Class 6.2

Acids and Bases

Friday, October 8
CHEM 462
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Table 8.3 From Jolly, "Modern Inorganic Chemistry" Aqueous pKa values of the binary hydrides of the nonmetals

CH_4 ~ 44	NH_3 39	H_2O 15.74	HF 3.15
SiH_4 ~ 35	PH_3 27	H_2S 6.89	HCl -6.3
GeH_4 25	AsH_3 ≤ 23	H_2Se 3.7	HBr -8.7
		H_2Te 2.6	HI -9.3

Acidic and Basic Oxides

- The oxides that one uses to form acids and bases in aqueous solution often have reactivity that reflects their acidic or basic character.
- Examples: Li_2O, CaO, and BaO react with water to form basic solutions and can react with acids directly to form salts. Likewise, SO_3, CO_2, and N_2O_5 form acidic aqueous solutions and can react directly with bases to give salts.

Oxides as Acid and Basic Anhydrides

Basic Oxides (usually "ionic")

$CaO + 2H_2O \longrightarrow Ca^{2+} + 2OH^-$,
moderately strong base

$[O^{2-}] + H_2O \longrightarrow 2OH^-$ $K > 10^{22}$

Alkali metal and alkaline earth oxides are basic (dissolve in acid).

Acidic Oxides (Acid Anhydrides)

element-oxygen (E–O) bond not broken on dissolution

either

an E – O – E group is hydrolyzed by water

or

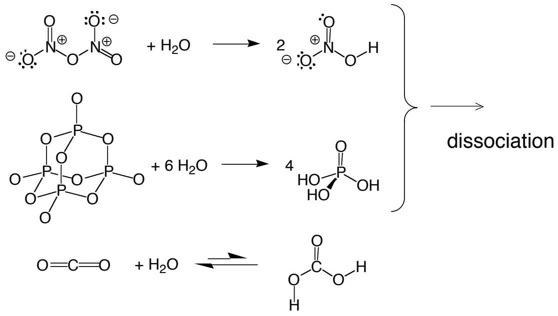
water is added across a double bond

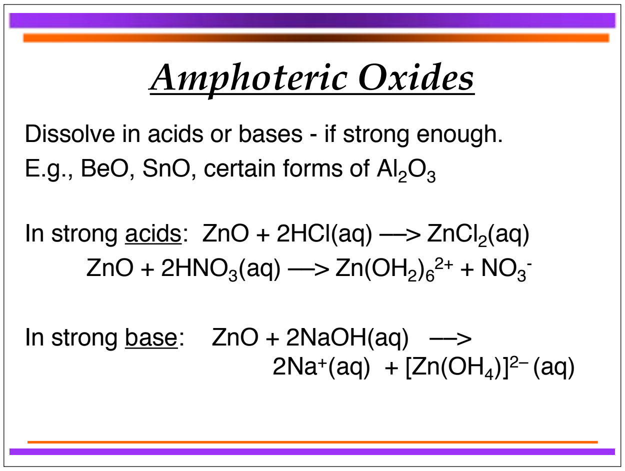
Acidic Oxides not soluble in water will dissolve in basic aqueous solutions to produce salts

e.g. $As_2O_3 + 2NaOH(aq) \longrightarrow 2NaH_2AsO_3$

(Often seen for anhydrides of weaker acids.)

Examples



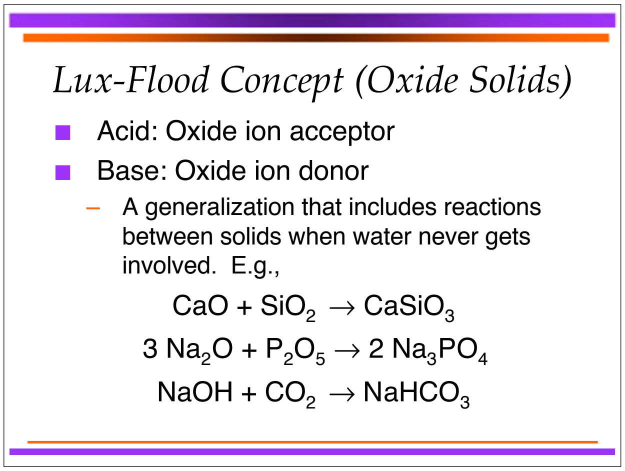


Amphoteric Oxides

Dissolve in acids or bases - if strong enough.
E.g., BeO, SnO, certain forms of Al_2O_3

