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

$CO_2(s)$ f.p. = -78.5˚C

"dry ice"

$$CO_{2(s)} \xrightarrow{>-78.5°C} CO_{2(g)}$$ 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
  $CN^-_{(aq)} + HCl_{(aq)} \rightarrow HCN_{(aq)} + Cl^-_{(aq)}$
  strong acid
  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

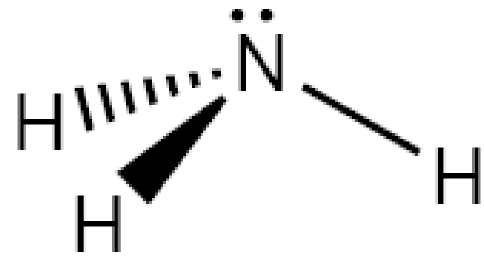
Nitrogen Cycle helps to maintain balance of N_2 in the atmosphere.

- Plants remove N_2 to make $\underline{NH_3}$
- Plants decay back to N_2

<u>Nitrogen Fixation:</u>

Name given to the reactions that microorganisms use to make <u>NH_3</u> from <u>N_2</u>.

<u>Ammonia:</u>



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

<u>Haber – Bosch Process:</u>

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

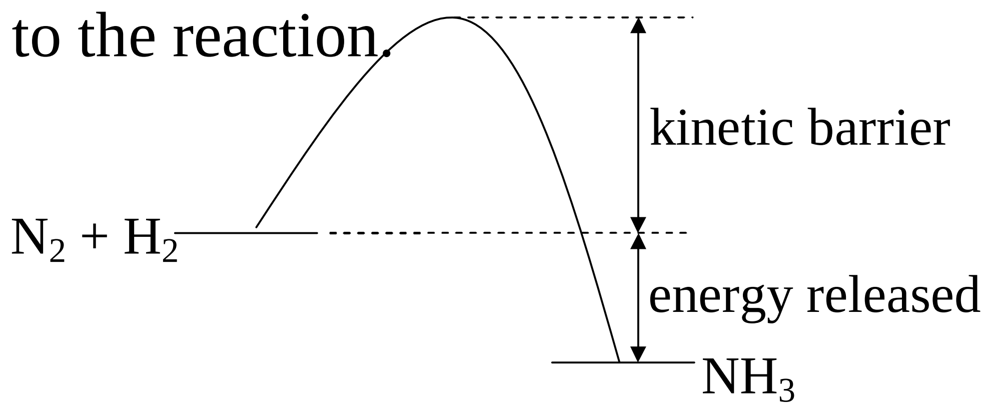
$$\Delta H = -92.38KJ$$

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 <u>exothermic.</u>

The extreme conditions are required because of the large <u>kinetic barrier</u> 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!!

$\boxed{\text{Amides}}$ 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:

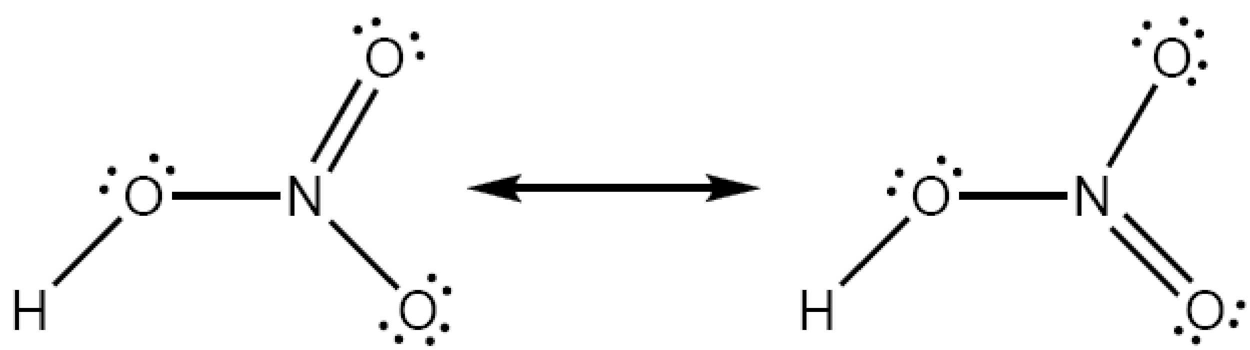
$NH_4^+Cl^-_{(aq)} + NaOH_{(aq)} \rightarrow NH_{3(aq)} + NaCl_{(aq)} + H_2O_{(l)}$

