Chem Rxs, Stoich__________ Z Ch 2.9, 4; H Ch 1-2, 1-3, 7-1, 7-2, 16-4–16-6

"The world of chemical events is like a stage on which scene after scene is enacted in a continuous succession. The players on this stage are the elements. To each of them is assigned a characteristic role, either that of supernumerary or that of an actor playing a part."

Clemens Alexander Winkler, 1897

Almost all the chemical processes which occur in nature ... take place between substances in solution." **Friedrich Wilhelm Ostwald**, 1890

(Nobel Prize for Chemistry in 1909 "in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction".)

4.9 – Acid-Base Reactions

Exam I Monday, September 20 (in one week)

quiz on Friday covering material since first quiz

you need to do the Grubbs test on your Exp 5 data and email the spreadsheet with any outliers clearly marked

REVIEW FROM WEDNESDAY

Solubility Rules

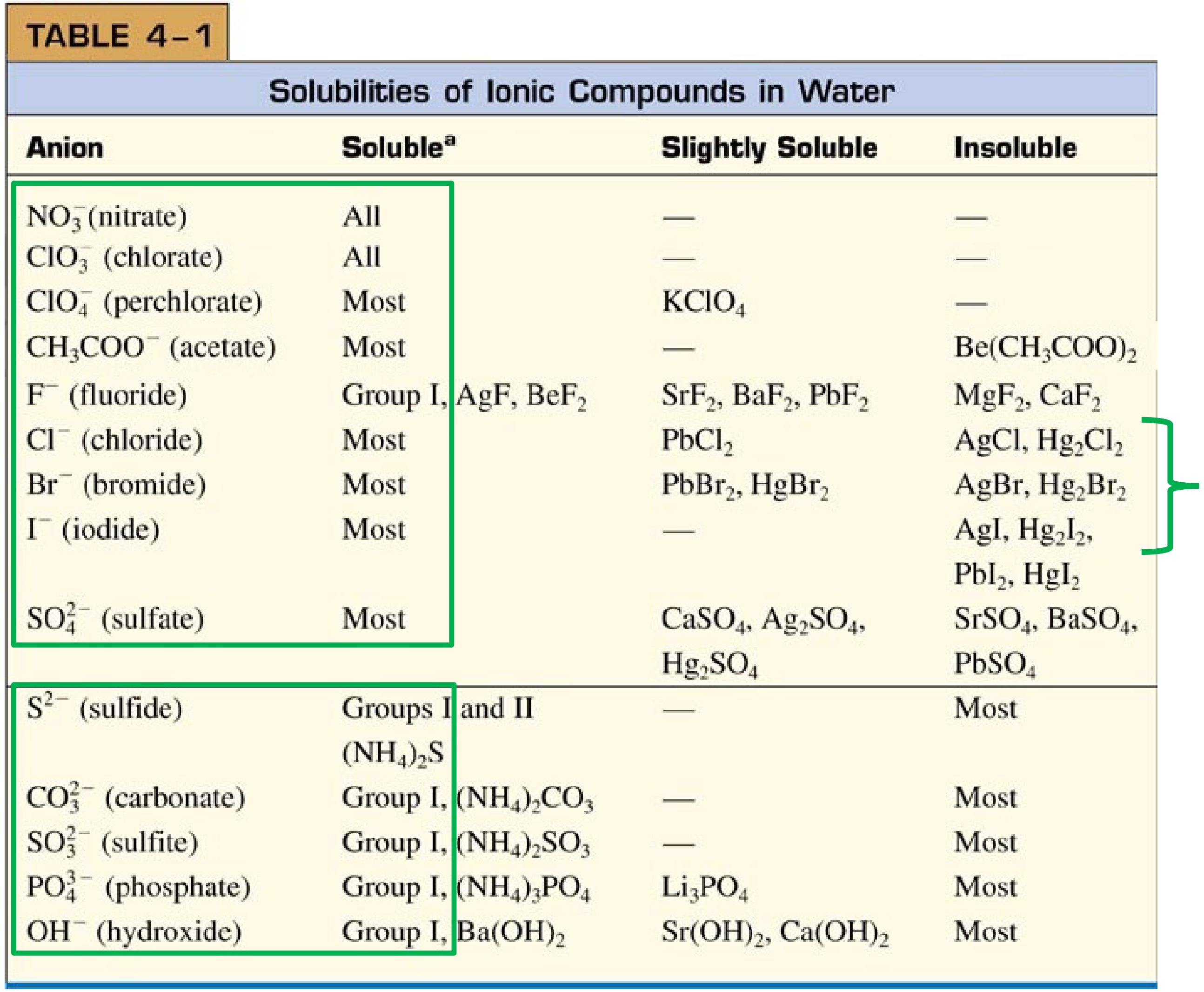


TABLE 4–1

Solubilities of Ionic Compounds in Water

Anion	Soluble[a]	Slightly Soluble	Insoluble
NO_3^- (nitrate)	All	—	—
ClO_3^- (chlorate)	All	—	—
ClO_4^- (perchlorate)	Most	$KClO_4$	—
CH_3COO^- (acetate)	Most	—	$Be(CH_3COO)_2$
F^- (fluoride)	Group I, AgF, BeF_2	SrF_2, BaF_2, PbF_2	MgF_2, CaF_2
