# Non aqueous Solvent liquid Ammonia

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An inorganic nonaqueous solvent is a solvent other than water, that is not an organic compound. Common examples are liquid ammonia, liquid sulfur dioxide, sulfuryl chloride and sulfuryl chloride fluoride, phosphoryl chloride, dinitrogen tetroxide, antimony trichloride, bromine pentafluoride, hydrogen fluoride, pure sulfuric acid and other inorganic acids. These solvents are used in chemical research and industry for reactions that cannot occur in aqueous solutions or require a special environment

The Brønsted theory encompasses any type of solvent that can donate and accept $H^+$H+ ions, not just aqueous solutions. The strength of an acid or a base varies depending on the solvent. Non-aqueous acid-base chemistry follows similar rules to those developed for acids and bases in water. For example in liquid ammonia, the solvent autodissociates in the reaction:

This equilibrium is analogous to the autodissociation of water, but has a smaller equilibrium constant ($K \approx 10^{-30}$). It follows by analogy to water that $NH_4^+$ is the strongest acid and $NH_2^-$ is the strongest base that can exist in liquid ammonia. Because ammonia is a basic solvent, it enhances the acidity and suppresses the basicity of substances dissolved in it. For example, the ammonium ion ($NH_4^+$) is a weak acid in water ($K_a = 6 \times 10^{-10}$), but it is a strong acid in ammonia. Similarly, acetic acid is weak in water but strong in ammonia. Solvent leveling in fact makes $CH_3COOH$ and $NH_4Cl$ both strong acids in ammonia, where they have equivalent acid strength.

Strong acids that are leveled in water have different acid strengths in acidic solvents such as HF or anhydrous acetic acid. For example, acid dissociation of HX in acetic acid ($CH_3COOH$) involves protonating the solvent to make its conjugate acid ($CH_3COOH_2^+$) and the $X^-$ anion. Because $CH_3COOH_2^+$ is a stronger acid that $H_3O^+$, the anion $X^-$ (which is a spectator in water) can become a weak base in $CH_3COOH$:

It follows that acidic solvents magnify the Brønsted basicities of substances that cannot accept protons in water. Conversely, basic solvents magnify the acidity of substances that cannot donate a proton to $OH^-$OH−.

The acidity and basicity of non-aqueous solvents is difficult to quantify precisely, but one good relative measure is the Hammett acidity function, $H_o$Ho, which is defined analogously to pH according to the Henderson-Hasselbach equation:

$$H_o = pK_a + \log([base][conjugate\ acid]$$

For non-aqueous solvents, or for acidic or basic compounds in dissolved in solvents that do not themselves dissociate, $H_o$ is a rough measure of the pH of the solvent or compound in question. Anhydrous HF and $H_2SO_4$ have $H_o$ values of approximately -10 and -12 respectively.

## Liquid ammonia: a non-aqueous solvent

Despite low boiling point (-33.4$^{o}$C), easy to handle.

Solubilities, relatively high dielectric constant (ammonia, $\varepsilon^{o}$= 26.7 @ -60$^{o}$C; water, $\varepsilon^{o}$ = 82 @ 18 deg.C).

=> ionic compounds can be soluble but the lower $\varepsilon^{o}$ compared to water means that salt with highly charged,
non-polarisable anions such as carbonates, sulphates, and phosphates are insoluble.

Self-ionization of ammonia is much "weaker" than water.

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

with $K \approx 10^{-30}$K≈10−30 @ 223K. Since ammonia is better proton acceptor than water, the ionization of acids is relatively enhanced in liquid ammonia. For example, acetic acid is a strong acid in liquid ammonia. Liquid ammonia will therefore tolerate very strong bases such as $C_5H_5^-$C5H5− that would otherwise be hydrolyzed in water.

Ammonia is kinetically stabilized to reduction (but easily oxidized) by many reagents, e.g., the reaction

$$Na + NH_3 \longrightarrow NaNH_2 + H_2(g)$$

and is very favorable but slow in the absence of a catalyst such as $Fe^{3+}$.

Much of the chemistry in liquid ammonia can be classified by analogy with related reactions in aqueous solutions. Comparison of the physical properties of $NH_3$NH3 with those of water shows $NH_3$NH3 has the lower melting point, boiling point, density, viscosity, dielectric constant and electrical conductivity; this is due at least in part to the weaker hydrogen bonding in $NH_3$NH3 and because such bonding cannot form cross-linked networks, since each $NH_3$NH3 molecule has only one lone pair of electrons compared with two for each $H_2O$ molecule.

