control potassium excretion, and buildup of blood concentrations of potassium (hyperkalemia) may trigger fatal cardiac arrhythmia.

8 - Applications:

About 93 % of the world potassium production was consumed by the fertilizer industry.

8 – 1 - Biological applications:

Potassium ions are an essential component of plant nutrition and are found in most soil types. Its primary use in agriculture, horticulture and hydroponic culture is as a fertilizer as the chloride (KCl), sulfate (K_2SO_4) or nitrate (KNO_3).

In animal cells, potassium ions are vital to cell function. They participate in the Na - K pump.

In the form of potassium chloride, it is used to stop the heart, e.g. in cardiac surgery and execution by lethal injection.

8 – 2 - Food applications:

Potassium ion is a nutrient necessary for human life and health. Potassium chloride is used as a substitute for table salt by those seeking to reduce sodium intake so as to control hypertension. The USDA lists tomato paste, orange juice, beet greens, white beans, potatoes, bananas and many other good dietary sources of potassium, ranked according to potassium content per measure shown.

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Potassium sodium tartrate, or Rochelle salt ($\text{K Na C}_4 \text{H}_4 \text{O}_6$) is the main constituent of baking powder. Potassium bromate (KBrO_3) is a strong oxidiser, used as a flour improver (E 924) to improve dough strength and rise height.

The sulfite compound, potassium bisulfite (KHSO_3) is used as a food preservative, for example in wine and beer - making (but not in meats). It is also used to bleach textiles and straw, and in the tanning of leathers.

8 – 3 - Industrial applications:

Potassium vapor is used in several types of magnetometers. An alloy of sodium and potassium, NaK (usually pronounced "nack"), that is liquid at room temperature, is used as a heat-transfer medium. It can also be used as a desiccant for producing dry and air - free solvents.

Potassium metal reacts vigorously with all of the halogens to form the corresponding potassium halides, which are white, water-soluble salts with cubic crystal morphology. Potassium bromide (KBr), potassium iodide (KI) and potassium chloride (KCl) are used in photographic emulsion to make the corresponding photosensitive silver halides.

Potassium hydroxide KOH is a strong base, used in industry to neutralize strong and weak acids and thereby finding uses in pH control and in the manufacture of potassium salts. Potassium hydroxide is also used to saponify fats and oils and in hydrolysis reactions, for example of esters and in industrial cleaners.

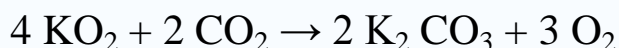
Potassium nitrate KNO_3 or saltpeter is obtained from natural sources such as guano and evaporites or manufactured by the Haber process and is the oxidant in gun powder (black powder) and an important agricultural fertilizer. Potassium cyanide KCN is used industrially to dissolve copper and precious metals particularly silver and gold by forming complexes; applications include gold mining, electro plating and electro forming of these metals. It is also used in organic synthesis to make nitriles. Potassium carbonate K_2CO_3 , also

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known as potash, is used in the manufacture of glass and soap and as a mild desiccant.

Potassium chromate (K_2CrO_4) is used in inks, dyes, and stains (bright yellowish - red colour), in explosives and fireworks, in safety matches, in the tanning of leather and in fly paper. Potassium fluorosilicate (K_2SiF_6) is used in specialized glasses, ceramics, and enamels. Potassium sodium tartrate, or Rochelle salt ($KNaC_4H_4O_6$) is used in the silvering of mirrors.

The superoxide KO_2 is an orange-colored solid used as a portable source of oxygen and as a carbon dioxide absorber. It is useful in portable respiration systems. It is widely used in submarines and spacecraft as it takes less volume than O_2 (g).

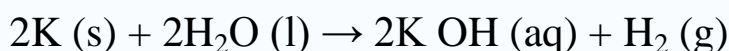


Potassium chlorate $KClO_3$ is a strong oxidant, used in percussion caps and safety matches and in agriculture as a weedkiller. Glass may be treated with molten potassium nitrate KNO_3 to make toughened glass, which is much stronger than regular glass.

Potassium cobalti nitrite $K_3 [Co (NO_2)_6]$ is used as artist's pigment under the name of Aureolin or Cobalt yellow.

9 – Precautions:

Potassium reacts very violently with water producing potassium hydroxide (KOH) and hydrogen gas.



This reaction is exothermic and temperature produced is sufficient to ignite the resulting hydrogen. It in turn may explode in the presence of oxygen. Potassium hydroxide is a strong alkali which causes skin burns.

Finely divided potassium will ignite in air at room temperature. The bulk metal will ignite in air if heated. Water makes a potassium fire worse. Because its density is 0.89, burning potassium floats which

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exposes it to more atmospheric oxygen. The water also produces potentially explosive hydrogen gas. Many common fire extinguishing agents are either ineffective or make a potassium fire worse. Sodium chloride (table salt), sodium carbonate (soda ash), and silicon dioxide (sand) are effective if they are dry. Some Class D dry powder extinguishers designed for metal fires are also effective. These powders deprive the fire of oxygen and cool the potassium metal. Nitrogen or argon are also effective.

Potassium reacts violently in the presence of halogens and will detonate in the presence of bromine. It also reacts explosively with sulphuric acid. During combustion potassium forms peroxides and superoxides . These peroxides may react violently with organics present such as oils. Both peroxides and superoxides may react explosively with metallic potassium.

Since potassium reacts with water vapor present in the air, it is usually stored under anhydrous mineral oil or kerosene. Unlike lithium and sodium, however, potassium should not be stored under oil indefinitely. If stored longer than 6 months to a year, dangerous shock-sensitive peroxides can form on the metal and under the lid of the container, which can detonate upon opening. It is recommended that potassium not be stored for longer than three months unless stored in an inert (oxygen free) atmosphere, or under vacuum.

Due to the highly reactive nature of potassium metal, it must be handled with great care, with full skin and eye protection being used and preferably an explosive resistant barrier between the user and the potassium.

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Potassium hydroxide

Contents

- 1 Introduction
- 2 Properties and structure
 - 2.1 Structure
 - 2.2 Solubility and desiccating properties
 - 2.3 Thermal stability
- 3 Reactions
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 - 3.3 Reactions with inorganic compounds
- 4 Manufacture
- 5 Uses
 - 5.1 Precursor to other potassium compounds
 - 5.2 Manufacture of biodiesel
 - 5.3 Manufacture of soft soaps
 - 5.4 As an electrolyte
 - 5.5 Niche applications

1 – Introduction :

Potassium hydroxide is an inorganic compound with the formula KOH. Along with sodium hydroxide, this colourless solid is a prototypical "strong base". It has many industrial and niche applications. Most applications exploit its reactivity toward acids and its corrosive nature. In 2005, an estimated 700,000 to 800,000 tons were produced. Approximately 100 times more NaOH than KOH is produced annually. KOH is noteworthy as the precursor to most soft and liquid soaps as well as numerous potassium - containing chemicals.

IUPAC name : Potassium hydroxide

Other names : Caustic potash

Potash lye

Potassia

Potassium hydrate

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Properties	
Molecular formula	KOH
Molar mass	56 g / mol
Appearance	white solid, deliquescent
Density	2.044 g / cm ³
Melting point	420 °C
Boiling point	1327 °C
Solubility in water	110 g / 100 mL (25 °C) 178 g / 100 mL (100 °C)
Solubility	soluble in alcohol , glycerol insoluble in ether, liquid ammonia
Acidity (pK _a)	13.5 (0.1 M)
Refractive index (n _D)	1.409
Crystal structure	Mono clinic
Hazards	
EU classification	Corrosive (C) , Harmful (Xn)
Flash point	Non - flammable
LD ₅₀	273 mg / kg

2 - Properties and structure:

Potassium hydroxide can be found in pure form by reacting sodium hydroxide with impure potassium. Potassium hydroxide is usually sold as translucent pellets, which will become tacky in air because KOH is hygroscopic. Consequently, KOH typically contains varying amounts of water (as well as carbonates, see below). Its dissolution in water is strongly exothermic, meaning the process gives off significant heat. Concentrated aqueous solutions are sometimes called potassium lyes. Even at high temperatures, solid KOH does not dehydrate readily.

2 – 1 - Structure;

At higher temperatures, solid KOH crystallizes in the NaCl motif. The OH group is either rapidly or randomly disordered so that the OH⁻ group is effectively a spherical anion of radius 1.53 Å (between Cl⁻ and F⁻ in size). At room temperature, the OH⁻ groups

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are ordered and the environment about the K^+ centers is distorted, with $K^+ \cdots OH^-$ distances ranging from 2.69 to 3.15 Å, depending on the orientation of the OH group. KOH forms a series of crystalline hydrates, namely the monohydrate $KOH \cdot H_2O$, the dihydrate $KOH \cdot 2H_2O$, and the tetrahydrate $KOH \cdot 4H_2O$.

2 – 2 - Solubility and desiccating properties:

Approximately 121 g of KOH will dissolve in 100 mL of water at room temperature (compared with 100 g of NaOH in the same volume). Lower alcohols such as methanol, ethanol, and propanols are also excellent solvents. The solubility in ethanol is about 40 g KOH / 100 mL.

Because of its high affinity for water, KOH serves as a desiccant in the laboratory. It is often used to dry basic solvents, especially amines and pyridines: distillation of these basic liquids from a slurry of KOH yields the anhydrous reagent.

2 – 3 - Thermal stability :

Like NaOH, KOH exhibits high thermal stability. The gaseous species is dimeric. Because of its high stability and relatively low melting point, it is often melt-cast as pellets or rods, forms that have low surface area and convenient handling properties.

3 - Reactions :

3 – 1 - As a base :

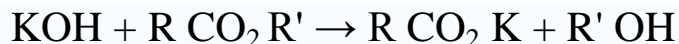
KOH is highly basic, forming strongly alkaline solutions in water and other polar solvents. These solutions are capable of deprotonating many acids, even weak ones. In analytical chemistry, titrations using solutions of KOH are used to assay acids.

3 – 2 - As a nucleophile in organic chemistry :

KOH, like NaOH, serves as a source of OH^- , a highly nucleophilic anion that attacks polar bonds in both inorganic and

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organic materials. In perhaps its most well-known reaction, aqueous KOH saponifies esters :

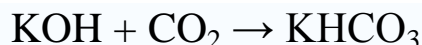


When R is a long chain, the product is called a potassium soap. This reaction is manifested by the "greasy" feel that KOH gives when touched - fats on the skin are rapidly converted to soap and glycerol.

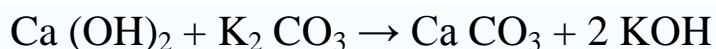
Molten KOH is used to displace halides and other leaving groups. The reaction is especially useful for aromatic reagents to give the corresponding phenols.

3 – 3 - Reactions with inorganic compounds:

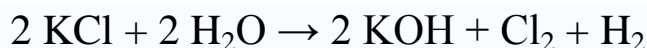
Complementary to its reactivity toward acids, KOH attacks oxides. Thus, SiO_2 is attacked by KOH to give soluble potassium silicates . KOH reacts with carbon dioxide to give bicarbonate:

**4 – Manufacture :**

Historically KOH was made by boiling a solution of potassium carbonate (potash) with calcium hydroxide (slaked lime), leading to a metathesis reaction which caused calcium carbonate to precipitate, leaving potassium hydroxide in solution:



Filtering off the precipitated calcium carbonate and boiling down the solution gives potassium hydroxide ("calcinated or caustic potash"). This method used potash extracted from wood ashes using slaked lime. It was the most important method of producing potassium hydroxide until the late 19th century, when it was largely replaced by the current method of electrolysis of potassium chloride solutions, analogous to the method of manufacturing sodium hydroxide :



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Hydrogen gas forms as a by-product on the cathode; concurrently, an anodic oxidation of the chloride ion takes place, forming chlorine gas as a byproduct. Separation of the anodic and cathodic spaces in the electrolysis cell is essential for this process.

5 - Use :

K OH and Na OH can be used interchangeably for a number of applications, although in industry, Na OH is preferred because of its lower cost.

5 – 1 - Precursor to other potassium compounds:

Many potassium salts are prepared by neutralization reactions involving KOH. The potassium salts of carbonate, cyanide, permanganate, phosphate, and various silicates are prepared by treating either the oxides or the acids with KOH. The high solubility of potassium phosphate is desirable in fertilizers. or a high solubility of a potassium - hydroxide .

5 – 2 - Manufacture of bio diesel :

Although more expensive than using sodium hydroxide, KOH works well in the manufacture of bio diesel by saponification of the fats in vegetable oil. Glycerin from potassium hydroxide - processed bio diesel is useful as an inexpensive food supplement for livestock, once the toxic methanol is removed.

5 – 3 - Manufacture of soft soaps :

The saponification of fats with KOH is used to prepare the corresponding "potassium soaps," which are softer than the more common sodium hydroxide - derived soaps. Because of their softness and greater solubility, potassium soaps require less water to liquefy, and can thus contain more cleaning agent than liquefied sodium soaps.

5 – 4 - As an electrolyte :

Aqueous potassium hydroxide is employed as the electrolyte in alkaline batteries based on nickel - cadmium and manganese dioxide -

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zinc. Potassium hydroxide is preferred over sodium hydroxide because its solutions are more conductive .

5 – 5 - Niche applications;

KOH attracts numerous specialized applications, which virtually all rely on its basic or degradative properties. KOH is widely used in the laboratory for the same purposes.

In chemical synthesis, the selection of KOH vs. NaOH is guided by the solubility for the resulting salt. Its corrosive properties make it useful as an ingredient in cleaning and disinfection of resistant surfaces and materials.

It is often the main active ingredient in chemical "cuticle removers."

KOH is also widely used as a way to remove hair from animal hides, leaving the hides in a solution of KOH and water for a few hours. It is used in resomation to dissolve human remains.

Aggressive bases will damage the cuticle of the hair shaft, and thus is useful for weakening the hair in preparation for shaving. Pre-shave products and shave creams such as Proraso contain Potassium Hydroxide in order to force the cuticle open and act as a hygroscopic agent to attract and force water into the shaft, causing further damage to the hair. In this state, the hair is more easily cut by razor blade.

FERTILIZERS SALTS

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ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**Ammonium ferric citrate****1 – Introduction :**

Ammonium ferric citrate is a food additive with E number E381 used as an acidity regulator. It is a green or reddish-brown powder which is very soluble in water.

Other uses for ammonium ferric citrate include water purification and printing (cyanotype). It is used as a reducing agent of metal salts of low activity like gold and silver and is also in a commonly used recipe with potassium ferri cyanide to make cyanotype prints. Ammonium ferric citrate is also used in Kligler iron deeps to determine hydrogen sulfide production in microbial metabolism.

Ammonium ferric citrate is present in Scottish carbonated soft drink Irn - Bru.

In medicine, ammonium ferric citrate is used as a contrast medium.

IUPAC Name: 2 – Hydroxy propane –1 , 2 , 3 – tri carboxylate,
Ammonium iron (3+) salt

Other Names : Ferric ammonium citrate;
Ammonium Iron (III) Citrate;
Ammonium ferric citrate;
Iron ammonium citrate;
Prothoate +

Molecular formula	$C_6 H_{5+4y} Fe_x N_y O_7$
Molar mass	Variable
Appearance	Reddish - brown powder

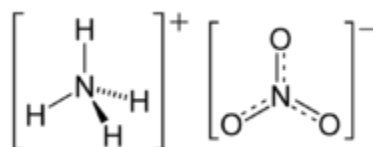
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Ammonium Nitrate

1 – Introduction ;

The chemical compound **ammonium nitrate**, the nitrate of ammonia with the chemical formula NH_4NO_3 , is a white crystalline solid at room temperature and standard pressure. It is commonly used in agriculture as a high - nitrogen fertilizer, and it has also been used as an oxidizing agent in explosives, including improvised explosive devices. It is the main component of ANFO, a very popular explosive.

Ammonium nitrate is used in cold packs, as hydrating the salt is an endothermic process.



Properties

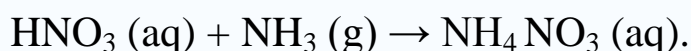
Molecular formula	$(\text{NH}_4)(\text{NO}_3)$
Molar mass	80 g / mol
Appearance	white solid
Density	1.725 g / cm^3 (20 °C)
Melting point	169.6 °C
Boiling point	<i>approx.</i> 210 °C decomp.
Solubility in water	118 g / 100 ml (0 °C)
	150 g / 100 ml (20 °C)
	297 g / 100 ml (40 °C)
	410 g / 100 ml (60 °C)
	576 g / 100 ml (80 °C)
	1024 g / 100 ml (100 °C)

Explosive data

Shock sensitivity	very low
Explosive velocity	5270 m / s
EU Index	not listed
LD ₅₀	2085 – 5300 mg / kg (oral in rats, mice)

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**2 – Production;**

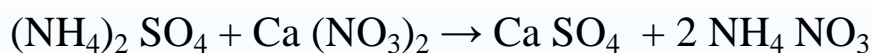
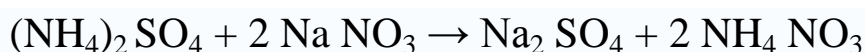
The processes involved in the production of ammonium nitrate in industry, although chemically simple, are technologically challenging. The acid - base reaction of ammonia with nitric acid gives a solution of ammonium nitrate :



For industrial production, this is done using anhydrous ammonia gas and concentrated nitric acid. This reaction is violent and very exothermic. After the solution is formed, typically at about 83% concentration, the excess water is evaporated to an ammonium nitrate (AN) content of 95 % to 99.9 % concentration (AN melt), depending on grade. The AN melt is then made into "prills" or small beads in a spray tower, or into granules by spraying and tumbling in a rotating drum. The prills or granules may be further dried, cooled, and then coated to prevent caking. These prills or granules are the typical AN products in commerce.

The Haber process combines nitrogen and hydrogen to produce ammonia, part of which can be oxidized to nitric acid and combined with the remaining ammonia to produce the nitrate. Another production method is used in the so - called Odda process.

Ammonium nitrate is also manufactured by amateur explosive enthusiasts by metathesis reactions:



Sodium sulfate is removed by lowering the temperature of the mixture. Since sodium sulfate is much less water-soluble than ammonium nitrate, it precipitates, and may be filtered off. For the reaction with calcium nitrate, the calcium sulfate generated is quite insoluble, even at room temperature.

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Transformations of the crystal states due to changing conditions (temperature, pressure) affect the physical properties of ammonium nitrate. The following crystalline states have been identified :

	System Temperature (°C)	State	Volume Change (%)
-	>169.6	liquid	-
I	169.6 to 125.2	cubic	+ 2.1
II	125.2 to 84.2	tetragonal	- 1.3
III	84.2 to 32.3	α - rhombic	+ 3.6
IV	32.3 to -16.8	β - rhombic	- 2.9
V	-16.8	tetragonal	-

The type V crystal is a quasi-cubic form which is related to caesium chloride, the nitrogens of the nitrates and the ammoniums are at the sites in a cubic array where Cs and Cl would be in the Cs Cl lattice.

4 - Ammonium Nitrate Disasters:

Ammonium nitrate decomposes into gases including oxygen when heated (non - explosive reaction) ; however, ammonium nitrate can be induced to decompose explosively by detonation. Large stockpiles of the material can be a major fire risk due to their supporting oxidation, and may also detonate, as happened in the Texas City disaster of 1947, which led to major changes in the regulations for storage and handling.

There are two major classes of incidents resulting in explosions:

- In the first case, the explosion happens by the mechanism of shock to detonation transition. The initiation happens by an explosive charge going off in the mass, by the detonation of a shell thrown into the mass, or by detonation of an explosive mixture in contact with the mass. The examples are Kriewald, Morgan (present - day Sayreville , New Jersey) Oppau, Tessengerlo and Traskwood.

