Largest use of CO_2 (~50%) is not a chemical use but a refrigerant

CO_2(s) f.p. = -78.5˚C
"dry ice"

$$CO_{2(s)} \xrightarrow{>-78.5^\circ C} CO_{2(g)}$$ sublimation

directly from solid to gas!

<u>How do you get liquid CO_2?</u>

You have to keep a pressure on the solid when it is melting.

CO_2 is a liquid → $CO_{2(l)}$ at 5.2 atm and -5.6˚C

- $CO_{2(l)}$ is used to extract caffeine from coffee. It leaves no harmful residues.
- $CO_{2(l)}$ is used in fire extinguishers. The more dense CO_2 will displace air around the burning material and keep O_2 from fueling the flames.
- ~25% of CO_2 produced is used in carbonation of beverages

"Chemistry of Soda"

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} + H_2O \rightleftharpoons HCO_3^-{}_{(aq)} + H_3O^+$$

TABLE 2.6 Some Polyatomic Ions

Ion	Name (Alternate Name in Parentheses)
NH_4^+	Ammonium ion
H_3O^+	Hydronium ion[a]
OH^-	Hydroxide ion
CN^-	Cyanide ion
NO_2^-	Nitrite ion
NO_3^-	Nitrate ion
ClO^-	Hypochlorite ion
ClO_2^-	Chlorite ion
ClO_3^-	Chlorate ion
ClO_4^-	Perchlorate ion
MnO_4^-	Permanganate ion
$C_2H_3O_2^-$	Acetate ion
CO_3^{2-}	Carbonate ion
HCO_3^-	Hydrogen carbonate ion (bicarbonate ion)[b]
SO_3^{2-}	Sulfite ion
SO_4^{2-}	Sulfate ion
HSO_4^-	Hydrogen sulfate ion (bisulfate ion)
CrO_4^{2-}	Chromate ion
$Cr_2O_7^{2-}$	Dichromate ion
PO_4^{3-}	Phosphate ion (orthophosphate ion)
HPO_4^{2-}	Monohydrogen phosphate ion
$H_2PO_4^-$	Dihydrogen phosphate ion

[a] You will only encounter this ion in aqueous solutions.

[b] Although "hydrogen carbonate ion" is formally correct, "bicarbonate ion" is what you will see and hear the most. We'll use "bicarbonate" too.

<u>CO_2 Reaction with Base:</u>

$CO_{2(aq)} + OH^-_{(aq)} \rightarrow HCO_3^-{}_{(aq)}$

$HCO_3^-{}_{(aq)} + OH^-_{(aq)} \rightarrow CO_3^{2-}{}_{(aq)} + H_2O_{(l)}$

<u>Other carbon compounds</u>

- Cyanides CN^-
  $[:C{\equiv}N:]^{-1}$ <u>strong base</u>
  NaCN sodium cyanide
  HCN hydrogen cyanide (weak acid)
- <u>Reaction of CN^- with water:</u>
  $CN^-_{(aq)} + H_2O \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$
  equilibrium
- <u>Reaction of CN^- with a strong acid:</u>
  strong base (CN^-)
  $CN^-_{(aq)} + HCl_{(aq)} \rightarrow HCN_{(aq)} + Cl^-_{(aq)}$
  strong acid (HCl)
  Reaction is complete!

<u>Properties of Cyanides</u>

- HCN is <u>extremely poisonous</u>

\- it was used in gas chambers. CN^- binds to the heme in your mitochondria that transport O_2. Not the same heme as CO which is your blood heme.