In strong acids: $ZnO + 2HCl(aq) \longrightarrow ZnCl_2(aq)$
$ZnO + 2HNO_3(aq) \longrightarrow Zn(OH_2)_6^{2+} + NO_3^-$

In strong base: $ZnO + 2NaOH(aq) \longrightarrow$
$2Na^+(aq) + [Zn(OH_4)]^{2-}(aq)$



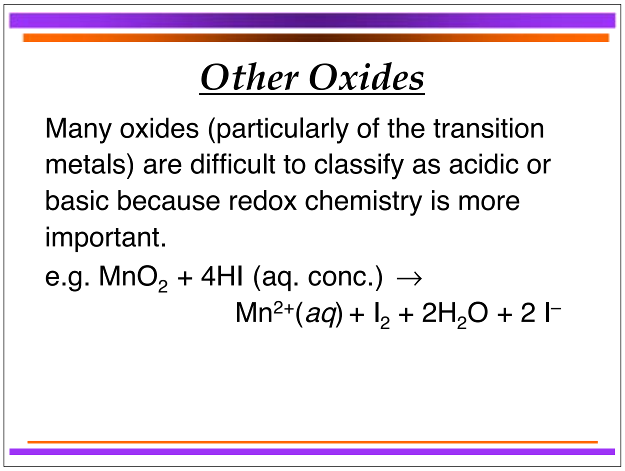
Lux-Flood Concept (Oxide Solids)

- Acid: Oxide ion acceptor
- Base: Oxide ion donor
  - A generalization that includes reactions between solids when water never gets involved. E.g.,

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$3\ Na_2O + P_2O_5 \rightarrow 2\ Na_3PO_4$$

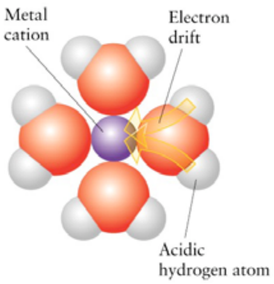
$$NaOH + CO_2 \rightarrow NaHCO_3$$



Other Oxides

Many oxides (particularly of the transition metals) are difficult to classify as acidic or basic because redox chemistry is more important.
e.g. $MnO_2 + 4HI$ (aq. conc.) $\rightarrow$
$Mn^{2+}(aq) + I_2 + 2H_2O + 2\ I^-$

Hydrolysis of Metal Complexes can give acidic solutions



pK_a's for $[M(H_2O)_6]^{n+}$	
$[Fe(H_2O)_6]^{3+}$	2.46
$[Cr(H_2O)_6]^{3+}$	3.89
$[Al(H_2O)_6]^{3+}$	4.85
$[Fe(H_2O)_6]^{2+}$	5.89
$[Cu(H_2O)_6]^{3+}$	7.49
$[Ni(H_2O)_6]^{2+}$	9.03

Examples of Acids From Solvolyzed Metals

Aqua Acids (solvolysis) Al^{3+} solutions are acidic

$AlCl_3(s) + H_2O \rightarrow Al^{3+}(aq) + Cl^-(aq)$

(w/sm. amts of water, HCl gas is evolved):

$AlCl_3 + H_2O \rightarrow$ "$Al(OH)_3$" + 3HCl
$\rightarrow$ $AlCl_2(OH)\cdot nH_2O$ complex
$AlCl(OH)_2 + mH_2O$

Highly charged cations with small radii make for stronger acids:

$[Fe(OH_2)_6]^{2+}$ fairly weak, $[Fe(OH_2)_6]^{3+}$ is much stronger. $r(Fe^{3+}) < r(Fe^{2+})$, the smaller, more highly charged (more polarizing) cation withdraws more e^- density from coordinated water.

