October 30th 2014

Acids and Bases

Conjugate Acids/Bases Pairs

- a Bronsted acid donates a proton
- a Bronsted base accepts a proton

- the conjugate base of a Bronsted acid is what is produced after the acid loses its proton
- the conjugate acid of a Bronsted base is what is produced after the base accepts a proton

- ex.; $CH_3COOH(aq) + H_2O(l)$ $CH_3COO^-(aq) + H_3O^+(aq)$

CH_3COOH/ CH_3COO^- is a conjugate acid/base pair

and H_3O^+/ H_2O is another conjugate acid/base pair

Conjugate Acid/Base Pairs

- example: What are the conjugate acid/base pairs in the following reactions?

  (a) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

  (b) $H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2\ H_2O(l)$

- answer:

  (a) NH_4^+/ NH_3 is a conjugate acid/base pair

  H_2O/ OH^- is a conjugate acid/base pair

  (b) H_3O^+/H_2O is a conjugate acid/base pair

  H_2O/ OH^- is a conjugate acid/base pair

- N.B. In each case, the acid is placed first and the base is second.

Acid/Base Properties in Water

- we just saw that water can lose a proton (to become OH^-) or can accept a proton (to become H_3O^+):
- water can self-ionize: $2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
- the equilibrium constant at 25°C for the self-ionization is (using H^+) for simplicity):

$$K = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} = [H^+][OH^-] = 1.0 \times 10^{-14}$$

- the concentrations of H^+ et OH^- are related to one another
    - if one is high, the other is low, since their product is fixed
- in a neutral solution, $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M

The pH: a Measure of Acidity

- a more practical measurment for the H^+ concentraiton is the pH (no units): $pH = -\log[H^+]$

- in an acidic solution: $pH < 7.00$
- in a basic solution: $pH > 7.00$
- in a neutral solution: $pH = 7.00$

- the pOH is less common: $pOH = -\log[OH^-]$

- the sum pH + pOH is always fixed: $pH + pOH = 14.00$

The pH: a Measure of Acidity

- example: Calculate the pH of a solution of HNO_3 wherein the concentration of hydrogen ions is 0.76 M.

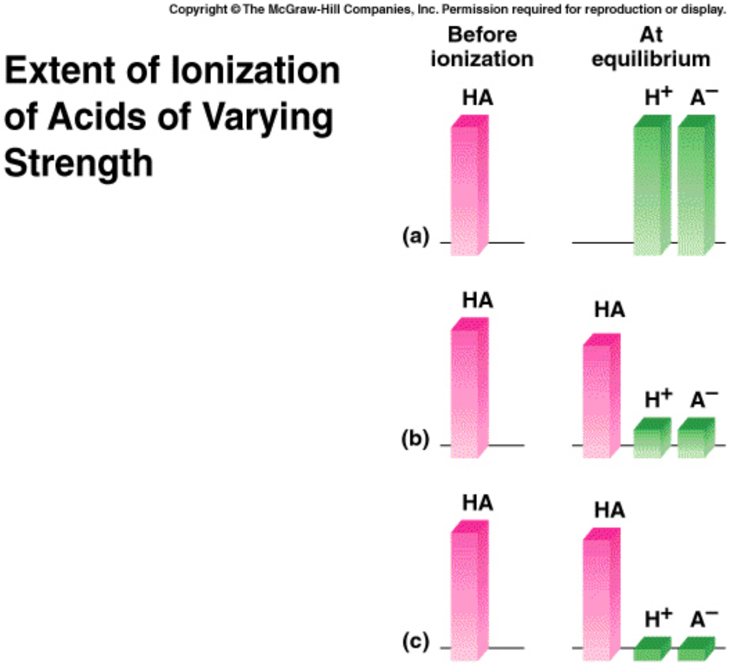
- answer: $pH = -\log[H^+] = -\log(0.76) = 0.12$

- example: The pH of certain fruit juice is 3.33. Calculate the H^+ concentration.