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- In the second case, the explosion results from a fire that spreads into the ammonium nitrate itself (Texas City, Brest, Oakdale), or from a mixture of ammonium nitrate with a combustible material during the fire (Repauno, Cherokee, Nadadores). The fire must be confined at least to a degree for successful transition from a fire to an explosion (a phenomenon known as "deflagration to detonation transition", or DDT). Pure, compact AN is stable and very difficult to ignite, and there are numerous cases when even impure AN did not explode in a fire.

Ammonium nitrate based explosives were used in the Oklahoma City bombing.

Ammonium nitrate decomposes in temperatures normally well above 200°C. However the presence of impurities (organic and/or inorganic) will often reduce the temperature point when heat is being generated. Once the AN has started to decompose then a runaway reaction will normally occur as the heat of decomposition is very large. AN evolves so much heat that this runaway reaction is not normally possible to stop. This is a well - known hazard with some types of N-P-K Fertilizers, and is responsible for the loss of several cargo ships.

In November 2009, a ban on ammonium sulfate, ammonium nitrate and calcium ammonium nitrate fertilizers was imposed in the Malakand Division - comprising the Dir, Swat, Chitral and Malakand districts of the North West Frontier Province (NWFP) of Pakistan, by the NWFP government, following reports that those chemicals were used by militants to make explosives. In January 2010, these substances were also banned in Afghanistan for the same reason.

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Di Ammonium Phosphate

1 – Introduction :

Di ammonium phosphate (DAP) (chemical formula $(\text{NH}_4)_2\text{HPO}_4$, IUPAC name **di ammonium hydrogen phosphate**) is one of a series of water-soluble ammonium phosphate salts which can be produced when ammonia reacts with phosphoric acid.

2 – Uses:

DAP is used as a fertilizer. When applied as plant food, it temporarily increases the soil pH, but over a long term the treated ground becomes more acidic than before upon nitrification of the ammonium. It is incompatible with alkaline chemicals because its ammonium ion is more likely to convert to ammonia in a high-pH environment.

DAP can be used a fire retardant. It lowers the combustion temperature of the material, decreases maximum weight loss rates, and causes an increase in the production of residue or char.^[2] These are important effects in fighting wildfires as lowering the pyrolysis temperature and increasing the amount of char formed reduces that amount of available fuel and can lead to the formation of a firebreak. It is the largest component of some popular commercial firefighting products.

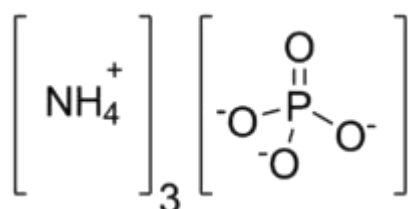
DAP is also used as a yeast nutrient in winemaking and brewing mead; as an additive in some brands of cigarettes purportedly as a nicotine enhancer ; to prevent afterglow in matches, in purifying sugar; as a flux for soldering tin, copper, zinc and brass; and to control precipitation of alkali - soluble and acid - insoluble colloidal dyes on wool.

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Tri Ammonium Phosphate

Ammonium phosphate is the salt of ammonia and phosphoric acid. It has the molecular formula $(\text{NH}_4)_3\text{PO}_4$ and consists of ammonium cations and phosphate anion. It is obtained as a crystalline powder upon mixing concentrated solutions of ammonia and phosphoric acid, or on the addition of excess of ammonia to the acid phosphate $(\text{NH}_4)_2\text{HPO}_4$. It is soluble in water, and the aqueous solution on boiling loses ammonia and the acid phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ is formed.

Ammonium phosphate is used as an ingredient in some fertilizers as a high source of elemental nitrogen. It is also used as a flame retardant in thermoplastic compositions.



IUPAC Name : ammonium phosphate

Other Names . Tri ammonium phosphate

Properties	
Molecular formula	$\text{H}_{12} \text{N}_3 \text{O}_4 \text{P} (\text{NH}_4)_3 \text{PO}_4$
Molar mass	149 g mol^{-1}
Solubility in water	25.0 g /100 g

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Ammonium sulfate

1 - Introduction :

Ammonium sulfate, $(\text{NH}_4)_2 \text{SO}_4$, is an inorganic chemical compound commonly used as a fertilizer. It contains 21% nitrogen as ammonium ions and 24 % sulfur as sulfate ions. Ammonium sulfate occurs naturally as the rare mineral mascagnite in volcanic fumaroles and due to coal fires on some dumps .

IUPAC Name	Ammonium sulfate
Other Names	ammonium sulfate (2:1) ; di ammonium sulfate ; sulfuric acid di ammonium salt ; mascagnite ; Actamaster ; Dolamin
Molecular Formula	$(\text{NH}_4)_2 \text{SO}_4$
Molar Mass	132 g / mol
Appearance	Fine white hygroscopic granules or crystals.
Density	1.77 g / cm ³ @ 50 °C
Melting Point	235 - 280 °C (decomposes)
Solubility in Water	70.6 g / 100 mL (0 °C) and 103.8 g / 100 mL (100 °C)
Critical relative humidity	79.2 % at 30 °C

2 – Properties ;

Ammonium sulfate is not soluble in alcohol or liquid ammonia. The compound is slightly hygroscopic and absorbs water from the air at relative humidity > 81% (at ca. 20°C) .

3 - Synthesis

Ammonium sulfate is prepared commercially by reacting ammonia with sulfuric acid (H_2SO_4). Ammonium sulfate is prepared

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commercially from the ammoniacal liquor of gas - works and is purified by recrystallization. It forms large rhombic prisms, has a somewhat saline taste and is easily soluble in water.

4 - Uses ;

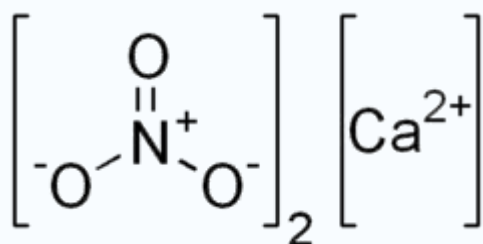
It is used largely as an artificial fertilizer for alkaline soils. In the soil the sulfate ion is released and forms bisulfate, lowering the pH balance of the soil (as do other sulfate compounds such as aluminium sulfate) , while contributing essential nitrogen for plant growth.

It is also used as an agricultural spray adjuvant for water soluble insecticides, herbicides, and fungicides. There it functions to bind iron and calcium cations that are present in both well water and plant cells. It is particularly effective as an adjuvant for 2 , 4 - D (amine) , glyphosate, and glufosinate herbicides.

It is also used in the preparation of other ammonium salts.

In biochemistry, ammonium sulfate precipitation is a common method for purifying proteins by precipitation. As such, ammonium sulfate is also listed as an ingredient for many United States vaccines per the Center for Disease Control.^[3]

Ammonium sulfate is also a food additive .

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**Calcium nitrate****1 – Introduction :**

Calcium nitrate, also called Norges saltpeter (Norwegian saltpeter) is the inorganic compound with the formula $\text{Ca}(\text{NO}_3)_2$. This colorless salt absorbs moisture from the air and is commonly found as a tetra hydrate. It is mainly used as a component in fertilizers. Nitro calcite is the name for a mineral which is a hydrated calcium nitrate that forms as an efflorescence where manure contacts concrete or limestone in a dry environment as in stables or caverns.

Other Names: Kalksalpeter,
Nitrocalcite,
Norwegian salt peter,
Lime nitrate

Properties

Molecular formula	$\text{Ca}(\text{NO}_3)_2$
Molar mass	164 g / mol (anhydrous) 236 g / mol (tetra hydrate)
Appearance	colorless
Density	2.504 g / cm^3 (anhydrous) 1.896 g / cm^3 (tetra hydrate)
Melting point	561 °C (anhydrous) 42.7 °C (tetra hydrate)
Boiling point	decomposes (anhydrous) 132 °C (tetra hydrate)
Solubility in water	<i>anhydrous:</i> 121.2 g / 100 mL (20 °C) 271.0 g / 100 mL (40° C)

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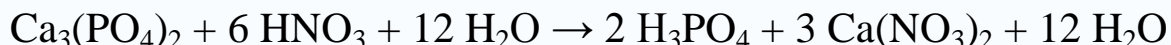
	<i>Tetra hydrate:</i>
	102 g / 100 mL (0 °C)
	129 g / 100 mL (20 °C)
	363 g / 100 mL (100 °C)
Solubility	dissolves in alcohol and acetone
Crystal structure	cubic (anhydrous) mono clinic (tetra hydrate)
Flash point	Non - flammable

2 - Production and reactivity :

Norges saltpeter was the first nitrogen fertilizer compound to be manufactured. Production began at Notodden, Norway in 1905. Most of the world's calcium nitrate is now made in Porsgrunn. It is produced by treating limestone with nitric acid, followed by neutralization with ammonia:



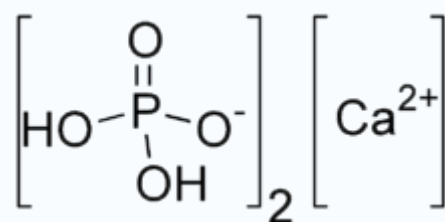
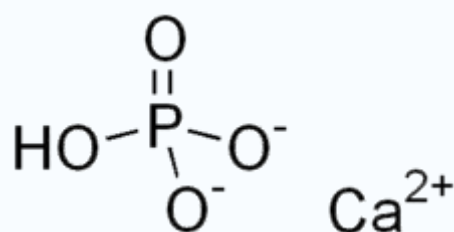
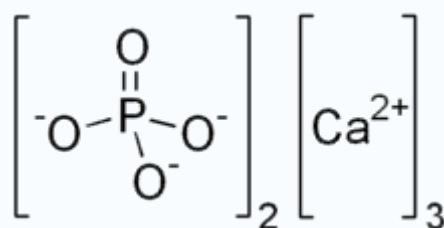
It is also a byproduct of the Odda Process for the extraction of calcium phosphate:



Like related alkaline earth metal nitrates (as well as LiNO_3), calcium nitrate decomposes upon heating to release nitrogen dioxide :

**3 - Use in fertilizer :**

The fertilizer grade (15.5 – 0 - 0 + 19 % Ca) is popular in the greenhouse and hydroponics trades; it contains ammonium nitrate and water, as the "double salt" $5 \text{Ca}(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3 \cdot 10\text{H}_2\text{O}$. Formulations lacking ammonia are also known: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (12.8 - 0 - 0 + 18.3 % Ca). A liquid formulation (9 - 0 - 0 + 11 % Ca) is also offered. An anhydrous, air - stable derivative is the urea complex $\text{Ca}(\text{NO}_3)_2 \cdot 4[\text{OC}(\text{NH}_2)_2]$, which has been sold as Cal - Urea.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**Calcium phosphate***Calcium dihydrogen phosphate**Calcium hydrogen phosphate**Tri calcium phosphate - $\text{Ca}_3(\text{PO}_4)_2$* **1 – Introduction :**

Calcium phosphate is the name given to a family of minerals containing calcium ions (Ca^{2+}) together with ortho phosphates PO_4^{3-} meta phosphates or pyro phosphates ($\text{P}_2\text{O}_7^{4-}$) and occasionally hydrogen or hydroxide ions.

It is the principal form of calcium found in bovine milk. Seventy percent of bone is made up of hydroxy apatite, a calcium phosphate mineral (known as bone mineral). Tooth enamel is also largely calcium phosphate.

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Unlike most other compounds calcium phosphate is increasingly insoluble at higher temperatures. Thus heating causes precipitation.

In milk it is found in higher concentrations than would be possible at the normal pH because it exists in a colloidal form in micelles bound to casein protein with Magnesium, zinc and citrate - collectively referred to as colloidal calcium phosphate (CCP) .

3 - Uses :

For the production of phosphoric acid and fertilizers, for example in the Odda process. Overuse of certain forms of calcium phosphate can lead to nutrient - containing surface runoff and subsequent adverse effects upon receiving waters such as algal blooms and eutrophication.

Calcium phosphate is used in baking as a raising agent, with E number E341. It is also used in cheese products.

Tri calcium phosphate is also used as a nutritional supplement^[2] and occurs naturally in cow milk, although the most common and economical forms for supplementation are calcium carbonate (which should be taken with food) and calcium citrate (which can be taken without food). Hydroxy apatite (e.g. calcium hydrogen phosphate) as a food supplement has not been currently studied well, so its usage as a supplement is discouraged.

It is used in a variety of dental products for re mineralization and as a diluents in some medications where it will give the tablet a grey colour in the absence of additional coloring agents.

Another practical application of the compound is its use in gene transfection of cells. It is not too well understood , but the calcium phosphate precipitate and DNA form a complex that is thought to help the DNA enter the cell.

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4 - Calcium phosphate compounds :

- Calcium phosphate : $\text{Ca}_3(\text{PO}_4)_2$
- Calcium di hydrogen phosphate, E341(i): $\text{Ca}(\text{H}_2\text{PO}_4)_2$
- Calcium hydrogen phosphate, E341(ii): CaHPO_4
- Tri calcium phosphate, E341(iii): $\text{Ca}_3(\text{PO}_4)_2$
- Tetra calcium phosphate : $\text{Ca}_4(\text{PO}_4)_2$

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Mono Calcium Phosphate

1 – Introduction :

Mono calcium phosphate is a chemical compound with the formula $\text{Ca}(\text{H}_2\text{PO}_4)_2$. It is commonly found as the monohydrate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

IUPAC Name : Calcium di hydrogen phosphate

Other Names : Acid calcium phosphate

Calcium acid phosphate

Calcium bi phosphate

Mono basic calcium phosphate

Mono calcium ortho phosphate

Calcium di ortho phosphate

Phosphoric acid calcium salt (2 : 1)

Molecular formula	$\text{Ca H}_4 \text{P}_2 \text{O}_8$
Molar mass	234 g / mol
Density	2.22 g / cm ³
Melting point	109 °C
Boiling point	203 °C (decomposes)

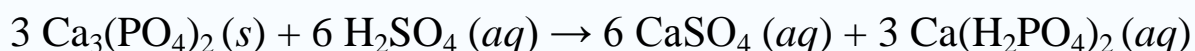
2 – Uses :

2 – 1 – Fertilizer:

Phosphorus is an essential nutrient and therefore is a common component of agricultural fertilizers. Tri calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ a major component of phosphate rock such as phosphorite, apatite, and other phosphate minerals, is too insoluble to be an efficient fertilizer. Therefore it can be converted into the more soluble mono calcium phosphate, generally by the use of sulfuric acid H_2SO_4 . The result is hydrated to turn the calcium sulfate into the di hydrate gypsum and sold as *super phosphate of lime*. Alternately phosphate rock may be treated with phosphoric acid to produce a purer form of mono calcium phosphate and is sold as *triple phosphate*.

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Super phosphate is a fertilizer produced by the action of concentrated sulfuric acid on powdered phosphate rock.



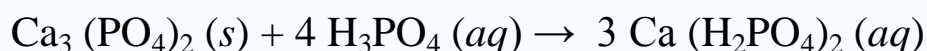
"In 1840, Justus Von Liebig wrote, 'The crops on the field diminish or increase in exact proportion to the diminution or increase of the mineral substances conveyed to it in manure.' Von Liebig was the first to discover that phosphate of lime in bone meal could be rendered more readily available to plants by treatment with sulfuric acid. Sir John Bennett Lawes about the same time discovered that phosphate rock underwent the same reaction and could be used as a source ingredient. In the 1840s, scientists found that coprolites could be dissolved in sulfuric acid to produce what became known as superphosphate. Bennett Lawes was the first to manufacture superphosphate at his factory in Deptford, England in 1842."

A large market for superphosphate was created in the second half of the 20th century by the development of aerial topdressing in New Zealand which allowed superphosphate to be spread economically over large areas.

Super phosphate can be created naturally in large quantities by the action of guano, or bird feces, resulting in deposits around sea bird colonies which can be mined. The most famous mining site is the island of Nauru in the South Pacific much of the "soil" from which was mined, creating temporary wealth for the inhabitants, but destroying their environment.

2 – 1 – 2 - Triple super phosphate:

Triple Super phosphate is a fertilizer produced by the action of concentrated phosphoric acid on ground phosphate rock.



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The active ingredient of the product, mono calcium phosphate, is identical to that of superphosphate, but without the presence of calcium sulfate that is formed if sulfuric acid is used instead of phosphoric acid. The phosphorus content of triple superphosphate (17 – 23 % P; 44 to 52 % P_2O_5) is therefore greater than that of superphosphate (7 - 9.5 % P; 16 to 22 % P_2O_5). Triple superphosphate was the most common phosphate (P) fertilizer in the USA until the 1960s, when ammonium phosphates became more popular. It is produced in granular and non granular form and is used both in fertilizer blends (with potassium and nitrogen fertilizers) and by itself.

2 -2 - Leavening agent :

Calcium di hydrogen phosphate is also used in the food industry as a leavening agent to cause baked goods to rise. Because it is acidic, when combined with an alkali ingredient – commonly sodium bicarbonate (baking soda) or potassium bicarbonate – it reacts to produce carbon dioxide and a salt. The carbon dioxide gas is what leavens the baked good. When combined in a ready-made baking powder, the acid and alkali ingredients are included in the right proportions such that they will exactly neutralize each other and not significantly affect the overall pH of the product.

Apart from acting as leavening agent, it also inhibits microbial activity because of the phosphate ions present in the molec .

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Di Calcium Phosphate

1 Introduction :

Di calcium phosphate, also known as calcium mono hydrogen phosphate, is a dibasic calcium phosphate. It is usually found as the di hydrate, with the chemical formula of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, but it can be thermally converted to the anhydrous form. It is practically insoluble in water, with a solubility of 0.02 g per 100 mL at 25 °C. It contains about 23 percent calcium in its anhydrous form.

IUPAC Name : Calcium hydrogen phosphate

Other Names : Calcium mono hydrogen phosphate

Phosphoric acid calcium salt (1:1)

Molecular Formula CaHPO_4

Molar Mass 136 g / mol

Density 2.929 g / cm³

Solubility in Water 0.02 g /100 mL

Hazards

EU Index Not listed

Flash point Non - flammable

2 – Uses :

Di calcium phosphate is mainly used as a dietary supplement in prepared break fast cereals, dog treats, enriched flour, and noodle products. It is also used as a tableting agent in some pharmaceutical preparations, including some products meant to eliminate body odor. It is used in poultry feed.

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Tri Calcium Phosphate

1 – Introduction ;

Tri calcium phosphate is a compound with formula $\text{Ca}_3(\text{PO}_4)_2$. It is also known as *calcium orthophosphate*, *tertiary calcium phosphate*, *tri basic calcium phosphate*, or "*bone ash*" (calcium phosphate being one of the main combustion products of bone).

It has an alpha and a beta crystal form, the alpha state being formed at high temperatures. As rock, it is found in Whit lockite .

IUPAC Name : Tri calcium di phosphate

Other Names : Whit loc kite

Molecular Formula $\text{Ca}_3\text{O}_8\text{P}_2$

Molar mass 310 g / mol

Appearance White amorphous powder

Density 3.14 g / cm³

Hazards

EU Index Not listed

Flash point Non -flammable

2 - General case :

In minerals, "calcium phosphate" refers to minerals containing calcium ions (Ca^{2+}) together with orthophosphates (PO_4^{3-}), meta phosphates or pyrophosphates ($\text{P}_2\text{O}_7^{4-}$) and occasionally hydrogen or hydroxide ions.

Especially, the common mineral apatite has formula $\text{Ca}_5(\text{PO}_4)_3\text{X}$, where X is F, Cl , OH, or a mixture; it is hydroxyapatite if the extra ion is mainly hydroxide. Much of the "tri calcium phosphate" on the market is actually powdered hydroxy apatite.