More than size is involved:

$r(Al^{3+}) < r(Fe^{3+})$ ionic radii, but $[Fe(OH_2)_6]^{3+}$ is stronger than $[Al(OH_2)_6]^{3+}$

Fe^{III}–O bonding probably more covalent (smaller electronegativity diff. than Al/O).

Acid-Base behavior of Metal Ions not so simple…

Ions like Al^{3+} and Fe^{3+} are often used as examples of cations that form acidic aqueous solutions, however acid-base equilibria for the "ions" are not simple.

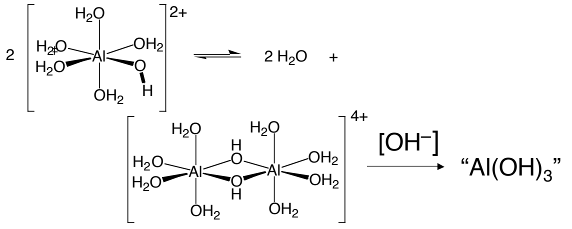
[Compare: $ClCH_2COOH$ $pK_a = 2.85$
— has a "normal" titration curve (pH vs. added base). What does it look like?.]

An acidic $[Al(OH_2)_6]^{3+}$ solution will not titrate this way. Why?

$[Al(OH_2)_6]^{3+}$ is deprotonated, then…

e.g., $[Al(OH_2)_6]^{3+} + CH_3COO^- \rightleftarrows [Al(OH_2)_5(OH)]^{2+} + CH_3COOH$

condensation occurs:

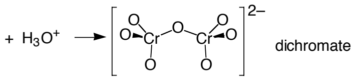


Transition Metals in High Ox. States: Acidic

Metals in very high oxidation states form strong, largely covalent, bonds with oxygen

—> weakens O-H bonds!

e.g. CrO_4^{2-} weak conjugate base of chromic acid



e.g. MnO_4^- very weak conjugate base of permanganic acid (both are powerful oxidants)

Lewis acids and Bases (orbital viewpoint)

(1) Metal cations (Lewis acids) & Ligands (Lewis bases)

(2) p-block Lewis Acids: Incomplete octets

e.g. $B(CH_3)_3$, $AlCl_3$

- Review of bonding
- Lewis acidity Trend for BX_3 (X = F, Cl, Br)?

$AlCl_3$: exists as Al_2Cl_6 in gas phase

Familiar application: Friedel-Crafts acylation

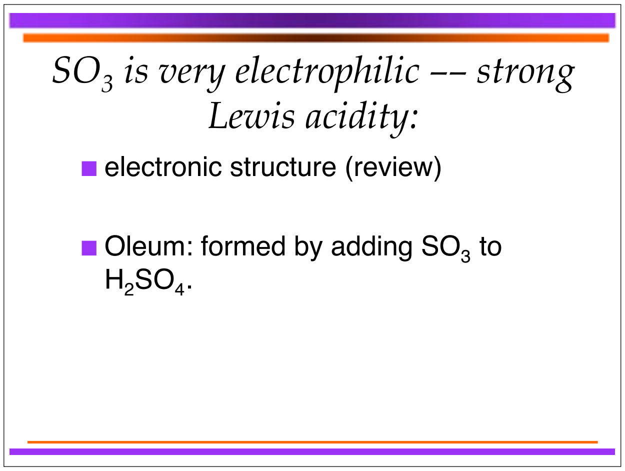
To be discussed later: Chloroaluminate based Ionic Liquids

Molecules with low-lying LUMOs

- E.g. (review CO_2 and SO_3 examples).

SO_2: can function as a Lewis acid or Lewis base:

- SO_2 as an acid (involvement of LUMO)
- SO_2 as a Lewis base - use of S-localized (HOMO) or O-localized lone-pairs



SO_3 is very electrophilic –– strong Lewis acidity:

- electronic structure (review)
- Oleum: formed by adding SO_3 to H_2SO_4.