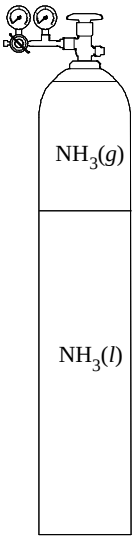
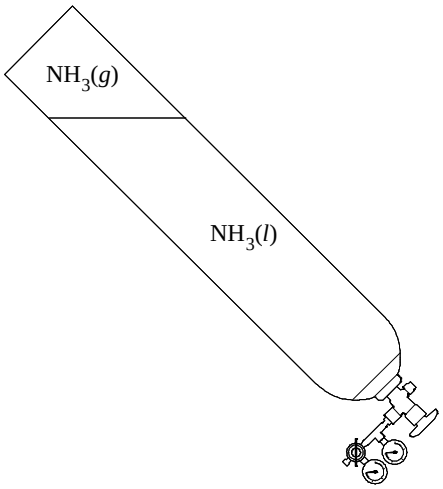
Liquid Ammonia in a Gas Tank



A full tank of ammonia gas under pressure contains mostly liquid with some gas in the space above.



If the tank is inverted, liquid ammonia can be delivered into a vessel.

☞ For ease of handling, we will use small lecture bottle tanks of ammonia (or a medium-sized tank with an aductor), which can be held in the inverted position with a clamp on a ring stand.

Properties of Liquid Ammonia vs. Water

- $NH_3(l)$ is decent ionizing solvent, which can be conveniently handled in an insulated vessel (Dewar) owing to its relatively high heat of vaporization.

	$NH_3(l)$	$H_2O(l)$
ΔH_{vap} (kJ/mol)	23.3	40.7
b.p. (^oC)	–33.35	100

- Both ammonia and water are extensively hydrogen bonded.

☞ Because of its high heat of vaporization, liquid ammonia in a Dewar at –33.35 ^oC evaporates slowly and smoothly, and the gaseous ammonia produced can easily be handled by a well functioning fume hood.

☛ Any room-temperature substance placed in liquid ammonia is "hot" and will cause significant boiling and/or bumping.

☛ Be sure you are wearing nitrile gloves and safety goggles throughout this experiment, especially when handling the liquid ammonia.

Acid-Base Chemistry

- Both $NH_3(l)$ and $H_2O(l)$ have an autodissociation equilibrium, which defines the strongest acid and base in the liquid.

  $2H_2O = H_3O^+ + OH^-$ $\quad K_w = 1.0 \times 10^{-14}$ at 25°C

  $2NH_3 = NH_4^+ + NH_2^-$ $\quad K = 1.9 \times 10^{-33}$ at –50°C

  - In water, H_3O^+ is the strongest possible acid, and OH^- is the strongest possible base.

  - In liquid ammonia, NH_4^+ is the strongest possible acid, and NH_2^- is the strongest possible base.

	$NH_3(l)$	$H_2O(l)$
Strong base solution	$NaNH_2$	NaOH
Strong acid solution	NH_4Cl	HCl

Alkali Metals in Liquid Ammonia

- Alkali metals (e.g., Na) in $NH_3(l)$ produce bronze colored solutions when concentrated (>1.0 M) and blue solutions when less concentrated.
  - In both cases, the solution contains solvated electrons.

$$M + (x + y)NH_3 \rightarrow M(NH_3)_x^+ + e(NH_3)_y^-$$

  - The more dilute blue solutions are strongly paramagnetic, becoming less so with increasing concentration.
  - In the concentrated solutions, extensive electron pairing occurs, making the bronze colored solutions less paramagnetic.

- Solutions of metals in liquid ammonia are very strong reducing agents and react very much like the free metals themselves.
  - The reduction process appears to involve free solvated electrons, $e(NH_3)_y^-$.

Reduction of Ammonia by Alkali Metals

- The resistance of ammonia itself to reduction provides a medium in which highly reduced states are thermodynamically stable.

- Alkali metals do react very slowly with NH_3 in a manner analogous to their behavior with water.

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$

  - The reaction is catalyzed by small amounts of any Fe(III) salt.

  - Catalytic mechanism is uncertain, but appears to involve rapid reduction of Fe^{3+} to produce finely divided Fe^{o}, which may be the actual catalytic agent.

Synthesis of $[Cr(NH_3)_6](NO_3)_3$ - A Two Step Preparation
First Step

- $[Cr(NH_3)_6]Cl_3$ is formed first by reacting $CrCl_3$ with NH_3 in liquid ammonia.

$$CrCl_3 + 6NH_3 \xrightarrow[NH_3(l)/NaNH_2]{} [Cr(NH_3)_6]Cl_3$$

  - If anhydrous $CrCl_3$ were simply allowed to react with liquid ammonia, a major product would be $[Cr(NH_3)_5Cl]Cl_2$.

  - The displacement of the last Cl^- proceeds very slowly unless catalytic amounts of $NaNH_2$ are present.
    - ☞ Therefore, $NaNH_2$ is produced before adding $CrCl_3$, by reacting $Na(s)$ with $NH_3(l)$ in the presence of a small amount of Fe^{3+}.

$$2Na + 2NH_3 \xrightarrow{Fe^{3+}} 2NaNH_2 + H_2$$

    - The greater nucleophilic character of NH_2^- as compared to NH_3 probably allows attack at the Cr atom with displacement of Cl^- to give $[Cr(NH_3)_5NH_2]^{2+}$.
      - This intermediate species either removes a proton from solvent NH_3 or acquires a proton when treated with nitric acid (next step) to produce the cation $[Cr(NH_3)_6]^{3+}$, which is precipitated as the relatively insoluble nitrate salt.

Synthesis of $[Cr(NH_3)_6](NO_3)_3$ - A Two Step Preparation
Second Step

- After decanting off $NH_3(l)$ a brown precipitate of impure $[Cr(NH_3)_6]Cl_3$ will remain.

- This precipitate is dissolved in warm (~40 ºC) 0.75 M HCl to neutralizing excess NH_3.
  - ☛Be ready to carry out the remaining steps rapidly or the product will decompose by reaction of $[Cr(NH_3)_6]^{3+}$ with Cl^- to form $[Cr(NH_3)_5Cl]^{2+}$.

- Filter and then treat with concentrated HNO_3 to form $[Cr(NH_3)_6](NO_3)_3$.

$$[Cr(NH_3)_6]Cl_3 + 3HNO_3 \rightarrow [Cr(NH_3)_6](NO_3)_3 + 3HCl$$

  - The product precipitates when chilled over an ice bath to give a dull yellow solid.

  ☛After washing and drying, weigh the sample in a *brown* tared sample bottle to protect it from decomposition in the light.

- Take a uv-vis spectrum of a dilute solution of your sample, print it out, and submit it with your report.