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An introduction to the amines

1.1 Introduction

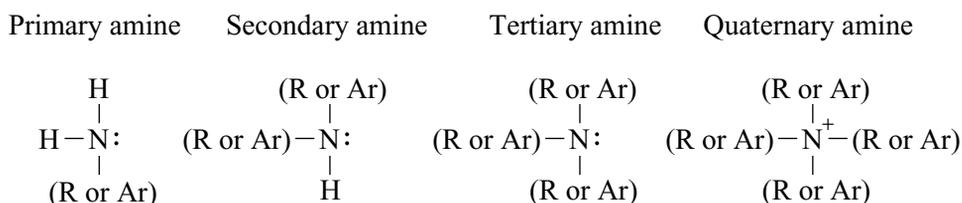
The amines are a group of chemical compounds that have the common feature of possessing nitrogen atoms that are sp^3 hybridized with three single bonds to other elements. Although there are many different types of amine, they all have similar features because somewhere in their molecular structures they possess a nitrogen atom. For many people one characteristic is that they possess an identifiable amine smell, which is often described as being rather like rotting fish.

Amines are named according to the IUPAC system from the corresponding parent alcohol, i.e. $C_2H_5-NH_2$ is ethylamine from C_2H_5-OH = ethyl alcohol. Substituents on carbon chains are identified by a number, and the prefix *N*- is used for substituents on the nitrogen atom. Other amines may be named in a similar manner but many aromatic and heterocyclic amines retain their trivial names such as indole, aniline and quinoline, all of which are universally accepted.

An idea of the importance of amines can be obtained from a crude analysis of the worldwide production of ammonia gas, which is around 170 million tonnes per year. Of this figure about 70% is used in the manufacture of fertilizers, 10% is used in the manufacture of nylon and 7% is used in the manufacture of explosives (via nitric acid). The remaining 13% is used for refrigeration applications, directly as a water solution for pH control and also for the production of organic and inorganic chemicals. The percentage of ammonia used in the production of amines (excluding caprolactam and hexamethylene diamine) is about 3% to 4% of the total worldwide output and accounts for around 5–7 million tonnes of ammonia per year. However, a sizeable fraction of the ammonia used in fertilizers may eventually end up in the form of amines during plant metabolism.

The simplest amine is ammonia, NH_3 , in which the central nitrogen atom is bonded to three hydrogen atoms which are all chemically equivalent. The replacement of hydrogen atoms in ammonia with other elements produces inorganic

amines such as trichloroamine, NCl_3 . The replacement of hydrogen atoms with other functional groups such as alkyl and aryl groups gives rise to organic amines which are categorized as follows. Replacement of one hydrogen atom by an alkyl group, R, or an aryl group, Ar, produces a primary alkyl amine R-NH_2 or a primary aryl amine Ar-NH_2 , respectively. Replacement of a second hydrogen with another alkyl or aryl group, R' or Ar', will produce a secondary alkyl amine, $\text{R-NH-R}'$, or a secondary aryl amine, $\text{Ar-NH-Ar}'$. Where the nitrogen atom is substituted with an alkyl group and an aryl group, the product is called a secondary alkyl aryl amine R-NH-Ar . Replacement of all hydrogen atoms with alkyl or aryl groups produces tertiary alkyl and aryl amines of the type $\text{R-NR}'\text{-R}''$ or $\text{Ar-NAr}'\text{-Ar}''$, or alkyl aryl variations like $\text{R-NAr}'\text{-Ar}$. Finally, tertiary amines can add on another molecule of an amine such as an amine hydrobromide to form a quaternary amine (e.g. $[\text{R-N(R}'\text{R}'')\text{-R}''']^+$) with a bromide counter ion. Examples of these amines are shown below.