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

$\Delta H = -1170$ 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:

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

With strong heating:

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

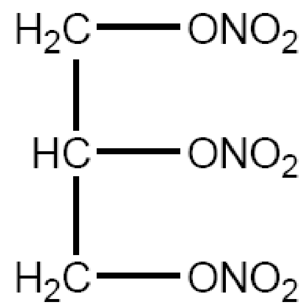
(2 moles solid → 2 + 1 + 4 = 7 moles of gas)

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)



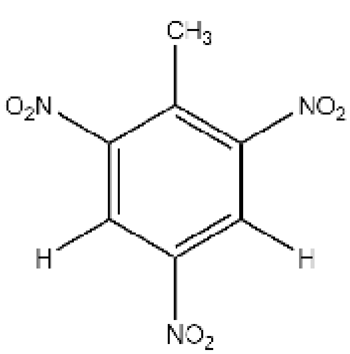
$4C_3H_5N_3O_9 \rightarrow 6N_2 + 12CO + 10H_2O + 7O_2$
Nitroglycerine
(4 molecules of liquid → 35 moles of gas!)

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)



$C_7H_5N_3O_6\ (s) \rightarrow$
$3N_2 + 7CO_2 + 5H_2O + 7C_{(s)}$
(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:

$$\underset{99.8\%}{^{16}O} \qquad \underbrace{^{17}O \qquad ^{18}O}_{0.2\%}$$

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:

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

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

Laboratory (small scale) Synthesis of O_2:

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

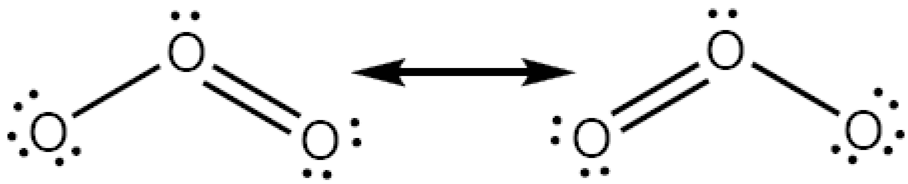
Uses of O_2:

(top 5th 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)**

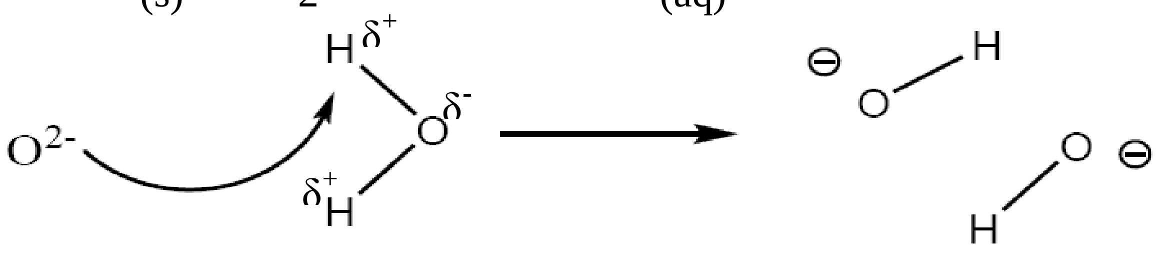
- Basic – ionic oxides (form with metals)
- Acidic – covalent oxides (form with non-metals, metalloids, some metals)
- Amphoteric – can be ionic or covalent (form with metals)

<u>Basic Oxides</u>

- 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

$\boxed{\text{Peroxides}}$ (O_2^{2-}) ox. state is O^{-1}

- Hydrogen peroxide: H_2O_2

- colorless liquid
- strong oxidizing agent
- used as a bleach, disinfectant

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

Exothermic!

- Alkali Metal Peroxides: M_2O_2

Na_2O_2

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

PERIODIC TABLE OF ELEMENTS

acidic oxides

Some acidic oxides throughout transition series

	1	2											3	4	5	6	7	8
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Hn (262)	106 Unh (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)									

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (256)

Amphoteric Oxides

PERIODIC TABLE OF ELEMENTS

many oxides of transition elements are amphoteric

	1	2											3	4	5	6	7	8
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
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90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (256)

Basic Oxides

PERIODIC TABLE OF ELEMENTS

some basic oxides throughout transition series

	1	2											3	4	5	6	7	8
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
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6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
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90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (256)