# 12.2: Reducing Agents

## 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:

$$\mathrm{M(s) + NH_3(l) \rightarrow \frac{1}{2}H_2(g) + M^+(am) + NH_2^-(am)} \tag{12.2.1}$$

where the (am) designation refers to an ammonia solution, analogous to (aq) used to indicate aqueous solutions. Without a catalyst, the reaction in Equation 12.2.1 tends to be rather slow. In many cases, the alkali metal amide salt ($\mathrm{MNH_2}$) 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.

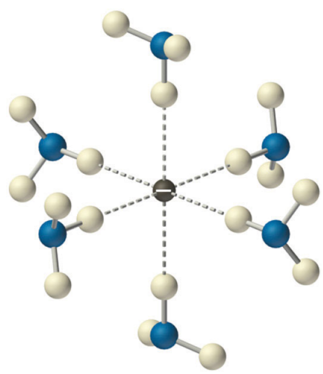


Figure 12.2.1: Solvated electrons. The presence of solvated electrons ($e^-$, $NH_3$) in solutions of alkali metals in liquid ammonia is indicated by the intense color of the solution and its electrical conductivity. (CC BY-SA-NC 3.0; anonymous)

Solutions of alkali metals in liquid ammonia are intensely colored and good conductors of electricity due to the presence of solvated electrons ($e^-$, $\mathrm{NH_3}$), 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 12.2.2) and conduct electricity about 10 times better than an aqueous $\mathrm{NaCl}$ 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.

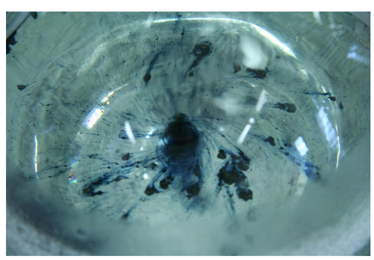
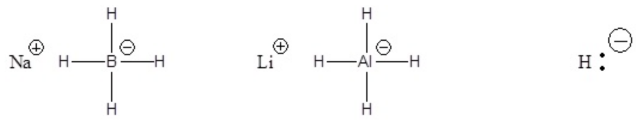


Figure 12.2.2: Alkali Metal–Liquid Ammonia Solutions. Most metals are insoluble in virtually all solvents, but the alkali metals (and the heavier alkaline earth metals) dissolve readily in liquid ammonia to form solvated metal cations and solvated electrons, which give the solution a deep blue color. Image copyrighted by the Klein research group (Christian Joest, 2013).

The most common sources of the hydride nucleophile are lithium aluminum hydride ($\mathrm{LiAlH_4}$) and sodium borohydride ($\mathrm{NaBH_4}$). 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 $\mathrm{LiAlH_4}$ is more polar, thereby, making $\mathrm{LiAlH_4}$ a stronger reducing agent.



**Sodium Borohydride** **Lithium Aluminum Hydride** **Hydride Nucleophile**