3 - Natural occurrence:

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It is found in nature as a rock in Morocco, Jordan , Philippines, Egypt, and Kola (Russia) and in smaller quantities in some other countries. The natural form is not completely pure, and there are some other components like sand and lime which can change the composition. In terms of P_2O_5 , most calcium phosphate rocks have a content of 30 % to 40 % P_2O_5 in weight.

The skeletons and teeth of vertebrate animals are composed of calcium phosphate, mainly hydroxy apatite.

4 - Uses :

Tri calcium phosphate is used in powdered spices as an anti - caking agent.

Calcium phosphate is an important raw material for the production of phosphoric acid and fertilizers, for example in the Odda process.

Calcium phosphate is also a raising agent (food additives) E341 . Is a mineral salt found in rocks and bones, it is used in cheese products.

It is also used as a nutritional supplement and occurs naturally in cow milk, although the most common and economical forms for supplementation are calcium carbonate (which should be taken with food) and calcium citrate (which can be taken without food).^[2] There is some debate about the different bio availabilities of the different calcium salts.

It is commonly used in porcelain and dental powders, and medically as an antacid or calcium supplement, although calcium carbonate is more common in this regard.

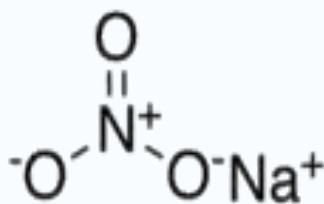
It can be used as a tissue replacement for repairing bony defects when autogenous bone graft is not feasible or possible.^{[3][4][5]} It may be used alone or in combination with a biodegradable, resorbable polymer such as poly glycolic acid. It may also be combined with autologous materials for a bone graft.

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Another practical application of the compound is its use in gene transfection. The calcium ions can make a cell competent (a euphemism for "rip holes in its membrane") to allow exogenous genes to enter the cell by diffusion. A heat shock afterwards then invokes the cell to repair itself. This is a quick and easy method for transfection, albeit a rather inefficient one.

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Sodium Nitrate



1 – Introduction :

Sodium nitrate is the chemical compound with the formula NaNO_3 . This salt, also known as "Chile saltpeter" or "Peru saltpeter" (to distinguish it from ordinary saltpeter, potassium nitrate), is a white solid which is very soluble in water. The mineral form is also known as **nitratine** or **soda niter**.

Sodium nitrate is used as an ingredient in fertilizers, pyrotechnics, as an ingredient in smoke bombs, as a food preservative, and as a solid rocket propellant, as well as in glass and pottery enamels; the compound has been mined extensively for those purposes.

The first shipment of Chile saltpeter to Europe arrived in England in 1820 or 1825, but didn't find any buyers and was dumped at sea in order to avoid customs toll. With time, however, the mining of South American saltpeter became a profitable business (in 1859, England alone consumed 47,000 metric tons). Chile fought against the allies Peru and Bolivia in the War of the Pacific 1879-1884 and took over the richest deposits. The world's largest natural deposits of caliche ore were in the Atacama desert of Chile, and many deposits were mined for over a century, until the 1940s, when its value declined dramatically in the first decades of the twentieth century (see Haber process).

Chile still has the largest reserves of caliche, with active mines in such locations as Pedro de Valdivia, Maria Elena and Pampa Blanca, and there it used to be called "white gold". Sodium nitrate, potassium nitrate, sodium sulfate and iodine are all obtained by the processing of caliche. The former Chilean saltpeter mining communities of

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Humberstone and Santa Laura were declared Unesco World Heritage sites in 2005.

Sodium nitrate is also synthesized industrially by neutralizing nitric acid with soda ash.

IUPAC Name : Sodium nitrate

Other Names : Caliche

Chile saltpeter

Nitrate of soda

Nitratine

Peru saltpeter

Soda niter

Molecular formula	NaNO_3
Molar mass	85 g / mol
Appearance	White powder or colorless crystals with sweet smell
Density	2.257 g / cm ³ , solid
Melting point	308 °C
Boiling point	380 °C decomp.
Solubility in water	92.1 g / 100 ml (25 °C) 180 g / 100mL (100 °C)
Solubility	Very soluble in ammonia; Soluble in alcohol
Refractive index (n_D)	1.587 (trigonal) 1.336 (rhombohedral)
Crystal structure	trigonal and rhombohedral
Std enthalpy of formation $\Delta_f H^\circ_{298}$	– 468 kJ/mol
Main hazards	Oxidant , irritant
Flash point	Non - flammable
LD ₅₀	3236 mg / kg

2 - Applications:

Sodium nitrate was used extensively as a fertilizer and a raw material for the manufacture of gunpowder in the late nineteenth

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century. Sodium nitrate has antimicrobial properties when used as a food preservative. It is found naturally in leafy green vegetables. It can also be combined with iron hydroxide to make a resin.

Sodium nitrate should not be confused with the related compound, sodium nitrite.

It can be used in the production of nitric acid by combining it with sulfuric acid and subsequent separation through fractional distillation of the nitric acid, leaving behind a residue of sodium bisulfate. Hobbyist gold refiners use sodium nitrate to make a hybrid aqua regia that dissolves gold and other metals.

Less common applications include its use as a substitute oxidizer used in fireworks as a replacement for potassium nitrate commonly found in black powder and as a component in instant cold packs.

Because sodium nitrate can be used as a Phase Change Material it may be used for heat transfer in solar power plants.

It is also used in the wastewater industry for the facultative microorganisms respiration. The growth of nitrosomonas will use the nitrate instead of oxygen to breath easier.

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Magnesium phosphate

1 – Introduction :

Magnesium phosphate is a general term for salts of magnesium and phosphate appearing in three forms:

- Magnesium phosphate mono basic ($\text{Mg}(\text{H}_2\text{PO}_4)_2$)
- Magnesium phosphate di basic (MgHPO_4)
- Magnesium phosphate tri basic ($\text{Mg}_3(\text{PO}_4)_2$)

Various forms have been used as laxatives and antacids.

2 - Safety:

Magnesium phosphate dibasic and tri basic are listed on FDA's Generally recognized as safe, or GRAS, list of substances

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**Di Magnesium Phosphate****1 – introduction :**

Di magnesium phosphate is a compound with formula MgHPO_4 . It is a magnesium acid salt of phosphoric acid.

It is one of the compounds that have E number E343^l

other names : Magnesium hydrogen phosphate;
Magnesium phosphate dibasic

Molecular formula HMgO_4P

Molar mass 120 g mol^{-1}

Density 2.13 g / cm^3 tri hydrate

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Magnesium sulfate

1 Introduction :

Magnesium sulfate is a chemical compound containing magnesium and sulfate, with the formula MgSO_4 . In its hydrated form the pH is 6.0 (5.5 to 7.0). It is often encountered as the heptahydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, commonly called **Epsom salts**. Anhydrous magnesium sulfate is used as a drying agent. Since the anhydrous form is hygroscopic (readily absorbs water from the air) and therefore harder to weigh accurately, the hydrate is often preferred when preparing solutions, for example in medical preparations. Epsom salts have traditionally been used as a component of bath salts.

IUPAC Name	Magnesium sulfate (anhydrous) ; Magnesium sulfate heptahydrate
Other Names	Magnesium sulphate ; Epsom salts; Bitter salts
Molecular formula	Mg SO_4 (anhydrous); $\text{Mg SO}_4 \cdot 7\text{H}_2\text{O}$
Molar Mass	120 g / mol
Appearance	white crystalline solid
Density	2.66 g/mL, solid
Melting point	1124°C <i>decomp.</i>
Solubility in water	25.5 g / 100 ml (20 °C)
Crystal structure	monoclinic (hydrate)

2 – Properties :

Magnesium sulfate makes an important contribution to the absorption of sound in seawater .

3 - Occurrence :

Magnesium sulfates are common minerals in geological environments. Their occurrence is mostly connected with supergene processes. Some of them are also important constituents of evaporitic

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potassium-magnesium (K – Mg) salts deposits. Almost all known mineralogical forms of Mg SO_4 occur as hydrates. Epsomite is the natural analogue of " Epsom salt " , mentioned above. Another hepta hydrate, the copper - containing mineral alpersite ($\text{Mg , Cu SO}_4 \cdot 7\text{H}_2\text{O}$) was also recently recognized. Both are however not the highest known hydrates of MgSO_4 , due to the recent terrestrial find of meridianiite, $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$, which is thought to also occur on Mars. Hexahydrate is the next lower (6) hydrate. Three next lower hydrates – penta hydrate (5) , starkeyite (4) and especially sanderite (2) are more rarely found. Kieserite is a monohydrate and is common among evaporitic deposits . Anhydrous magnesium sulfate was reported from some burning coal dumps, but never treated as a mineral.

4 - Applications :

In agriculture and gardening, magnesium sulfate is used to correct magnesium deficiency in soil (magnesium is an essential element in the chlorophyll molecule). It is most commonly applied to potted plants, or to magnesium - hungry crops, such as potatoes, roses, tomatoes, and peppers. The advantage of magnesium sulfate over other magnesium soil amendments (such as dolomitic lime) is its high solubility.

Anhydrous magnesium sulfate is commonly used as a desiccant in organic synthesis due to its affinity for water. During work-up, an organic phase is saturated with magnesium sulfate until it no longer forms clumps. The hydrated solid is then removed with filtration or decantation. Other inorganic sulfate salts such as sodium sulfate and calcium sulfate may also be used in the same way.

Magnesium sulfate is used as in bath salts, particularly in flotation therapy where high concentrations raise the bath water's specific gravity, effectively making the body more buoyant. This property is also used to restore some Lava lamps damaged by being shaken by exchanging the water and adding drops of a concentrated solution until sustainable buoyancy is reached. Traditionally, it is also used to prepare foot baths, intended to soothe sore feet. The reason for the inclusion of the salt is partially cosmetic: the increase in ionic strength prevents some of the temporary skin wrinkling ("pruning")

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which is caused by prolonged immersion of extremities in pure water. However, magnesium sulfate can also be absorbed into the skin, reducing inflammation. It is also used in many bottled water ingredients. It may also be used as a coagulant for making tofu.^[2]

Magnesium sulfate hepta hydrate is also used to maintain the magnesium concentration in marine aquaria which contain large amounts of stony corals as it is slowly depleted in their calcification process. In a magnesium-deficient marine aquarium calcium and alkalinity concentrations are very difficult to control because magnesium stabilizes these ions in the saltwater and prevents their spontaneous precipitation into calcium carbonate.^[3] It is also recommended for dropsy treatment for fish .

An old remedy for diarrhea in adult chickens is 1/2 tsp per bird per day added to their feed.

5 - Medical use :

Oral magnesium sulfate, or magnesium hydroxide, is commonly used as a saline laxative. Epsom salts are also available in a gel form for topical application in treating aches and pains.

Indications for its use are

- Replacement therapy for hypomagnesaemia.
- Magnesium sulfate is the first - line anti arrhythmic agent for Torsades de pointes in cardiac arrest under the 2005 ECC guidelines.
- As a bronchodilator after beta-agonist and anti cholinergic agents have been tried, e.g. in severe exacerbations of asthma^[6]. Recent studies have revealed that magnesium sulfate can be nebulized to reduce the symptoms of acute asthma . It is commonly administered via the intravenous route for the management of severe asthma attacks.
- Users of Epsom salts in the gel form have reported significant and lasting reduction of pain associated with fibromyalgia and osteoporosis .

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- A 2004 research study showed that both magnesium and sulfate are absorbed through the skin when bathing in 1 % solution .
- Magnesium sulfate can be used to treat pre-eclampsia in pregnant women .
- Magnesium sulfate can also delay labor in the case of premature labor, to delay preterm birth.
- Intravenous magnesium sulfate may be able to prevent cerebral palsy in preterm babies .
- Solutions of sulfate salts such as Epsom salts may be given as first aid for barium poisoning .
- Magnesium sulfate paste has been used as an agent for dehydrating (drawing) boils and carbuncles.
- Magnesium sulfate solution has also been shown to be an effective aid in the fight against blemishes and acne when applied directly to problematic areas, usually in poultice form.
- Magnesium sulfate when used through soaking, can soothe muscle pains and help improve rough patches in the skin.
- The body's magnesium level increases when soaking with magnesium sulfate which is necessary for serotonin, a mood - regulating neurotransmitter that may increase feelings of relaxation and well – being .
- Soaking in a warm bath containing Epsom Salt (magnesium sulfate) can be beneficial to soothe and relieve Herpes outbreak symptoms, such as itching and lesions relating to Genital Herpes and Shingles .

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Potassium chloride

1 – Introduction :

The chemical compound **potassium chloride** (KCl) is a metal halide salt composed of potassium and chlorine. In its pure state it is odorless. It has a white or colorless vitreous crystal, with a crystal structure that cleaves easily in three directions. Potassium chloride crystals are face-centered cubic. Potassium chloride is occasionally known as "muriate of potash," particularly when used as a fertilizer. Potash varies in color from pink or red to white depending on the mining and recovery process used. White potash, sometimes referred to as soluble potash, is usually higher in analysis and is used primarily for making liquid starter fertilizers. KCl is used in medicine, scientific applications, food processing and in judicial execution through lethal injection. It occurs naturally as the mineral sylvite and in combination with sodium chloride as sylvinite.

Other Names :	Sylvite , Muriate of potash
Molecular formula	KCl
Molar mass	74.5 g / mol
Appearance	white crystalline solid
Odor	odorless
Density	1.984 g / cm ³
Melting point	790 °C
Boiling point	1420 °C (sublimes)
Solubility in water	28.1 g / 100 ml (0 °C)
	34.4 g / 100 ml (20 °C)
	56.7 g / 100 ml (100 °C)
Solubility	soluble in ether , glycerol , alkalies
	slightly soluble in alcohol
Refractive index (n_D)	1.33743

2 - Chemical properties:

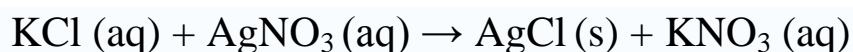
In chemistry and physics it is a very commonly used standard, for example as a calibration standard solution in measuring electrical conductivity of (ionic) solutions, since carefully prepared KCl

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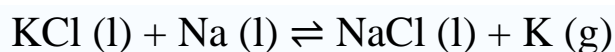
solutions have well-reproducible and well - repeatable measurable properties.

Solubility of KCl in various solvents (g KCl / 100 g of solvent at 25 °C)[2]	
H ₂ O	36
Liquid ammonia	0.04
Liquid sulfur dioxide	0.041
Methanol	0.53
Formic acid	19.2
Sulfolane	0.004
Acetonitrile	0.0024
Acetone	0.000091
Formamide	6.2
Acetamide	2.45
Dimethyl formamide	0.017– 0.05

Potassium chloride can react as a source of chloride ion. As with any other soluble ionic chloride, it will precipitate insoluble chloride salts when added to a solution of an appropriate metal ion:



Although potassium is more electropositive than sodium, KCl can be reduced to the metal by reaction with metallic sodium at 850 °C because the potassium is removed by distillation



This method is the main method for producing metallic potassium. Electrolysis (used for sodium) fails because of the high solubility of potassium in molten KCl.

As with other compounds containing potassium, KCl in powdered form gives a lilac flame test result.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**3 - Physical properties:**

Potassium chloride has a crystalline structure like many other salts. Its structure is face - centered cubic. Its lattice constant is roughly 630 pico meters. Some other properties are

- Transmission range: 210 nm to 20 μm
- Transmittivity = 92 % at 450 nm and rises linearly to 94% at 16 μm
- Refractive index = 1.456 at 10 μm
- Reflection Loss = 6.8 % at 10 μm (two surfaces)
- dN / dT (expansion coefficient) = $-33.2 \times 10^{-6} / ^\circ\text{C}$
- dL / dT (refractive index gradient) = $40 \times 10^{-6} / ^\circ\text{C}$
- Coefficient of absorption: 0.001 cm^{-1}
- Thermal conductivity = $0.036 \text{ W}/(\text{cm}\cdot\text{K})$

4 - Production:

Potassium chloride occurs naturally as sylvite, and it can be extracted from sylvinit. It is also extracted from salt water and can be manufactured by crystallization from solution, flotation or electrostatic separation from suitable minerals. It is a by-product of the making of nitric acid from potassium nitrate and hydrochloric acid.

	
<i>Sylvite</i>	<i>Sylvinit</i>

5 – Uses :

The majority of the potassium chloride produced is used for making fertilizer, since the growth of many plants is limited by their potassium intake. As a chemical feedstock it is used for the

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manufacture of potassium hydroxide and potassium metal. It is also used in medicine, scientific applications, food processing, and as a sodium-free substitute for table salt (sodium chloride).

Potassium chloride is used as the third of a three - drug combination in lethal injection. Additionally, KCl is used (albeit rarely) in fetal intracardiac injections in second- and third-trimester induced abortions.

It is sometimes used in water as a completion fluid in petroleum and natural gas operations, as well as being an alternative to sodium chloride in household water softener units. KCl is useful as a beta radiation source for calibration of radiation monitoring equipment because natural potassium contains 0.0118% of the isotope ^{40}K . One kilogram of KCl yields 16350 becquerels of radiation consisting of 89.28% beta and 10.72 % gamma with 1.46083 MeV. Potassium chloride makes up 70 % of Ace Hardware's pet and vegetation-friendly "Ice Melt" though inferior in melting quality to calcium chloride ($-18\text{ }^{\circ}\text{C}$) v . ($-31.7\text{ }^{\circ}\text{C}$) . It is also used in various brands of bottled water, as well as in bulk quantities for fossil fuel drilling purposes.

Potassium chloride was once used as a fire extinguishing agent, used in portable and wheeled fire extinguishers. Known as Super - K dry chemical, it was more effective than sodium bicarbonate - based dry chemicals and was compatible with protein foam. This agent fell out of favor with the introduction of potassium bicarbonate (Purple-K) dry chemical in the late 1960s, which was much less corrosive and more effective. Rated for B and C fires.

Along with sodium chloride and lithium chloride, potassium chloride is used as a flux for the gas welding of aluminium.

Potassium chloride is also an optical crystal with a wide transmission range from 210 nm to 20 μm . While cheap, KCl crystal is hygroscopic. This limits its application to protected environments or short term uses such as prototyping. Exposed to free air, KCl optics will "rot". Whereas KCl components were formerly used for infrared optics .

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Potassium chloride has also been used to create heat packs which employ exothermic chemical reactions, but these are no longer being created due to cheaper and more efficient methods such as the oxidation of metals ('Hot Hands', one time use products) or the crystallization of sodium acetate (multiple use products).

6 - Biological and medical properties:

Potassium is vital in the human body and oral potassium chloride is the common means to replenish it, although it can also be diluted and given intravenously. It can be used as a salt substitute for food, but due to its weak, bitter, unsalty flavor, it is usually mixed with regular salt (sodium chloride), for this purpose to improve the taste (for example, in Morton Lite Salt). Medically it is used in the treatment of hypokalemia and associated conditions, for digitalis poisoning, and as an electrolyte replenisher. Brand names include K - Dur, Klor - Con, Micro - K, and Kaon Cl. Side effects can include gastrointestinal discomfort including nausea and vomiting, diarrhea and bleeding of the digestive tract. Overdoses cause hyperkalemia which can lead to paresthesia, cardiac conduction blocks, fibrillation, arrhythmias, and sclerosis.

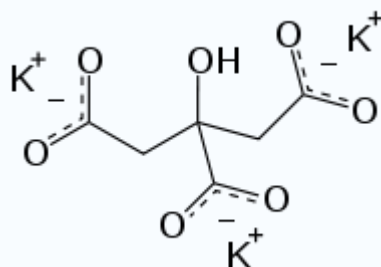
The lethal effects of potassium chloride overdoses has led to its use in lethal injection. Jack Kevorkian's thanatron machine injected a lethal dose of potassium chloride into the patient, which caused the heart to stop functioning, after a sodium thiopental-induced coma was achieved. A similar device, the German 'Perfusor', also uses potassium chloride as a suicide aid.

