Highlights of last lecture

Standard states

- 1 atm, 1 M, 298 K, element in usual form

Heat of formation

- The heat of formation of an element in its standard state is defined as zero
- Knowledge of $\Delta H_f$ for different chemical species allows accurate prediction of reaction enthalpy
- $\Delta H_r = \sum \Delta H_f \text{(products)} - \sum \Delta H_f \text{(reactants)}$

Fuels

- Four common types of fuel: solid, petroleum, hypergolic, cryogenic
Interregnum: Nitrogen Chemistry

**Purpose:** To reinforce several earlier concepts in one application: Nitrogen Chemistry

**Earlier concepts:** Shapes (Lewis structures), Thermochemistry, Oxidation numbers, Bonding, IR Spectroscopy

**Themes:** Nitrogen fuels
Nitrogen fixation and bioavailability
Nitrogen oxides in the atmosphere
What makes an explosive?

What is the chemical requirement of a high explosive?

Most high explosives contain nitrogen. Why?

Why are compounds sometimes explosive, and sometimes fuels, or even safer?

\[
\begin{align*}
\text{C}_3\text{H}_5\text{N}_3\text{O}_9 & \quad \text{(nitroglycerine)} \\
\text{NH}_4\text{NO}_3 & \quad \text{ammonium nitrate} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{CH}_3 & \quad \text{(TNT)}
\end{align*}
\]
What makes an explosive?

What is the chemical requirement of a high explosive?

ANS: The reaction must produce a large amount of energy (exothermic), released in the form of a pressure wave (i.e. PV-type work is done).

**nitroglycerine**

\[
C_3H_5N_3O_9 (l) \rightarrow 1.5N_2(g) + 3CO_2(g) + 2.5H_2O(g) + 0.25O_2(g)
\]

7.25 moles of gas produced for each mole of nitroglycerine

**trinitrotoluene (TNT)**

\[
C_7H_5N_3O_6(s) \rightarrow 6CO(g) + 2.5H_2(g) + 1.5N_2(g) + C(s)
\]

10 moles of gas produced for each mole of TNT

PLUS! The reaction is very exothermic, therefore the gases are hot and expand even more rapidly.
What makes an explosive?

- Reaction energy diagram

\[ \Delta H^\circ \]
Transition States

\[ \text{BrCH}_3 + \text{OH}^- \rightarrow \text{Br}^- + \text{CH}_3\text{OH} \]

TRANSITION STATE or ACTIVATED COMPLEX

- geometry through which system must pass between reactant and product
- higher energy than reactants or products
- not a stable molecule!
Transition States

- Forward reaction is **EXOTHERMIC**, Reverse reaction is **ENDOTHERMIC**

\[
\text{BrCH}_3 + \text{OH}^- \rightarrow \text{Br}^- + \text{CH}_3\text{OH}
\]

\[
\Delta H_{\text{rxn}}
\]

- **\( E_a \) (fwd)**
- **\( E_a \) (rev)**

**Transition States**
Activation energies affect the rate at which reactions occur (Kinetics - see later).

Large activation energies lead to slow reactions since only a small fraction of reagents have enough energy to overcome the activation energy barrier to convert into products.

Small activation energies generally lead to fast reactions since a large fraction of reagents have enough energy to overcome the activation energy barrier. Single component reagents with low $E_a$ and large negative $\Delta H \Rightarrow$ Explosives.
What makes an explosive?

Why are compounds sometimes explosive, and sometimes useful fuels?

Hint: Where is the oxidant?

\[
\text{nitroglycerine} \\
C_3H_5N_3O_9 (l) \rightarrow 1.5N_2(g) + 3CO_2(g) + 2.5H_2O(g) + 0.25 O_2(g)
\]
What makes an explosive?

Most high explosives contain nitrogen. Why?

trinitrotoluene (TNT)

\[ C_7H_5N_3O_6(s) \rightarrow 6 \text{CO}(g) + 2.5 \text{H}_2(g) + 1.5 \text{N}_2(g) + \text{C}(s) \]
Properties of N-compounds

HIGHLY VARIED!

Incredibly stable: \( \text{N}_2 \)

Extremely explosive: trinitrotoluene (TNT)

Strong acid \( \text{HNO}_3 \)

Weak base \( \text{NH}_3 \)

Photochemical smog: \( \text{NO}_2 \)

Biologically important: NO + amino acids

nitroglycerine
# Oxidation states of N

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Compounds</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N^{V}$</td>
<td>$\text{HNO}_3 / \text{NO}_3^-$</td>
<td>Strong acid</td>
</tr>
<tr>
<td>$N^{IV}$</td>
<td>$\text{NO}_2, \text{N}_2\text{O}_4$</td>
<td>Smog</td>
</tr>
<tr>
<td>$N^{III}$</td>
<td>$\text{HNO}_2 / \text{NO}_2^-$</td>
<td>Weak acid / weak base</td>
</tr>
<tr>
<td>$N^{II}$</td>
<td>$\text{NO}$</td>
<td>Smog + biology</td>
</tr>
<tr>
<td>$N^{I}$</td>
<td>$\text{N}_2\text{O}$</td>
<td>Greenhouse gas + laughing gas</td>
</tr>
<tr>
<td>$N^0$</td>
<td>$\text{N}_2$</td>
<td>Stable</td>
</tr>
<tr>
<td>$N^{-I}$</td>
<td>$\text{NH}_2\text{OH}$</td>
<td></td>
</tr>
<tr>
<td>$N^{-II}$</td>
<td>$\text{N}_2\text{H}_4$</td>
<td>Hydrazine, rocket fuel</td>
</tr>
<tr>
<td>$N^{-III}$</td>
<td>$\text{NH}_3 / \text{NH}_4^+$</td>
<td>Weak base / weak acid</td>
</tr>
</tbody>
</table>
Revision: elemental nitrogen

Standard State: $\text{N}_2 \ (g)$

N: $1s^2 \ 2s^2 \ 2p^3 = [\text{He}] \ 2s^2 \ 2p^3$ (5 valence electrons)

$\Delta H_{\text{atom}} = \text{bond enthalpy} = 945 \text{ kJ/mol (very strong)}$

MO structure
Hydrides of N

Two main hydrides:

Ammonia, NH$_3$
- Oxidation state of N = -3
- Essential in the nitrogen cycle for life (see later)

Hydrazine, N$_2$H$_4$
- Oxidation state of N = -2
- Rocket fuel
Halides of N

Halides of formula \( \text{NX}_3 \)
- molecular compounds;
- trigonal pyramidal structure

\( \text{NF}_3 \): colourless gas, fluorinating agent
\( \text{NCl}_3 \): explosive liquid, industrial use as bleach
\( \text{NBr}_3 \): unstable
\( \text{NI}_3 \): only stable in presence of water
Oxides of nitrogen

- Nitrous oxide
- Nitric oxide
- Nitrogen dioxide
- Nitrate radical

All present in atmosphere, See next lecture
Oxoacids of N

HNO$_3$; nitric acid
- strong acid and strong oxidiser;
- colourless liquid;
- in nitrate ion all N-O bonds are equal, B.O.$\sim$1.3;
- nitrate salts are mostly soluble.

HNO$_2$; nitrous acid
- weak acid
- nitrite salts are generally soluble
Example questions

CONCEPTS
- N-compounds
- Explosive vs controlled reactions
- Basic info about hydrides, halides, oxides, etc