Cl^- (chloride)	Most	$PbCl_2$	$AgCl$, Hg_2Cl_2
Br^- (bromide)	Most	$PbBr_2$, $HgBr_2$	$AgBr$, Hg_2Br_2
I^- (iodide)	Most	—	AgI, Hg_2I_2, PbI_2, HgI_2
SO_4^{2-} (sulfate)	Most	$CaSO_4$, Ag_2SO_4, Hg_2SO_4	$SrSO_4$, $BaSO_4$, $PbSO_4$
S^{2-} (sulfide)	Groups I and II $(NH_4)_2S$	—	Most
CO_3^{2-} (carbonate)	Group I, $(NH_4)_2CO_3$	—	Most
SO_3^{2-} (sulfite)	Group I, $(NH_4)_2SO_3$	—	Most
PO_4^{3-} (phosphate)	Group I, $(NH_4)_3PO_4$	Li_3PO_4	Most
OH^- (hydroxide)	Group I, $Ba(OH)_2$	$Sr(OH)_2$, $Ca(OH)_2$	Most

Group I, NH_4^+ always soluble

Ag^+
Hg_2^{2+}

REVIEW FROM WEDNESDAY

Precipitation Reactions

For example: if aqueous solutions of sodium chloride and silver nitrate were mixed, the solubility table identifies silver chloride as an insoluble species so

1. balanced equation:

$$NaCl(\textit{aq}) + AgNO_3(\textit{aq}) \rightarrow AgCl(\textit{s}) + NaNO_3(\textit{aq})$$

2. **total ionic** equation: [never break apart (*s*), (*l*), (*g*)]

$$Na^+(\textit{aq}) + Cl^-(\textit{aq}) + Ag^+(\textit{aq}) + NO_3^-(\textit{aq}) \rightarrow$$

$$AgCl(\textit{s}) + Na^+(\textit{aq}) + NO_3^-(\textit{aq})$$

3. **net ionic** equation (contains the **CHEMISTRY**):