7 – Precautions:

Orally, KCl is toxic in excess; the LD₅₀ is around 2.5 g / kg (meaning that a lethal dose for 50 % of people weighing 75 kg is about 190 g). Intravenously this is reduced to just over 100 mg / kg, but of more concern are its severe effects on the cardiac muscles; high doses can cause cardiac arrest and rapid death, ergo its aforementioned use as the third and final drug delivered in the lethal injection process.

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Potassium citrate



1 – Introduction :

Potassium citrate is a potassium salt of citric acid with the molecular formula $C_6H_5K_3O_7$. It is a white, slightly hygroscopic crystalline powder. It is odorless with a saline taste.

As a food additive, potassium citrate is used to regulate acidity. Medicinally, it may be used to control kidney stones derived from either uric acid or cystine.

IUPAC name : Tri potassium Citrate

Properties

Molecular formula	$C_6H_5K_3O_7$
Molar mass	306 g / mol
Appearance	white powder , hygroscopic
Odor	odorless
Density	1.98 g / cm ³
Melting point	180 °C
Boiling point	230 °C
Solubility in water	soluble
Solubility	soluble in glycerin insoluble in ethanol (95%)

Hazards

LD ₅₀	170 mg / kg (IV, dog)
------------------	-----------------------

2 - Uses :

Potassium citrate is rapidly absorbed when given by mouth and is excreted in the urine as the carbonate. It is, therefore, effective in

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reducing the pain and frequency of urination when these are caused by highly acidic urine. It is used for this purpose in dogs and cats, but is chiefly employed as a non-irritating diuretic.

Potassium citrate is an effective way to treat/manage gout and arrhythmia, if the patient is hypokalemic. In common with other substances that render the urine alkaline, it may be used to reduce the danger of crystalluria during sulfonamide therapy.

It is widely used to treat urinary calculi (kidney stones), and is often used by patients with cystinuria. A study of 500 patients with recurrent stones found that it reduced the frequency of stones from 2 per year to a half per year. It is also used in many soft drinks as a buffering agent.

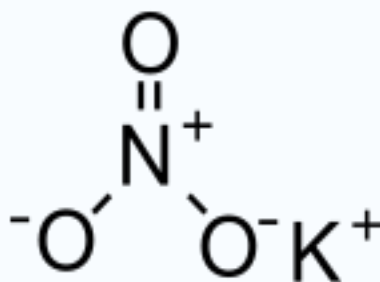
3 - Administration :

Potassium citrate is usually administered by mouth in dilute aqueous solution. This is because of its somewhat caustic effect on the stomach lining, and the potential for other mild health hazards.

The maximum allowable over-the-counter (OTC) dose for elemental potassium is regulated by the FDA to be no more than 100 mg (approximately 3 % of the daily allowance). Potassium citrate contains 32.28 % potassium.

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Potassium Nitrate



1 – Introduction :

Potassium nitrate is a chemical compound with the chemical formula KNO_3 . A naturally occurring mineral source of nitrogen, KNO_3 constitutes a critical oxidizing component of black powder / gun powder. In the past it was also used for several kinds of burning fuses, including slow matches. Potassium nitrate readily precipitates from mixtures of salts, and decomposing urine was the main commercial source of the nitrate ion, through various means, from the Late Middle Ages and Early Modern era through the 19th century.

Its common names include **salt petre** (**salt peter** in American English), from Medieval Latin *sal petræ*: "stone salt" or possibly "Salt of Petra", **nitrate of potash**, and **nitre** (American **niter**). For specific information about the naturally occurring mineral, see **niter**. The name **Peru salt petre** or **Chile salt petre** (American "Peru saltpeter" or "Chile saltpeter") is applied to sodium nitrate, a similar nitrogen compound that is also used in explosives and fertilizers. The major problem of using the cheaper sodium nitrate in gunpowder is its tendency to go damp.

Other Names : Saltpetre
Nitrate of potash
Vesta powder

Properties

Molecular Formula KNO_3

Molar Mass 101 g / mol

Appearance white solid

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Odor	odorless
Density	2.109 g / cm ³ (16 °C)
Melting point	334 °C
Boiling point	400 °C decomp.
	13.3 g / 100 mL (0 °C)
Solubility in water	36 g / 100 mL (25 °C)
	247 g / 100 mL (100 °C)
Solubility	slightly soluble in ethanol
	soluble in glycerol, ammonia

Structure

Crystal structure	Ortho rhombic, Aragonite
-------------------	--------------------------

Hazards

EU Index	Not listed
Main hazards	Oxidant
Flash point	Non - flammable
LD ₅₀	3750 mg / kg

2 – Description:

Potassium nitrate is the oxidising component of black powder. Before the large - scale industrial fixation of nitrogen through the Haber process, major sources of potassium nitrate were the deposits crystallizing from cave walls and the draining of decomposing organic material. Dung-heaps were a particularly common source: ammonia from the decomposition of urea and other nitrogenous materials would undergo bacterial oxidation to produce nitrates. These often contained calcium nitrate, which could be converted to potassium nitrate by the addition of potash from wood ashes. It was and is also used as a component in some fertilizers. Potassium nitrate when used by itself as a fertilizer has an NPK rating of 13 - 0 - 44. Potassium nitrate was once thought to induce impotence, and is still falsely rumored to be in institutional food (such as military fare) as an anaphrodisiac; these uses would be ineffective, since potassium nitrate has no such properties. However, potassium nitrate successfully combats high blood pressure and was once used as a hypotensive. Other nitrates and

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nitrites such as glyceryl trinitrate (nitroglycerin), amyl nitrite and isosorbide derivatives are still used to relieve angina.

3 - History of production:

Historically, niter-beds were prepared by mixing manure with either mortar or wood ashes, common earth and organic materials such as straw to give porosity to a compost pile typically 1.5 meters high by 2 meters wide by 5 meters long.^[3] The heap was usually under a cover from the rain, kept moist with urine, turned often to accelerate the decomposition and leached with water after approximately one year. The liquid containing various nitrates was then converted with wood ashes to potassium nitrate, crystallized and refined for use in gun powder.

Urine has also been used in the manufacture of saltpetre for gunpowder. In this process, stale urine placed in a container of straw hay is allowed to sour for many months, after which water is used to wash the resulting chemical salts from the straw. The process is completed by filtering the liquid through wood ashes and air-drying in the sun. Saltpetre crystals can then be collected and added to sulfur and charcoal to create black powder. Potassium nitrate could also be harvested from accumulations of bat guano in caves. This was the traditional method used in Laos for the manufacture of gun powder for Bang Fai rockets.

The earliest known complete purification process for potassium nitrate is described in 1270 by the Arab chemist and engineer Hasan al-Rammah of Syria in his book *al-Furusiyya wa al-Manasib al-Harbiyya* ('The Book of Military Horsemanship and Ingenious War Devices'), where he first described the use of potassium carbonate (in the form of wood ashes) to remove calcium and magnesium salts from the potassium nitrate.

During the 19th century and until around World War I, potassium nitrate was produced on an industrial scale, first by the Birkeland – Eyde process in 1905, and then later from ammonia produced by the

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much more efficient Haber process. Today practically all nitrates are produced from the oxidation of ammonia made by the Haber process.

4 – Uses:

Potassium nitrate is also used as a fertilizer, in amateur rocket propellants, and in several fireworks such as smoke bombs.

In the process of food preservation, potassium nitrate has been a common ingredient of salted meat since the Middle Ages, but its use has been mostly discontinued due to inconsistent results compared to more modern nitrate and nitrite compounds. Even so, saltpetre is still used in some food applications, such as charcuterie and the brine used to make corned beef. Sodium nitrate (and nitrite) have mostly supplanted potassium nitrate's culinary usage, as they are more reliable in preventing bacterial infection than saltpetre. All three give cured salami and corned beef their characteristic pink hue.

In the European Union, the compound is referred to as E252.

It is commonly used in pre - rolled cigarettes to maintain an even burn of the tobacco.

As a fertilizer, it is used as a source of nitrogen and potassium, two of the macro nutrients for plants.

Potassium nitrate is also the main component (usually about 98 %) of tree stump remover, as it accelerates the natural decomposition of the stump.

Potassium nitrate is also commonly used in the heat treatment of metals as a solvent in the post - wash. The oxidizing, water solubility and low cost make it an ideal short - term rust inhibitor.

It has also been used in the manufacture of ice cream and can be found in some toothpastes for sensitive teeth . Recently, the use of potassium nitrate in toothpastes for treating sensitive teeth has increased dramatically, despite the fact that it has not been conclusively shown to reduce dentine hypersensitivity.

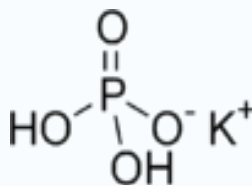
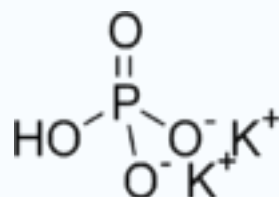
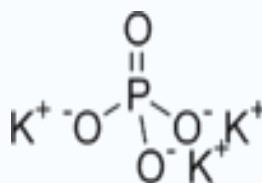
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Potassium nitrate is also one of the three components of black powder, along with powdered charcoal (substantially carbon) and sulfur, where it acts as an oxidizer. When subjected to the flame test it produces a lilac flame due to the presence of potassium.

Saltpetre is thought to decrease sex drive, but there is no scientific evidence to support that the substance causes such an effect.

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Potassium Phosphate

*Mono potassium phosphate**Dipotassium phosphate**Tripotassium phosphate*

Introduction :

Potassium phosphate is a generic term for the salts of potassium and phosphate ions including:

- Mono potassium phosphate (KH_2PO_4)
- Di potassium phosphate (K_2HPO_4)
- Tri potassium phosphate (K_3PO_4)

As food additives, potassium phosphates have the E number E340 .

The ratio of potassium to phosphate in K-Phos solution is 3:4.3 ($\text{K}:\text{PO}_4$). The ratio of potassium to phosphate in K-Phos Neutral packets for oral administration is 1:1 , 14.25 mEq potassium and 14.25 mmol phosphate per packet.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**Mono potassium phosphate****1 – Introduction :**

Mono potassium phosphate (also **potassium di hydrogen phosphate, KDP**, or **mono basic potassium phosphate, MKP**) -- KH_2PO_4 -- is a soluble salt which is used as a fertilizer, a food additive and a fungicide. It is a source of phosphorus and potassium. It is also a buffering agent. When used in fertilizer mixtures with urea and ammonium phosphates, it minimizes escape of ammonia by keeping the pH at a relatively low level.

Fertilizer grade MKP contains the equivalent of 52 % P_2O_5 and 34 % K_2O , and is labeled 0 – 52 – 34 . MKP is often used as a nutrient source in the greenhouse trade and in hydroponics.

It is one of the components of Gatorade (used as both an emulsifier and pH buffer) and is used as an additive in cigarettes.

At 400 °C it decomposes, by loss of water, to potassium metaphosphate (KPO_3)

IUPAC name : Potassium di hydrogen phosphate

Other names : Potassium phosphate mono basic

Phosphoric acid ,

Mono potassium salt

Molecular formula	KH_2PO_4
Molar mass	136 g / mol
Appearance	White powder deliquescent
Density	2.338 g / cm ³
Melting point	252.6 °C
Boiling point	400 °C, dec
Solubility in water	33 g / 100 ml
Solubility	insoluble in alcohol
Crystal structure	tetragonal
EU Index	Not listed
Flash point	Non - flammable

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**2 - Nonlinear optics use:**

As a crystal, it is noted for its non - linear optical properties. Used in optical modulators and for non-linear optics such as SHG (second harmonic generation).

Also to be noted is **KD*P**, Potassium dideuterium phosphate, with slightly different properties. Highly deuterated KDP is used in nonlinear frequency conversion of laser light instead of protonated (regular) KDP due to the fact that the replacement of protons with deuterons in the crystal shifts the third overtone of the strong OH molecular stretch to longer wavelengths, moving it mostly out of the range of the fundamental line at ~ 1,064 nm of neodymium based lasers. Regular KDP has absorbances at this wavelength of around 4.7 - 6.3 % / cm of thickness while highly deuterated KDP has absorbances of typically less than 8 % / cm.

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Di Potassium Phosphate

1 – Introduction :

Dipotassium phosphate (K_2HPO_4) - also phosphoric acid, dipotassium salt; dipotassium hydrogen orthophosphate; potassium phosphate, dibasic - is a highly water - soluble salt which is often used as a fertilizer, food additive and buffering agent. It is a common source of phosphorus and potassium.

2 - Safety:

As a food additive, Dipotassium phosphate is on the FDA's Generally recognized as safe, or GRAS, list of substances^[1]. It is used in non - dairy creamers to prevent coagulation.

It is some times sold as a food additive to help with headaches.

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Tri potassium phosphate

1 – Introduction ;

Tripotassium phosphate is a water-soluble ionic salt which has the chemical formula K_3PO_4 . It is used as a food additive for its properties as an emulsifier, foaming agent and whipping agent.^[1] In combination with fatty acids, it is a potential antimicrobial agent in poultry processing. As a fertilizer, its proportions of N, P_2O_5 , and K_2O are 0 - 33 - 67, making it one of the few fertilizer compounds in which the nutrient percentages have a total of 100 % .

IUPAC name : Tri potassium phosphate

Molecular formula K_3PO_4

Molar mass 212 g / mol

Appearance white powder deliquescent

Density 2.564 g / cm³ (17 °C)

Melting point 1380 °C

Solubility in water 90 g / 100 mL (20 °C)

Solubility In soluble in alcohol

Hazards

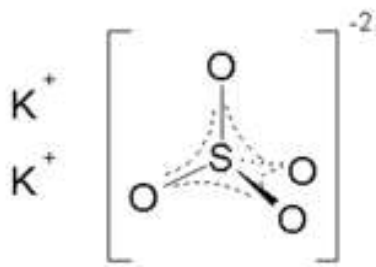
EU Index Not listed

Main hazards Irritant

Flash point Non - flammable

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Potassium Sulfate



Contents :

- 1 introduction
- 2 History
- 3 Natural resources
- 4 Manufacture
- 5 Properties
- 6 Uses
- 7 Potassium hydrogen sulfate

1 – Introduction :

Potassium sulfate (K_2SO_4), or **potassium sulphate**, also called **sulphate of potash**, **arcanite**, or archaically known as **potash of sulfur**, is a non - flammable white crystalline salt which is soluble in water. The chemical is commonly used in fertilizers, providing both potassium and sulfur.

Other names : Potassium sulphate

Molecular formula K_2SO_4

Molar mass 174 g / mol

Appearance White crystalline solid

Density 2.66 g / cm³

Melting point 1069 °C, 1342 K, 1956 °F

Boiling point 1689 °C, 1962 K, 3072 °F

11.1 g / 100 ml (20 °C)

Solubility in water 12 g / 100 mL (25 °C)

24 g / 100 mL (100 °C)

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Solubility	slightly soluble in glycerol insoluble in acetone, alcohol, CS ₂
Crystal structure	orthorhombic

Hazards

EU Index	Not listed
Main hazards	Irritant
Flash point	Non - flammable
LD ₅₀	6600 mg / kg

2 – History:

Potassium sulfate (K₂SO₄) has been known since early in the 14th century, and it was studied by Glauber, Boyle and Tachenius. In the 17th century it was named *arcanuni* or *sal duplicatum*, as it was a combination of an acid salt with an alkaline salt. It was also known as *vitriolic tartar*.

3 - Natural resources:

The mineral form of potassium sulfate, namely arcanite, is relatively rare. Natural resources of potassium sulfate are minerals abundant in the Stassfurt salt. These are cocrystalisations of potassium sulfate and sulfates of magnesium calcium and sodium. The minerals are :

- Kainite, MgSO₄ · KCl · H₂O
- Schönite, K₂SO₄ · MgSO₄ · 6 H₂O
- Leonite, K₂SO₄ · MgSO₄ · 4 H₂O
- Langbeinite, K₂SO₄ · 2 MgSO₄
- Glaserite, K₃ Na (SO₄)₂
- Polyhalite, K₂SO₄ · MgSO₄ · 2 CaSO₄ · 2 H₂O

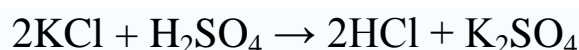
From some of the minerals like kainite, the potassium sulfate can be separated, because the corresponding salt is less soluble in water.

With potassium chloride kieserite MgSO₄ • 2 H₂O can be transformed and then the potassium sulfate can be dissolved in water.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**4 – Manufacture :**

The process for manufacturing potassium sulfate is similar to that used for the manufacture of sodium sulfate.

- Potassium sulfate can be synthesised by reaction of potassium chloride with sulfuric acid according to the Leblanc process. Potassium Sulfate is produced according to the following chemical equation:



- The Hargreaves process uses sulfur dioxide, oxygen and water and potassium chloride as the starting materials to produce potassium sulfate. Hydrochloric acid evaporates off. SO_2 is produced through the burning of sulfur.

5 - Properties :

The anhydrous crystals form a double six - sided pyramid, but are in fact classified as rhombic. They are transparent, very hard and have a bitter, salty taste. The salt is soluble in water, but insoluble in solutions of potassium hydroxide (sp. gr. 1.35), or in absolute ethanol. It melts at 1078 °C .

6 – Uses :

The principal use of potassium sulfate is as a fertilizer. The crude salt is also used occasionally in the manufacture of glass.

7 - Potassium hydrogen sulfate :

Potassium hydrogen sulfate or bisulfate, KHSO_4 , is readily produced by mixing K_2SO_4 with an equivalent no. of moles of sulfuric acid. It forms rhombic pyramids, which melt at 197 °C. It dissolves in three parts of water at 0°C. The solution behaves much as if its two congeners, K_2SO_4 and H_2SO_4 , were present side by side of each other uncombined; an excess of ethanol the precipitates normal sulfate (with little bisulfate) with excess acid remaining.

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The behavior of the fused dry salt is similar when heated to several hundred degrees; it acts on silicates, titanates, etc., the same way as sulfuric acid that is heated beyond its natural boiling point does. Hence it is frequently used in analytical chemistry as a disintegrating agent. For information about other salts that contain sulfate .

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Borax

Contents

- 1 Introduction
- 2 Uses
 - 2.1 Buffer
 - 2.2 Co - complexing
 - 2.3 Flux
 - 2.4 Small-scale mining
 - 2.5 Putty
 - 2.6 Food additive
 - 2.7 Other uses
- 3 Natural sources
- 4 Toxicity
- 5 Chemistry

1 – Introduction :

Borax, also known as **sodium borate**, **sodium tetra borate**, or **disodium tetra borate**, is an important boron compound, a mineral, and a salt of boric acid. It is usually a white powder consisting of soft colorless crystals that dissolve easily in water.

Borax has a wide variety of uses. It is a component of many detergents, cosmetics, and enamel glazes. It is also used to make buffer solutions in biochemistry, as a fire retardant, as an anti-fungal compound for fiber glass, as an insecticide, as a flux in metallurgy, a texturing agent in cooking, and as a precursor for other boron compounds.

The term *borax* is used for a number of closely related minerals or chemical compounds that differ in their crystal water content, but usually refers to the decahydrate. Commercially sold borax is usually partially dehydrated.

The word *borax* is from Persian and originates in the Middle-Persian *būrak*.

