Dinitrogen

- $\text{N}_2$ is chemically very unreactive, mp $-210^\circ\text{C}$, bp $-195.8^\circ\text{C}$; its great bond strength, $\Delta H_{\text{diss}} = 945.41 \text{ kJ/mol}$, $d_{\text{N,N}} = 109.76 \text{ pm}$, and great thermodynamic stability causes many nitrogen compounds to be endothermic.
- The $\text{N}_2$ lone pairs are very low in energy and are much less available for donation than the isoelectronic CO.
- The $\pi^*$ molecular orbitals are very high in energy ($\pi$ bonds are very strong) and $\pi$-backbonding is less favored.
- A large HOMO-LUMO energy gap makes it hard to promote electrons or reduce dinitrogen.
- Dinitrogen is a non-polar molecule, isoelectronic with: CO, NO$,^+$, CN$,^-$, C$_2^2-$, and similar to HC$_2^-$, H$_2$C$_2$.

Molecular Orbital Diagram - Dinitrogen

Note the two $\pi$-bonds are stronger than the $\sigma$-bond due to bond compression.
Reactions of Dinitrogen

Nitrides and nitrogen oxides:

\[ 6 \text{Li} + \text{N}_2 \rightarrow 2 \text{Li}_3\text{N} \]

Many small metals (Mg, Al, Ti) react with dinitrogen at elevated temperatures.

\[ \text{N}_2 + \text{O}_2 \rightarrow \text{NO}_x \]

Dinitrogen "fixation" during electrical storms and high temperature combustion contributes to soil fertility & "acid rain."

Dinitrogen coordinates to some metal complexes:

\[ [\text{Ru(NH}_3)_5(\text{H}_2\text{O})]^2+ + \text{N}_2 \rightarrow [\text{Ru(NH}_3)_5(\text{N}_2)]^{2+} + \text{H}_2\text{O} \]

\[ [\text{MoCl}_4(\text{PMe}_2\text{Ph})_2]^+ + 2 \text{N}_2 \rightarrow [\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_2] \]

Dinitrogen Coordination:

\[ \eta^1 \text{most common} \quad \text{bis-}\eta^1 \text{impt in fixation} \quad \mu\text{-bis-}\eta^2 \quad \eta^2 \text{rare} \]

Nitrides – Nitrido Complexes

\[ ^{14}\text{N} 99.634\%, \ I = 1 \quad ^{15}\text{N} 0.366\%, \ I = \frac{1}{2} \]

Ionic:

\[ 3 \text{Ca} + \text{N}_2 \rightarrow \text{Ca}_3\text{N}_2 \quad \text{also Li, Mg, Zn, Ti other small cations.} \]

\[ \text{Al}_2\text{O}_3 + \text{N}_2 + \text{C}_x \rightarrow 2\text{AlN} + 3\text{CO} \]

Covalent:

\[ \text{Si}_3\text{N}_4 \quad \text{Network covalent - with alumina in hi tech ceramics.} \]

\[ \text{S}_3\text{N}_4 \quad \text{Molecular, all have some type of d-p bonding.} \]

\[ \text{P}_3\text{N}_5 \quad \] (some have network bonding)

Metallic:

Transition metals (Zr, Ti, Cr) in cubic and hexagonal close packed lattices, N fits into octahedral sites.

Nitrides – Nitrido Complexes

Nitrido:

\[ \text{OsO}_4 + \text{NH}_3 \rightarrow \text{H}_3\text{O}^+ \quad [\text{N}\overset{\text{Os}}{\text{O}}]^- \]

Linear:

\[ \text{M} = \text{N} = \text{M} \quad \text{180°} \]

\[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

\[ \text{H}_2\text{O} - \text{Ru} = \text{N} = \text{Ru} - \text{OH}_2 \]

Trigonal:

\[ \text{M} = \text{N} = \text{M} \]

\[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

\[ [\text{Ni}_{12}\text{(SO}_4)_6(\text{H}_2\text{O})_3]^+ \]

Tetrahedral:

\[ \text{M} = \text{N} = \text{M} \]

\[ \text{M} \quad \text{M} \quad \text{M} \]

\[ [\text{N}\left(\text{HgMe}_2\right)\text{]}^+ \]
Azides – Azido Compounds

Ionic Azides:
\[ \text{N}_3^- : \hat{\text{N}} - \hat{\text{N}} - \hat{\text{N}}^- \]  iso-electronic with \[ \text{O} - \text{C} - \text{O} \]
\[ \delta_{\text{N-N}} = 116 \text{ pm} \]
Ionic azides are stable, the ion is symmetrical, the alkali metal salts are commercially available.