$$Ag^+(\textit{aq}) + Cl^-(\textit{aq}) \rightarrow AgCl(\textit{s})$$

REVIEW FROM WEDNESDAY

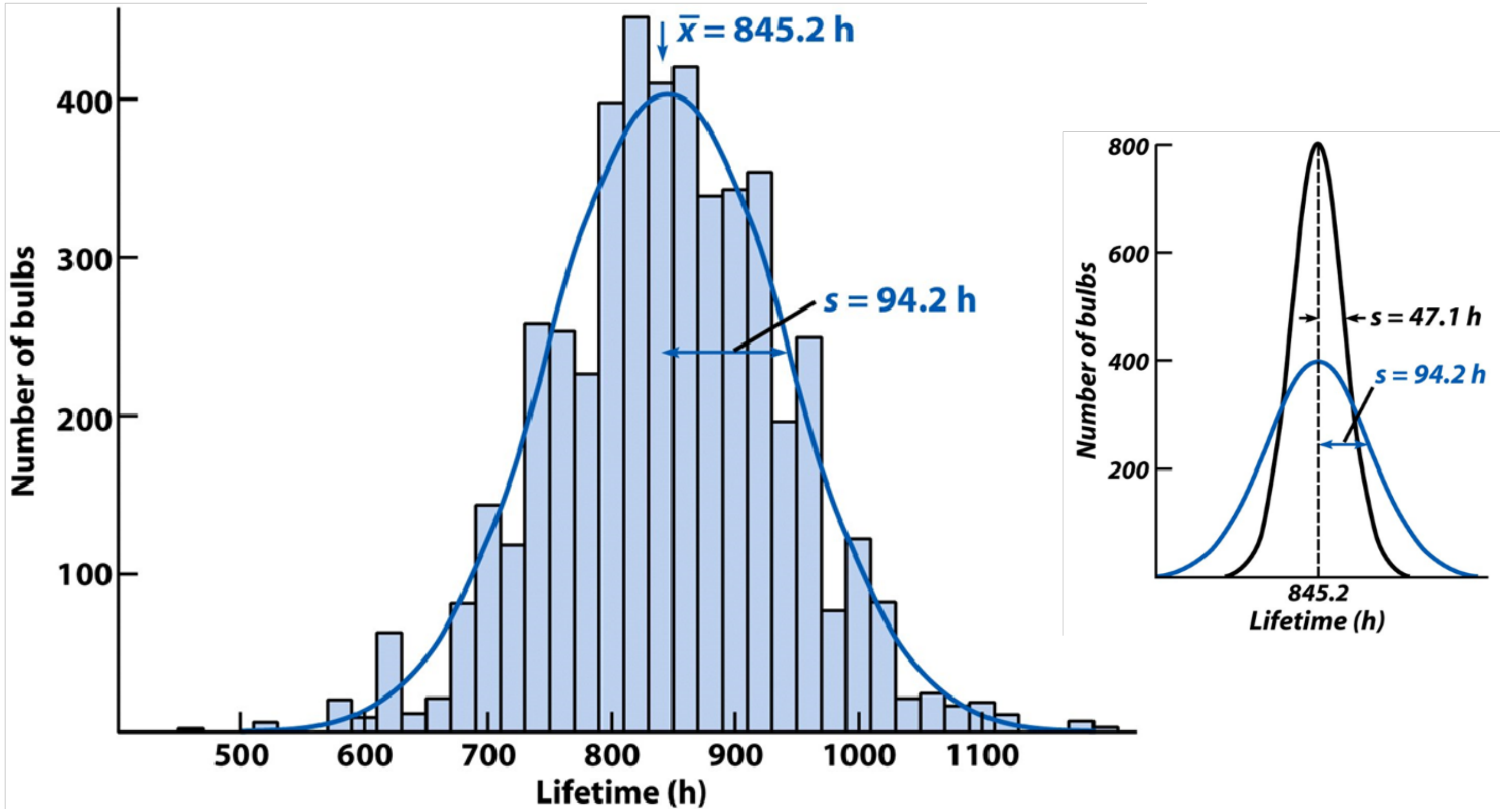
Statistics

H_Exp 5 (next week)

H Ch 4

H 4-1 - Gaussian Distribution

Central Limit Theorem – random variable



REVIEW FROM WEDNESDAY

H 4-6 – Grubbs Test

To determine whether a particular data point can be excluded based upon its questionable veracity, form the Grubbs statistic, G.

$$\boxed{G_{\text{calculated}} = \frac{|x_{\text{questionable}} - <x>|}{s}}$$

If $G_{\text{calculated}} > G_{\text{table}}$ then the point can be excluded with the chosen confidence level (here 95%). The mean and standard deviation will need to be recalculated. Hint: generally do not exclude a data point unless you are certain that an error occurred in its measurement. **Never** exclude more than one point. Always use a value of G of at least a 95% confidence level.