- NaCN is also lethal

Hemoglobin in blood is based on Fe

Heme in mitrochondria is Cu based

Nitrogen

- 78% of air is N_2
- 25-30 million tons N_2/ year

Industrial Preparation of N_2:

$$\text{Air} \xrightarrow{\textit{liquify}} \begin{array}{l} N_2 \text{ (collected first)} \\ Ar \\ O_2 \end{array}$$

Uses of N_2:

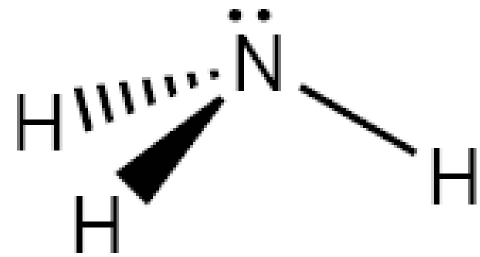
- Enhanced oil recovery – to force oil from subterranean deposits (~30% of N_2 made)
- Coolant (low b.p. 77k (-196˚C)) freezing perishables (meat, seafood)
- Unreactive gas in chemical industry used as a blanketing atmosphere

Nitrogen Cycle helps to maintain balance of N_2 in the atmosphere.

- Plants remove N_2 to make NH_3
- Plants decay back to N_2

Nitrogen Fixation:
Name given to the reactions that microorganisms use to make NH_3 from N_2.

Ammonia:



- Sharp odor
- Irritates lungs. Can cause death if inhaled in large quantities
- Used as a fertilizer by injecting directly into the soil

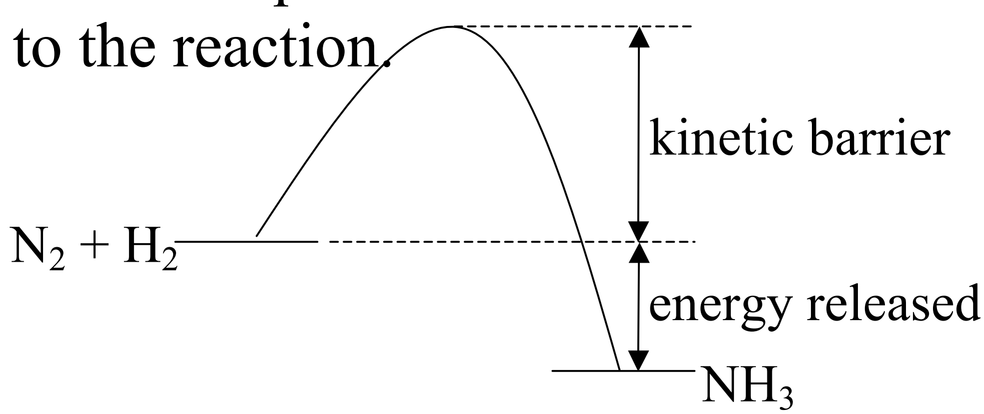
Haber – Bosch Process:

$$N_2(g) + 3H_2(g) \xrightleftharpoons{\text{catalysts}} 2NH_3(g)$$

$$\Delta H = -92.38KJ$$

requires a catalyst and high pressure $\begin{Bmatrix} 100-300atm \\ 450-500°C \end{Bmatrix}$

ΔH = -92.38KJ is the heat of reaction.
Negative ΔH means exothermic.
The extreme conditions are required because of the large kinetic barrier to the reaction.



Properties of NH_3:

- b.p. -33.4˚C
- f.p. -77.7˚C
- very soluble in H_2O due to H-bonding ability. It is a weak base in H_2O.

$NH_{3(aq)} + H_2O \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$
(an equilibrium exists in H_2O)

- Reacts completely with strong acids
  $NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$

- Dissolves Group IA, IIA metals
  $Na + NH_{3(l)} \rightarrow Na^+ + NH_{3(l)} + e^-$
  The e^- is "solvated" by NH_3!!

Amides NH_2^-

- NH_2^- is a powerful base and is found in combination with metals such as Na^+ and K^-
- Amides react with H_2O to give strongly basic solutions.
  $NaNH_2 + H_2O \rightarrow NH_{3(aq)} + NaOH_{(aq)}$
  (very exothermic reactions!)

