Within this module will be the primary discussion about the chemistry of nitrogen and its ability and inability of forming reactions with certain main group elements. Although nitrogen is considered a relatively inert element, it is fully capable of creating some very active compounds.

Nitrogen and the Main Group Elements

Nitrogen exists in a natural gaseous state as an inert (chemically inactive) non-polar diatomic molecule ($N_2$). The natural diatomic molecule of nitrogen is held tightly together by a strong triple bond between the two nitrogen atoms, which requires an immense amount of energy in order to break the bonds, thus the reason as to why nitrogen is primarily viewed as relatively nonreactive. In connection with the main group elements of the periodic table (groups 1-2 and groups 13-18), nitrogen does not generate many reactions with the main group elements due to the strong triple bond keeping the nitrogen atoms together, which makes it difficult and most of the time impossible to create reactions. Aside from its inert characteristics, nitrogen is also accountable for creating many active compounds and making up about 78% of the air we breathe. In reaction with a few of the main group elements, nitrogen is capable of producing successful compounds despite its triple bond.

Reactions With Group 1: Alkali Metals (Li, Na, K, Rb, and Cs)

General characteristics of the alkali metals include:

- relatively abundant
- high chemical reactivity (the most active metals)
- low melting and boiling points
- largest atomic and ionic radii
- highly metallic character
- low first ionization energy (they lose their valence electrons easily creating a strong reducing character)

Although the alkali metals possess a high chemical reactivity characteristic, lithium is the only element of the alkali metals to react with nitrogen gas at room temperature. The reaction between elemental lithium and nitrogen gas proceeds as follows producing the ionic (salt-like) lithium nitride ($Li_3N$):

$$Li(s) + N_2(g) \rightarrow 2Li_3N(s)$$

When water is added to the lithium nitride, the lithium nitride hydrolyzes (decomposes by reacting with water) into ammonia and lithium hydroxide:

$$Li_3N(s) + 3H_2O(l) \rightarrow 3Li^+(aq) + OH^-(aq) + NH_3(aq)$$

On account of the nitrogen ion having a ‘3-’ oxidation state ($N^{3-}$), it is a strong Bronsted base (a compound that accepts a hydrogen ion) causing all ionic nitride and water reactions to exhibit similar structure reactions to that of the lithium nitride and water reaction, forming ammonia molecules and hydroxide ions. The heavier alkali metals are seen to be chemically inactive in regards to nitrogen upon heating or under ambient states. Due to this idleness, the notion that nitrides are
unable to form through traditional chemical conditions has been formed. Since the nitride ion holds a high formal charge \( (N^{3-}) \) and contains an adverse molar ratio of cations to anions (3:1), it is impossible to form a stable ionic structure in alkali metal and nitrogen reactions due to the unfulfilled necessities required for a stable solid material.

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**Reactions With Group 2: Alkaline Earth Metals (Be, Mg, Ca, Sr, and Ba)**

General characteristics of the alkaline earth metals include:

- fairly reactive
- low melting and boiling points, but higher than alkali metals
- large atomic and ionic radii, but smaller than those of the alkali metals
- more metallic than alkali metals
- higher ionization energies than alkali metals

All alkaline earth metals are competent to producing their appropriate nitrides in reaction with nitrogen with a required vast amount of heat. The basic structure of reactions with an alkaline earth metal and nitrogen are as follows:

\[
\ce{3M_{(s)} + N_{2 (g)} ->\[\Delta\] M_3N_{2 (s)}}\]

\((M = \text{Be, Mg, Ca, Sr, or Ba})\)

Nitrides of the alkaline earth metals are ionic and solid in nature except for beryllium nitride \((\text{Be}_3\text{N}_2)\), which is covalent and unpredictable. Decompositions of the alkaline earth metal nitrides occur upon heating:

\[
\ce{M_3N_{2 (s)} ->\[\Delta\] 3M_{(s)} + N2 (g)}}\]