$G_{\text{calc}} < G_{\text{table}}$ => do not drop point

$G_{\text{calc}} > G_{\text{table}}$ => drop point

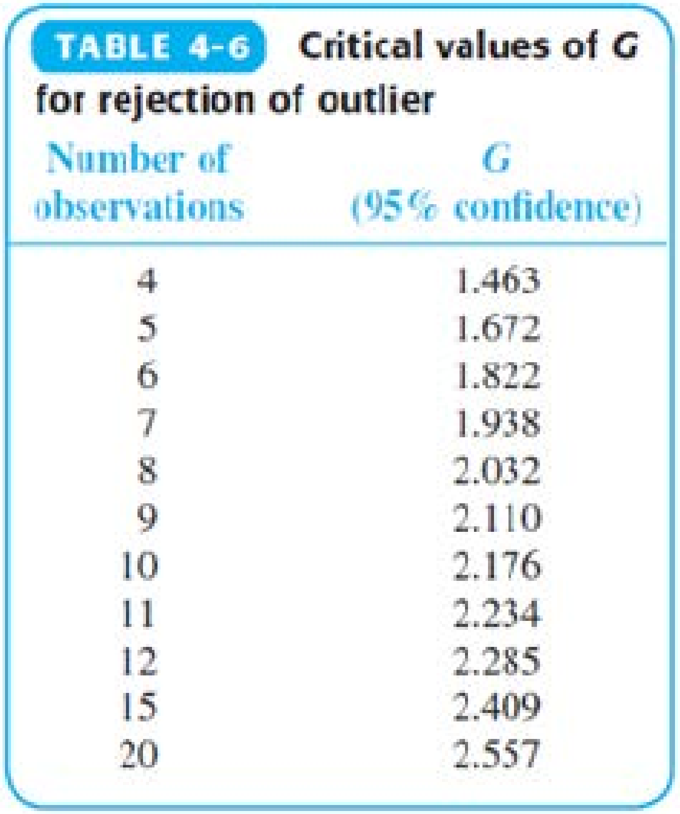


TABLE 4-6 Critical values of *G* for rejection of outlier

Number of observations	*G* (95% confidence)
4	1.463
5	1.672
6	1.822
7	1.938
8	2.032
9	2.110
10	2.176
11	2.234
12	2.285
15	2.409
20	2.557

REVIEW FROM WEDNESDAY

H 4-2 – *F* Test: Comparison of Standard Deviations

To compare the standard deviations of two different sets of measurements to determine if they are or are not statistically the same

n_1 measurements, $<x_1>$ mean, s_1 standard deviation
n_2 measurements, $<x_2>$ mean, s_2 standard deviation

determine

$$F_{\text{calculated}} = (s_1 / s_2)^2 \text{ where } F \geq 1$$

F_{table} = FINV(0.05,dof1,dof2), dof1 = $n_1 - 1$, dof2 = $n_2 - 1$

EXCEL

$F_{\text{calc}} < F_{\text{table}}$ => statistically the same at 95% confidence
$F_{\text{calc}} > F_{\text{table}}$ => statistically different

REVIEW FROM WEDNESDAY

H 4-4 – Case 2 : Comparing Means

To compare the means of two different sets of measurements to determine if they are statistically the same or different

n_1 measurements, $<x_1>$ mean, s_1 standard deviation
n_2 measurements, $<x_2>$ mean, s_2 standard deviation

if $F_{calc} < F_{table}$

determine: s_{pooled}, t_{calc}

t_{table} = TINV(0.05,**dof**)

EXCEL

$t_{calc} < t_{table}$ => stat. the same
$t_{calc} > t_{table}$ => stat. different

$$t_{\text{calculated}} = \frac{|<x_1> - <x_2>|}{s_{\text{pooled}}}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

