Ammonia

Ammonia					
101.7 pm H H H 107.8°					
	Identifiers				
CAS number	7664-41-7 [1] 🗸				
PubChem	222 ^[2] (anhydrate) \checkmark , 12896473 ^[3] (monohydrate) \checkmark , 22321416 ^[4] (dihydrate) \checkmark				
ChemSpider	$217^{[5]}$ (anhydrate) \checkmark , 11338614 ^[6] (dihydrate) \checkmark				
EC number	231-635-3 ^[7]				
UN number	UN 1005				
KEGG	C00014 ^[8]				
MeSH	Ammonia ^[9]				
ChEBI	16134 ^[10]				
RTECS number	BO0875000				
SMILES					
InChI					
InChI key	QGZKDVFQNNGYKY-UHFFFAOYSA-N				
Beilstein Reference	3587154				
Gmelin Reference	79				
3DMet	B00004 ^[11]				
Properties					
Molecular formula	NH ₃				
Molar mass	17.031 g/mol				
Appearance	Colourless gas with strong pungent odour				
Density	0.86 kg/m ³ (1.013 bar at boiling point) 0.73 kg/m ³ (1.013 bar at 15 °C) 681.9 kg/m ³ at -33.3 °C (liquid) ^[12] 817 kg/m ³ at -80 °C (transparent solid) ^[13]				

Melting point	-77.73 °C, unknown operator: u'\u2212' K, unknown operator: u'\u2212' °F					
Boiling point	-33.34 °C, unknown operator: u'\u2212' K, unknown operator: u'\u2212' °F					
Solubility in water	47% (0 °C) 31% (25 °C) 28% (50 °C) ^[14]					
Acidity (pK_a)	9.2 (H ₂ O) 10.5 (DMSO)					
Basicity (pK_b)	4.75					
	Structure					
Molecular shape	Trigonal pyramid					
Dipole moment	1.42 D					
Hazards						
EU Index	007-001-00-5 (anhydrous) 007-001-01-2 (solutions)					
EU classification	Toxic (T) Corrosive (C) Dangerous for the environment (N)					
R-phrases	R10, R23, R34, R50					
S-phrases	(\$1/2), \$9, \$16, \$26, \$36/37/39, \$45, \$61					
NFPA 704						
Flash point	flammable gas (see text)					
Autoignition temperature	651 °C					
Explosive limits	15–28%					
U.S. Permissible exposure limit (PEL)	50 ppm (25 ppm ACGIH- TLV; 35 ppm STEL)					
	Related compounds					
Other cations	Phosphine Arsine Stibine					
Related nitrogen hydrides	Hydrazine Hydrazoic acid					
Related compounds	Ammonium hydroxide					
✓ (what is this?) (verify) ^[15] Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa) Infobox references						

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3 . It is a colourless gas with a characteristic pungent odour. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food 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 tonnes.^[16] It is used in commercial cleaning products.

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 °C, (-28.012 °F) 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 °C) being the typical high concentration commercial product.^[17] Household ammonia ranges in concentration from 5 to 10 weight percent ammonia.

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 makes 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 NH₄⁺. The latter has the shape of a regular tetrahedron and is isoelectronic with methane. It is known to have the highest specific heat capacity of any substance.

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 NH₃ to neutralize excess acid.^[18] 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*.

History

The Romans called the ammonium chloride deposits they collected from near the Temple of Jupiter Amun (Greek Ἄμμων Ammon) in ancient Libya 'sal ammoniacus' (salt of Amun) because of proximity to the nearby temple.^[19] 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*.^[20]

In the form of sal-ammoniac (nushadir), ammonia was important to the Muslim alchemists as early as the 8th century, first mentioned by the Islamic chemist Jābir ibn Hayyān,^[21] 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.^[22]



This high-pressure reactor was built in 1921 by BASF in Ludwigshafen and was re-erected on the premises of the University of Karlsruhe in Germany.

Gaseous ammonia was first isolated by Joseph Priestley in 1774 and

was termed by him *alkaline air*.^[23] Eleven years later in 1785, Claude Louis Berthollet ascertained its composition.