\((M = \text{Be, Mg, Ca, Sr, or Ba})\)

Nitrides of alkaline earth metals may also react with water producing ammonia:

\[
\ce{M_3N_{2 (s)} + 6H_2O (l) \rightarrow 3M(OH)_{2 (aq)} + 2NH_3 (g)}
\]

\((M = \text{Be, Mg, Ca, Sr, or Ba})\)

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**Reactions With Main Group 13-18 Elements**

General characteristics of non-metals include:

- high ionization energies
- poor conductors of heat
- ability to gain electrons easily
- brittle
- little or no metallic luster

With the larger numbered groups of the main group elements, the elements (most of which are non-metals) experience a decrease in electronegativities causing these elements and nitrogen to form compounds with more covalent (chemical
bonds formed by sharing electrons between atoms) character, contrasting from the ionic compounds formed by groups 1 and 2. For group 13 elements (B, Al, Ga, In, and Ti), they produce compounds of the form MN (M = B, Al, Ga, In, or Ti). Most non-metals retain multiple oxidation states and as they remain in their highest oxidation state, they present a diminishing inclination to generate stable binary nitrides. Main group elements B, Al, Ga, In, Si, Ge, and P, in their maximum oxidation states, are the only elements known to react with nitrogen in successfully producing their appropriate binary nitrides, BN, AlN, GaN, InN, Si$_3$N$_4$, Ge$_3$N$_4$, and P$_3$N$_5$, respectively. The instability of the bond between a non-metal and nitrogen seem to be accountable for the nonexistence of their correlated binary nitrides. Other binary covalent nitrides include (CN)$_2$, As$_4$N$_4$, S$_2$N$_2$, and S$_4$N$_4$.

References

Problems
1. Write a balanced equation for the formation of a binary nitride when nitrogen reacts with:
   - A) An alkali metal
   - B) An alkaline earth metal

2. Write a balanced equation showing the reaction of any ionic nitride with water.

3. Write a balanced equation showing that, when heated, PCl$_5$ and NH$_4$Cl produce phosphorous nitride and hydrochloric acid.

4. Fully provide and explain the characteristics of both metals and non-metals that make it impossible for the existence of some binary nitrides with their corresponding elements.

5. Write a balanced equation of the decomposition of magnesium nitride with water.

Answers
1. **A)** $6\text{Li} \ (s) + \text{N}_2 \ (g) \rightarrow 2\text{Li}_3\text{N} \ (s)$. This is the only answer for because lithium is the only element of the alkali metals to react with nitrogen at room temperature.

2. **B)** $3\text{M} \ (s) + \text{N}_2 \ (g) \rightarrow \text{M}_3\text{N}_2 \ (s)$. Answers may vary. M must be replaced by either of the group 2 alkaline earth metals.

3. $\text{Li}_3\text{N} \ (s) + 3\text{H}_2\text{O} \ (l) \rightarrow 3\text{Li}^+ \ (aq) + \text{OH}^- \ (aq) + \text{NH}_3 \ (aq)$. Answers may vary. Reactants must always be an ionic nitride and water. Product must always contain OH$^-$ and NH$_3$.

4. $3\text{PCl}_5 \ (s) + 5\text{NH}_4\text{Cl} \ (s) \rightarrow \text{P}_3\text{N}_5 \ (s) + 20\text{HCl} \ (aq)$
4. **Metal characteristics**: heavy and inert alkali metals, metals binding with nitrogen that contain a high oxidation state, and unfavorable molar ratio of 3:1 (cations:anion).

**Non-metal characteristics**: multiple high oxidation states, decreasing electronegativities, covalent bonding, and unstable bonds between non-metal and nitrogen.

5. \( \text{Mg}_3\text{N}_2 (s) + 16\text{H}_2\text{O} (l) \rightarrow 3\text{Mg(OH)}_2 (s) + 2\text{NH}_3 (aq) \)

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