H 4-4 – Case 2 : Comparing Means

To compare the means of two different sets of measurements to determine if they are statistically the same or different

n_1 measurements, $<x_1>$ mean, s_1 standard deviation
n_2 measurements, $<x_2>$ mean, s_2 standard deviation

if $F_{calc} > F_{table}$

determine: dof, t_{calc}

t_{table} = TINV(0.05,**dof**)

EXCEL

$t_{calc} < t_{table}$ => stat. the same
$t_{calc} > t_{table}$ => stat. different

$$t_{\text{calculated}} = \frac{|<x_1> - <x_2>|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}}$$

$$\frac{\text{degrees of}}{\text{freedom}} = \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{\dfrac{(s_1^2/n_1)^2}{n_1 - 1} + \dfrac{(s_2^2/n_2)^2}{n_2 - 1}}$$

H 4-3 – The Meaning of 95% Confidence

You make n measurements and report

$$\text{confidence interval} = \langle x \rangle \pm t_{95}\, s/\sqrt{n}$$

$\langle x \rangle$ mean t_{95} from *t*-table *s* standard deviation

which => that the true mean will be found within a range of $ts/\sqrt{n}$ of your mean with a level of certainty of 95% if you were to repeat the *n* measurements many times (95% of the sets of *n* measurements would include the true mean)

Properties of Arrhenius Acids and Bases

Arrhenius acids - produce $H^+(aq)$ ions upon dissolution in water

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

Arrhenius bases - produce $OH^-(aq)$ ions upon dissolution in water

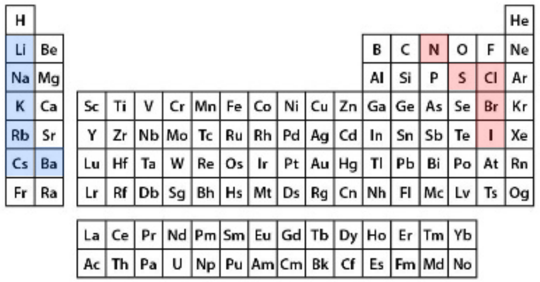
$$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2\,OH^-(aq)$$

Definition works since pure water ionizes to a very small extent in a process called **autoionization**

$$H_2O(aq) \rightarrow H^+(aq) + OH^-(aq)$$

Water is both an Arrhenius acid and an Arrhenius base. A substance having both acidic and basic properties is called **amphoteric**.

Strong Acids and Strong Bases



seven strong acids to know

hydrochloric acid	HCl
hydrobromic acid	HBr
hydroiodic acid	HI
perchloric acid	$HClO_4$
chloric acid	$HClO_3$
sulfuric acid	H_2SO_4
nitric acid	HNO_3

soluble strong bases to know

lithium hydroxide	$LiOH$
sodium hydroxide	$NaOH$
potassium hydroxide	KOH
rubidium hydroxide	$RbOH$
cesium hydroxide	$CsOH$
barium hydroxide	$Ba(OH)_2$

Neutralization of Arrhenius Acid with Arrhenius Base

neutralization - reaction of an Arrhenius acid with an Arrhenius base to form a **salt** (**ionic compound not containing OH^-**) and water; driving force is the formation of stable, low energy water

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

net ionic equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

What about ammonia?

Modified Definition of Arrhenius Acids and Bases

Arrhenius acids - increase concentration of $H^+(aq)$ above that present in pure water by reacting with water

Arrhenius bases - increase concentration of $OH^-(aq)$ above that present in pure water by reacting with water – for ammonia

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

Broadens the applicable chemistry.