The Haber-Bosch 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,^[16] 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.^[24]

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.

Synthesis and production

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.^[25] The People's Republic of China produced 28.4% of the worldwide production (increasingly from coal as part of urea synthesis)^[26] followed by India with 8.6%, Russia with 8.4%, and the United States with 8.2%.^[25] About 80% or more of the ammonia produced is used for fertilizing agricultural crops.^[25]



Before the start of World War I, most ammonia was obtained by the dry distillation^[27] 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^[28] such as quicklime, the salt most generally used being the chloride (sal-ammoniac) thus:

 $2 \text{ NH}_{4}\text{Cl} + 2 \text{ CaO} \rightarrow \text{CaCl}_{2} + \text{Ca(OH)}_{2} + 2 \text{ NH}_{3}$

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:

 $\mathrm{H_2} + \mathrm{RSH} \rightarrow \mathrm{RH} + \mathrm{H_2S}~(\mathrm{g})$

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:

 $H_2S + ZnO \rightarrow ZnS + H_2O$

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

 $CH_4 + H_2O \rightarrow CO + 3 H_2$

In the next step, the water gas shift reaction is used to convert the carbon monoxide into carbon dioxide and more hydrogen:

 $CO + H_2O \rightarrow CO_2 + H_2$

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:

 $CO + 3 H_2 \rightarrow CH_4 + H_2O$ $CO_2 + 4 H_2 \rightarrow CH_4 + 2 H_2O$

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):

$$3 H_2 + N_2 \rightarrow 2 NH_3$$

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 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.

Biosynthesis

In certain organisms, ammonia is produced from atmospheric nitrogen 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_7MoS_0 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.

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 $-33.3 \,^{\circ}$ C, and solidifies at $-77.7 \,^{\circ}$ C to white crystals. The crystal symmetry is cubic, Pearson symbol cP16, space group P2₁3 No.198, lattice constant 0.5125 nm.^[29] Liquid ammonia possesses strong ionising 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.

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/cm³ 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 chlorine is present in excess, then the highly explosive nitrogen trichloride (NCl₂) 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.^[30]

Ammonia may be conveniently deodorized by reacting it with either sodium bicarbonate or acetic acid. Both of these reactions form an odourless ammonium salt.

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.^[31]

 $NH_3 + HCl \rightarrow NH_4Cl$

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 skin to lessen the effects of acidic animal poisons, such as from insects and jellyfish.

Acidity

Although ammonia is well known as a strong 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:

 $2 \text{Li} + 2 \text{NH}_3 \rightarrow 2 \text{LiNH}_2 + \text{H}_2$

Self-dissociation

Like water, ammonia undergoes molecular autoionisation to form its acid and base conjugates:

 $2 \operatorname{NH}_{3}(l) \rightleftharpoons \operatorname{NH}_{4}^{+}(aq) + \operatorname{NH}_{2}^{-}(aq)$

At standard pressure and temperature, $[NH_4^+][NH_2^-] = 10^{-30} \text{ M}^2$.

Combustion

The combustion of ammonia to nitrogen and water is exothermic:

 $4 \text{ NH}_3 + 3 \text{ O}_2 \rightarrow 2 \text{ N}_2 + 6 \text{ H}_2\text{O} (g) (\Delta H^o_r = -1267.20 \text{ kJ/mol})$

The standard enthalpy change of combustion, ΔH_c^{o} , 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:

 $4 \text{ NH}_3 + 5 \text{ O}_2 \rightarrow 4 \text{ NO} + 6 \text{ H}_2\text{O}$

A subsequent reaction leads to water and N₂O

The combustion of ammonia in air is very difficult in the absence of a catalyst (such as platinum gauze), as the temperature of the flame is usually lower than the ignition temperature of the ammonia-air mixture. The flammable range of ammonia in air is 16-25%.^[32]