The properties of amines are largely controlled by the electronic characteristics of the electron pair on the central nitrogen atom (or atoms for bi- and polyfunctional amines), which is able to act as a Lewis Base and use the lone pair of electrons for donation. The ability of the nitrogen atom to donate its lone pair of electrons in chemical reactions is modified by the presence of the functional groups bonded to the nitrogen atom that can increase or decrease this ability. Generally electron density in s orbitals is held more strongly by the atomic nucleus and is less available for donation. Therefore amines with sp^3 hybridization are generally better at donating electrons to electrophiles than amines or nitrogen-containing molecules with sp^2 hybridization, which have a greater proportion of s character. This helps to explain why acetonitrile is a weaker base than ethylamine. However, because the chemistry and properties of amines are so strongly determined by the electron lone pair on the nitrogen atom it is important to look into the properties of the element nitrogen before trying to understand the behaviour of amines.

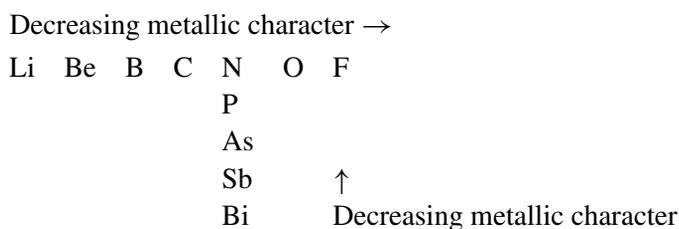
1.2 Nitrogen

The Earth's atmosphere contains about 75.5% of nitrogen by weight; this is equivalent to around 4000 billion tonnes of nitrogen gas. Nitrogen is a colourless,

odourless, diatomic gas and is actually the single most abundant element accessible to Man in an uncombined state. In its combined state nitrogen is the thirtythird most abundant element next to gadolinium. Without nitrogen, life as we know it would not exist on Earth: nitrogen is an essential part of proteins, which are about 15% nitrogen (by weight). Mankind had known for centuries that air was composed of two fractions, a part which would burn and a part which would not. The discovery of nitrogen as a chemical element in 1772 is credited to Rutherford [1] (although it was isolated at the same time by Scheele and Cavendish [2]). Rutherford's experiment was to burn carbon in a limited supply of air. After combustion Rutherford removed the carbon dioxide with potassium hydroxide and named the remaining gas 'residual air'. The name nitrogen was proposed in 1790 by Jean-Antoine Chaptal when it was discovered that this residual air was a constituent of nitric acid and nitrates.

Lavoisier preferred the name azote (from the Greek meaning no-life) because of its asphyxiating properties; this name is still used in France and is the root of chemical names such as azo, diazo, azide, etc. In German nitrogen is called Stickstoff from the verb 'to stricken' ('to suffocate').

In order to understand the chemistry of the amines it is important to understand how nitrogen's position at the top of Group V in the first row of the Periodic Table (see below) can explain its unique properties which also characterize the behaviour of the amines.

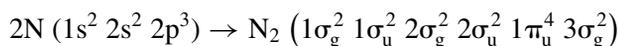


Nitrogen has the smallest atomic number of the elements in Group V, and this usually results in differences in chemical behaviour from the other elements in the group (this is known as 'the first row anomaly'). Nitrogen also lies near the middle of the first period of the p block, which means that it should display a pronounced lack of metallic character. From its position in the Periodic Table it would most probably be predicted that nitrogen would have little tendency to form ions but would have a large variety of oxidation states. However, nitrogen has only four available orbitals in its valence shell ($1s^2 2s^2 2p^3$) and there are no d orbitals available. This limits to four the maximum number of covalent bonds that a nitrogen atom can make. Also because one valence orbital is occupied by a lone electron pair in neutral molecules, nitrogen can form only three bonds. From its small size (interatomic radius 1.10 Å)

