

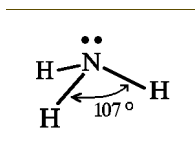
Chemical of the Week

AMMONIA, NH₃

Almost everyone has smelled the sharp, penetrating odor of ammonia, NH₃. As the active product of “smelling salts,” the compound can quickly revive the faint of heart and light of head. But more than a sniff of this toxic, reactive, and corrosive gas can make one very ill indeed. It can, in fact, be fatal. Ammonia is pretty nasty stuff. Nevertheless, it is also an extremely important bulk chemical widely used in fertilizers, plastics, and explosives.

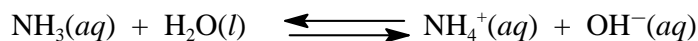
The melting and boiling points of ammonia, -77.7°C and -33.5°C , respectively, are both considerably higher than the corresponding properties of its chemical “cousins,” PH₃ and AsH₃. This failure of NH₃ to follow the usual trend of decreasing melting and boiling points with decreasing molecular weights indicates abnormally strong intermolecular attractions. The forces involved stem from hydrogen bonding, a consequence of the high electronegativity of nitrogen and the small size of the hydrogen atom.

The NH₃ molecule has a large dipole moment, and this is consistent with its geometry, a trigonal pyramid.



The electronic arrangement in nitrogen obeys the octet rule. The four pairs of electrons (three bonding pairs and one non-bonding lone pair) repel each other, giving the molecule its non-planar geometry. The H–N–H bond angle of 107 degrees is close to the tetrahedral angle of 109.5 degrees. Because of this, the electronic arrangement of the valence electrons in nitrogen is described as sp³ hybridization of atomic orbitals.

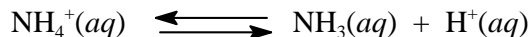
The polarity of NH₃ molecules and their ability to form hydrogen bonds explains to some extent the high solubility of ammonia in water. However, a chemical reaction also occurs when ammonia dissolves in water. In aqueous solution, ammonia acts as a base, acquiring hydrogen ions from H₂O to yield ammonium and hydroxide ions.



The production of hydroxide ions when ammonia dissolves in water gives aqueous solutions of ammonia their characteristic alkaline (basic) properties. The double arrow in the equation indicates that an equilibrium is established between dissolved ammonia gas and ammonium ions. Not all of the dissolved ammonia reacts with water to form ammonium ions. A substantial fraction remains in the molecular form in solution. In other words, ammonia is a weak base. A quantitative indication of this strength is given by its base ionization constant:

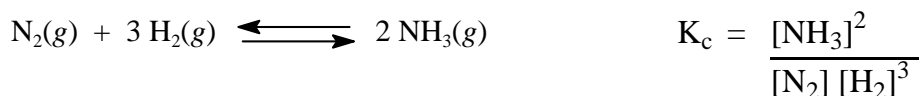
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} \text{ at } 25^{\circ}\text{C}$$

In contrast, the ammonium ion acts as a weak *acid* in aqueous solution because it dissociates to form hydrogen ion and ammonia.



The ammonium ion is found in many common compounds, such as ammonium chloride, NH_4Cl . Typically, ammonium salts have properties similar to the corresponding compounds of the Group IA alkali metals.

The commercial production of ammonia by the direct combination of nitrogen and hydrogen is an example of equilibrium in the gaseous state. The equation for the reaction and its equilibrium constant expression are



At 300°C , K_c has a value of 9.6, indicating that at this temperature, an appreciable amount of NH_3 forms from N_2 and H_2 . Because the reaction gives off heat ($\Delta H^\circ = -92.0 \text{ kJ}$ for the equation above), increasing the temperature drives the reaction to the left. Thus, K_c decreases with increasing temperature. The equilibrium mixture at 500°C contains less NH_3 than at 300°C or at 100°C . If one is in the business of making ammonia (and money), the object is to make as much NH_3 as possible as quickly as possible. The temperature dependence of the equilibrium constant suggests that working at low temperatures is better because more ammonia is obtained at equilibrium. Alas, equilibrium isn't everything! All chemical reactions slow down as the temperature decreases. While a low temperature favors a high equilibrium yield of ammonia, it also dictates that a long time will be required to obtain the yield. The ideal method is a balance between yield and speed.

A great asset in the production of ammonia is a catalyst which speeds the reaction between nitrogen and hydrogen. Early in this century, a German academic chemist, Fritz Haber, and an industrial colleague, Carl Bosch, found that a mixture of Fe_2O_3 and Fe_3O_4 catalyzes this reaction at temperatures in the range of 400°C to 600°C . The yield of ammonia was further enhanced by working at gas pressures between 200 and 400 atmospheres. In the balanced equation for the reaction, the number of moles of product (2NH_3) is less than the total number of moles of reactants ($\text{N}_2 + 3\text{H}_2$). Therefore, high pressures drive the reaction forward, decreasing the number of moles of gas in the mixture. Although now modified and improved, the Haber-Bosch process continues to be the most common method for making ammonia. The nitrogen is obtained from liquefied air, and the hydrogen is usually from natural gas decomposed by heating.

The Haber-Bosch process is also an example of the complex impact of chemistry upon life. At the start of World War I, Germany was dependent upon the natural nitrate deposits of Chile for the nitrogen compounds required to manufacture explosives. The Allied blockade of South American ports soon cut off this supply. Had it not been for the alternative source of nitrogen compounds provided by the direct synthesis of ammonia, Germany most likely would have been forced to surrender several years before 1918. By prolonging the war, the Haber-Bosch process indirectly cost thousands of lives. However, over the years, the fertilizer produced by the same process has increased crop yields around the globe and spared millions from starvation.