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IUPAC Name : Sodium tetra borate decahydrate

Properties

Molecular Formula	$\text{Na}_2 \text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ or $\text{Na}_2 [\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$
Molar mass	381 g / mol
Appearance	white solid
Density	1.73 g /cm ³ (solid)
Melting point	743 °C
Boiling point	1575 °C

2 – Uses :**2 – 1 – Buffer :**

Sodium borate is used in biochemical and chemical laboratories to make buffers, e.g. for gel electrophoresis of DNA, such as TBE or the newer SB buffer or BBS (borate buffered saline) in coating procedures. Borate buffers (usually at pH 8) are also used as preferential equilibration solution in DMP - based crosslinking reactions.

2 – 2 - Co – Complexing:

Borax as a source of borate has been used to take advantage of the co-complexing ability of borate with other agents in water to form complex ions with various substances. Borate and a suitable polymer bed are used to chromatograph non-glycosylated hemoglobin differentially from glycosylated hemoglobin (chiefly HbA1c), which is an indicator of long term hyperglycemia in diabetes mellitus. Borate and a proprietary synthetic amino acid, Deselex (from Henkel) have been used to complex water "hardness" cations to make a non-precipitating water "softener". Borate alone does not have a high affinity for "hardness" cations.

2 – 3 – Flux:

A mixture of borax and ammonium chloride is used as a flux when welding iron and steel. It lowers the melting point of the unwanted iron oxide (*scale*), allowing it to run off. Borax is also used

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mixed with water as a flux when soldering jewelry metals such as gold or silver. It allows the molten solder to flow evenly over the joint in question. Borax is also a good flux for 'pre-tinning' tungsten with zinc - making the tungsten soft - solderable.

2 – 4 - Small - scale mining :

Borax is replacing mercury as the preferred method for extracting gold in small - scale mining facilities. The method is called the borax method and was first discovered in Sweden and used in the Philippines.

2 – 5 - Putty :

When a borax - water solution is mixed with PVA glue (wood glue), a rubbery precipitate is formed which is the result of cross-linking in the polymer.

2 – 6 - Food additive :

Borax, given the E number *E285*, is used as a food additive in some countries but is banned in the United States. In consequence certain foods, such as caviar, produced for sale in the U.S. contain higher levels of salt to assist preservation.^[5] Its use in cooking is to add a firm rubbery texture to the food, or as a preservative. In oriental cooking it is mostly used for its texturing properties. In China it was found to have been added to hand-pulled noodles (*lamian*) and some Cheung Fun recipes . In Indonesia it is a common, but forbidden, additive to such foods as noodles, meatballs and steamed rice. The country's Directorate of Consumer Protection warns of the risk of liver cancer with high consumption over a period of 5 – 10 years.

2 – 7 - Other uses :

- Component of detergents
- Ingredient in enamel glazes
- Component of glass, pottery, and ceramics
- Fire retardant
- Anti - fungal compound for fiberglass and cellulose insulation

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- Insecticide to kill ants, cockroaches and fleas
- Precursor for sodium perborate monohydrate that is used in detergents, as well as for boric acid and other borates
- Tackifier ingredient in casein, starch and dextrin based adhesives
- Precursor for Boric acid, a tackifier ingredient in polyvinyl acetate, polyvinyl alcohol based adhesives
- Treatment for thrush in horses' hooves
- Used to make indelible ink for dip pens by dissolving shellac into heated borax
- Curing agent for snake skins
- Curing agent for salmon eggs, for use in sport fishing for salmon
- Swimming pool buffering agent to control the pH
- Neutron absorber, used in nuclear reactors and spent fuel pools to control reactivity and to shut down a nuclear chain reaction
- In agriculture it can be used as a fertilizer to correct boron-poor soils; however, it is required in small amounts. Excess can cause injury to plants.^[7]
- To clean the brain cavity of a skull for mounting
- To color fires with a green tint^[8]
- Borax can be used as an additive in ceramic slips and glazes to improve fit on wet, greenware, and bisque.
- Borax was traditionally used to coat dry-cured meats such as hams to protect them from becoming fly-blown during further storage.
- Borax is found in some vitamins, such as Puritan's Pride Multi - Day.
- For stopping car radiator and engine block leaks^[9]

3 - Natural sources;

Borax occurs naturally in evaporite deposits produced by the repeated evaporation of seasonal lakes. The most commercially important deposits are found in Turkey, Boron, California, and Searles Lake, California. Also, it has been found at many other locations in the Southwestern United States, the Atacama desert in Chile, and in

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Tibet and Romania. Borax can also be produced synthetically from other boron compounds.

4 – Toxicity :

Borax, sodium tetraborate decahydrate, is not acutely toxic.^[10] Its LD₅₀ (median lethal dose) score is tested at 2.66 g / kg in rats .This does not mean that it is safe, merely that a significant dose of the chemical is needed to cause severe symptoms or death. The median lethal dose for humans tends to differ for a given compound from that of rats. Simple exposure can cause respiratory and skin irritation. Ingestion may cause gastrointestinal distress including nausea, persistent vomiting, abdominal pain, and diarrhea. Effects on the vascular system and brain include headaches and lethargy, but are less frequent. *"In severe poisonings, a beefy red skin rash affecting palms, soles, buttocks and scrotum has been described. With severe poisoning, erythematous and exfoliative rash, unconsciousness, respiratory depression, and renal failure."*

A reassessment of boric acid / borax by the United States Environmental Protection Agency Office of Pesticide Programs found potential developmental toxicity (especially effects on the testes).^[13] Boric acid solutions used as an eye wash or on abraded skin are known to be especially toxic to infants, especially after repeated use because of its slow elimination rate .

5 – Chemistry :

The term *borax* is often used for a number of closely related minerals or chemical compounds that differ in their crystal water content:

- Anhydrous borax ($\text{Na}_2\text{B}_4\text{O}_7$)
- Borax penta hydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$)
- Borax deca hydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)

Borax is generally described as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. However, it is better formulated as $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$, since borax contains the $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ ion. In this structure, there are two four - coordinate

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boron atoms (two BO_4 tetra hedra) and two three-coordinate boron atoms (two BO_3 tri angles).

Borax is also easily converted to boric acid and other borates, which have many applications. Its reaction with hydro chloric acid to form boric acid is:



If left exposed to dry air, it slowly loses its water of hydration and becomes the white and chalky mineral tincalconite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) .

When borax is added to a flame, it produces a yellow green color.^[15] This property has been tried in amateur fireworks, but borax in this use is not popular because its waters of hydration inhibit combustion of compositions and make it an inferior source of the boron which is responsible for most of the green color, and which is over whelmed by the yellow contributed to the flame by sodium.

However, commercially available borax can be mixed with flammables such as methanol to give the characteristic green flame of boron when ignited, which then slowly gives way to the characteristic yellow-orange flame of the sodium.

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ORGANIC FERTILIZERS

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Compost

1 – Introduction :

Compost is a combination of decomposed plant and animal materials and other organic materials that are being decomposed largely through aerobic decomposition into a rich black soil. The process of composting is simple and practiced by individuals in their homes, farmers on their land, and industrially by industries and cities.

Compost soil is very rich soil and used for many purposes. A few of the places that it is used are in gardens, landscaping, horticulture, and agriculture. The compost soil itself is beneficial for the land in many ways, including as a soil conditioner, a fertilizer to add vital humus or humic acids, and as a natural pesticide for soil. In ecosystems, compost soil is useful for erosion control, land and stream reclamation, wetland construction, and as landfill cover .

2 - History :

Composting as a recognized practice dates to at least the early Roman era since Pliny the Elder (AD 23 - 79) who refers to compost in his writings. Traditionally, composting was to pile organic materials and let them stand for about a year, or until the next planting season, at which time the materials would be ready for soil application. The main advantage of this method is that little working time or effort is required from the composter and it fits in naturally with agricultural practices in temperate climates.

Disadvantages (from the modern perspective) are that space is used for a whole year, some nutrients might be leached due to exposure to rainfall, and disease producing organisms, some weeds, weed seeds and insects may not be adequately controlled.

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Composting was somewhat modernized beginning in the 1920s in Europe as a tool for organic farming . The first industrial station for the transformation of urban organic materials into compost was set up in Wels / Austria in the year 1921. The early personages most cited for propounding composting within farming are for the German - speaking world Rudolf Steiner, founder of a farming method called bio dynamics, and Annie Francé - Harrar, who was appointed on behalf of the government in Mexico and supported the country 1950-1958 to set up a large humus organization in the fight against erosion and soil degradation. In the English-speaking world it was Sir Albert Howard who worked extensively in India on sustainable practices and Lady Eve Balfour who was a huge proponent of composting. Composting was imported to America by various followers of these early European movements in the form of persons such as J.I. Rodale (founder of Rodale Organic Gardening), E.E. Pfeiffer (who developed scientific practices in biodynamic farming), Paul Keene (founder of Walnut Acres in Pennsylvania), and Scott and Helen Nearing (who inspired the back – to - land movement of the 1960s). Coincidentally, some of these personages met briefly in India - all were quite influential in the U.S. from the 1960s into the 1980s.

There are many modern proponents of rapid composting which attempt to correct some of the perceived problems associated with traditional, slow composting. Many advocate that compost can be made in 2 to 3 weeks. Many such short processes involve a few changes to traditional methods, including smaller, more homogenized pieces in the compost, controlling carbon to nitrogen (CN) ratio at 30 to 1 or less, and monitoring the moisture level more carefully. However, none of these parameters differ significantly from early writings of Howard and Balfour, suggesting that in fact modern composting has not made significant advances over traditional a few months time .For this reason and others, many modern scientists who deal with carbon transformations are skeptical that there is a " super – charged " way to get nature to make compost rapidly.

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They also point to the fact that it is the structure of the natural molecules - such as carbohydrates, proteins, and cellulose - that really dictate the rate at which microbial - mediated transformations are possible.

3 - Ingredients :

Given enough time, all biodegradable material will oxidize to "compost". One objective of composting today is to treat readily degradable materials that may otherwise enter landfills, and decompose anaerobically, releasing greenhouse gases. Most small - scale domestic systems are not maintained at the thermophilic temperatures required to eliminate possible pathogens and disease vectors, or deter vermin, therefore pet droppings, meat scrap, and dairy products are best left to larger scale high-rate, aerobic composting systems. A local organics recycling facility may operate such a system. However, hobby animal manure (horses , goats , sheep , chickens) , fruit and vegetable food things and Garden materials are excellent raw materials for home composting.

Major bio degradable materials used:

- | | |
|--------------|--------------|
| • Card board | • Paper |
| • Fish | • Sea weed |
| • Fruit | • Tree bark |
| • Leaves | • Vegetables |

Inorganic additives:

- Agricultural lime
- Rock dust
- Soil
- Sand

4 – Uses :

Compost is generally recommended as an additive to soil, or other matrices such as coir and peat, as a tilth improver,

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supplying humus and nutrients. It provides a rich *growing medium*, or a porous, absorbent material that holds moisture and soluble minerals, providing the support and nutrients in which plants can flourish, although it is rarely used alone, being primarily mixed with soil, sand, grit, bark chips, vermiculite, perlite, or clay granules to produce loam.

Generally, direct seeding into a compost is not recommended due to the speed with which it may dry and the possible presence of phytotoxins which may inhibit germination,^{[4][5][6]} and the possible tie up of nitrogen by incompletely decomposed lignin . It is very common to see blends of 20 – 30 % compost used for transplanting seedlings at cotyledon stage or later.

5 - As alternative to land filling :

As concern about landfill space increases, worldwide interest in recycling by means of composting is growing, since composting is a process for converting decomposable organic materials into useful stable products. Industrial scale composting in the form of in - vessel composting, aerated static pile composting, and anaerobic digestion takes place in most Western countries now, and in many areas is mandated by law. There are process and product guidelines in Europe that date to the early 1980s (Germany, Holland, Switzerland) and only more recently in the UK and the US. In both these countries, private trade associations within the industry have established loose standards, some say as a stop-gap measure to discourage independent government agencies from establishing tougher consumer-friendly standards. See: UK^[9] and for the US see ^[10]. The USA is the only Western country that does not distinguish sludge-source compost from green - composts, and by default in the USA 50 % of states expect composts to comply in some manner with the federal EPA 503 rule promulgated in 1984 for sludge products. Compost is regulated in Canada and Australia as well.

Composting

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1 – Introduction :

Composting is the purposeful biodegradation of organic matter, such as yard and food waste. The decomposition is performed by micro - organisms, mostly bacteria, but also yeasts and fungi. In low temperature phases a number of macro-organisms, such as springtails, ants, nematodes , isopods and red wigglers also contribute to the process, as well as soldier fly, fruit flies and fungus gnats. There are a wide range of organisms in the decomposer community .

- A *biodegradable* material is capable of being broken down under the action of microorganisms into carbon dioxide, water and biomass. It may take a very long time for some material to biodegrade depending on its environment (e.g. wood in an arid area versus paper in water). Many contaminating materials not dealt with in common composting are in fact "biodegradable", and may be dealt with via bioremediation, or other special composting approaches.

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- A *compostable* material biodegrades substantially under specific composting conditions. It is metabolized by the microorganisms, being incorporated into the organisms or converted into humus. The size of the material is a factor in determining compost ability, and mechanical particle size reduction can speed the process. Large pieces of hardwood may not be compostable under a specific set of composting conditions, whereas sawdust of the same type of wood may be. Some biodegradable materials are only compostable under very specific conditions, usually with an industrial process .

2 – Importance :

Composting up cycles organic kitchen and yard waste and manures into an extremely useful humus - like, soil end product, permitting the return of vital organic matter, nutrients, and particularly bacteria, that are vital to plant nutrition to the soil. Managed aerobic composting arranges environmental conditions so they are optimal for the natural processes to take place. There is a popular expression: "compost happens", but it is helpful to engineer the best possible circumstances for large amounts of organic waste to decompose quickly and efficiently, with the greatest conservation of useful nutrients and mass. Uncontrolled composting is when compost "happens", and although that may be functional in some circumstances, as with forest floor detritus, a neglected heap of kitchen and yard wastes will more likely result in "smells happen", or "rodents happen" long before useful compost does.

Long used in subsistence farming and home gardening for creating garden - ready soil, composting is becoming increasingly important and better understood as a tool for reducing municipal solid waste, and reducing the amount of green waste going into landfills. The decomposition of organic material sent to landfills is a principal cause of methane, an important greenhouse gas, making reduction of organic waste being land filled a key element in the fight against climate

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change. In general, net greenhouse gas emissions for landfills tend to be higher than that for composting facilities. In suburban and rural areas, much of the organic waste could be removed from the waste stream by promoting home composting, where consumers compost their yard waste and kitchen scraps on their own land, regardless of whether the material is ever actively re-used as "soil". In urban areas with dwellings predominantly lacking individual yard space, there are indoor small scale composting alternatives, such as vermicomposting and bokashi composting.

3 - Materials :

Composting organisms require four equally important things to work effectively :

- Carbon ("C" or carbohydrates) , for energy - the microbial oxidation of carbon produces the heat.
 - High carbon materials tend to be brown and dry
- Nitrogen ("N" or protein), to grow and reproduce more organisms to oxidize the carbon.
 - High nitrogen materials tend to be green (or colorful, like fruits and vegetables) and wet .
- Oxygen, for oxidizing the carbon, the decomposition process .
- Water , in the right amounts to maintain activity without causing anaerobic conditions.

Certain ratios of these elements will provide beneficial bacteria with the nutrients to work at a rate that will heat up the pile. In that process much water will be released as vapor ("steam"), and the oxygen will be quickly depleted, explaining the need to actively manage the pile. The hotter the pile gets, the more often added air and water is necessary; the air/water balance is critical to maintaining high temperatures until the materials are broken down. At the same time, too much air or water also slows the process, as does too much C (or too little N) .

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The most efficient composting occurs with a C : N mix of about 30 to 1. All organics have both carbon and nitrogen, but amounts vary widely, with characteristics noted above (dry / wet , brown / green). Fresh grass clippings have an average ratio of about 15 to 1 and dry autumn leaves about 50 to 1 depending on species. Mixing equal parts by volume approximates the ideal C:N range. Few individual situations will provide the ideal mix of materials at any point in time - in this respect, home composting is like horseshoes, perfect is great, but close still works. Observation of amounts, and consideration of different materials^[11] as a pile is built over time, can quickly achieve a workable technique for the individual situation.

Ingredients that are primarily carbon include:

- Dry , straw - type material, such as cereal straws and corn stalks
- Dry leaves (best shredded , as with a rotary mower , to prevent matting)
- Wood , as coarse or fine (may compact) sawdust, or ground wood waste

Paper and card board, both unprinted and printed are not recommended as both the inks and paper contain materials such as pigments, clays, binders, etc that are not biodegradable. While these insoluble ingredients are not toxic, they will not readily break down as other biodegradable materials. In addition, paper will decompose very slowly interfering with the composting process.

Ingredients with relatively high nitrogen content include:

- Green plant material, like crop residues, new shoots, hay (especially alfalfa), grass clippings and weeds.
- Manure from poultry , humans, pets, and herbivorous animals such as horses, cows and llamas.
- Kitchen waste - fruit and vegetable cooked waste and trimmings , juicing - pulp residue, tea and coffee grounds, meat , bones , eggs .

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For "back yard" composting, mixing the materials as they are added increases the rate of decomposition, as does reduced particle size (ie, chopped, shredded), or materials can be added in alternating layers, about 15 centimeters thick. Keeping a carbon "cache" handy to the pile for covering and mixing with fresh wet additions (lawn clippings, kitchen scraps) is simplest. Special additions or activators are not necessary, although some sprinklings of good garden loam as a first pile is built will aid more rapid working by *inoculating* it with beneficial soil bacteria, and some of the material from the first finished batch can be used in the subsequent mixes. Adding soil also provides grit to help earthworms digest, as well as providing particles for finished compost to aggregate with to create humus. Agricultural lime is not necessary - the bacteria prefer a slightly acidic pH, and their processing invariably results in a near-neutral product. Sea weed meal, rock dust or rock flour, and other trace element amendments are best added to the finished compost, or directly to the garden.

4 – Approaches :

4 – 1 - Active (Intensively Managed) :

An active compost heap, steaming on a cool morning. The heap is kept warm by the exothermic action of the bacteria as they decompose the organic matter.

Hot thermo philic composting is essential with some materials, such as meat and other animal products, dairy products, eggs, grease, cooking oil, manure of non-herbivores, and residuals from the treatment of wastewater, in order to kill pathogens; but these materials are not generally recommended in home composting because of the likelihood of creating odors and attracting rodents. Human waste can be composted by industrial methods as well as composting toilets. When high temperatures are reached, the resulting compost can be safely used for agricultural or horticultural purposes, providing local health regulations are met. Humanure fertilizer (as opposed to

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night soil) is used throughout the developing world and is becoming more accepted as a garden amendment in the developed world.

Hot, aerobic composting is conducted at close to the ideal conditions noted above, allowing thermo philic bacteria to thrive. These aerobic bacteria break down material faster, producing less odor, fewer pathogens, and less greenhouse gas than cool, uncontrolled, or accidental anaerobic methods. Commercial scale composting operations actively control the composting conditions (C : N ratio, moisture level and air), usually in a closed environment (in-vessel composting, tunnel composting or aerated static pile composting), where air is fan forced through the mass, and moisture added with sprayers, or conserved via the enclosure, with computer monitored probes detecting conditions.

In Thailand an aerated static pile system is in use by farmer groups at over 400 sites. The process needs only 30 days to finish without manual turning, with 10 metric tons of compost produced per month. A 38 centimeters (15 in) squirrel - cage blower with 2.2 kilowatts (3.0 hp) motor is used to force air through 10 covered static piles of compost twice a day. The raw materials consist of agricultural wastes and animal manure in the ratio of 3:1 by volume.