Table 1.1. *The properties of nitrogen*

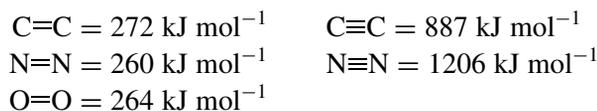
Boiling point	77.36 K
Freezing point	63.26 K
Critical pressure	33.54 bar (3398.44 Pa)
Transition $\alpha \rightarrow \beta$	35.62 K
Enthalpy of transition	228.9 kJ mol ⁻¹
Enthalpy of vapourization	5577 J mol ⁻¹
Enthalpy of fusion	719.6 J mol ⁻¹
Dissociation energy	944.7 kJ mol ⁻¹
Atomic mass	14.0067
Electronegativity	3.04 (Pauling)
Interatomic radius (N ₂)	1.10 Å
Isotopic abundance	99.634% ¹⁴ N, 0.366% ¹⁵ N

it can be predicted that the element nitrogen would have a tendency to form multiple bonds. For example, the formation of the nitrogen molecule N₂ can be represented as



Of the ten molecular orbitals, the four that make up $1\sigma_u$ and $2\sigma_u$ are anti-bonding. The bond order in the nitrogen molecule (N₂) is therefore $(10-4)/2 = 3$.

However, the triple-bonded N₂ molecule has a high stability. For example, the bond energies of double-bonded N, C and O are all similar but there is a big difference in the bond energies between double- and triple-bonded nitrogen and carbon.



As the bond energies of double-bonded carbon-carbon and nitrogen-nitrogen are similar, it might be predicted that the bond energy of triple-bonded nitrogen-nitrogen would similarly be around 615 kJ mol⁻¹ higher. However, the bond strength increases by 946 kJ/mol⁻¹, so the nitrogen-nitrogen triple bond is 331 kJ mol⁻¹ more stable than might be predicted. The high stability of the nitrogen molecule is the reason why nitrogen gas is such a major constituent of the Earth's atmosphere and why so many compounds of nitrogen are unstable and often explosive. Nitrogen gas reacts only with some transition metal complexes, with carbides and with nitrogen-fixing bacteria. The physical properties of nitrogen are given in Table 1.1.



Trigonal pyramidal

Tetrahedral

Figure 1.1. The trigonal pyramidal and tetrahedral geometries of substituted nitrogen compounds.

Because the electronic configuration of nitrogen in its ground state (^4S) is $1s^2 2s^2 2p^3$, nitrogen is one of the most electronegative elements (exceeded only by oxygen and fluorine). The nitrogen atom may complete its octet of electrons by:

- (i) formation of the N^{3-} nitride ion, e.g. in lithium nitride;
- (ii) formation of three electron-pair bonds, e.g. NH_3 or N_2 ;
- (iii) formation of two electron-pair bonds plus electron gain, e.g. $[\text{NH}_2]^-$;
- (iv) formation of four electron-pair bonds plus electron loss, e.g. $[\text{NH}_4]^+$;
- (v) formation of the N_5^+ ion (e.g. $\text{N}_5(\text{Sb}_2\text{F}_4)$) or the N_5^- ion.

It is the ease with which nitrogen forms four electron-pair bonds to generate quaternary ions with the loss of an electron that defines the chemistry of nitrogen and also the chemistry of the amines.

The conversion of three electron-pair bonds around a central nitrogen atom to four bonds with electron loss results in a change of geometry, as shown in Figure 1.1.

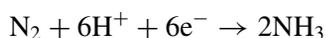
In instances when the R groups are very large, steric crowding may produce a trigonal planar NR_3 molecule rather than a trigonal pyramidal form. It might be expected that all four bonds in tetrahedral nitrogen would be equivalent (three electrons from 2p and one electron from the $2s^2$) and experimentally this has been proved [3] by measurement of all four bonds in the ammonium ion. These bonds have been shown to have equal valence angles of 109.5° . In ammonia the bond angle is 107° and not 90° , which might be predicted from the contribution from the three electrons in the 2p orbital. This is indicative of orbital hybridization taking place. The importance of ammonia will now be examined in greater detail.