Ammonium NH_4^+

- NH_4^+ is slightly acidic
- Reacts with bases:

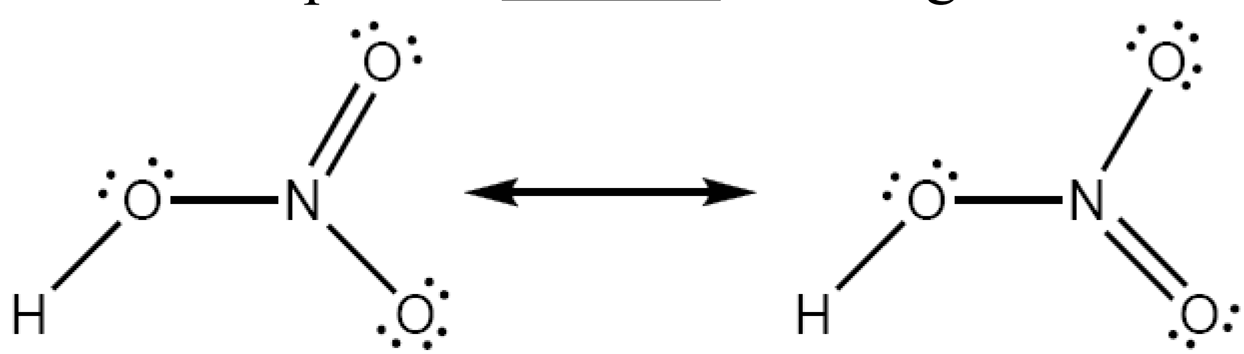
$$NH_4^+Cl^-_{(aq)} + NaOH_{(aq)} \rightarrow NH_{3(aq)} + NaCl_{(aq)} + H_2O_{(l)}$$

Nitrides N^{3-}

- N^{3-} combined with metals
- (i.e. Mg_3N_2, Li_3N) are ionic
- N^{3-} combined with non-metals (i.e. P_3N_5, BN) are covalent

Nitric Acid HNO_3

The most important oxo acid of nitrogen



Resonance forms of Lewis structure

Ostwald Process to make Nitric Acid:

- Very important reaction
- Discovered by the German scientist Ostwald in 1902
- It's discovery is thought to have prolonged WWI because Germany had been cut off from importing nitrate salts from Chile by the Allies. Nitrates are used in explosives.

Oswald Process is 3 steps:

(1) $4NH_{3(g)} + 5O_{2(g)} \xrightarrow[750\text{-}900\ ^{o}C]{Pt/Rh} 4NO_{(g)} + 6H_2O_{(g)}$

$\Delta H = -1170$ KJ

Very exothermic!

(Ammonia to nitric oxide)

(2) $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

This is down-stream from the $NH_3 + O_2$ reaction (1).

(nitric oxide to nitrogen dioxide)

(3) $3NO_{(g)} + H_2O \rightarrow 2HNO_{3(aq)} + NO_{(g)}$

(nitrogen dioxide to nitric acid and nitric oxide)

Overall:

$NH_{3(g)} + 2O_{2(g)} \rightarrow HNO_{3(aq)} + H_2O$

Uses of Nitric Acid HNO_3

1) To make NH_4NO_3 for fertilizers

$NH_3 + HNO_3 \rightarrow NH_4NO_3$

2) To make NH_4NO_3 for explosives

Alfred Nobel, a Swedish chemist, discovered how to safely handle nitroglycerine with the NH_4NO_3 and amassed a fortune, some of which he used to fund the Nobel Prizes.

NH_4NO_3 is unstable.

Decomposition of NH_4NO_3:

Under mild conditions:

$NH_4NO_3(s) \xrightarrow{200\text{-}260\ ºC} N_2O(s) + 2H_2O(g)$

With strong heating:

$2NH_4NO_3(s) \xrightarrow{>300\ ºC} 2N_2(g) + O_2(g) + 4H_2O(g)$

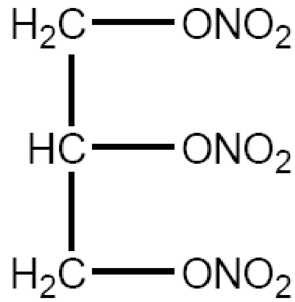
(2 moles solid → 2 + 1 + 4 = 7 moles of gas)

Rapid expansion occurs!

The violent explosion of a ship being loaded with fertilizer (NH_4NO_3) in Texas City, Texas took the lives of ~600 persons in 1947.