Solvolysis: synthesis of amides

$$OPCl_3+6NH_3 \longrightarrow OP(NH_2)_3+3NH_4Cl$$

$$SiCl_4+8NH_3 \longrightarrow Si(NH_2)_4+4NH_4Cl$$

Metatheses reactions: solubility reversals

$$RCl+AgNO_3 \xrightarrow{H_2O} AgCl(s)+RNO_3$$

$$AgCl+KNO_3 \xrightarrow{NH_3} KCl(s)+AgNO_3$$

$$Ba(NO_3)_2+2AgCl \xrightarrow{NH_3} BaCl_2(ppt)+2AgNO_3$$

Sodamide as a base

$$Na+NH_3 \longrightarrow NaNH_2+H_2(g)$$

$$NaNH_2+C_5H_6 \longrightarrow NaC_5H_5+NH_3$$

NaCpNaCp (useful reagent)

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Solvated electron as a reducing agent (Birch reduction), many examples of compounds in very unusual low oxidation states.

$$[Ni(CN)_4]^{2-} +Na \xrightarrow{NH_3} [Ni(CN)_4]^{4-}$$

$$Fe(CO)_5+Na \xrightarrow{NH_3} [Fe(CO)_4]^{2-}$$

$$Mo(CO)_6+Na \xrightarrow{NH_3} [Mo(CO)_4]^{4-}$$

$$[Pt(NH_3)_4]^{2+} +Na \xrightarrow{NH_3} [Pt(NH_3)_4]$$

Reduction of salts of Group IV and V elements give polyhedral anions, many examples. $Ge_9^{4-}$, $Sn_5^{2-}$, $Sn_9^{3-}$, $Pb_5^{2-}$, $Bi_4^{2-}$, $P_7^{2-}$ $As_6^{4-}$

## Liquid Ammonia Solutions

A remarkable feature of the alkali metals is their ability to dissolve reversibly in liquid ammonia. Just as in their reactions with water, reacting alkali metals with liquid ammonia eventually produces hydrogen gas and the metal salt of the conjugate base of the solvent—in this case, the amide ion ($NH_2^-$) rather than hydroxide:

$$M(s)+NH_3(l) \longrightarrow \frac{1}{2}H_2(g)+M^+(am)+NH_2^-(am)$$

where the (am) designation refers to an ammonia solution, analogous to (aq) used to indicate aqueous solutions. Without a catalyst, the reaction in Equation 9.6D.59.6D.5 tends to be rather slow. In many cases, the alkali metal amide salt ($MNH_2$) is not very soluble in liquid ammonia and precipitates, but when dissolved, very concentrated solutions of the alkali metal are produced. One mole of Cs metal, for example, will dissolve in as little as 53 mL (40 g) of liquid ammonia. The pure metal is easily recovered when the ammonia evaporates.

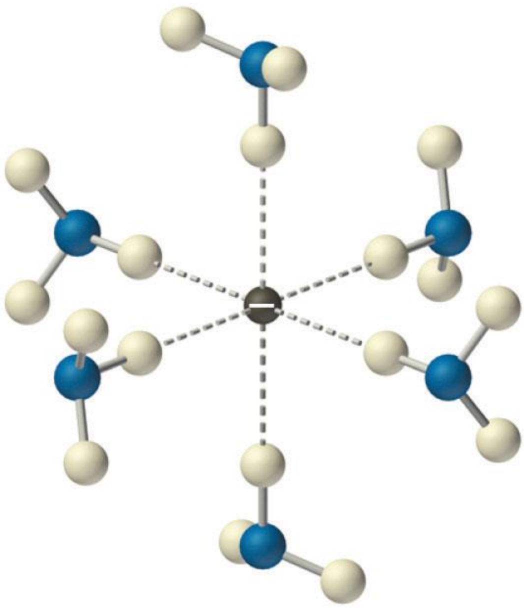

***Figure** 1: Solvated electrons. The presence of solvated electrons ($e^-$, $NH_3$) in solutions of alkali metals in liquid ammonia is indicated by the intense color of the solution and its electrical conductivity.*

Solutions of alkali metals in liquid ammonia are intensely colored and good conductors of electricity due to the presence of solvated electrons ($e^-$, $NH_3$), which are not attached to single atoms. A solvated electron is loosely associated with a cavity in the ammonia solvent that is stabilized by hydrogen bonds. Alkali metal–liquid ammonia solutions of about 3 M or less are deep blue (Figure 21.11) and conduct electricity about 10 times better than an aqueous NaCl solution because of the high mobility of the solvated electrons. As the concentration of the metal increases above 3 M, the color changes to metallic bronze or gold, and the conductivity increases to a value comparable with that of the pure liquid metals.