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 $-NH_2$ 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-bromopropanoic 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 Mg_3N_2 , and when the gas is passed over heated sodium or potassium, sodamide, $NaNH_2$, and potassamide, KNH_2 , 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 λ^5 -amine, or more commonly, ammonium hydride. This crystalline solid is only stable under high pressure, and decomposes back into trivalent ammonia and hydrogen gas at normal conditions. This substance is was once investigated as a possible solid rocket fuel in 1966.^[33]

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:

- **Tetraamminediaquacopper(II)**, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, a characteristic dark blue complex formed by adding ammonia to solution of copper(II) salts. Known as Schweizer's reagent.
- **Diamminesilver(I)**, $[Ag(NH_3)_2]^+$, 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 $[CrCl_3(NH_3)_3]$ 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.

$$\text{Hg}_2\text{Cl}_2 + 2 \text{ NH}_3 \rightarrow \text{Hg} + \text{HgCl}(\text{NH}_2) + \text{NH}_4^+ + \text{Cl}^-$$

Interstellar formation and destruction

Formation mechanisms

The interstellar abundance for ammonia has been measured for a variety of environments. The $[NH_3]/[H_2]$ ratio has been estimated to range from 10^{-7} in small dark clouds^[34] up to 10^{-5} in the dense core of the Orion Molecular Cloud Complex.^[35] Although a total of 18 total production routes have been proposed,^[36] the principal formation mechanism for interstellar NH₃ is the reaction:

$$\mathrm{NH}_{4}^{+} + \mathrm{e}^{-} \rightarrow \mathrm{NH}_{3} + \mathrm{H}_{2}$$

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.^[37] 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 NH₄⁺ abundance of 3×10^{-7} and an electron abundance of 10^{-7} typical of molecular clouds, the formation will proceed at a rate of 1.6×10^{-9} cm⁻³s⁻¹ in a molecular cloud of total density 10^{5} cm⁻³.^[38]

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.^[39] As an example of the minor contribution





other formation reactions play, the reaction:

$$H_2 + NH_2 \rightarrow NH_3 + H$$

has a rate constant of 2.2×10^{-15} . Assuming H₂ densities of 10^5 and NH₂/H₂ ratio of 10^{-7} , this reaction proceeds at a rate of 2.2×10^{-12} , more than 3 orders of magnitude slower that the primary reaction above.

Some of the other possible formation reactions are:

$$H^{-} + NH_{4}^{+} \rightarrow NH_{3} + H_{2}^{-}$$
$$PNH_{3}^{+} + e^{-} \rightarrow P + NH_{3}^{-}$$

Destruction mechanisms

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.^[40] A review of interstellar ammonia cites the following reactions as the principal dissociation mechanisms:^[41]

(1) $\operatorname{NH}_3 + \operatorname{H}_3^+ \rightarrow \operatorname{NH}_4^+ + \operatorname{H}_2$ (2) $\operatorname{NH}_3 + \operatorname{HCO}^+ \rightarrow \operatorname{NH}_4^+ + \operatorname{CO}$

with rate constants of 4.39×10^{-9} ^[42] and 2.2×10^{-9} , ^[43] 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 $[NH_3]/[H_2] = 10^{-5}$, $[H_3^+]/[H_2] = 2 \times 10^{-5}$, $[HCO^+]/[H_2] = 2 \times 10^{-9}$, and total densities of $n = 10^5$, typical of cold, dense, molecular clouds. ^[44] 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^{++} .

Uses

Fertilizer

Approximately 83% (as of 2004) 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.^[16]

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:^[45]

 $\rm NH_3 + 2 O_2 \rightarrow HNO_3 + H_2O$

Nitric acid is used for the production of fertilizers, explosives, and many organonitrogen compounds.

Cleaner

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Household 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 grime. Household ammonia ranges in concentration from 5 to 10 weight percent ammonia.