Acid and Base Anhydrides

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

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

$P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(aq)$

to find the acid/base add enough **units of H_2O** to the anhydride

Acid and Base Anhydrides

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

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

$P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(aq)$

$2\ HNO_3(aq) - \text{'}H_2O\text{'} \rightarrow N_2O_5(g)$

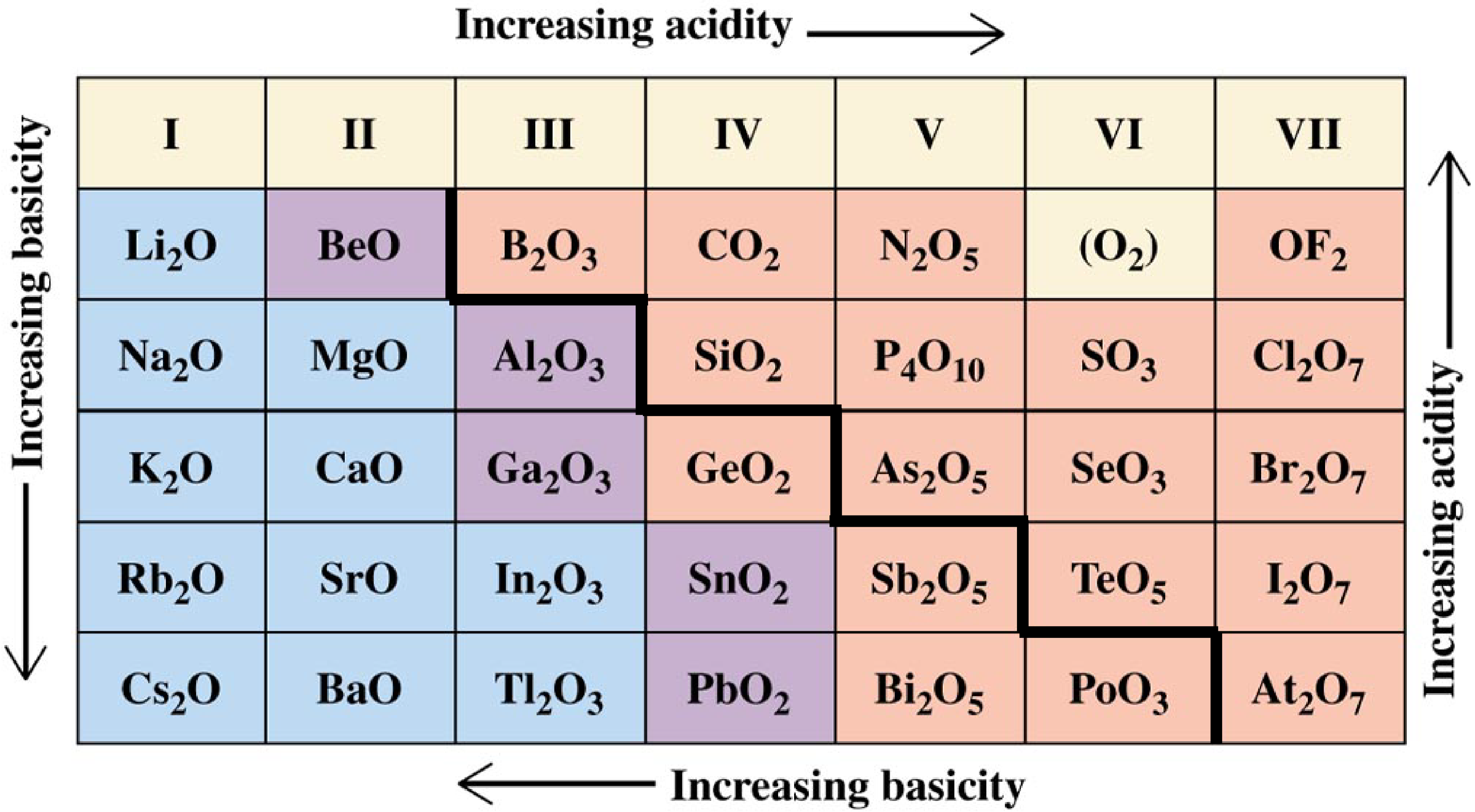
$Ba(OH)_2(s) - \text{'}H_2O\text{'} \rightarrow BaO(s)$

$2\ HBrO_4(aq) - \text{'}H_2O\text{'} \rightarrow Br_2O_7(g)$

---

to find the anhydride "subtract" enough **units of H_2O** from the acid/base to remove all of the hydrogens