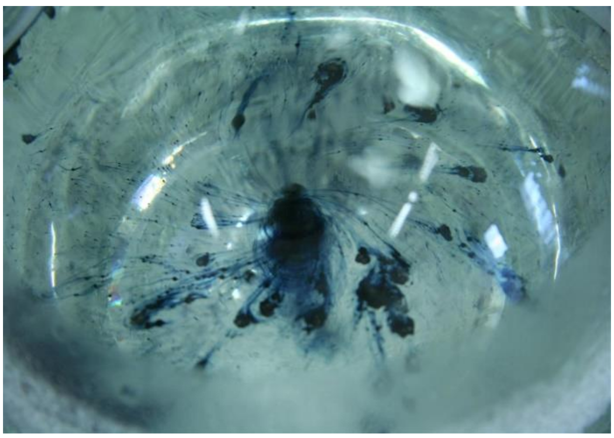

***Figure** 2:* Alkali Metal–Liquid Ammonia Solutions. *Most metals are insoluble in virtually all solvents, but the alkali metals (and the heavier alkaline earth metals) dissolve readily in* *liquid ammonia to form solvated metal cations and solvated electrons, which give the solution a deep blue color.. .*

The most common sources of the hydride Nucleophile are lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). Note! The hydride anion is not present during this reaction; rather, these reagents serve as a source of hydride due to the presence of a polar metal-hydrogen bond. Because aluminum is less electronegative than boron, the Al-H bond in $LiAlH_4$ is more polar, thereby, making $LiAlH_4$ a stronger reducing agent.

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$NH_3$ is more polarisable than $H_2O$,
so salts with more polarisable anions are more soluble,
hence the solubility trends.

$F^- < Cl^- < Br^- < I^-$

$PO_4^{3-} < SO_4^{2-} < OAc^- < NO_3$

specific solvation: $NH_3$ is a better a-donor than $H_2O$ and ammine complexes are formed,
especially with the later transition ($Ni^{2+}$, $Cu^{2+}$) and B metals ($Ag^+$, $Zn^{2+}$).
Hence higher solubilities for compounds of these metals than those of the A-metals.

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Liquid ammonia will therefore tolerate very strong bases such as

$C_5H_5^-$ which would otherwise be hydrolysed in water.

Ammonia is kinetically stabilized to reduction (but easily oxidized) by many reagents, e.g., the reaction;

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is very favourable but slow in the absence of a catalyst such as $Fe^{3+}$.

## Reactions and applications

### Solvolysis: synthesis of amides

$$OPCl_3 + 6NH_3 \longrightarrow OP(NH_2)_3 + 3NH_4Cl$$

$$SiCl_4 + 8NH_3 \longrightarrow Si(NH_2)_4 + 4NH_4Cl$$

### Metatheses reactions: solubility reversals

*In water*,

$$RCl + AgNO_3 \longrightarrow AgCl(ppt) + RNO_3$$

*In ammonia*

$$AgCl + KNO_3 \longrightarrow RCl(ppt) + AgNO_3$$

$$Ba(NO_3)_2 + 2AgCl \longrightarrow BaCl_{2(ppt)} + 2AgNO_3$$

## Alkali metals in liquid ammonia

### Sodamide as a base

$$Na + NH_3 \longrightarrow NaNH_2 + H_2(g)$$

NaNH2 + C5H6 ⟶ NaC5H5 + NH3

NaCp (useful reagent)

Solvated electron as a reducing agent (Birch reduction),
many examples of compounds in very unusual low oxidation states.

$$[Ni(CN)_4]^{2-} + Na/liq\text{-}NH_3 \longrightarrow [Ni(CN)_4]^{4-}$$

$$Fe(CO)_5 + Na/liq\text{-}NH_3 \longrightarrow [Fe(CO)_4]^{2-}$$

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$$[Pt(NH_3)_4]^{2+} + Na/liq\text{-}NH_3 \longrightarrow [Pt(NH_3)_4]$$

Reduction of salts of Group IV and V elements give polyhedral anions, many examples.

$Ge_9^{4-}$, $Sn_5^{2-}$, $Sn_9^{3-}$, $Pb_5^{2-}$, $Bi_4^{2-}$, $P_7^{2-}$ $As_6^{4-}$

## QUESTIONS:

What is the difference between ammonia and liquid ammonia?

What happens when anhydrous ammonia is mixed with water?

How dangerous is anhydrous ammonia?

What does anhydrous ammonia do to a person?
CHEMICAL PROPERTIES
Most deaths from **anhydrous ammonia** are caused by severe damage to the throat and lungs from a direct blast to the face. When large amounts are inhaled, the throat swells shut and victims suffocate. Exposure to vapors or liquid also **can** cause blindness.

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What is the formula of liquid ammonia?

What drug is made with anhydrous ammonia?

What does ammonia do to lungs?

Does urine contain ammonia?

Can ammonia be mixed with water?

At what temperature does ammonia become liquid?

Does ammonia dissolve in water?

What dissolves in ammonia?

How do you dissolve a gas in a liquid?

Why does ammonia need ice?

What is liquid ammonia?

Is ammonia an acid or base?

Is ammonia D harmful?

What contains ammonia?

Does ammonia affect pH?

How does ammonia kill you?

What is the main use of ammonia?

What is ammonia disease?

How do you make a 25% ammonia solution?

How dangerous is anhydrous ammonia?

What does anhydrous ammonia do to a person?

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