1.3 The history of ammonia and its importance to mankind

In 2002 the total annual usage of fertilizers worldwide was around 135 million tonnes. This figure represents around 90 million tonnes of fixed nitrogen, which is

expected to rise to a requirement of 100 million tonnes of fixed nitrogen per year in 2010. The most widely used fertilizer is urea, of which 50 million tonnes alone were used as fertilizer in 2002. The balance of the nitrogen-containing fertilizers consisted of nitrates (such as calcium nitrate and ammonium nitrate), ammonium salts (such as diammonium phosphate, calcium ammonium nitrate, ammonium potassium chloride and ammonium phosphate chloride) and others such as aqua ammonia (aqueous ammonia solution) and dicyandiamide. Until the 1950s, ammonium nitrate was the single most widely used fertilizer but more recently urea (with 46.7% nitrogen content) has become the single most important fertilizer. In the USA the use of aqua ammonia seems to be growing, but its usage is still tiny compared with the widespread use of urea.

Prior to the development of industrial nitrogen-fixation processes, the only fixed nitrogen available for assimilation by plants and animals came either from oxidation of atmospheric nitrogen during lightning storms or from the biological fixation of nitrogen by microorganisms present in the soil and also in certain plants and algae. The microorganisms that can convert nitrogen to ammonia produce an enzyme complex called nitrogenase, which catalyses the reaction.



Nitrogenase consists of two high-molecular-weight components called molybdoferredoxin and azoferredoxin. They are able to fix atmospheric nitrogen because they contain small metallic iron/sulphur and iron/molybdenum centres, which fix and reduce nitrogen. It is thought that the Fe/Mo centres bind to nitrogen and the Fe/S centres are responsible for its reduction. Reactive sites containing Fe_4S_4 units have been identified in azoferredoxin.

In free soil, bacteria can assimilate about 50 kg of nitrogen per hectare per year. However, when the soil is planted with legumes, clover or alfalfa this figure rises to 250 kg of nitrogen per year. The principles of crop rotation have been known since the Middle Ages in Europe, even though the importance of nitrogen to plant metabolism remained a mystery.

Once fixed, nitrogen can enter the biological nitrogen cycle; it is oxidized by other bacteria, e.g. nitrosomas and nitrobacters, and can be incorporated into amino acids and then into proteins. Animals are able to obtain fixed nitrogen either by eating plants (herbivores) or by eating other animals (carnivores).

Every nitrogen atom in industrially produced chemical compounds today comes either directly or indirectly from ammonia. In addition to the production of fertilizers, once ammonia has been converted to nitric acid it is essential for the production of plastics and fibres such as polyamides, urea-formaldehyde resins, polyurethanes and polyacrylonitrile. However, to get a true appreciation of the importance of

ammonia to mankind we have to look back to 1798 when the philosopher T. R. Malthus proposed the principle of population [4], stating:

In the absence of any external constraints, the world's population always increases in geometric progression, while the production of food increases in arithmetic progression.

Put another way, Malthus predicted that at some point in the future the planet would not be able to produce enough food to feed mankind. Malthus was essentially correct in this principle but advances in science and agricultural technology have increased the worldwide production of food and so postponed the Malthusian final outcome.

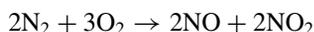
In 1840 Justus von Liebig studied plant nutrition and established the importance of fixed nitrogen for the growth of plants [5]. Justus von Liebig is nowadays considered to be the father of the concept of fertilizers. In the mid nineteenth century the major natural resources of fixed nitrogen were sodium nitrate from Chilean saltpetre, and guano (bird excrement) from islands in the Pacific Ocean (the term saltpetre alone is misleading as Chilean saltpetre is sodium nitrate whereas Indian saltpetre is potassium nitrate). Synthetic fixed nitrogen could be obtained in limited quantities from the destructive distillation of coal as ammonium sulphate. Competing with fertilizers for the world supply of fixed nitrogen were the dyestuffs industry and, after the discovery of dynamite in 1866, the emerging explosives industry.