Acid and Base Anhydrides



I	II	III	IV	V	VI	VII
Li_2O	BeO	B_2O_3	CO_2	N_2O_5	(O_2)	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_5	I_2O_7
Cs_2O	BaO	Tl_2O_3	PbO_2	Bi_2O_5	PoO_3	At_2O_7

Reactions of Acids and Bases: ACID + BASE → SALT + WATER

chemistry contained in net ionic equation (or **WHY YOU NEED TO KNOW YOUR IONS**)

ACIDS react with

1. **bases**

BASES react with

1. **acids**

-------------------- **salt and water** --------------------

$$2\ HBr(aq) + Ba(OH)_2(aq) \rightarrow BaBr_2(aq) + 2\ H_2O(l)$$

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

$$2\ HBr(aq) + Ba(OH)_2(aq) \rightarrow BaBr_2(aq) + 2\ H_2O(l)$$

$$HBr \longrightarrow H^+ + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Br}}:^-$$

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2\ H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^-$$

REMEMBERING THE STRUCTURE FOR WATER

WE CAN UNDERSTAND ITS FORMATION BY THE ADDITION OF THE ACIDIC PROTON (H^+) TO THE BASIC HYDROXIDE (OH^-) TO FORM THE STABLE MOLECULAR COMPOUND (COVALENT BONDS) H_2O.

ACIDS react with

2. **metal oxides**

BASES react with

2. **nonmetal oxides**

-------------------- **salt and water** --------------------

$2\ HCl(aq) + MnO(s) \rightarrow$
$MnCl_2(aq) + H_2O(l)$

$2\ NaOH(aq) + Cl_2O_5(g) \rightarrow$
$2\ NaClO_3(aq) + H_2O(l)$

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

$2\ OH^-(aq) + Cl_2O_5(g) \rightarrow 2\ ClO_3^-(aq) + H_2O(l)$

$2\ HCl(aq) + MnO(s) \rightarrow MnCl_2(aq) + H_2O(l)$

THIS REACTION CAN BE BEST SEEN BY RECOGNIZING MnO AS IONIC SO THAT OXYGEN IS PRESENT AS THE OXIDE ANION, O^{2-}, AND

$$:\ddot{\underset{..}{O}}:^{2-} + 2H^{+} \longrightarrow H-\ddot{\underset{..}{O}}-H$$

ACIDS react with

3. **carbonates**
hydrogen carbonates

+ **$CO_2(g)$**

$HNO_3(aq) + NaHCO_3(s) \rightarrow$
$CO_2(g) + NaNO_3(aq) + H_2O(l)$

$H^+(aq) + NaHCO_3(s) \rightarrow$
$CO_2(g) + Na^+(aq) + H_2O(l)$

also **sulfites** and **hydrogen sulfites**

-------------------- **salt and water** --------------------

BASES react with

3. **ammonium salts**

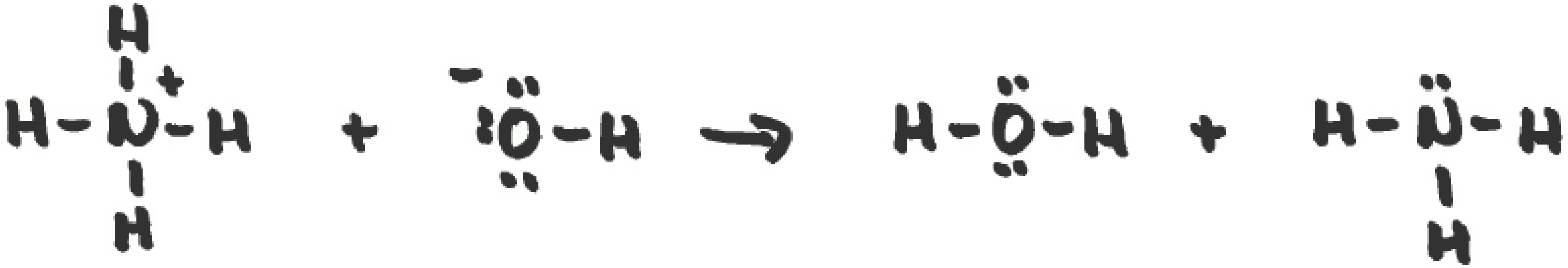
+ **$NH_3(g)$**

$2\ KOH(aq) + (NH_4)_2SO_4(aq) \rightarrow$
$2\ NH_3(g) + K_2SO_4(aq) + 2\ H_2O(l)$