Minor and emerging uses

Refrigeration – R717

Because of its favourable vaporization properties, ammonia is an attractive refrigerant.^[16] It was commonly used prior to the popularisation of chlorofluorocarbons (Freons). Anhydrous ammonia is widely used in industrial refrigeration applications and hockey rinks because of its high energy efficiency and low cost. The Kalina cycle, which is of growing importance to geothermal power plants, depends on the wide boiling range of the ammonia-water mixture. Ammonia is used less frequently in commercial applications, such as in grocery store freezer cases and refrigerated displays due to its toxicity.

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.^[46]

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. 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.

Ammonia has been proposed as a practical alternative to fossil fuel for internal combustion engines.^[47] The calorific value of ammonia is 22.5 MJ/kg (9690 BTU/lb) 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.



Drawing of an Ammoniacal Gas Engine Streetcar in New Orleans (1871) by Alfred Rudolph Waud

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 ^[47] ^[48] (the combustion products are nitrogen and water). In 1981 a Canadian company converted a 1981 Chevrolet Impala to operate using ammonia as fuel.^[49] ^[50]

Ammonia engines or ammonia motors, using ammonia as a working fluid, have been proposed and occasionally used ^[51]. The principle is similar to that used in a fireless locomotive, but with ammonia as the working fluid, instead of steam or compressed air. Ammonia engines were used experimentally in the 19th century by Goldsworthy Gurney in the UK and in streetcars in New Orleans in the USA.

Antimicrobial 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."^[52] Anhydrous ammonia has been shown effective as an antimicrobial agent for animal feed^[53] and is currently used commercially to reduce or eliminate microbial contamination of beef.^[54] ^[55] ^[56] 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.^[57] 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.^[58]

As a stimulant in sports

Ammonia has found significant use in various sports – particularly the strength sports of powerlifting and Olympic weightlifting as a respiratory stimulant.

Textile

Liquid ammonia is used for treatment of cotton materials, give a properties like mercerisation using alkalies. In particular, it is used for pre-washing of wool.^[59]

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. Because of 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).

Woodworking

Ammonia was historically used to darken quartersawn white oak in Arts & Crafts and Mission style furniture. Ammonia fumes react with the natural tannins in the wood and cause it to change colours.^[60]

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 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.^[62]

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.^[63] 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



(hyperammonemia). Likewise, defects in the enzymes responsible for the urea cycle, such as ornithine transcarbamylase, lead to hyperammonemia. Hyperammonemia 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.^[64]

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 the renal tubules, combine with a hydrogen ion, and thus allow for further acid excretion.^[65]



Reference ranges for blood tests, comparing blood content of ammonia (shown in yellow near middle) with other constituents.

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.^[66]

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 °C is about 10^{-33} mol²·L⁻².

Solubility of salts

		NH ₃)
Ammonium acetate	253.2	
Ammonium nitrate	389.6	
Lithium nitrate	243.7	
Sodium nitrate	97.6	
Potassium nitrate	10.4	
Sodium fluoride	0.35	
Sodium chloride	3.0	
Sodium bromide	138.0	
Sodium iodide	161.9	
Sodium thiocyanate	205.5	

Solubility (g of salt per 100 g liquid

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 (77 °F).

Solutions of metals

Liquid ammonia will dissolve the alkali metals and other electropositive 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.

Redox properties of liquid ammonia

	<i>E</i> ° (V, ammonia)	E° (V, water)
$Li^+ + e^- \rightleftharpoons Li$	-2.24	-3.04
$K^+ + e^- \rightleftharpoons K$	-1.98	-2.93
$Na^+ + e^- \rightleftharpoons Na$	-1.85	-2.71
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.53	-0.76
$\mathrm{NH}_4^+ + \mathrm{e}^- \rightleftharpoons \frac{1}{2}\mathrm{H}_2 + \mathrm{NH}_3$	0.00	_
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	+0.43	+0.34
$Ag^+ + e^- \rightleftharpoons Ag$	+0.83	+0.80

The range of thermodynamic stability of liquid ammonia solutions is very narrow, as the potential for oxidation to dinitrogen, E° (N₂ + 6NH₄⁺ + 6e⁻ \rightleftharpoons 8NH₂), 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.

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, $(NH_d)_2PtCl_6$.