Covalent Azides:
\[ \text{HN}_3, \text{RN}_3, \text{Pb(N}_3)_2, \text{HgN}_3 \]

Hydrazoic acid, \( pK_a = 4.77 \), pungent, revolting odor, very toxic. Concentrated and anhydrous acids are explosive.
\[ \Delta H_f^\circ = 269.5 \text{ kJ/mol} \]
\[ \Delta G_f^\circ = 327.2 \text{ kJ/mol} \]
A very energetic molecule, heavy metal salts are used as detonators for explosives, not hygroscopic, reliable.

Hydrides

Ammonia: \[ \text{NH}_3, K_b = 1.8 \times 10^{-5} \] \( \text{NH}_4^+ \)
Largest industrial commodity on a molar basis.

\[ \text{RBr} + \text{NH}_3 \to \text{RNH}_3^+ \text{Br}^- \]
Ammonia and amines are weak bases ammonium ions are weak acids. Tetraalkylammonium hydroxide is a strong base.

Hydrazine: \[ \text{H}_2\text{NNH}_2, K_b = 8.5 \times 10^{-7} \] \( \text{H}_2\text{NNH}_3^+ \)
\[ K_b = 8.9 \times 10^{-16} \] \( \text{H}_3\text{NNH}_3^+ \) A strong acid

\[ \text{L-P-L repulsions make the H-N bond long and weak.} \]
\[ \text{gauche conformation torsion angle } 90^\circ - 95^\circ \]
\[ 1e,2e,4e \text{ reducing agent, stronger in base than acid.} \]
\[ 1e \text{ } E^{\text{red}} = -1.74 \text{ V acid} \]
\[ 1e \text{ } E^{\text{red}} = -2.42 \text{ V base} \]

Hydrazide Ligand:

Less Common Binary Hydrides

Diazine: \[ \text{HNNH} \]
\[ \text{trans more stable} \]
\[ \text{Ligand important in nitrogen fixation.} \]

Cyclotriazene: \[ \text{N} \]
\[ \text{(triazidine)} \]

Triazane: \[ \text{H}_2\text{NNHH}_3 \]
\[ \text{(aminohydrazine)} \]

Tetrazane: \[ \text{H}_2\text{NNHNHNH}_2 \]
\[ \text{(diaminohydrazine)} \]

trans-2-Tetrazene

Several "binary hydrides" can be made such as ammonium and hydrazinium azide salts; dimers and trimers of hydrazoic acid or triaziridine.
**Hydroxylamine & Nitrogen Fixation**

**Hydroxylamine:** \(\text{H}_2\text{NOH} \quad \text{K}_b = 6.6 \times 10^{-9} \quad \text{H}_3\text{NOH}^+\)

Trans conformation in the crystal

Made by the reduction of ammonium nitrite in a gel using aqueous bisulfite/sulfur dioxide, Raschig Synthesis.

Industrially used as reducing agent, absorbent for nitrogen oxides.

Forms Oximes with aldehydes and ketones:

\[
\text{C}=\text{O} + \text{H}_2\text{NOH} \rightarrow \text{C}=(\text{ON})\text{H} + \text{H}_2\text{O}
\]

**Nitrogen Fixation:**

\[
\text{M} \rightarrow \text{N} = \text{N}\quad \text{M}
\]

\[
\text{M} \rightarrow \text{N} = \text{N} \quad \text{M}
\]

\[
\text{M} \rightarrow \text{N} = \text{NH}_2
\]

\[
\text{M} \rightarrow \text{N} = \text{NH}_2
\]