Sustained, high temperatures may destroy insects, larvae, and weed seeds, but no compost will be totally sterilized by high temperatures alone. This is because the reduction of available substrate (e.g. water soluble carbon) for bacteria growth must also accompany heating. In a hot compost where the temperature exceeds 55 °C (131 °F) for several weeks, the ability of most organisms to survive is of course compromised, and there are temperature standards, such as in the USA EPA-503 rule, based on early suppositions about this (1980-era). Nevertheless, many organisms in nature can survive extreme temperatures, including extremophiles such as *Thermus thermophilus* which play an important role in thermogenic

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composting, as well as pathogens such as *Clostridium*. The necessary second stage of any composting is maturation, a period allowing the dissipation of readily available substrates for pathogen proliferation and any phyto – toxins remaining from the process or contaminating ingredients (eg:chemical residues) and achieving a state of nutrient stability (low C:N ratio) that will not have an impact on Nitrogen availability in the receiving soil. It is a popular - and dangerous - misnomer of the composting industry that once a pile gets hot for a short period of time, pathogen content is eliminated. Very recent studies of *E. coli* O157 show survival in hot composting out to 120 days.

For backyard composters, carbon and nitrogen ratios in various ingredients and the calculations required to get the ideal mixture can be intimidating, so rules of thumb exist for approximating it by ingredient types and condition, as mentioned in Materials above. If the pile is built in a short period, and has a good mix of materials (C:N) and a coarse structure, with about 50 % moisture (" like a squeezed out sponge "), the temperature should rise within days to as high as 60 °C . When the temperature begins to fall, more air is needed, usually added by turning the pile or using an agitating tool, and moisture may be needed at the same time. Turning or other aeration is usually needed about every 6–10 days to maintain the highest heat levels until the material is fairly uniformly broken down to un recognize ability, and temperatures no longer rebound. A pile that has been maintained at peak temperatures may be ready for maturing in as little as 30 days, but rarely sooner than 60 days. Another 30–60 days maturing should suffice to allow passing the a plant growth test - depending on the plant species chosen.

To achieve thermo philic decomposition, a compost bin is best about 1 cubic meter , or 1 meter wide, 1 metre (3 ft) tall, and as long as desired for windrow composting. This provides enough insulating mass to build up heat but also allows oxygen infiltration. The center of the pile heats up the most, so regular turning/mixing is needed for insuring all material spends some

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time in the hottest area. When turning the pile results in no further temperature rise, the active aerobic phase is complete, and the mass may be turned out to a maturing pile. When the matured material has a dark brown crumbly appearance and the smell of rich damp earth, it is ready to use.

The natural sequence of the decomposition community involved will be:

- 0 – 15 °C psychrophiles predominate, beginning the heating process as they multiply
- 15 – 40 °C mesophiles take over, psychrophiles die off or are relegated to the borders
- 40 – 70 °C thermophiles work at their peak, including consuming many other bacteria

At the lower temperatures and around the borders, there will also be various fungal activity, as well as larger organisms, getting their share - a very dry, cooler pile may be attractive to ants, and gastropods may visit very wet piles. As the temperature returns to ambient at the end of the process, the sequence reverses, including new organisms that prefer the more degraded materials. Added heat and pile insulation may be useful in the coldest weather, but is not ordinarily necessary, and is not desirable if it interferes with aeration or natural convective evaporation. Keeping the top dry and burying fresh additions in the center of a pile will be effective during winter conditions until heating resumes in spring.

4 – 2 - Compost Odor :

Odor is generally the most frequent and serious complaint from neighbors of compost facilities. The first and most important task for the operator is to determine what problematic odors are present and where they are being generated. Only then can appropriate remedial actions be taken.

Compost that is properly made under aerobic conditions will have an earthy aroma that is not offensive. However, partly

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decomposed feed stocks or poor composting techniques can generate problematic odors including ammonia, hydrogen sulfide (the smell of rotten eggs) and volatile fatty acids (VFAs). VFAs are compounds for which most people have very little tolerance. While determining that there is an odor may seem simple, identifying the source and cause of problematic odors at a compost facility can be complex. Sites are large open areas with many potential odor - producing sources, and odors travel in unpredictable ways.

It is essential to determine whether odors are generated by piles of incoming material that have not yet been incorporated, or from a specific compost pile, standing water, holding pond or another source. Identification of the source of the problem is important because the actions required to remedy each of these problems will differ.

Determine the Cause Odors occur at compost facilities for several reasons. Identifying the type of odor can give an indication of the root cause of the problem.

Ammonia An ammonia smell is usually generated in a compost pile that contains too much nitrogen-rich material such as fresh grass. Incoming material can already generate ammonia odors if it has been closed up in plastic bags for very long. Ammonia can also be generated when carbon has been supplied to the piles in particles that are too large, such as uncut brush. In either of these examples, there is too much nitrogen in the original mix for the amount of available carbon (low C:N ratio). An ammonia odor can also sometimes indicate a pH level that is too high.

Hydrogen sulfide A smell of hydrogen sulfide (rotten eggs) indicates that anaerobic conditions are present. Anaerobic conditions form if there are not enough air spaces through which air can flow. This can be caused by too much moisture and/or a lack of aeration. A pile with too much moisture will lack adequate aeration because too many of the air spaces are filled

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with water. Anaerobic conditions can also develop when the pile becomes compacted or air flow through the pile is short circuited. Compaction occurs when there are not enough large or rigid particles such as wood chips to maintain structure and air spaces in the mass. Short circuiting is a term used to describe the tendency of air to follow the route (channels) of least resistance through the pile. Channeling most often occurs in a compost pile that is not mixed during the composting process. In short circuiting, air flows preferentially through the channels rather than being distributed evenly throughout the mass. Although air does pass through the pile when short circuiting occurs, there are areas within the pile with no air, creating localized anaerobic conditions. Rapidly falling temperatures within a compost pile can be an indication that short circuiting is causing the odor problem.

Volatile Fatty Acids (VFAs) VFA's are not only offensive to the olfactory senses, their presence can contribute to phytotoxicity problems in finished compost. Like hydrogen sulfide odors, VFA odors are generated by microbial decomposition that occurs under anaerobic conditions. Because VFAs are generated under anaerobic conditions, it is necessary to determine why those conditions exist and eliminate them.

Ammonia If the ammonia odor is related to an imbalance in the amount of carbon and nitrogen in the recipe (C : N ratio), add more carbon - rich material such as leaves or wood chips. It is important that the particle size of the carbon source is small enough that it can be used by microbes. A carbon source such as brush or very large wood chips may need to be chipped or ground to a smaller particle size. High pH (greater than 8) can cause excessive ammonia loss and kill bacterial decomposers. If the pH level of a compost pile is greater than 8 , add acidic material such as leaves or sulfates and avoid adding more alkaline material to the pile.

Hydrogen sulfide Hydrogen sulfide odors (rotten eggs) indicate that anaerobic conditions are present within the

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compost pile. This is either because the material is too wet or because there is insufficient aeration. If the hydrogen sulfide odor is caused by wetness, add dry bulking agent, remix and place piles in an area where they won't be located in standing water. If insufficient aeration is related to poor structure or compaction, add bulking agent and remix the pile. If airflow through the pile is uneven (short circuiting) , turning piles more frequently should eliminate the problem.

VFAs Occurrence of VFAs also indicates that anaerobic conditions are present within the compost pile. The remedy applied should be the same as when hydrogen sulfide odors are present. If malodorous conditions persist despite taking the actions previously described, it may be necessary to time the turning of compost piles carefully. Turning is best when done with sensitive receptors in mind, such as when it is raining or when the wind direction is opposite of where sensitive receptors are located.

4 – 3 - Passive (Non – intensive) Composting :

Ambient composting, typical of "sheet composting" methods espoused in early organic farming, usually results in temperatures not climbing substantially above background temperatures, hence the expression ambient. It is slower, and is the more common type of composting in domestic gardening, particularly in home composting where compost piles are less than 1.3 cu. yd (1 cubic meter) in volume. Such composting systems may be in open or closed containers of wood or plastic, or in open exposed piles. Kitchen scraps are put in the garden compost bin and left untended. This scrap bin can have a very high water content which reduces aeration, and may become odorous. To improve drainage and airflow, and reduce odor, carbon-rich materials, or 'browns', such as wood chips, shredded bark, leaves, or twigs may be added to mix and cover each wet addition, or holes made occasionally in the pile. The amount of attention may vary from none through occasional to "regular".

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4 - In nature :

An unusual form of composting in nature is seen in the case of the mound - builders (megapodes) of the Australasian region. These Megapodes are fowl - sized birds famous for building nests in the form of compost heaps containing organic litter, in which they incubate their eggs. The male birds work assiduously to maintain the correct incubation temperatures, by adding and removing litter from the compost pile.

Forest floor detritus is the natural fertilizing material in temperate forests. Soil dwelling organisms slowly decompose the continuously deposited litter from below, returning the nutrients to the soil for bacterial conversion to forms useful to the native vegetation. This is a natural form of mulching or sheet composting.

5 - Vermicomposting:

Worm composting or vermicomposting is a method using Red Wiggler worms in a container to process kitchen waste. Moistened high - carbon bedding such as shredded paper is used as a base to which the food waste is added, and the worms and micro-organisms convert the materials to rich compost called worm castings, a nutrient and microbially rich material. Worm composting can be done indoors, allowing year-round composting, and providing apartment dwellers with a means of recycling food waste.

6 - Industrial systems;

Industrial composting systems are increasingly being installed as a waste management alternative to landfills, along with other advanced waste processing systems. Mechanical sorting of mixed waste streams combined with anaerobic digestion or in-vessel composting, is called mechanical biological treatment, increasingly used in developed countries due to regulations controlling the amount of organic matter allowed in landfills. Treating biodegradable waste before it

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enters a landfill reduces global warming from fugitive methane; untreated waste breaks down anaerobically in a landfill, producing landfill gas that contains methane, a potent greenhouse gas.

Large-scale composting systems are used by many urban centers around the world. Co-composting is a technique which combines solid waste with de-watered bio solids, although difficulties controlling inert and plastic contamination from Municipal solid waste makes this approach less attractive. The world's largest MSW co-composter is the Edmonton Composting Facility in Edmonton, Alberta, Canada, which turns 220,000 tonnes of residential solid waste and 22,500 dry tonnes of bio solids per year into 80,000 tonnes of compost. The facility is 38,690 meters², equivalent to 4 ½ Canadian football fields, and the operating structure is the largest stainless steel building in North America, the size of 14 NHL rinks.

Molasses based Distilleries all over the world generate large amount of effluent termed as spent wash or vinasse. For each liter of alcohol produced, around 8 liters of effluent is generated. This effluent has COD of 1,50,000 PPM and BOD of 60,000 PPM and even more. This effluent needs to be treated and the only effective method for conclusive disposal is by Composting. Sugar Factories generate press mud / cachaza during the process and the same has about 30% fibers as Carbon and has large amount of water. This pressmud is dumped on prepared land in the form of 100 meters long windrows of 3 meters X 1.5 meters and spent wash is sprayed on the windrow while the windrow is being turned. Composting machines called Windrow King, Windrow Prince and Windrow Queen are used for this applications. These machines help consume spent wash of about 2.5 times of the volume of the press mud. Which means that a 100 meters of windrow accommodates about 166 MT of pressmud and uses about 415 M3 of Spent wash in 50 days. Microbial Culture TRIO COM - CULT is used about 1 Kg per MT of press mud for fast de-composing of the spent wash. Lakhs of M3 of spent wash is being composted all over the

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world in countries like India, Colombia, Brazil, Thailand, Indonesia, South Africa etc. Composting machines Windrow King/Prince/Queen of various capacities of 336 HP, 153 HP and 80 Hp are being used all over the world for this application round the clock. The technology of composting spent wash / Vinasse is called TAS BIO - COM. The compost yard has to be prepared as per the norms of local countries however it has to be prepared in such a way that the land is impervious and does not allow the liquid effluent to pass down into the earth. The compost yard has to be located at a place where the smell of composting operations is not allowed to spread, as any composting operation generates foul smell. The compost thus generated, is of excellent quality and is rich in nutrients and it takes care of balance of nature. The products derived from nature go back to nature.

7 - Agriculture :

Compost is an important source of nutrients commonly used in modern agriculture. Through steaming, compost can be sanitized and prepared for further use.

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Urea

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1 – Introduction :

Urea or **carbamide** is an organic compound with the chemical formula $(\text{NH}_2)_2\text{CO}$. The molecule has two amine ($-\text{NH}_2$) residues joined by a carbonyl ($-\text{CO}-$) functional group.

Urea serves an important role in the metabolism of nitrogen - containing compounds by animals and is the main nitrogen - containing substance in the urine of mammals. Being solid, colorless, odorless, neither acidic nor alkaline, highly soluble in water, and relatively non - toxic, urea is widely used in fertilizers as a convenient source of nitrogen. Urea is also an important raw material for the chemical industry. The synthesis

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of this organic compound by Friedrich Wöhler in 1828 from an inorganic precursor was an important milestone in the development of chemistry.

The terms **urea** and **carbamide** are also used for a class of chemical compounds sharing the same functional group $RR'N-CO-NRR'$, namely a carbonyl group attached to two organic amine residues. Examples include carbamide peroxide, allantoin, and hydantoin. Ureas are closely related to biurets and related in structure to amides, carbamates, diimides, carbodiimides, and thiocarbamides.

IUPAC name : Di ammonium ethanol
(as organic compound),
Carbonyl di amide
(as inorganic compound)

Other Names : Carbamide,
Carbonyl di amide,
Carbonyl di amine

Molecular formula	CH_4N_2O
Molar mass	60 g mol^{-1}
Appearance	White solid
Density	1.32 g / cm^3
Melting point	$132.7 - 135 \text{ }^\circ\text{C}$
Solubility in water	$108 \text{ g / 100 ml (20 }^\circ\text{C)}$
	$167 \text{ g / 100 ml (40 }^\circ\text{C)}$
	$251 \text{ g / 100 ml (60 }^\circ\text{C)}$
	$400 \text{ g / 100 ml (80 }^\circ\text{C)}$
	$733 \text{ g / 100 ml (100 }^\circ\text{C)}$

Hazards

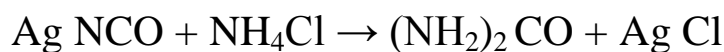
EU Index	Not listed
Flash point	Non - flammable

2 – History:

Urea was first discovered in urine in 1773 by the French chemist Hilaire Rouelle. In 1828, the German chemist Friedrich

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Wöhler obtained urea by treating silver isocyanate with ammonium chloride in a failed attempt to prepare ammonium cyanate :



This was the first time an organic compound was artificially synthesized from inorganic starting materials, without the involvement of living organisms. The results of this experiment implicitly discredited vitalism: the theory that the chemicals of living organisms are fundamentally different from inanimate matter. This insight was important for the development of organic chemistry. His discovery prompted Wöhler to write triumphantly to Berzelius: "I must tell you that I can make urea without the use of kidneys, either man or dog. Ammonium cyanate is urea." For this discovery, Wöhler is considered by many the father of organic chemistry.

3 - Physiology:

Urea is synthesized in the body of many organisms as part of the urea cycle, either from the oxidation of amino acids or from ammonia. In this cycle, amino groups donated by ammonia and L - aspartate are converted to urea, while L - ornithine, citrulline, L - argininosuccinate, and L - arginine act as intermediates. Urea production occurs in the liver and is regulated by N – acetyl glutamate. Urea is found dissolved in blood (in the reference range of 2.5 to 7.5 m mol / liter) and is excreted by the kidney as a component of urine. In addition, a small amount of urea is excreted (along with sodium chloride and water) in sweat.

Amino acids from ingested food which are not used for the synthesis of proteins and other biological substances are oxidized by the body, yielding urea and carbon dioxide, as an alternative source of energy. The oxidation pathway starts with the removal of the amino group by a trans aminase , the amino group is then fed into the urea cycle.

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Ammonia (NH_3) is another common byproduct of the metabolism of nitrogenous compounds. Ammonia molecules are smaller, more volatile and more mobile than urea's. If allowed to accumulate, ammonia would raise the pH in cells to toxic levels. Therefore many organisms convert ammonia to urea, even though this synthesis has a net energy cost. Being practically neutral and highly soluble in water, urea is a safe vehicle for the body to transport and excrete excess nitrogen.

3 – 1 - In humans :

The handling of urea by the kidneys is a vital part of human metabolism. Besides its role as carrier of waste nitrogen, urea also plays a role in the countercurrent exchange system of the nephrons, that allows for re absorption of water and critical ions from the excreted urine. Urea is reabsorbed in the inner medullary collecting ducts of the nephrons, thus raising the osmolarity in the medullary inter stitium surrounding the thin ascending limb of the loop of Henle, which in turn causes water to be reabsorbed. By action of the urea transporter 2, some of this reabsorbed urea will eventually flow back into the thin ascending limb of the tubule, through the collecting ducts, and into the excreted urine.

This mechanism, which is controlled by the antidiuretic hormone, allows the body to create hyperosmotic urine, that has a higher concentration of dissolved substances than the blood plasma. This mechanism is important to prevent the loss of water, to maintain blood pressure, and to maintain a suitable concentration of sodium ions in the blood plasma.

3 – 2 - In other species :

In aquatic organisms the most common form of nitrogen waste is ammonia, while land - dwelling organisms convert the toxic ammonia to either urea or uric acid. Urea is found in the urine of mammals and amphibians, as well as some fish. Birds and saurian reptiles have a different form of nitrogen metabolism, that requires less water and leads to nitrogen being

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excreted in the form of uric acid. It is noteworthy that tadpoles excrete ammonia but shift to urea production during metamorphosis. Despite the generalization above, the urea pathway has been documented not only in mammals and amphibians but in many other organisms as well, including birds, invertebrates, insects, plants, yeast, fungi, and even microorganisms

4 - Uses :

4 – 1 – Agriculture :

More than 90 % of world production of urea is destined for use as a nitrogen - release fertilizer. Urea has the highest nitrogen content of all solid nitrogenous fertilizers in common use (46.7 %). Therefore, it has the lowest transportation costs per unit of nitrogen nutrient.

In the soil, it hydrolyses to ammonia and carbon dioxide. The ammonia is oxidized by bacteria in the soil to nitrate which can be absorbed by the plants. Urea is also used in many multi-component solid fertilizer formulations. Urea is highly soluble in water and is, therefore, also very suitable for use in fertilizer solutions (in combination with ammonium nitrate: UAN), e.g., in 'foliar feed' fertilizers. For fertilizer use, granules are preferred over prills because of their narrower particle size distribution which is an advantage for mechanical application.

The most common impurity of synthetic urea is biuret, which impairs plant growth.

Urea is usually spread at rates of between 40 and 300 kg/ha but rates vary. Smaller applications incur lower losses due to leaching. During summer, urea is often spread just before, or during rain to minimize losses from volatilization (process wherein nitrogen is lost to the atmosphere as ammonia gas). Urea is not compatible with other fertilizers.

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Because of the high nitrogen concentration in urea, it is very important to achieve an even spread. The application equipment must be correctly calibrated and properly used. Drilling must not occur on contact with or close to seed, due to the risk of germination damage. Urea dissolves in water for application as a spray or through irrigation systems.

In grain and cotton crops, urea is often applied at the time of the last cultivation before planting. In high rainfall areas and on sandy soils (where nitrogen can be lost through leaching) and where good in-season rainfall is expected, urea can be side- or top-dressed during the growing season. Top-dressing is also popular on pasture and forage crops. In cultivating sugarcane, urea is side-dressed after planting, and applied to each ratoon crop.