- answer: $pH = 3.33 \quad \therefore \quad -\log[H^+] \quad \therefore \quad \log[H^+] = -3.33$

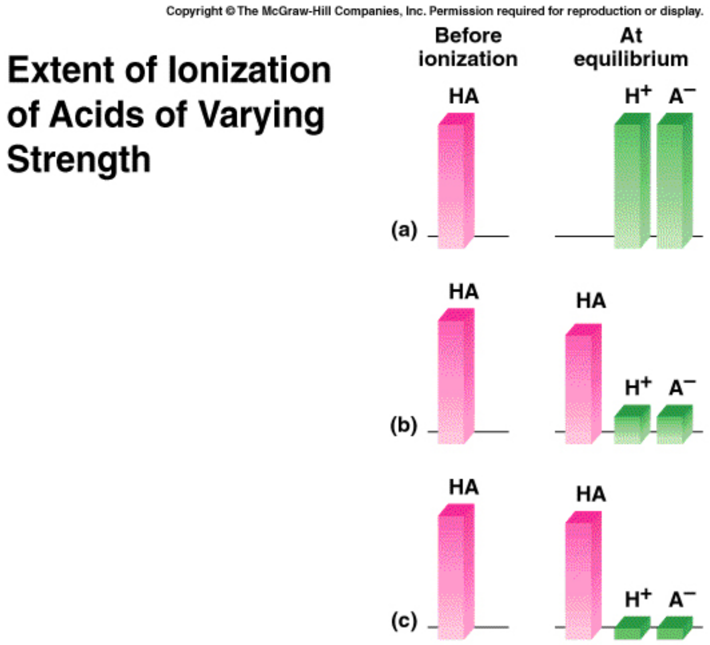
$$[H^+] = 10^{-3.33} = 4.7 \times 10^{-4}\ \text{M}$$

Strong Acids and Strong Bases



- a strong acid is a strong electrolyte that completely ionizes in water
  - ex.; HCl, HNO_3, H_2SO_4
- a weak acid is a weak electrolyte that partially ionizes in water
  - ex.; HF, CH_3COOH, NH_4^+

Strong Acids and Strong Bases



Extent of Ionization of Acids of Varying Strength

- a strong base is a strong electrolyte that ionizes completely in water
    - ex.; any alkali metal hydroxide (ex.; NaOH)
- a weak base is a weak electrolyte only partially ionizes in water
    - ex.; $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Strong Acids and Strong Bases

- for a given conjugate acid/base pair, if there is a strong acid, its conjugate base will be very weak and vice versa

- the H_3O^+ is the strongest acid possible that can exist in an aqueous solution
  - a stronger acid would react with H_2O

    ex.; $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

- the OH^- is the strongest base possible that can exist in an aqueous solution
  - a stronger base would react with H_2O

    ex.; $O^{2-}(aq) + H_2O(l) \rightleftharpoons 2\ OH^-(aq)$

Strong Acids and Bases

- example: Calculate the pH of a $Ba(OH)_2$ solution at 1.5×10^{-2} M.

- answer: For each $Ba(OH)_2$, there are two OH^-.

If we have 1.5×10^{-2} M de $Ba(OH)_2$, we have

3.0×10^{-2} M de OH^-.

The pOH is therefore $-\log(3.0 \times 10^{-2}) = 1.52$.

- The pH is therefore $14.00 - 1.52 = 12.48$.

Weak Acids and Ionization Constants for Acids

- the dissociation of a weak acid is not complete

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + A^{-}(aq)$$

- the equilibrium constant for the above reaction is the ionization constant of the acid, K_a

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

- when the acid is stronger, its K_a is larger

- we can calculated the concentrations of all species at equilibrium with the method we saw in the chapter on chemical equilibrium

Weak Acids and Ionization Constants for Acids

- to calculate the equilibrium concentrations of acids, we make the following approximations
  - 1) the H^+ concentration before adding the acid (1.0×10^{-7} M) is negligible
  - 2) at a first approximation, the quantity of acid that dissociates is negligible

- once we find x (the quantity of dissociated acid), we can verify if x is less than ~ 5% of the initial quantity of acid.
  - **yes**: we have the value of x and can find all concentrations
  - **no**: we must solve for x, without making the second approximation

Weak Acids and Ionization Constants of Acids

- example: Calculate the equilibrium H^+, A^-, and HA in a 0.20 M solution of HA. The K_a value for HA is 2.7×10^{-4}.