Interstellar space

Ammonia was first detected in interstellar space in 1968, based on microwave emissions from the direction of the galactic core.^[67] 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.^[41] 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:

NH₃, ¹⁵NH₃, NH₂D, NHD₂, and ND₃

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.^[68] 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.^[69]

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.

Single antenna detections

Radio observations of NH₃ from the Effelsberg 100-m Radio 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.^[70] The 25 m Chilbolton telescope in England detected radio signatures of ammonia in H II regions, HNH₂O 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.^[71]

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.^[72]

Interferometric studies

VLA observations of NH_3 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.^[73]

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.^[74] NH₃ was also monitored by VLA towards a sample of four galactic ultracompact HII regions: G9.62+0.19, G10.47+0.03, G29.96-0.02, and G31.41+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.^[75]

Infrared detections

Absorption at 2.97 micrometres due to solid ammonia was recorded from interstellar grains in the Becklin-Neugebauer Object and probably in NGC 2264-IR as well. This detection helped explaining the physical shape of previously poorly understood and related ice absorption lines.^[76]

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.^[77]

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 NH₃. 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.^[78]

Ammonia 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.^[79]

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.

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 previous 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 NH₃ 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.

UC HII regions

Ultra-compact HII regions are among the best tracers of high-mass star formation. The dense material surrounding UCHII 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 outflows and hot cores originating from forming stars.

Extragalactic detection

Ammonia 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).

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.^[80] 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 ^[81] 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.^[80] 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 (3,500 gallons).^[82]



The world's longest ammonia pipeline, running from the TogliattiAzot plant in Russia to Odessa in Ukraine.

Toxicity and storage information

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.



Hydrochloric acid sample releasing HCl fumes, which are reacting with ammonia fumes to produce a white smoke of ammonium chloride.

Household 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.^[83]

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 mol/L); "concentrated" solutions are usually prepared at >25% by weight. A 25% (by weight) solution has a density of 0.907 g/cm³, and a solution which has a lower density will be more concentrated. The European Union classification of ammonia solutions is given in the table.

Concentration by weight (w/w)	Molarity	Concentration mass/volume (w/v)	Classification	R-Phrases
5-10%	2.87—5.62 mol/L	48.9–95.7 g/L	Irritant (Xi)	R36/37/38
10-25%	5.62-13.29 mol/L	95.7–226.3 g/L	Corrosive (C)	R34
>25%	>13.29 mol/L	>226.3 g/L	Corrosive (C) Dangerous for the environment (N)	R34, R50

S-Phrases: (S1/2), S16, S36/37/39, S45, S61.

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.

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/m^3), 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.

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.

Mapping of industrial releases in the United States

One tool that maps releases of ammonia [84] to particular locations in the United States^[85] and also provides additional information about such releases is TOXMAP. TOXMAP is a Geographic Information System (GIS) from the Division of Specialized Information Services of the United States National Library of Medicine (NLM) that uses maps of the United States to help users visually explore data from the United States Environmental Protection Agency's (EPA) Toxics Release Inventory and Superfund Basic Research Programs. TOXMAP is a resource funded by the US Federal Government. TOXMAP's chemical and environmental health information is taken from NLM's Toxicology Data Network (TOXNET)^[86] and PubMed, and from other authoritative sources.

See also

- Ammonia (data page)
- Ammonia production
- Chlorination
- Forming gas
- · Relative cost of electricity generated by different sources
- Water purification

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External links

- International Chemical Safety Card 0414 ^[87] (anhydrous ammonia), ilo.org.
- International Chemical Safety Card 0215^[88] (aqueous solutions), ilo.org.
- National Pollutant Inventory Ammonia^[89], npi.gov.au.
- CID 222^[2] from PubChem
- (French) Institut national de recherche et de sécurité ^[90]
- Emergency Response to Ammonia Fertilizer Releases (Spills) ^[91] for the Minnesota Department of Agriculture.ammoniaspills.org
- National Institute for Occupational Safety and Health Ammonia Page ^[92], cdc.gov

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