In irrigated crops, urea can be applied dry to the soil, or dissolved and applied through the irrigation water. Urea will dissolve in its own weight in water, but it becomes increasingly difficult to dissolve as the concentration increases. Dissolving urea in water is endothermic, causing the temperature of the solution to fall when urea dissolves.

As a practical guide, when preparing urea solutions for fertigation (injection into irrigation lines), dissolve no more than 30 kg urea per 100 L water.

In foliar sprays, urea concentrations of 0.5 % – 2.0 % are often used in horticultural crops. Low - biuret grades of urea are often indicated.

Urea absorbs moisture from the atmosphere and therefore is typically stored either in closed/sealed bags on pallets, or, if stored in bulk, under cover with a tarpaulin. As with most solid fertilizers, storage in a cool, dry, well - ventilated area is recommended.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**4 – 2 - Chemical industry :**

Urea is a raw material for the manufacture of many important chemical compounds, such as

- Various plastics, especially the urea - formaldehyde resins.
- Various adhesives, such as urea- formaldehyde or the urea - melamine - formaldehyde used in marine plywood.
- Potassium cyanate, another industrial feedstock.
- Urea nitrate, an explosive.

4 - 3 - Automobile systems :

Urea is used in SNCR and SCR reactions to reduce the NO_x pollutants in exhaust gases from combustion, for example, from power plants and diesel engines. The Blue Tec system, for example, injects water - based urea solution into the exhaust system. The ammonia produced by decomposition of the urea reacts with the nitrogen oxide emissions and is converted into nitrogen and water within the catalytic converter.

4 – 4 - Other commercial uses :

- A stabilizer in nitrocellulose explosives.
- A component of animal feed, providing a relatively cheap source of nitrogen to promote growth.
- A non - corroding alternative to rock salt for road de-icing, and the resurfacing of snowboarding half pipes and terrain parks.
- A flavor - enhancing additive for cigarettes.
- A main ingredient in hair removers such as Nair or Veet.
- A browning agent in factory-produced pretzels.
- An ingredient in some hair conditioners, facial cleansers, bath oils, skin softeners, and lotions.
- A reactant in some ready - to - use cold compresses for first-aid use, due to the endothermic reaction it creates when mixed with water.

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- A cloud seeding agent, along with other salts.
- A flame - proofing agent, commonly used in dry chemical fire extinguisher charges such as the urea-potassium bicarbonate mixture.
- An ingredient in many tooth whitening products.
- An ingredient in dish soap.
- Along with ammonium phosphate, as a yeast nutrient, for fermentation of sugars into ethanol.
- A nutrient used by plankton in ocean nourishment experiments for geo engineering purposes.
- As an additive to extend the working temperature and open time of hide glue.
- As a solubility - enhancing and moisture-retaining additive to dye baths for textile dyeing or printing.

4 – 5 - Laboratory uses :

Urea in concentrations up to 10 M is a powerful protein denaturant as it disrupts the non covalent bonds in the proteins. This property can be exploited to increase the solubility of some proteins. A mixture of urea and choline chloride is used as a deep eutectic solvent, a type of ionic liquid.

Urea can in principle serve as a hydrogen source for subsequent power generation in fuel cells. Urea present in urine/wastewater can be used directly (though bacteria normally quickly degrade urea.) Producing hydrogen by electrolysis of urea solution occurs at a lower voltage (0.37 v) and thus consumes less energy than the electrolysis of water (1.2 v).

4 – 6 - Medical use :

Urea is used in topical dermatological products to promote rehydration of the skin. If covered by an occlusive dressing , 40 % urea preparations may also be used for non surgical debridement of nails. This drug is also used as an ear wax removal aid .

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Certain types of instant cold packs (or ice packs) contain water and separated urea crystals. Rupturing the internal water bag starts an endothermic reaction and allows the pack to be used to reduce swelling.

Like saline, urea injection is used to perform abortions. It is also the main component of an alternative medicinal treatment referred to as urine therapy .

The blood urea nitrogen (BUN) test is a measure of the amount of nitrogen in the blood that comes from urea. It is used as a marker of renal function .

Urea labeled with carbon -14 or carbon -13 is used in the urea breath test, which is used to detect the presence of the bacteria *Helicobacter pylori* (*H. pylori*) in the stomach and duodenum of humans, associated with ulcers. The test detects the characteristic enzyme urease, produced by *H. pylori*, by a reaction that produces ammonia from urea. This increases the pH (reduces acidity) of the stomach environment around the bacteria. Similar bacteria species to *H. pylori* can be identified by the same test in animals such as apes , dogs , and cats

5 - Terrorism:

Ahmed Ressam , the al - Qaeda Millennium Bomber, used urea as one of the components in the explosives that he prepared to bomb Los Angeles International Airport on New Year's Eve 1999 / 2000; the explosives could have produced a blast 40 x greater than that of a devastating car bomb.

6 - Synthetic production :

Urea is produced on a scale of some 100,000,000 tons per year world wide.

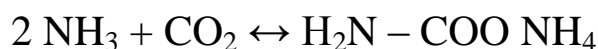
6 – 1 - Industrial methods :

For use in industry, urea is produced from synthetic ammonia and carbon dioxide. Large quantities of carbon dioxide

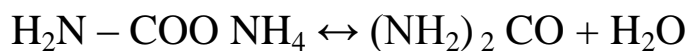
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are produced during the manufacture of ammonia from coal or from hydrocarbons such as natural gas and petroleum - derived raw materials. Such point sources of CO₂ facilitate direct synthesis of urea.

The basic process, developed in 1922, is also called the Bosch - Meiser urea process after its discoverers. The various urea processes are characterized by the conditions under which urea formation takes place and the way in which unconverted reactants are further processed. The process consists of two main equilibrium reactions, with incomplete conversion of the reactants. The first is an exothermic reaction of liquid ammonia with dry ice to form ammonium carbamate (H₂N – COO NH₄) :



The second is an endothermic decomposition of ammonium carbamate into urea and water:



Both reactions combined are exothermic.

Unconverted reactants can be used for the manufacture of other products, for example ammonium nitrate or sulfate, or they can be recycled for complete conversion to urea in a total-recycle process.

Urea can be produced as prills, granules, pellets, crystals, and solutions. Solid urea is marketed as prills or granules. The advantage of prills is that, in general, they can be produced more cheaply than granules. Properties such as impact strength, crushing strength, and free - flowing behavior are, in particular, important in product handling, storage, and bulk transportation. Typical impurities in the production are biuret and isocyanic acid:



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The biuret content is a serious concern because it is often toxic to the very plants that are to be fertilized. Urea is classified on the basis of its biuret content .

6 -2 - Laboratory processes :

Ureas in the more general sense can be accessed in the laboratory by reaction of phosgene with primary or secondary amines, proceeding through an iso cyanate intermediate. Non-symmetric ureas can be accessed by reaction of primary or secondary amines with an iso cyanate.

7 - Chemical properties :

7 – 1 - Molecular and crystal structure:

The urea molecule is planar. In solid urea, the oxygen center is engaged in two N - H - O hydrogen bonds. The resulting dense and energetically favorable hydrogen-bond network is probably established at the cost of efficient molecular packing: The structure is quite open, the ribbons forming tunnels with square cross - section. The carbon in urea is described as sp^2 hybridized, the C - N bonds have significant double bond character, and the carbonyl oxygen is basic compared to, say, formaldehyde. Urea's high aqueous solubility reflects its ability to engage in extensive hydrogen bonding with water.

By virtue of its tendency to form a porous frameworks, urea has the ability to trap many organic compounds. In these so - called clathrates, the organic "guest" molecules are held in channels formed by interpenetrating helices comprising of hydrogen-bonded urea molecules. This behavior can be used to separate mixtures, e.g. in the production of aviation fuel and lubricating oils, and in the separation of paraffins.

As the helices are inter connected, all helices in a crystal must have the same molecular handedness. This is determined when the crystal is nucleated and can thus be forced by seeding.

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The resulting crystals have been used to separate racemic mixtures.

7 – 2 – Reactions :

Urea reacts with alcohols to form urethanes. Urea reacts with malonic esters to make barbituric acids.

8 – Safety:

Urea can be irritating to skin, eyes, and the respiratory tract. Repeated or prolonged contact with urea in fertilizer form on the skin may cause dermatitis.

High concentrations in the blood can be damaging. Ingestion of low concentrations of urea, such as are found in typical human urine, are not dangerous with additional water ingestion within a reasonable time - frame. Many animals (e.g., dogs) have a much more concentrated urine and it contains a higher urea amount than normal human urine; this can prove dangerous as a source of liquids for consumption in a life-threatening situation (such as in a desert).

Urea can cause algal blooms to produce toxins, and its presence in the runoff from fertilized land may play a role in the increase of toxic blooms.

The substance decomposes on heating above melting point, producing toxic gases, and reacts violently with strong oxidants, nitrites, inorganic chlorides, chlorites and perchlorates, causing fire and explosion.

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Urea cycle

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- 2 Function
- 3 Reactions
- 4 Regulation
 - 4.1 N-Acetyl glutamic acid
 - 4.2 Substrate concentrations
- 5 Pathology
- 6 Additional images

1 – Introduction :

The **urea cycle** (also known as the **ornithine cycle**) is a cycle of biochemical reactions occurring in many animals that produces urea $(\text{NH}_2)_2\text{CO}$ from ammonia (NH_3) . This cycle was the first metabolic cycle discovered (Hans Krebs and Kurt Henseleit, 1932). In mammals, the urea cycle takes place primarily in the liver, and to a lesser extent in the kidney.

2 – Function :

Organisms that cannot easily and quickly remove ammonia usually have to convert it to some other substance, like urea or uric acid, which are much less toxic. Insufficiency of the urea cycle occurs in some genetic disorders (inborn errors of metabolism), and in liver failure. The result of liver failure is accumulation of nitrogenous waste, mainly ammonia, which leads to hepatic encephalopathy .

3 – Reactions :

The urea cycle consists of five reactions: two mitochondrial and three cytosolic. The cycle converts two amino groups, one from NH_4^+ and one from Asp, and a carbon atom from HCO_3^- , to the relatively nontoxic excretion product urea at the cost of four "high - energy" phosphate bonds (3 ATP

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hydrolyzed to 2 ADP and one ATP to AMP). Orn is the carrier of these carbon and nitrogen atoms.

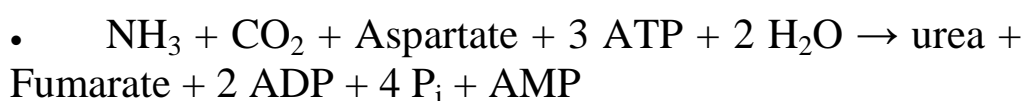
Reactions of the urea cycle :

Step	Reactant	Product	Catalyzed by	Location
1	$2\text{ATP} + \text{HCO}_3^- + \text{NH}_4^+$	carbamoyl phosphate + $2\text{ADP} + \text{P}_i$	CPS1	mitochondria
2	carbamoyl phosphate + ornithine	citrulline + P_i	OTC	mitochondria
3	citrulline + aspartate + ATP	argininosuccinate + AMP + PP_i	ASS	cytosol
4	argininosuccinate	Arg + fumarate	ASL	cytosol
5	Arg + H_2O	ornithine + urea	ARG1	cytosol

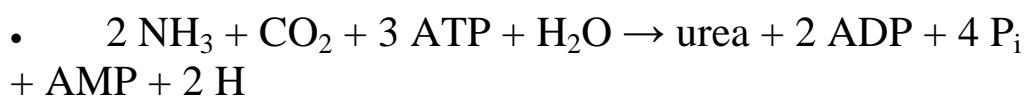
The reactions of the urea cycle

- 1 L - ornithine
 - 2 Carbamoyl phosphate
 - 3 L-citrulline
 - 4 Arginino succinate
 - 5 Fumarate
 - 6 L- arginine
 - 7 Urea
- L-Asp L-aspartate
 CPS-1 carbamoyl phosphate synthetase I
 OTC Ornithine transcarbamylase
 ASS argininosuccinate synthetase
 ASL argininosuccinate lyase
 ARG1 arginase 1

Overall energy requirement:



Overall equation of the urea cycle:

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Note that reactions related to the urea cycle also cause the reduction of 2 NADH, so the urea cycle releases slightly more energy than it consumes. These NADH are produced in two ways:

- One NADH molecule is reduced by the enzyme glutamate dehydrogenase in the conversion of glutamate to ammonium and α - ketoglutarate. Glutamate is the non-toxic carrier of amine groups. This provides the ammonium ion used in the initial synthesis of carbamoyl phosphate.
- The fumarate released in the cytosol is converted to malate by cytosolic fumarase. This malate is then converted to oxaloacetate by cytosolic malate dehydrogenase, generating a reduced NADH in the cytosol. Oxalo acetate is one of the keto acids preferred by trans aminases, and so will be recycled to aspartate , maintained the flow of nitrogen into the urea cycle.

The two NADH produced can provide energy for the formation of 5 ATP, a net production of one high energy phosphate bond for the urea cycle. However, if gluconeogenesis is underway in the cytosol, the latter reducing equivalent is used to drive the reversal of the GAPDH step instead of generating ATP.

The fate of oxalo acetate is either to produce aspartate via oxidative deamination or to be converted to phosphoenol pyruvate, which is a substrate to glucose.()

An excellent way to memorize the Urea Cycle is to remember the phrase "Ordinarily Careless Crappers Are Also Frivolous About Urination." The first letter of each word corresponds to the order in which reactants are combined to give products or intermediates that break apart as one progresses through the cycle.

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**4 - Regulation;****4 – 1 - N –Acetyl glutamic acid :**

The synthesis of carbamoyl phosphate and the urea cycle are dependent on the presence of N Ac Glu, which allosterically activates CPS1. Synthesis of NAc Glu by NAGS, is stimulated by Arg - allosteric stimulator of NAGS, and Glu - a product in the trans amination reactions and one of NAGS's substrates, both of which are elevated when free amino acids are elevated. So, Arg is not only a substrate for the urea cycle reactions but also serves as an activator for the urea cycle .

4 – 2 - Substrate concentrations:

The remaining enzymes of the cycle are controlled by the concentrations of their substrates. Thus, inherited deficiencies in the cycle enzymes other than ARG1 do not result in significant decrease in urea production (the total lack of any cycle enzyme results in death shortly after birth). Rather, the deficient enzyme's substrate builds up, increasing the rate of the deficient reaction to normal.

The anomalous substrate buildup is not without cost, however. The substrate concentrations become elevated all the way back up the cycle to NH_4^+ , resulting in hyperammonemia (elevated $[\text{NH}_4^+]_p$).

Although the root cause of NH_4^+ toxicity is not completely understood, a high $[\text{NH}_4^+]$ puts an enormous strain on the NH_4^+ -clearing system, especially in the brain (symptoms of urea cycle enzyme deficiencies include mental retardation and lethargy). This clearing system involves GLUD1 and GLUL, which decrease the 2OG and Glu pools. The brain is most sensitive to the depletion of these pools. Depletion of 2OG decreases the rate of TCAC, whereas Glu is both a neurotransmitter and a precursor to GABA, another neurotransmitter.

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5 - Pathology:

Anomalies of the urea cycle cause urea cycle disorders:

- ornithine transcarbamoylase deficiency
- Carbamoyl phosphate synthetase deficiency
(Ornithine translocase deficiency)
- Argininosuccinic aciduria
- Argininemia
- Hyperornithinemia, hyperammonemia,
homocitrullinuria syndrome (HHH syndrome)
- Lysinuric protein intolerance
- Citrullinemia
- N-Acetylglutamate synthase deficiency

Most of them are associated with hyperammonemia.

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Urea phosphate

1 – Introduction :

Urea phosphate is an organic compound of carbon, hydrogen, nitrogen, oxygen and phosphorus. Its formula is $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$. It is made by reacting urea with phosphoric acid.

It is sometimes used as a fertilizer; as such, its NPK formula is 17 - 44 - 0. It is soluble in water, and produces a strongly acidic solution. Urea phosphate is sometimes added to blends which contain calcium nitrate and magnesium nitrate to produce water-soluble formulas such as 15-5-15 , 13-2-20 , and 13 - 2 - 13. The acidity of urea phosphate allows Ca, Mg and P to co-exist in solution. Under less acidic conditions, there would be precipitation of Ca - Mg phosphates. Urea phosphate is often used in Drip irrigation to clean the pipe system.

Extension and supplements

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Macronutrient & Micronutrient Fertilizers

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 - 2.1 Macronutrients and micronutrients
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1 – Introduction :

Fertilizers are soil amendments applied to promote plant growth . They are usually applied directly onto the soil, but can also be applied onto leaves (foliar feeding) . The main nutrients added in fertilizer are : nitrogen , phosphorus , and potassium but other nutrients are added in smaller amounts .

Fertilizers can be either organic (e.g. manure) or inorganic (mined or synthesized chemically). Organic fertilizers and some mined inorganic fertilizers have been used for centuries whereas chemically - synthesized inorganic fertilizers were only developed on an industrial scale in the 20th century . Increased understanding and use of fertilizers was an important part of the industrial green revolution of the 20th century.

2 - Chemical content :

Fertilizers typically provide , in varying proportions , the three major plant nutrients : nitrogen , phosphorus , and potassium , known short hand as N-P-K . They may also provide secondary plant nutrients such as calcium , sulfur , magnesium . Micronutrients may be provided : boron , chlorine , manganese , iron , zinc , copper , molybdenum and selenium .

2 – 1 - Macronutrients and micronutrients :

Fertilizers can be classified by their macronutrients and micronutrients content . There are six macronutrients : nitrogen , phosphorus , and potassium , often termed " primary macronutrients " because their availability is usually managed with NPK fertilizers , and the " secondary macronutrients " : calcium , magnesium , and sulfur which are required in roughly similar quantities but whose availability is often managed as part of liming and manuring practices rather than fertilizers .

The macronutrients are consumed in larger quantities and normally present as a whole number or tenths of percentages in plant tissues .

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There are many micronutrients , required in concentrations ranging from 5 to 100 parts per million (ppm) by mass . Plant micronutrients include iron (Fe) , manganese (Mn) , boron (B) , copper (Cu) , molybdenum (Mo) , nickel (Ni), chlorine (Cl) , and zinc (Zn) .

2 – 2 - Macronutrient fertilizers :

Synthesized materials are also called **artificial** , and may be described as **straight** , where the product predominantly contains the three primary ingredients of nitrogen (N) , phosphorus (P) , and potassium (K) , (known as **N-P-K fertilizers** or **compound fertilizers** when elements are mixed intentionally) .

2 – 2 – 2 Reporting of N-P-K :

Such fertilizers are named according to the content of these three elements. For example, if nitrogen is the main element, the fertilizer is often described as a **nitrogen fertilizer**.

Regardless of the name, however, they are labeled according to the relative amounts of each of these three elements, by weight (i.e, mass fraction) . The percent of nitrogen is reported directly. However , phosphorus is reported as the mass fraction of phosphorus pent oxide (P_2O_5) , the anhydride of phosphoric acid , and potassium is reported as the mass fraction of potassium oxide (K_2O) , which is the anhydride of potassium hydroxide .

Fertilizer composition is expressed in this fashion for historical reasons in the way it was analyzed (conversion to ash for P and K mass fractions) ; this practice dates back to Justus von Liebig .

2 – 2 – 2 - 'Mass fraction' conversion to elemental values :

Since the N-P-K reporting described does not give the actual fraction of the respective elements , (some packaging

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also reports elemental mass fractions) . The UK fertilizer - labeling regulations allow for additionally reporting elemental mass fractions of phosphorous and potassium , rather than phosphoric acid and potassium hydroxide, (but must be listed in parentheses after standardized values) . The regulations specify the factors for converting from the P_2O_5 and K_2O values to the respective P and K elemental values as follows:

In phosphorous pent oxide , phosphorous constitutes 43.6 % of the total mass . Thus, the official UK mass fraction (percentage) of elemental phosphorus is 43.6 % .