- answer: $[H^+] = x$, $[A^-] = x$, and $[HA] = 0.20 - x \approx 0.20$ M

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \therefore \quad 2.7 \times 10^{-4} = \frac{x^2}{0.20} \quad \therefore \quad x = 7.3 \times 10^{-3}$$

verify our approximation: $\dfrac{7.3 \times 10^{-3}}{0.20} \times 100\% = 3.7\%$

our approximation is acceptable, therefore

$[H^+] = 7.3 \times 10^{-3}$ M

$[A^-] = 7.3 \times 10^{-3}$ M

$[HA] = 0.20 - 7.3 \times 10^{-3} = 0.19$ M

Weak Acids and Ionization Constants of Acids

- example: What is the pH of a 0.122 M solution of a monoacid with a K_a value of 5.7×10^{-4}?

- answer: $[H^+] = x$, $[A^-] = x$, and $[HA] = 0.122 - x \approx 0.122$ M

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \therefore \quad 5.7 \times 10^{-4} = \frac{x^2}{0.122} \quad \therefore \quad x = 8.34 \times 10^{-3}$$

verify our approximation: $$\frac{8.34 \times 10^{-3}}{0.122} \times 100\% = 6.8\%$$

we cannot make the approximation that $[HA] \approx 0.122$ M

Weak Acids and Ionization Constants of Acids

- answer: $[H^+] = x$, $[A^-] = x$, and $[HA] = 0.122 - x$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \therefore \quad 5.7 \times 10^{-4} = \frac{x^2}{0.122 - x}$$

$$x^2 + 5.7 \times 10^{-4}\, x - 6.954 \times 10^{-5} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \therefore \quad x = 8.06 \times 10^{-3} \quad \text{ou} \quad -8.63 \times 10^{-3}$$

- the second value of x is not acceptable

- therefore, $[H^+] = 8.06 \times 10^{-3}$ M, and $pH = -\log(8.06 \times 10^{-3}) = 2.09$

Weak Acids and Ionization Constants of Acids

- example: A 0.060 M solution of a monoacid has a pH of 3.44. Calculate the value of K_a for this acid.

- answer: if pH = 3.44, $[H^+] = 10^{-3.44} = 3.63 \times 10^{-4}$ M

$$[A^-] = [H^+] = 3.63 \times 10^{-4}\ \text{M}$$

$$[HA] = 0.060 - 3.63 \times 10^{-4} = 0.0596$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(3.63 \times 10^{-4})^2}{0.0596}$$

$$K_a = 2.2 \times 10^{-6}$$

- 1.22 g of a monoacid, HA, is dissolved in water to produce a 25.0 mL solution. The initial pH of this solution is 1.17. To neutralize this acid, we need 17.7 mL of an aqueous 0.250 M NaOH solution.
  - a) What is the molar mass of HA?
  - b) What is the value of the ionization constant for HA?

Diacids and Polyacids

- a diacid or polyacid can release two or more protons per molecule

- the ionization occurs stepwise

- each step has an ionization constant

$$\text{eg.;}H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

- the ionization constant becomes smaller after each ionization step ($K_{a2} < K_{a1}$)

- see table 16.4 for examples of diacids and polyacids

Diacids and Polyacids

- example: Calculate the concentrations of $C_2H_2O_4$, of $C_2HO_4^-$, of $C_2O_4^{2-}$, and of H^+ in an 0.20 M oxalic acid ($C_2H_2O_4$). For oxalic acid, K_{a1}= 6.5 x 10^{-2} and K_{a2}= 6.1 x 10^{-5}.

