Inorganic Chemistry

Second year
1st semester

Oxides

Oxygen forms oxides by direct combination with all elements of periodic table (except the noble gases and noble metals Au, Pd, Pt). The reaction is generally exothermic but some proceed slowly and requires heating to supply energy necessary to break the strong O=O bond. Then the reaction becomes exothermic

Classification of oxides

1- Classification of oxides according to ΔH_f^o & ΔG_f^o

Formation of oxides increase (or ΔH_f^o & ΔG_f^o increase) within a period from right to left

within a period from right to left

$$Li_2O > BeO > B_2O_3 > CO_2 > N_2O_3 > F_2O$$

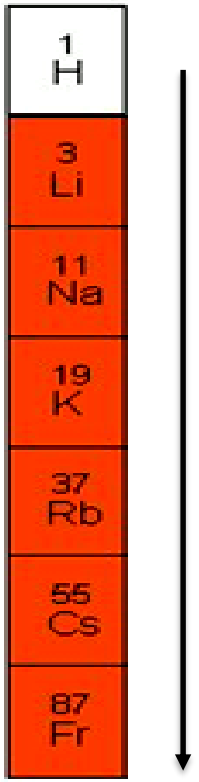
Increased stability of oxides

Exothermic **Endothermic**

ΔG_f° and ΔH_f^o decrease or heat evolved decrease down the group with increased atomic number (Z) of elements

H_f^o Li_2O = -72 K cal. / mol Δ

ΔH_f^o Na_2O = - 45 K cal. / mol .



Decrease of ΔG° and ΔH_f^o Of M_2O

2- Classification according to acidic & basic properties

A- Water soluble oxides

i- Acidic oxides

increase $[H_3O^+]$ when dissolved in H_2O

B_2O_3, CO_2, N_2O_3,NO_2, N_2O_5, P_4O_6,P_4O_{10},SO_2, SO_3, Cl_2O_7

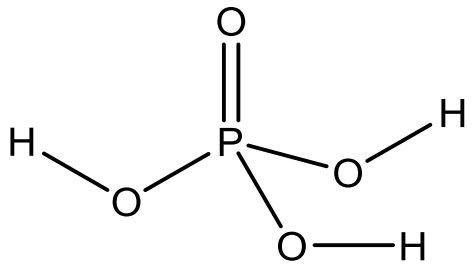
ii- Basic oxides

Increase pH when dissolved in H_2O

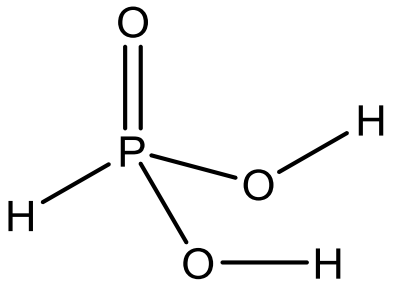
Na_2O,BaO,CaO,Rb_2O, Tl_2O

i- Acidic water soluble oxides

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4 \xrightarrow{H_2O} 4H_3O^+ + 4H_2PO_4^-$$



$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3 \xrightarrow{H_2O} 4H_3O^+ + 4H_2PO_3^-$$



ii- Basic water soluble oxides

$$Na_2O + H_2O \rightarrow 2Na^+_{aq} + 2OH^-_{aq}$$

basic

B – Water insoluble oxides

- i- Acidic oxides
- ii- Basic oxides
- iii- Amphoteric oxides

i- Acidic water insoluble oxides

They are insoluble in H_2O but react with strong bases to form water- soluble salts

$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3 + H_2O \longrightarrow 2Na^+_{aq} + SiO_3^{=}{}_{aq}$$

ii- Basic water Insoluble oxides

These are insoluble in H_2O but soluble in acidic solutions e.g. MnO , NiO

$$MnO\ (s) + 2H^+_{\ aq} \rightarrow Mn^{2+}_{\ aq} + H_2O$$

$$NiO\ (s) + 2H^+_{\ aq} \rightarrow Ni^{2+}_{\ aq} + H_2O$$

iii- Amphoteric oxides

Insoluble in water but soluble in strong basic & strong acidic solutions e.g. ZnO, Al_2O_3, Cr_2O_3

$$ZnO\ (s) + NaOH \rightarrow Na_2ZnO_2 \xrightarrow{2OH^-,\ H_2O} [Zn(OH)_4]^{2-} + 2Na^+_{\ aq}$$