Other Nitrogen Explosives

<u>Nitroglycerine</u>
$C_3H_5N_3O_9$
(liquid)



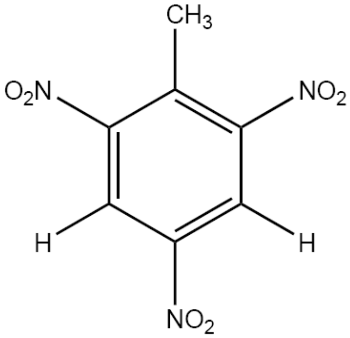
$4C_3H_5N_3O_9 \rightarrow 6N_2 + 12CO + 10H_2O + 7O_2$
Nitroglycerine
(4 molecules of liquid → 35 moles of gas!)

The expanding gases cause a violent detonation but no smoke!

<u>Dynamite</u> – this is a mixture of
Nitroglycerine/NH_4NO_3/wood pulp/$CaCO_3$

(this is a filter used to neutralize any acids that may form during storage)

<u>TNT</u> – trinitrotoluene (solid)



$C_7H_5N_3O_6$ (s) →
$3N_2 + 7CO_2 + 5H_2O + 7C_{(s)}$
(15 moles of gas)

huge entropy increase

Oxygen

50% of all atoms on earth are oxygen.
61% of all atoms in earth's crust are O.
(crust is 16-40 km thick)

O_2
- Diatomic
- Colorless, odorless, tasteless

Allotropes:
(different molecular forms of the same element)
- O_2
- O_3

Isotopes: Three for O:

^{16}O	^{17}O	^{18}O
99.8%	0.2%	

Dry air is ~ 21% of O_2 → this has not changed for millions of years due to the oxygen cycle in nature which maintains the balance.

Oxygen consumed ≡ oxygen produced

- respiration
- decay
- combustion of fuels

- photosynthesis by cholorophyll-containing organisms

Photosynthesis

$$nCO_2 + nH_2O \xrightarrow{\text{sunlight}} (CH_2O)_n + nO_2$$

carbohydrates (especially glucose)

Note: >50% of all O_2 from photosynthesis comes from photoplankton in oceans

- The cycle continues when decay, respiration and combustion take O_2 back to CO_2 and H_2O.

Q What would happen if the oxygen cycle did not maintain O_2 concentration in air at ~21%?

A
Everything would burn out of control - forest fires, house fires etc.,

Why?

Because the rates of reactions increase with higher concentrations of reagents.

Industrial Production of O_2:

$$\text{Air} \xrightarrow{\text{liquify}} \text{Liquid Air} \rightarrow \begin{array}{l} N_2 \ (1) \\ Ar \ (2) \\ O_2 \ (3) \end{array}$$

N_2, Ar boil off first; wait to collect pure O_2

Laboratory (small scale) Synthesis of O_2:

$$2\ KClO_{3(s)} \xrightarrow[150\text{-}200\ ^{o}C]{MnO_2\ (cat)} 3O_{2(g)} + 2KCl_{(s)}$$

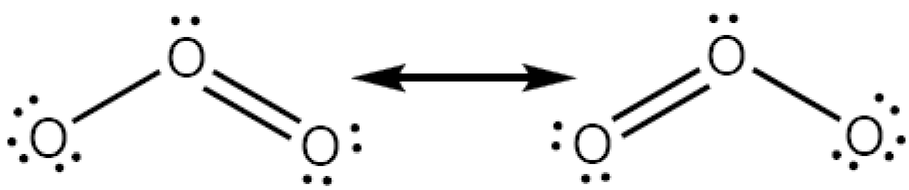
Uses of O_2:

(top 5^{th} chemical in the U.S. ~ 19 million tons)

1) steel industry – blast furnaces
2) chemical industry – plastics
3) sewage treatment – aerobic bacteria
4) health industry – respirators
5) rocket industry – fuel

Ozone O_3

Pungent odor
Lewis structure/VSEPR



- Importance of O_3 for life:
  It absorbs hυ in the UV range which screens us from this harmful radiation
  $$O_3 + \text{UV light} \rightarrow O_2 + O$$

- Oxidizing Ability of O_3
  Very strong oxidant in basic and acidic media.
  Second only to fluorine in its oxidizing ability

- Ozone is a dangerous pollutant in smog. It attacks trees, fabrics, rubber, plastics, & lungs!