- answer: we start with the first equilibrium

$$[H^+] = x, \qquad [C_2HO_4^-] = x, \qquad [C_2H_2O_4] = 0.20 - x \approx 0.20$$

$$K_{a1} = \frac{[H^+][C_2HO_4^-]}{[C_2H_2O_4]} \quad \therefore \quad 6.5 \times 10^{-2} = \frac{x^2}{0.20} \quad \therefore \quad x = 0.114$$

verify the approximation $\quad \dfrac{0.114}{0.200} \times 100\% = 57\%$

- we cannot make the approximation that $[C_2H_2O_4] \approx 0.20$ M

Diacids and Polyacids

- answer:

$$[H^+] = x, \qquad [C_2HO_4^-] = x, \qquad [C_2H_2O_4] = 0.20 - x$$

$$K_{a1} = \frac{[H^+][C_2HO_4^-]}{[C_2H_2O_4]} \quad \therefore \quad 6.5 \times 10^{-2} = \frac{x^2}{0.20 - x} \quad \therefore \quad x^2 + 0.065x - 0.013 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \therefore \quad x = 0.0861 \text{ ou } -0.184$$

- the second answer is not acceptable

- therefore $[H^+] = 0.086$ M
  $[C_2HO_4^-] = 0.086$ M
  $[C_2H_2O_4] = 0.11$ M

Diacids and Polyacids

- answer: We must also find $[C_2O_4^{2-}]$. We make the approximation that this second dissociation does not affect $[C_2HO_4^-]$ and $[H^+]$ from the first dissociation

$$C_2HO_4^-(aq) \rightleftharpoons H^+(aq) + C_2O_4^{2-}(aq)$$

$$[C_2O_4^{2-}] = x, \quad [H^+] = 0.086 + x, \quad [C_2HO_4^-] = 0.086 - x$$

$$K_{a1} = \frac{[H^+][C_2O_4^{2-}]}{[C_2HO_4^-]} \quad \therefore \quad 6.1 \times 10^{-5} = \frac{(0.086)(x)}{(0.086)} \quad \therefore \quad x = 6.1 \ \times 10^{-5}$$

- verify the approximation: $\frac{6.1 \times 10^{-5}}{0.086} \times 100\% = 0.07\%$

- our approximation is acceptable, therefore

$[C_2H_2O_4] = 0.11$ M
$[C_2HO_4^-] = 0.086$ M
$[C_2O_4^-] = 6.1 \times 10^{-5}$ M
$[H^+] = 0.086$ M

Weak Bases and Ionization Constants of Bases

- We treat weak bases the same way we do for weak acids

- ex.; $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3} a_{H_2O}} = \frac{[NH_4^+][OH^-]}{[NH_3](1)}$$

$$K_b = 1.8 \times 10^{-5}$$

- K_b is the ionization constant of the base

Weak Bases and the the Ionization Constants of Bases

- example: Calculate the pH of a 0.26 M methylamine(CH_3NH_2) solution. $K_b = 4.4 \text{ x } 10^{-4}$ for methylamine.

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

- answer: $[CH_3NH_3^+] = x$, $[OH^-] = x$, and $[CH_3NH_2] = 0.26 - x \approx 0.26$

$$K_a = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} \quad \therefore \quad 4.4 \times 10^{-4} = \frac{x^2}{0.26} \quad \therefore \quad x = 0.011$$

verify the approximation: $\frac{0.011}{0.26} \times 100\% = 4.2\%$

- our approximation is acceptable, therefore pOH = -log(0.011) = 1.96, therefore pH = 14.0 - 1.96 = 12.04

The Relation Between Ionization Constants of a Conjugate Acid/Base Pair

- for a weak acid

$$\mathrm{HA(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{A^-(aq)} \qquad K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

- for its conjugate base

$$\mathrm{A^-(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{HA(aq)} + \mathrm{OH^-(aq)} \qquad K_b = \frac{[\mathrm{OH^-}][\mathrm{HA}]}{[\mathrm{A^-}]}$$

- multiplying both ionization constants yields

$$K_a K_b = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \times \frac{[\mathrm{OH^-}][\mathrm{HA}]}{[\mathrm{A^-}]} = [\mathrm{H^+}][\mathrm{OH^-}] = K_{\mathrm{water}}$$