$OH^-(aq) + NH_4^+(aq) \rightarrow NH_3(g) + H_2O(l)$

$2\ KOH(aq) + (NH_4)_2SO_4(aq) \rightarrow 2\ NH_3(g) + K_2SO_4(aq) + 2\ H_2O(l)$

As Before, Lewis Structures Elucidate The Reaction Where The Strong Base OH^- Plucks A Proton Off NH_4^+ To Make Water, Leaving Ammonia Behind:



Generally If A Reaction Can Make Water It Does.

Stoichiometry of Acid-Base Titrations

balanced equation
concentrations
end-point = equivalence point (end-point: indicator, potentiometric)

EX 10. A 25.0 mL sample of acetic acid (CH_3COOH) requires 28.33 mL of 0.953 M NaOH to reach the phenolphthalein end-point. What is the concentration of acetic acid?

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H2O(l)$$

25 mL

28.33 mL
0.953 M

$$n_A = (VM)_A = n_B = (VM)_B$$

Stoichiometry of Acid-Base Titrations

balanced equation
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$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H2O(l)$$

25 mL

28.33 mL
0.953 M

$$n_A = (VM)_A = n_B = (VM)_B \Rightarrow$$

$$M_A = (VM)_B / V_A = (28.33)(0.953) / 25.0 = 1.0799 \Rightarrow \mathbf{1.08\ M}$$

H-Nonmetal

Rule 1: (**without the presence of H_2O**)
like ionic compounds: cation + anion
hydrogen _ide

Examples:

HCl	hydrogen chloride
HF	hydrogen fluoride
H_2S	hydrogen sulfide
H_2Se	hydrogen selenide

Rule 2: (H acids, **when dissolved in H_2O**)
hydro_ic acid

Examples:

HCl	hydrochloric acid
HF	hydrofluoric acid
H_2S	hydrosulfuric acid
H_2Se	hydroselenic acid

Comment:

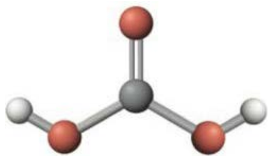
(a) These H-containing compounds are named as if they were ionic. (b) Often the (*aq*) in the formulas of the acids is omitted when it is obvious from the context that they are acids.

H-Oxyanion

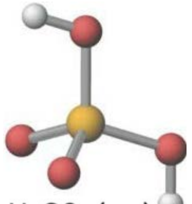
Rule 1: (**without the presence of H_2O**)
like ionic compounds: cation + anion
hydrogen hypo_ite
hydrogen _ite
hydrogen _ate
hydrogen per_ate

Rule 2: (HO acids, **when dissolved in H_2O**)

hypo_ous acid
_ous acid
_ic acid
per_ic acid



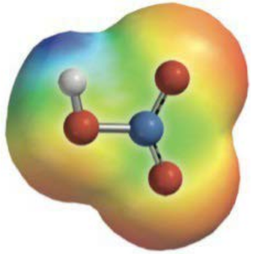
$H_2CO_3(aq)$



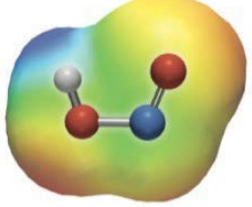
$H_2SO_4(aq)$

Examples:

HClO	hypochlorous acid
$HClO_2$	chlorous acid
$HClO_3$	chloric acid
$HClO_4$	perchloric acid
HNO_2	nitrous acid
HNO_3	nitric acid
H_2SO_3	sulfurous acid
H_2SO_4	sulfuric acid
H_3PO_4	phosphoric acid



nitric acid, HNO_3



nitrous acid, HNO_2