- at 0.0000005% O_3 in air (0.5 parts per million) young children and elderly people are at risk
- at 0.000001% O_3 (1 ppm) O_3 is dangerous to everyone

Oxides

All elements except Noble gases form oxides

Three catagories: **(THIS IS ALL REVIEW)- we covered it already – this will be on the final**

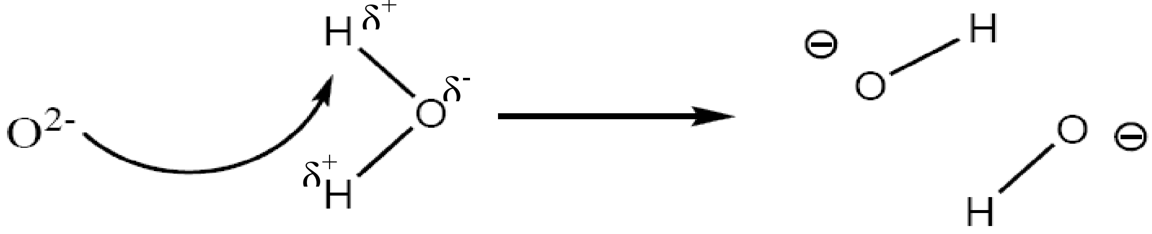
- Basic – ionic oxides (form with metals)
- Acidic – covalent oxides (form with non-metals, metalloids, some metals)
- Amphoteric – can be ionic or covalent (form with metals)

Basic Oxides

- Form OH^- in H_2O
- Groups I, IA (except Be), In, Tl, some transition metals

Examples:

$NaO_{(s)} + H_2O \rightarrow 2NaOH_{(aq)}$



$MgO_{(s)} + H_2O \rightarrow Mg(OH)_{2(s)}$ (insoluble hydroxide)

Acidic Oxides

- Form acids in water
- All non-metals except noble gases. SO_3, SO_2, NO, NO_2, SiO_2, Sb_2O_3, etc., and some transition elements

Examples:
$SO_3 + H_2O \rightarrow H_2SO_{4(aq)}$
$CrO_3 + H_2O \rightarrow H_2CrO_{4(aq)}$

Amphoteric Oxides

- Can be either acidic or basic
- Al, Ga, Sn, Pb and most transition metals
- They can neutralize acid or base

Example: Al_2O_3 (amphoteric)

(C) $Al_2O_{3(s)} + 2OH^-_{(aq)} + 7H_2O \rightarrow 2[Al(H_2O)_2(OH)_4]^-_{(aq)}$

(B) $Al_2O_{3(s)} + 6H^+_{(aq)} + 9H_2O \rightarrow 2[Al(H_2O)_6]^{3+}_{(aq)}$

In reaction (A), Al_2O_3 is an acid
In reaction (B), Al_2O_3 is a base

How do you predict if a transition metal oxide will be acidic, basic or amphoteric?

Two trends

Trend 1
The higher the oxidation state of the metal, the more covalent (acidic) it will be.

Trend 2
The lower the oxidation state of the metal, the more ionic (basic) it will be.

Consider: $Cr^{+2}O$, $Cr_2^{+3}O_3$, $Cr^{+6}O_3$
Most ionic is CrO (lowest ox. state)
Most covalent is CrO_3 (highest ox. state)
∴ CrO would be basic
CrO_3 would be acidic
Cr_2O_3 would be amphoteric

Practice these:
Mn_2O_3, MnO, $[MnO_4]^-$
OsO_4, OsO_2, OsO

Peroxides

(O_2^{2-}) ox. state is O^{-1}

- Hydrogen peroxide: H_2O_2
- colorless liquid
- strong oxidizing agent
- used as a bleach, disinfectant

$$H_2O_2 \xrightarrow{\Delta} H_2O + \frac{1}{2}O_2$$

Exothermic!

- Alkali Metal Peroxides: M_2O_2

Na_2O_2

K_2O_2 $\quad M^+ \; {}^-O\text{-}O^- \; M^+$