The Relation Between Ionization Constants of a Conjugate Acid/Base Pair

- the fact that $K_aK_b = K_{eau}$ is not surprising since the sum of both reactions is

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

$$K_a = \frac{K_{water}}{K_b} \qquad \text{and} \qquad K_b = \frac{K_{water}}{K_a}$$

- the stronger an acid becomes, the weaker its conjugate base will become and vice versa
- example: for acetic acid, $K_a = 1.8 \times 10^{-5}$. What is the K_b value for the acetate anion (its conjugate base)?
- answer:

$$K_b = \frac{K_{eau}}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Acid/Base Properties of Salts

- the hydrolysis of a salt is the reaction between the anion and/or the cation derived from the salt and water

- for a salt where the cation is the conjugate acid of a strong base and the anion is the conjugate base of a strong acid, the ions of the salt do not react with water and the pH ≈ 7.0

  - ex.; $NaNO_3$ is produced by the reaction of NaOH and HNO_3

  for the dissociation: $NaNO_3(s) \xrightarrow{H_2O} Na^+(aq) + NO_3^-(aq)$

  the produced ions to not interact with water

  - the salt is said to be neutral

Salts that Produce Base Solutions

- ex.; when we dissolve sodium acetate in water

$$CH_3COONa(s) \xrightarrow{H_2O} Na^+(aq) + CH_3COO^-(aq)$$

- The Na^+ cation does not react with water, but the anion CH_3COO^- reacts with water

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

- the solution becomes basic

- this salt is called a base salt

Salts that Produce Acid Solutions

- ex.; when we dissolve ammonium chloride in water

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$$

- The Cl^- anion does not react with water, but the cation NH_4^+ reacts with water

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

- the solution becomes acidic

- this salt is called an acid salt

Salts Where the Cation and Anion Hydrolyze

- if both the cation and anion react with water, the relative strength of the acid and base of the salt that will determine the pH of the solution

  - if $K_b > K_a$: basic solution
  - if $K_b < K_a$: acidic solution
  - if $K_b \approx K_a$: nearly neutral solution

- for an amphoteric ion, the larger ionization constant will dominate

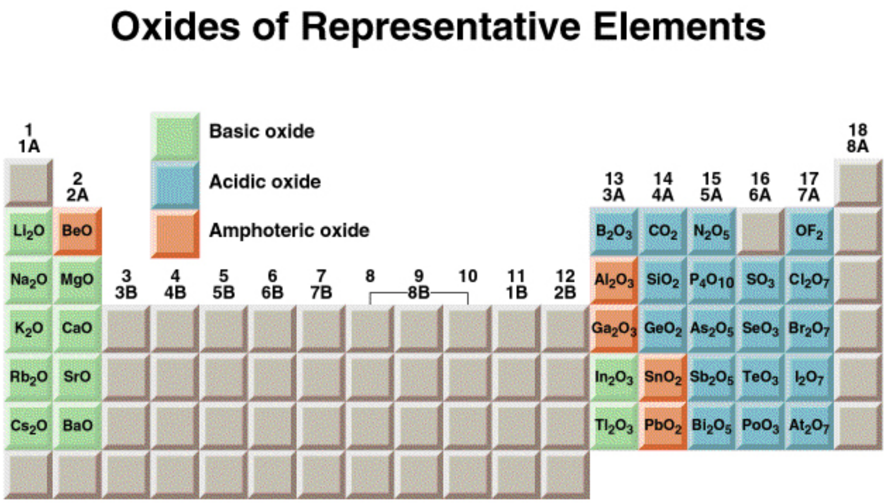
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_a = 4.8 \times 10^{-11}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2CO_3(aq) \qquad K_b = 2.4 \times 10^{-8}$$

therefore, a sodium bicarbonate solution is basic

- We dissolve 0.1344 g of a monoacid, HA, in water to produce a 25.0 mL solution. In order to neutralize this acid, we need 36.2 mL of a 0.122 M NaOH solution.
  (a) What is the molar mass of this monoacid?
  (b) If the pH at the equivalence point is 11.22, what is the value of K_b for $A^-(aq)$?