Strong base

$$ZnO\ (s) + 2H^+_{\ aq} \rightarrow Zn^{2+}_{\ aq} + H_2O$$

Strong acid (HCl,H_2SO_4)

$$Al_2O_3(s) + 2NaOH \rightarrow 2NaAlO_2 + H_2O \xrightarrow{2OH^-,\ H_2O} 2Na^+_{\ aq} + [Al(OH)_4]^-_{aq}$$

$$Al_2O_3\ (s) + 6H^+_{\ aq} \rightarrow 2Al^{3+}_{\ aq} + 3H_2O$$

3- Classification according to bonding nature

i- Ionic oxides : IA , IIA oxides M_2O & MO , they crystallize in antifluorite structure (C.N. of metal = 4 and C.N. of anion O^{2-} = 8 , they exists in electrostatic attraction in the crystal lattice , they are basic in nature

ii- Covalent oxides : molecular oxides (acid anhydride) exist as gases , examples : oxides of light nonmetal s: F_2O , NO , SO_3 , SO_2 bond between oxygen and other atom is covalent in character due to small Δ EN . Most non metal oxides are acidic (P_4O_{10} , CO_2 N_2O_3) Some are neutral(NO, N_2O, halogen oxides, noble gases oxides)

iii- Oxides of metalloids and heavy nonmetals : They are solid with polymeric structure (SiO_2 , SnO_2 , GeO_2) or discrete molecules As_4O_{10} , P_4O_{10} , P_4O_6 , Sb_4O_6 , SeO_2 (polymer) TeO_2 (polymer)they with slightly basic or acidic properties

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Normal oxides of representative elements in max. ox. state

Increased basic and ionic character

IA	IIA	IIIA	IVA	VA	VIA	VIIA
Li_2O	*BeO	B_2O_3	CO_2	N_2O_5		F_2O
Na_2O	MgO	*Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
K_2O	CaO	*Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O_7
Rb_2O	SrO	In_2O_3	*SnO_2	Sb_2O_5	TeO_3	I_2O_7
Cs_2O	BaO	Tl_2O_3	*PbO_2	Bi_2O_5	PoO_3	At_2O_7

Increase of acidic and covalent character

basic

acidic

* amphoteric

Oxides of heavy post transition metals of period 6 : The formula:

Gr	13	14	15	16
	Tl_2O,	PbO ,	Bi_2O_3 ,	PoO_2
	+1	+2	+3	+4

are stable Ox. state

Increased basicity

are more stable than the formula:

Tl_2O_3 ,	PbO_2 ,	Bi_2O_5 ,	PoO_3
(unstable)		(oxidizing)	
+3	+4	+5	+6

Ox. state

Increased basicity

because of Inert or unreactive s^2 electrons

Oxides of main transition metal series

Oxides of 1st Transition series

3	4	5	6	7	8	9	10	11
IIIA	IVA	VA	VIA	VIIA	VIIIA			IB
Sc_2O_3	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO
(b)	(b)	(b,red)	(b,red)	(b)	(b)	(b)	(b)	(b)
	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3	Co_2O_3		Cu_2O
	(b)	(b)	(am)	(b,ox)	(am)	(am)		(b)
	TiO_2	VO_2	CrO_3	MnO_2				
	(am)	(am)	(ac,ox)	(am)				
		V_2O_5		Mn_2O_7				
		(ac)		(ac,ox)				

ac acidic, b basic, am amphoteric, red reducing, ox oxidizing

+2 becomes more stable and +3 less stable

Increased stability of higher ox. State and their oxides increased and so their acidic property

↓

FeO_4	not isolated
RuO_4	decomp.
OsO_4	isolated

Increased stability of lower oxidation state

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Fe_2O_3	FeO	stable
Ru_2O_3	RuO	unstable
Os_2O_3	OsO	unstable

Mixed Oxides

Mixed oxides: two types of oxides in one binary oxide containing the same metal ion but in two different oxidation states in the crystal lattice. e.g. :

Fe_3O_4 magnetite (black) ($FeO.\ Fe_2O_3$) (insoluble in H_2O)
FeO basic(pale green) , Fe_2O_3 am(red brown)

Pb_3O_4 red lead (red) ($2PbO.\ PbO_2$) (insoluble in H_2O)
PbO(yellow) basic, PbO_2 am(brown)