**Nitrogen Halides**

\[
\text{NF}_3, \text{NCl}_3, \text{NBr}_3, \text{NI}_3
\]

\[
\text{NH}_3, \text{NH}_4^+\text{HF}^-\quad \text{electrolysis}
\]

\[
\text{NH}_4^+\text{Cl}^-\quad \text{electrolysis}
\]

\[
\text{NH}_3 + \text{I}_3^- \rightarrow \text{N}_2\text{H}_4 + 3 \text{HCl}
\]

\[
\text{N}_2\text{F}_4 + 2 \text{HF} \rightarrow \text{N}_2\text{F}_3 + 2 \text{HF}
\]

\[
\text{N}_2\text{F}_2 + \text{SbF}_3 \rightarrow \text{N}_2\text{F}_4 + \text{SbF}_4^-
\]

**Nitrogen Halides**

\[
\text{NF}_3 \quad \text{mp} -206.6^\circ \quad \text{bp} -139.0^\circ
\]

Stable, \(\Delta G = -23.3 \text{ kJ/mol}\), colorless, low dipole moment, low reactivity.

\[
\text{N}_2\text{F}_2 \quad \text{mp} -206.8^\circ \text{bp} -129.0^\circ
\]

\[
\text{N}_2\text{F}_2 \quad \text{mp} -165.5^\circ \text{bp} -73^\circ
\]

\[
\text{N}_2\text{F}_3 \quad \text{mp} -172^\circ \text{bp} -111.4^\circ
\]

Cis isomer more reactive, attacks glass. Trans isomer does not attack glass.

**NF\(_3\)\** [SbF\(_4\)]

Many salts known, oxidizer for chemical lasers.
## Nitrosyl & Nitril Halides

<table>
<thead>
<tr>
<th>Nitrosyl halides: XNO</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>Cl</td>
<td>Br</td>
</tr>
<tr>
<td>mp °C</td>
<td>-132.5</td>
<td>-59.6</td>
<td>-56</td>
</tr>
<tr>
<td>bp °C</td>
<td>-59.9</td>
<td>-6.4</td>
<td>-0</td>
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<tr>
<td>ΔH_f (kJ/mol)</td>
<td>-66.5</td>
<td>+51.7</td>
<td>+82.2</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Nitryl halides: XNO₂</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>Cl</td>
<td></td>
</tr>
<tr>
<td>mp °C</td>
<td>-166</td>
<td>-145</td>
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</tr>
<tr>
<td>bp °C</td>
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<td>-15.9</td>
<td></td>
</tr>
<tr>
<td>ΔH_f (kJ/mol)</td>
<td>-80</td>
<td>+13</td>
<td></td>
</tr>
</tbody>
</table>

**BF₃, AsF₅, AlCl₃**

**H₂O**

*Potent solvents for dissolving metals.*

## Oxides of Nitrogen

### Dinitrogen Monoxide

Isoelectronic with carbon dioxide & NO₂⁺. Very unreactive, very stable gas, anesthetic (laughing gas), greenhouse gas. Natural source, microbial degradation of NH₄NO₃(Nitrous Oxide).

### Nitrogen Monoxide

A stable free radical, paramagnetic, colorless, bp -151.8 °C. Little tendency to dimerize. Oxidation to NO₂ has a negative temperature coefficient.

## Nitric Oxide as a Ligand – Bent Nitrosyls

- **Linear:** NO⁺
  - M–N–O
  - v(NO) = 1650-1690 cm⁻¹. Common with early transition metals and middle transition metals in higher oxidation states.

- **Bent:**
  - Gp A: (2 electron donor)
    - M–N–O
    - v(NO) = 1500-1690 cm⁻¹. Common with late transition metals and middle transition metals in lower oxidation states.
  - Gp B: (1 electron donor)
    - M–N–O
    - v(NO) = 1200-1400 cm⁻¹. Bonding modes of NO:

*Note: Diagrams and equations are not rendered in this text format.*
Nitric Oxide as a Ligand

Oxides of Nitrogen

Dinitrogen Trioxide:

\[ \text{NO}_2 \xrightarrow{\text{NO} + \text{NO}_2} \text{NO}_2 \text{O}_2 \]

\( m.p. -100.1^\circ \text{C} \)

Light blue solid, intense blue liquid, turns green as NO dissociates, color becomes less intense.