Acidic, Basic, and Amphoteric Oxides



Oxides of Representative Elements

🟩 Basic oxide
🟦 Acidic oxide
🟧 Amphoteric oxide

1 1A	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
🟩 Li_2O	🟧 BeO	🟦 B_2O_3	🟦 CO_2	🟦 N_2O_5		🟦 OF_2	
🟩 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	

- oxides often react with water

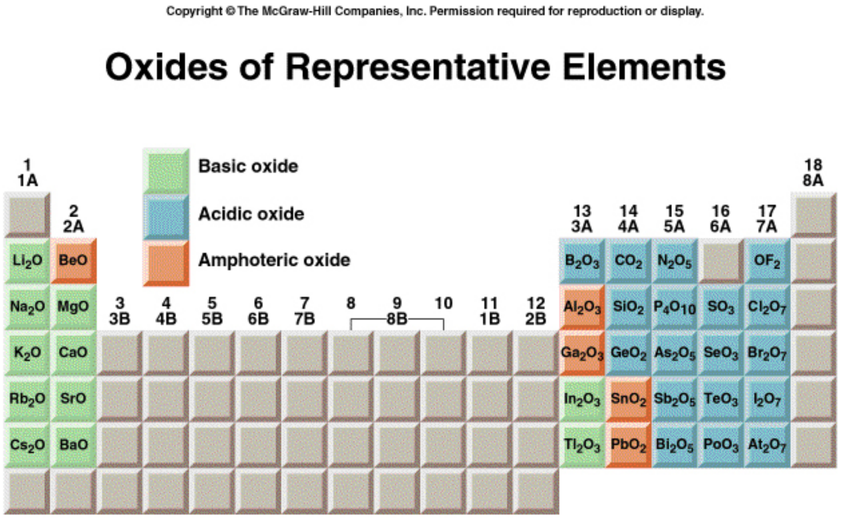
- in general, a metal oxide reacts with water yielding a base (the oxide is basic)

- examples:

$$Na_2O(s) + H_2O(l) \longrightarrow 2\ NaOH(aq)$$

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

Acidic, Basic, and Amphoteric Oxides



- in general, the oxide of a non-metal reacts with water yielding an acid (the oxide is acidic)

- examples

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

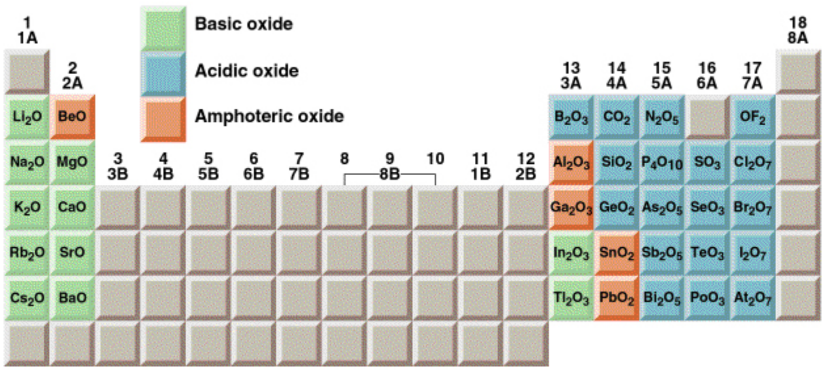
$$N_2O_5(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq)$$

$$P_4O_{10}(g) + 6\,H_2O(l) \longrightarrow 4\,H_3PO_4(aq)$$

- the first reaction explains why rain is naturally acidic (pH ≈ 5.5) and the second reaction explains the acid rain phenomenon

Acidic, Basic, and Amphoteric Oxides

Oxides of Representative Elements



- the oxide of a transition metal with a high oxidation state is often an acid

- ex.; permanganic acid

$$Mn_2O_7(l) + H_2O(l) \longrightarrow 2\,HMnO_4(aq)$$

- ex.; chromic acid

$$CrO_3(s) + H_2O(l) \longrightarrow H_2CrO_4(aq)$$