In 1898 Sir William Crookes warned in his presidential address to the British Association for the Advancement of Science that the supply of fixed nitrogen for agriculture was rapidly reaching a point where it was insufficient to support the world's rapidly increasing population (i.e. the world's population was not far from reaching the Malthusian limit) [6]. Sir William's address must be understood in view of the fact that the reserves of Chilean saltpetre and guano were known to be limited and it was thought that they could not sustain the needs of agriculture and industry for the rest of the twentieth century.

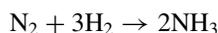
The fixation of atmospheric nitrogen was seen as the solution to this problem, but at the time there was no satisfactory fixation process that could be carried out on a large scale at a low cost. For example, the atmospheric discharge of high-voltage electricity had been studied by Cavendish at the end of the eighteenth century [2] and had been discovered to produce small quantities of nitric and nitrous acids. However, the thermodynamic equilibrium concentration of nitric oxide is very low at normal temperatures. Although this was not a practical route it did at least provide an example to scientists working at the time that the fixation of atmospheric nitrogen might be technically feasible. In principle in order to 'fix' atmospheric nitrogen it is necessary first to break the nitrogen–nitrogen triple bond, and at the end of

the nineteenth century there were three methods by which this was thought to be possible.

- (i) By combining nitrogen with oxygen to form nitric oxides (as studied by Cavendish).



- (ii) By combining nitrogen with hydrogen to form ammonia.



- (iii) By the use of active chemical compounds capable of splitting the $\text{N}\equiv\text{N}$ bond under energetic conditions.

(In the twentyfirst century the use of biotechnology and enzymes has emerged as a fourth possibility, but a low-cost method for producing fixed nitrogen by this process is still one of the remaining goals of science.)

At the beginning of the twentieth century the two most advanced methods for the fixation of atmospheric nitrogen were the Cyanamide Process developed by Adolf Frank and Nikodem Caro in 1895 [7] and the Electric Arc Process, first successfully developed commercially in 1904 by Kristian Birkeland and Samuel Eyde [8]. In 1902 the Electric Arc Process was the first ammonia-synthesis process to be run on a commercial scale at Niagara in the USA. The process used an electric arc, which heated air to 3000 °C and produced dilute nitric acid. The commercial venture was started by two Americans, Bradley and Lovejoy, who raised around USD 1 million in share capital. The concentration of the air after passing through the arc was around only 2% nitric oxide and the plant was closed two years later as it was not commercially viable and the share capital was exhausted. Although the energy consumption of the Arc Process was enormous the process was commercialized for a second time by Norsk Hydro in Notodden, Norway, in 1904. By 1908 this plant was producing 7000 tonnes of fixed nitrogen per year. Eyde and Birkeland succeeded where Bradley and Lovejoy had failed primarily because of three factors: first, because of the availability of cheap hydroelectric power in Notodden; second because of relatively cheaper labour costs in Norway compared with the USA (Norway was not a rich country in the early 1900s and it was common for several families working at Notodden to share single rooms together with their children in hostels near the plant); and third, because of the Birkeland furnace, which was the most energy-efficient furnace of its time.

The plant at Notodden operated throughout the First World War and, together with a sister plant at Rjukan, reached a production of over 30 000 tonnes per year with a power consumption of 60 000 kW per tonne of fixed nitrogen. Fortunately in Norway cheap hydroelectric power was available to operate the arc but if fossil fuels had been used the energy requirement would have been around 600 GJ per