Nitrogen Dioxide & Dinitrogen Tetroxide

Isoelectronic with \( \text{B}_2\text{F}_4 \) & \( \text{C}_2\text{O}_4^{2-} \) whose C-C and B-B bonds are of normal length.

Does not autoionize, but ionic intermediates form in high dielectric solvents. An intermediate in the production of nitric acid.

Nitric Acid:

\[ \text{NH}_3 + \text{NO} \xrightarrow{\text{H}_2\text{O}} \text{N}_2\text{O}_4 \xrightarrow{\text{H}^+} \text{HNO}_3 + \text{HNO}_2 \]

Oxides of Nitrogen

Dinitrogen Pentoxide:

\[ 2 \text{HNO}_3 \xrightarrow{70^\circ \text{C}} \text{N}_2\text{O}_5 \]

Oxoacids – Oxoanions:

Hyponitrous Acid - Hyponitrite

\( \text{HONO} = \text{NOH} \)

pK\text{a} = 6.9 \text{ - } 11.6

Isotenic with nitramide pK\text{a} = 6.6

Weak dibasic acid of unknown structure. Stable for weeks in acidic solution, decomposes at pH \( \geq 4 \).

Na\text{NO}_2 = \text{NaNO}_2

Salts are stable, reducing. "trans" by vibrational spect. "Cis" ion known as a ligand.

Many "non-EAN" nitrosyls are cis-hyponitriles.
Oxoacids – Oxoanions

Hyponitric Acid - Hyponitrates:

\[
\begin{align*}
\text{Acid is known only in solution and is explosive.} \\
\text{Na}_2\text{N}_2\text{O}_2 \xrightarrow{\text{aq}} \beta-\text{N}_2\text{O}_3^{2-} \xrightarrow{\text{slow}} \text{N}_2\text{O}_2^{2-} \xrightarrow{100^\circ\text{C}} \text{N}_2\text{O}_4^{2-} \\
\end{align*}
\]

Nitroxylic (Hydronitrous) Acid - Nitroxolate Anion:

"Acid Explosive"

\[
2 \text{NaNO}_2 + 2 \text{Na} \rightarrow \text{N}_2\text{O}_4^{2-}
\]

Oxoacids – Oxoanions

Nitrous Acid - Nitrites

\[
\begin{align*}
\text{45 kJ/mol barrier to rotation} \quad \text{nitrile is a very versatile ligand} \\
\text{N} \quad \text{O} \quad \text{N} \\
\text{M} \quad \text{N} \quad \text{O} \quad \text{N} \\
\text{M} \quad \text{O} \quad \text{N} \quad \text{O} \\
\text{O} \quad \text{N} \quad \text{O} \quad \text{N} \\
\end{align*}
\]

Nitric Acid - Nitrates

\[
\begin{align*}
\text{Almost planar gas, } \ell_{\text{cis}} \text{ tension } 2^\dagger \\
\text{bp } 82.5^\circ\text{C}. \text{ Nitric Acid will form H-bonded complexes with nitrate.} \\
\text{The nitrate ligand may coordinate in a manner similar to nitrile and may use all three oxygen atoms.} \\
\end{align*}
\]

Orthonitrate:

\[
\begin{align*}
\text{Na}_2\text{O}_3 + \text{NaNO}_3 \xrightarrow{\text{aq}} \text{H}_2\text{NO}_4^{\text{2-}} \xrightarrow{\text{100 pm}} \text{[N}_4\text{O}_6\text{]}^{\text{2+}} \xrightarrow{\text{3 NO}_3^{\text{2-}}} \text{NO}_3^{\text{2-}} + 3 \text{NO}_3^{\text{2-}} \\
\end{align*}
\]

Tetrahedral anion, very short N-O bond due to strong polar interactions.
Many metal nitrates melt at "low" temperatures without decomposition
LiNO₃ (255°C); CsNO₃ (419°C); AgNO₃ (212°C).