Likewise , the mass fraction (percentage) of elemental potassium is 83 % . $[K] = 0.83 \times [K_2O]$

Thus an 18–51–20 fertilizer contains , by weight, 18 % elemental nitrogen (N) , 22 % elemental phosphorus (P) , and 16 % elemental potassium (K).

3 - History of Fertilizer :

While manure , cinder and iron making slag have been used to improve crops for centuries , the use of fertilizers is one of the great innovations of the Agricultural Revolution of the 19th Century.

4 - Inorganic fertilizers (synthetic fertilizer) :

Fertilizers are broadly divided into *organic fertilizers* (composed of enriched organic matter—plant or animal) , or *inorganic fertilizers* (composed of synthetic chemicals and / or minerals) .

Inorganic fertilizer is often synthesized using the Haber - Bosch process , which produces ammonia . This ammonia is used as a feedstock for other nitrogen fertilizers (e.g. urea and anhydrous ammonium nitrate UAN) . These concentrated products may be diluted with water to form a concentrated liquid fertilizer . Ammonia can also be used in the Odda Process

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in combination with rock phosphate and potassium fertilizer to produce compound fertilizers .

Major users of nitrogen - based fertilizer

Country	Total N consumption (Mt pa)	Amount used for feed & pasture
China	18.7	3.0
USA	9.1	4.7
France	2.5	1.3
Germany	2.0	1.2
Brazil	1.7	0.7
Canada	1.6	0.9
Turkey	1.5	0.3
UK	1.3	0.9
Mexico	1.3	0.3
Spain	1.2	0.5
Argentina	0.4	0.1

4 – 1 – Application :

Synthetic fertilizers are commonly used to treat fields used for growing maize , followed by barley , sorghum , rapeseed , soy and sunflower . One study has shown that application of nitrogen fertilizer on off - season cover crops can increase the biomass (and subsequent green manure value) of these crops , while having a beneficial effect on soil nitrogen levels for the main crop planted during the summer season .

4 – 2 – Over – fertilization Or Fertilizer burn :

Over - fertilization of a vital nutrient can be as detrimental as under fertilization . " Fertilizer burn " can occur when too

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much fertilizer is applied , resulting in a drying out of the roots and damage or even death of the plant .



Fertilizer burn

4 – 3 - Trace mineral depletion :

Many inorganic fertilizers do not replace trace mineral elements in the soil which become gradually depleted by crops . This depletion has been linked to studies which have shown a marked fall (up to 75 %) in the quantities of such minerals present in fruit and vegetables .

In Western Australia deficiencies of zinc , copper , manganese , iron and molybdenum were identified as limiting the growth of broad - acre crops and pastures in the 1940s and 1950s . Soils in Western Australia are very old , highly weathered and deficient in many of the major nutrients and trace elements . Since this time these trace elements are routinely added to inorganic fertilizers used in agriculture in this state .

4 – 4 - Energy consumption :

The production of synthetic ammonia currently consumes about 5 % of global natural gas consumption , which is some what under 2 % of world energy production .

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Natural gas is overwhelmingly used for the production of ammonia, but other energy sources, together with a hydrogen source, can be used for the production of nitrogen compounds suitable for fertilizers. The cost of natural gas makes up about 90 % of the cost of producing ammonia. The increase in price of natural gas over the past decade, along with other factors such as increasing demand, have contributed to an increase in fertilizer price.

4 – 5 – Long - Term Sustainability :

Inorganic fertilizers are now produced in ways which cannot be continued indefinitely. Potassium and phosphorus come from mines (or saline lakes such as the Dead Sea) and such resources are limited. While atmospheric nitrogen is effectively unlimited (forming over 70 % of atmospheric gases), relatively few plants engage in nitrogen fixation (conversion of atmospheric nitrogen to a plant - accessible form) . To make nitrogen accessible to plants, nitrogen fertilizers are synthesized using fossil fuels such as natural gas and coal, which are limited.

5 - Organic fertilizers

Organic fertilizers include naturally - occurring organic materials, such as manure, worm castings, compost, sea weed, guano and peat moss, or naturally occurring mineral deposits (e.g. salt peter) . In addition to increasing yield and fertilizing plants directly, organic fertilizers can improve the health and long - term productivity of soil. Organic nutrients increase the abundance of soil organisms by providing organic matter and micronutrients for organisms such as fungal mycorrhiza, which aid plants in absorbing nutrients. It is believed by some that 'organic' agricultural methods are more environmentally friendly and better maintain soil organic matter (SOM) levels .

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5 – 1 - Comparison with inorganic fertilizer :

Organic fertilizer nutrient content , solubility , and nutrient release rates are typically all lower than inorganic fertilizers . One study found that over a 140 - day period , after 7 leaching :

- * Organic fertilizers had released between 25 % and 60 % of their nitrogen content .
- * Controlled release fertilizers (CRFs) had a relatively constant rate of release .
- * Soluble fertilizer released most of its nitrogen content at the first leaching .

In general , the nutrients in organic fertilizer are both more dilute and also much less readily available to plants . According to UC IPM, all *organic fertilizers* are classified as ' slow – release ' fertilizers , and there fore cannot cause nitrogen burn .

Non concentrated organic fertilizers with dilute concentrations of nutrients have greater transport and application costs .

Organic fertilizers from treated sewage, composts and other sources can be quite variable from one batch to the next. Without batch testing the amounts of applied nutrient cannot be precisely known. And they are just as good as regular fertilizers.

5 – 2 - Sources :

5 – 2 - 1 – Animal :

Animal - sourced Urea and Urea - Formaldehyde (from urine) , are suitable for application organic agriculture, while pure synthetic forms of urea are not . The common thread that can be seen through these examples is that *organic* agriculture attempts to define itself through minimal processing (e.g. via chemical energy such as petroleum) , as well as being naturally-occurring or via natural biological processes such as composting.

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Sewage sludge use in organic agricultural operations in the U.S. has been extremely limited and rare due to USDA prohibition of the practice (due to toxic metal accumulation , among other factors) . The USDA now requires 3rd - party certification of high - nitrogen liquid organic fertilizers sold in the U.S .

5 - 2 – 2 – Plant :

Cover crops are also grown to enrich soil as a green manure through nitrogen fixation from the atmosphere ; as well as phosphorus (through nutrient mobilization) content of soils . Minerals such as mined rock phosphate , sulfate of potash and lime stone are considered *inorganic fertilizers* , though by a contain no (carbon) molecules .

5 - 2 – 3 – Mineral :

Naturally mined powdered limestone , mined rock phosphate and sodium nitrate , are *inorganic* . and are energetically - intensive to harvest , yet are still approved for usage in organic agriculture in *minimal* amounts . This is a contradictory stance however , because high - concentrate plant nutrients (in the form of salts) obtained from dry lake beds by farmers for centuries in a very minimal fashion are excluded from consideration by most *organic* enthusiasts and many governmental definitions of *organic agriculture* . No such dichotomy between organic and chemical exists .

6 - Environmental effects of fertilizer use :

6 – 1 – Water :

6 – 1 – 1 – Eutrophication :

The nitrogen - rich compounds found in fertilizer run - off is the primary cause of a serious depletion of oxygen in many parts of the ocean , especially in coastal zones ; the resulting lack of dissolved oxygen is greatly reducing the ability of these

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areas to sustain oceanic fauna . Visually, water may become cloudy and / or discolored (green , yellow , brown , or red) . About half of all the lakes in the United States are now eutrophic , while the number of oceanic dead zones near inhabited coastlines are increasing . As of 2006 , the application of nitrogen fertilizer is being increasingly controlled in Britain and the United States . If eutrophication *can* be reversed , it may take decades before the accumulated nitrates in groundwater can be broken down by natural processes .

High application rates of inorganic nitrogen fertilizers in order to maximize crop yields , combined with the high solubility of these fertilizers leads to increased runoff into surface water as well as leaching into groundwater . The use of ammonium nitrate in *inorganic* fertilizers is particularly damaging , as plants absorb ammonium ions preferentially over nitrate ions , while excess nitrate ions which are not absorbed dissolve (by rain or irrigation) into runoff or groundwater .

6 -2 – 2 - Blue Baby Syndrome :

Nitrate levels above 10 mg / L (10 ppm) in ground water can cause ' blue baby syndrome' (acquired methemoglobinemia), leading to hypoxia (which can lead to coma and death if not treated) .

6 - 2 – Soil :

3 – 2 – 1 – Acidification :

Nitrogen - containing inorganic fertilizers in the form of nitrate and ammonium cause soil acidification .

6 -2 – 2 - Toxic persistent organic compounds :

Dioxins , poly chlorinated di benzo – p - dioxins (PCDDs) , and poly chlorinated di benzo furans (PCDFs) have been detected in fertilizers and soil amendments .

ADANA UNIVERSITY – INDUSTRY JOINT RESEARCH CENTER**6 – 2 - 3 - Heavy metal accumulation :**

The concentration of up to 100 mg / kg of cadmium in phosphate minerals increases the contamination of soil with cadmium . Uranium is another example of a contaminant often found in phosphate fertilizers ' Eventually these heavy metals can build up to unacceptable levels and build up in produce .

Steel industry wastes , recycled into fertilizers for their high levels of zinc (essential to plant growth) , wastes can include the following toxic metals : lead , arsenic , cadmium , chromium , and nickel . The most common toxic elements in this type of fertilizer are mercury , lead , and arsenic .

Also, highly - radioactive Polonium - 210 contained in phosphate fertilizers is absorbed by the roots of plants and stored in its tissues . Tobacco derived from plants fertilized by rock phosphates contains Polonium - 210 which emits alpha radiation estimated to cause about 11,700 lung cancer deaths each year world wide .

For these reasons , it is recommended that nutrient budgeting , through careful observation and monitoring of crops, take place to mitigate the effects of excess fertilizer application .

6 – 3 - Atmosphere :

Through the increasing use of nitrogen fertilizer , which is added at a rate of 120 million tons per year presently to the already existing amount of reactive nitrogen , nitrous oxide (N_2O) has become the third most important greenhouse gas after carbon dioxide and methane, with a global warming potential 296 times larger than an equal mass of carbon dioxide, while it also contributes to stratospheric ozone depletion .

Storage and application of some nitrogen fertilizers in some weather or soil conditions can cause emissions of the potent green house gas — nitrous oxide . Ammonia gas (NH_3)

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may be emitted following application of ' inorganic ' fertilizers and / or manures and slurries .

The use of fertilizers on a global scale emits significant quantities of greenhouse gas into the atmosphere. Emissions come about through the use of :

- * - animal manures and urea , which release methane , nitrous oxide , ammonia , and carbon dioxide in varying quantities depending on their form (solid or liquid) and management (collection , storage , spreading)
- * - fertilizers that use nitric acid or ammonium bicarbonate , the production and application of which results in emissions of nitrogen oxides , nitrous oxide , ammonia and carbon dioxide into the atmosphere .

By changing processes and procedures , it is possible to mitigate some , but not all , of these effects on anthropogenic climate change .

6 – 4 - Increased pest problems :

Excessive nitrogen fertilizer applications can also lead to pest problems by increasing the birth rate , longevity and overall fitness of certain agricultural pests .

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A	P
Aheylite	Panethite
Aldermanite	Phosphophyllite
Alforsite	Phosphorite
Alluaudite	Pseudomalachite
Althausite	Purpurite
Althupite	Pyromorphite
Amblygonite	R
Anapaite	Robertsite
Apatite	S
Archerite	Saleeite
Arctite	Santabarbaraite
Arthurite	Scorzalite
Augelite	Seamanite
Autunite	Segelerite
B	Struvite
Beraunite	Svanbergite
Bergenite	T
Berlinite	Taranakite
Beryllonite	Torbernite
Bisbee Blue	Triplite
Brazilianite	Triploidite
Brianite	Turquoise
Brushite	U
C	Ulrichite
Cacoxenite	Upalite
Childrenite	V
Coconinoite	Vantasselite
Cyrllovite	Variscite
D	Vauquelinite
Delvauxite	Vauxite
Diadochite	Vivianite
E	W
Eosphorite	Wagnerite

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F	Wardite
Fluor apatite	Wavellite
Fluorcapthite	Whitlockite
Francolite	Woodhouseite
G	X
Graftonite	Xanthoxenite
H	Xenotime
Hazenite	Z
Henwoodite	Zanazziite
Herderite	
Hopeite	P
Hureaulite	Panethite
Hydroxylapatite	Phosphophyllite
J	Phosphorite
Jarosewichite	Pseudomalachite
K	Purpurite
Kolbeckite	Pyromorphite
L	R
Lazulite	Robertsite
Libethenite	S
Lithiophilite	Saleeite
M	Santabarbaraite
Metatorbernite	Scorzalite
Monazite	Seamanite
Moroxite	Segelerite
N	Struvite
Natrophilite	Svanbergite
Nissonite	T
O	Taranakite
Odontolite	Torbernite
	Triplite
	Triploidite
	Turquoise
	U
	Ulrichite

Pozzolan

1 – Introduction :

A **pozzolan** is a material which, when combined with calcium hydroxide, exhibits cementitious properties. Pozzolans are commonly used as an addition (the technical term is "cement extender") to Portland cement concrete mixtures to increase the long - term strength and other material properties of Portland cement concrete, and in some cases reduce the material cost of concrete. Pozzolans are primarily vitreous siliceous materials which react with calcium hydroxide to form calcium silicates; other cementitious materials may also be formed depending on the constituents of the pozzolan.

The pozzolanic reaction may be slower than the rest of the reactions that occur during cement hydration, and thus the short-term strength of concrete made with pozzolans may not be as high as concrete made with purely cementitious materials; conversely, highly reactive pozzolans, such as silica fume and high reactivity meta kaolin can produce "high early strength" concrete that increase the rate at which concrete gains strength.

The first known pozzolan was pozzolana, a volcanic ash, for which the category of materials was named. The most commonly used pozzolan today is fly ash, though silica fume, high-reactivity meta kaolin, ground granulated blast furnace slag, and other materials are also used as pozzolans.

A pozzolan is a siliceous or aluminosiliceous material, which is highly vitreous. This material independently has few/fewer cementitious properties, but in the presence of a lime-rich medium like calcium hydroxide, shows better cementitious properties towards the later day strength (> 28 days) . The mechanism for this display of strength is the reaction of silicates with lime to form secondary cementitious phases (calcium silicate hydrates with a lower C / S ratio) which display gradual strengthening properties usually after 7 days.

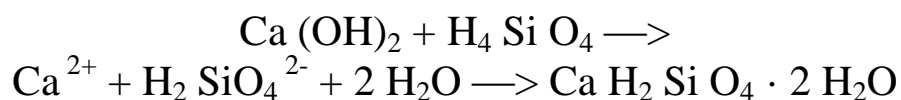
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The extent of the strength development depends upon the chemical composition of the pozzolan : the greater the composition of alumina and silica along with the vitreous phase in the material, the better the pozzolanic reaction and strength display.

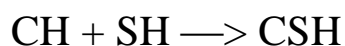
Many pozzolans available for use in construction today were previously seen as waste products, often ending up in landfills. Use of pozzolans can permit a decrease in the use of Portland cement when producing concrete, this is more environmentally friendly than limiting cementitious materials to Portland cement. As experience with using pozzolans has increased over the past 15 years, current practice may permit up to a 40 percent reduction of Portland cement used in the concrete mix when replaced with a carefully designed combination of approved pozzolans. When the mix is designed properly, concrete can utilize pozzolans without significantly reducing the final compressive strength or other performance characteristics .

2 - Pozzolanic reaction :

At the basis of the Pozzolanic reaction stands a simple acid - base reaction between calcium hydroxide, also known as Portlandite , or $(\text{Ca}(\text{OH})_2)$, and silicic acid (H_4SiO_4 , or $\text{Si}(\text{OH})_4$) For simplifying, this reaction can be schematically represented as following :



or summarized in abbreviated notation of cement chemists :



The product of general formula ($\text{CaH}_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$) formed is a calcium silicate hydrate, also abbreviated as CSH in cement chemist notation. The ratio Ca / Si , or C / S , and the

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number of water molecules can vary and the here above mentioned stoichiometry may differ.

As the density of CSH is lower than that of portlandite and pure silica, a consequence of this reaction is a swelling of the reaction products. This reaction may also occur with time in concrete between alkaline cement pore water and poorly-crystalline silica aggregates. This delayed process is also known as alkali silica reaction, or alkali - aggregate reaction, and may seriously damage concrete structures because the resulting volumetric expansion is also responsible for spalling and decrease of the concrete strength.

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Pumice

1 – Introduction :

Pumice is a textural term for a volcanic rock that is a solidified frothy lava typically created when super - heated, highly pressurized rock is violently ejected from a volcano. It can be formed when lava and water are mixed. This unusual formation is due to the simultaneous actions of rapid cooling and rapid depressurization. The depressurization creates bubbles by lowering the solubility of gases (including water and CO₂) dissolved in the lava, so that they rapidly exsolve (like the bubbles of CO₂ that appear when a carbonated drink is opened). The simultaneous cooling then freezes the bubbles in the matrix.

2 - Properties :

Pumice is composed of highly micro vesicular glass **pyroclastic with very thin, translucent bubble walls of extrusive igneous rock**. It is commonly, but not exclusively of silicic or felsic to intermediate in composition (e.g., rhyolitic, dacitic, andesite , pantellerite , phonolite , trachyte) , but basaltic and other compositions are known. Pumice is commonly pale in color, ranging from white, cream, blue or grey, to green-brown or black. It forms when volcanic gases exsolving from viscous magma nucleate bubbles which cannot readily decouple from the viscous magma prior to chilling to glass. Pumice is a common product of explosive eruptions (plinian and ignimbrite-forming) and commonly forms zones in upper parts of silicic lavas. Pumice has an average porosity of 90 %, and initially floats on water.

Scoria differs from pumice in being denser, with larger vesicles and thicker vesicle walls; it sinks rapidly. The difference is the result of the lower viscosity of the magma that forms scoria. When larger amounts of gas are present, the result is a finer-grained variety of pumice known as **pumicite**. Pumice is considered a glass because it has no crystal structure. Pumice

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varies in density according to the thickness of the solid material between the bubbles; many samples float in water. After the explosion of Krakatoa, rafts of pumice drifted through the Pacific Ocean for up to 20 years, with tree trunks floating among them. In fact, pumice rafts disperse and support several marine species. In 1979, 1984 and 2006, underwater volcanic eruptions near Tonga created large pumice rafts, some as large as 30 kilometres that floated hundreds of kilo metres to Fiji.

There are two main forms of vesicles. Most pumice contains tubular micro vesicles that can impart a silky or fibrous fabric. The elongation of the micro vesicles occurs due to ductile elongation in the volcanic conduit or, in the case of pumiceous lavas, during flow. The other form of vesicles are subspherical to spherical and result from high vapor pressure during eruption.

3 – Uses :

Pumice is widely used to make lightweight concrete or insulative low-density breeze blocks. When used as an additive for cement, a fine-grained version of pumice called pozzolan is mixed with lime to form a light-weight, smooth, plaster-like concrete. This form of concrete was used as far back as Roman times. Roman engineers used it to build the huge dome of the Pantheon and as construction material for many aqueducts.

It is also used as an abrasive, especially in polishes, pencil erasers, cosmetic exfoliants, and to produce stone - washed jeans. "Pumice stones" are often used in beauty salons during the pedicure process to remove dry and excess skin from the bottom of the foot as well as calluses. It was also used in ancient Greek and Roman times to remove excess hair. Finely ground pumice is added to some toothpastes and heavy - duty hand cleaners (such as Lava soap) as a mild abrasive.