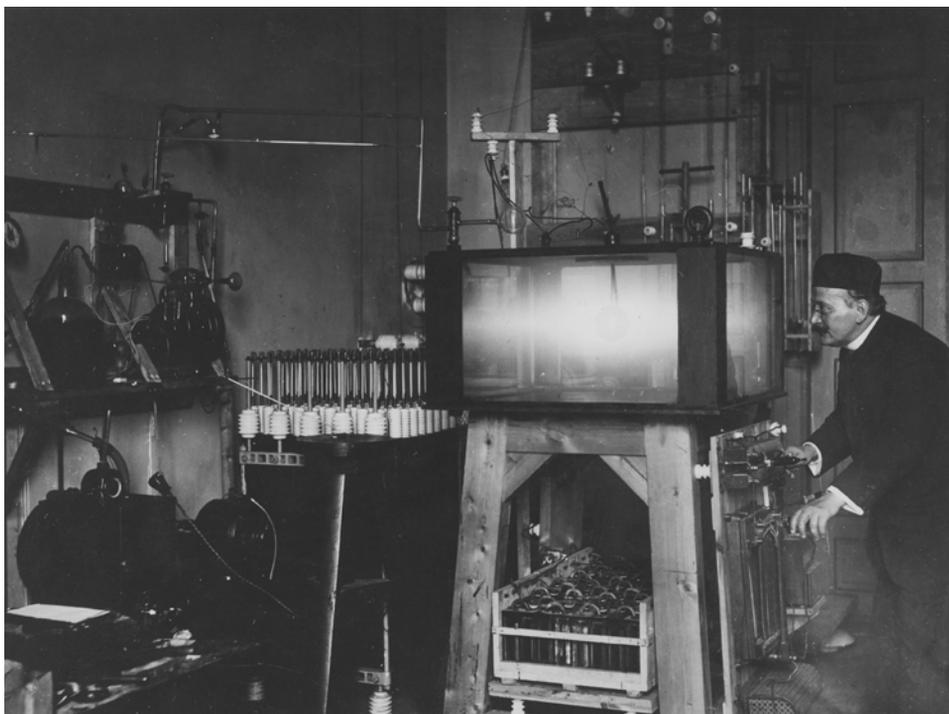


Figure 1.2. Birkeland at work in his laboratory on the Arc Process. (Photo © Hydro Media, reproduced with permission of Norsk Hydro a.s.)

tonne of fixed nitrogen. The Arc Process was abandoned in the 1920s as it was by then obsolete and had been overtaken by newer technology. However, the 36 furnaces at Notodden and at the sister plant in Rjukan were in use right up until 1940. At the time of writing (in 2003), Norsk Hydro have established a museum at the Notodden site in Norway. This museum contains many historical documents and some of the original laboratory equipment used by Birkeland. A photograph of Birkeland's laboratory is shown in Figure 1.2, and Figure 1.3 shows a photograph of the Notodden plant.

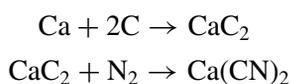
Schoenherr, working at BASF in Germany, also demonstrated an electric arc furnace in 1905, and in 1912 BASF and the Norwegians decided jointly to build a new plant in Norway with increased capacity. However, this project was shelved as the First World War intervened and also, shortly after agreeing to enter this joint venture, BASF had demonstrated another more energetically feasible ammonia synthesis process called the Haber–Bosch Process.

In the Cyanamide Process coke and limestone were reacted in a furnace to form calcium carbide, which then reacts with nitrogen to form calcium cyanamide. The hydrolysis of calcium cyanamide with steam, or more slowly with water, produces



Figure 1.3. The plant at Notodden. (Photo © Hydro Media, reproduced with permission Norsk Hydro a.s.)

ammonia. This allows calcium cyanamide to be used directly as a fertilizer or as a source of ammonia gas.



Although this process uses 190 GJ per tonne of fixed ammonia this was about a quarter of the amount used by the Arc Process and so it was useful for operation in areas without cheap hydroelectricity. The Cyanamide Process was first operated commercially in 1905 in Westeregeln in Germany and by 1934 about 11% of the world's fixed nitrogen was obtained from this process. The Cyanamide Process fell into decline after the Second World War and is no longer operated on a commercial scale.

At the beginning of the twentieth century the synthesis of ammonia by the direct combination of hydrogen and nitrogen was thought to be impractical. Although Bertholet had established in 1784 that ammonia consisted of hydrogen and nitrogen and had also established the elemental ratio between them [9], there seemed to