AP CHEMISTRY NOTES- CHAPTER 16 ACIDS & BASES: AQUEOUS EQUILIBRIA

16.1 Acids and Bases Review

Arrhenius definition:

- Acids increase ________________________________
- Bases increase ________________________________

Traditional acids only exhibit what are considered characteristic acidic properties in aqueous solution.
Ex. HCl, not acidic in pure form or if dissolved in benzene.
But is highly soluble in water and is electrolytic.

Con. HCl is up to 37% HCl by weight in a saturated solution.
That is **450L** of HCl(g) at 1 atm dissolved in a liter of water.

The characteristic species for acids is the hydrated proton.
For simplicity, this is usually represented as: ______

Polar water molecules cause the ionization of HCl molecules: $HCl \dashrightarrow H^+ + Cl^-$

or $HCl(aq) + H_2O(l) \dashrightarrow H_3O^+(aq) + Cl^-(aq)$

H_3O^+ is the **hydronium ion:** seen frequently in chemical reaction representations.

This however is probably not very accurate. Realistically, the specie is probably more like $H_5O_2^+$ or $H_9O_4^+$
Whatever representation is used, in acidic solutions, acid molecules transfer protons to water.

16.2 Brønsted-Lowry Theory

In this definition

- Acids are _____________________
- Bases are ______________________

*Water need not necessarily be involved (but it usually is.)

OH^- is an excellent proton acceptor. ****Important note: the hydroxide ion is the strongest basic species that can exist in water solution. Other ions may be stronger bases, but they form hydroxides immediately upon contact with water. Ex. N^{-3}.** $N^{-3} + 3\ H_2O \rightarrow$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ is the equation for a traditional acid base **neutralization**. It is the common net ionic equation for all such reactions.

Here is another important reaction that you should know well:

$NH_3(aq) + H_2O(l) \rightleftharpoons$
Base Acid

The reaction is an equilibrium and so is reversible. In this case, NH_4^+ is the acid and OH^- the base.

Conjugate Acid-Base Pairs

When a Brønsted acid donates a proton, **it becomes a potential proton acceptor**, making it a Brønsted base. This is called a ______________________________________.

Similarly, a base accepts a proton becoming its ____________________________.

Strong acids have _______________ conjugate bases.

Weak acids have _______________ conjugate bases.

Similar for bases.

Ex: HCl is a very strong acid. Its conjugate base the ______ion is such a weak proton acceptor that it doesn't even act like a base. It is most often a spectator ion in solution.

- See p. 574 for an excellent table of conjugate acid/base pairs and their relative strengths.

Important note: In aqueous solution, the H^+ ion is the strongest acid possible.

16.3 The Autoionization of Water

Write the equation for the auto ionization of water:

____

This process occurs spontaneously but in low proportions.

At room temperature, only one molecule in every 10^8 transfers a proton. This equates to about 1 g of protons in an Olympic sized swimming pool full of water.

*Note: the forward reaction is endothermic, and so the degree of ionization goes up with rising temperature.

A simpler way to write the equation is: $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

16.4 The pH Scale.

We can write Kc for this equilibrium (remember, as a pure liquid, water is left out since its concentration is essentially constant.)

This is a **"special K"** (Part of a balanced breakfast, along with 2 eggs, bacon, buttered toast with jelly, coffee, milk, orange juice, a One-A-Day® vitamin and a cheese Danish.)

K values that apply to special, common equilibrium equations are given a subscript that designates them as such. For the ionization of water, we use _______.

$\mathbf{K_w}$ is called the 'ionization product constant for water.'

- Both H^+ and OH^- have equal concentrations.
- At 25ºC, $[H^+] = [OH^-] = 1.0 \times 10^{-7}M$
- Therefore, K_w = __________________________

This is an important value, and you should remember it.

Since hydrogen and hydroxide ions appear in equal concentration, this 'solution' is **neutral**.

Note: Contrary to popular belief, rumor and opinion, water is hardly ever neutral, unless it has been distilled and heated to about 80ºC to drive all gases from the liquid.

In acidic solutions $[H^+] > [OH^-]$ and in basic solutions $[H^+] < [OH^-]$.

The concentrations of the 2 ions are <u>inversely proportional</u>.

Write the mathematical formula for calculating pH. (The symbol 'pH' comes from the French *pouvoire* of hydrogen. *Pouvoire* means 'strength' or 'power'.)

- pH = ___________________
- **Note: pH is a logarithmic scale. So a change in pH of 2 units means a change in [H^+] of <u>100 fold</u>, not 2 fold.**
- **pH 7 is neutral.**
- **The normal range of the pH scale is from __________________.**
- **It is possible to have pH values outside this range.**
- **Solutions with pH < 7 are __________________.**
- **Solutions with pH > 7 are __________________.**

pOH can be calculated in the same way as pH: pOH = __________________________.

- **pH + pOH = _______.**
- **[H^+] x [OH^-] = 1.0 x 10^{-14}**

While it is not difficult to calculate pOH, convention usually calls for pH, even with a basic solution. If given a basic solution (like 0.4M NaOH) go ahead and calculate pOH and simply take 14 - pOH to get pH. Simple.
***Note: all pH and pOH problems use base$_{10}$ logs, and not natural logs. Be sure you can do these problems comfortably with your calculator. Example problems are in the chapter.**
There is a very nice table of some common acids and bases, their pH values and ionic concentrations on p. 576 in the text.

Measuring pH.

pH can be measured in a couple of different ways. (Wait a minute, if you start a sentence with 'pH' should the 'p' be capitalized? Life's little mysteries just never end, do they?)
One way to measure pH or pH changes is with **color indicators**.
Most indicators are molecular dyes which are **weak acids**. When the molecule is in tact (with hydrogen(s) attached, it is one color. When the molecule ionizes, releasing an H^+, it becomes a different color.

Most indicators have ______ possible colors, although some have _____ with 2 transition points.

There is a good table showing several indicators, their colors and transitional pH's on p. 578.

_____________________________ is a mixture of several dyes that gives a rainbow of colors with changing pH.

Sometimes the changes are not very sharp making the indicator of questionable value, however, they are still widely used especially in acid/base **titrations**.

Another, more accurate way to measure pH is with an electronic **pH meter**. These use a special probe sensor to measure electrical potential in a solution. There is still some debate as to exactly how these things work, and they are notoriously fickle instruments.

16.5 Strong Acids and Bases

Strong acids ionize completely in water. These are the strong acids you should know. Memorize their names and formulas.

HCl	______________________	$HClO_3$	______________________
HBr	______________________	$HClO_4$	______________________
HI	______________________	H_2SO_4	______________________
HNO_3	______________________		

There are others, such as chromic or tungstic acids that are also very strong, but they are also very uncommon, so the list above should serve. Consider that all other acids not listed above are weak.

If you wish to review the system for naming acids, you must be extra nice to the instructor and perhaps offer some bribe or small sacrifice (peanut M&Ms® work well.)

Strong bases include the column________and _________ metal hydroxides and oxides.
These are strong mostly because they dissolve in water (Col. IA better than IIA), whereas the oxides and hydroxides of other metals dissolve poorly and so do not put enough hydroxide ions in solution to be strong.

Even some of the Column IIA hydroxides do not dissolve very well (e. g. $Mg(OH)_2$ and $Be(OH)_2$. Calcium hydroxide is the most common Column II base. It is used in __________.
(**Special tip**: If you mix Philips® Milk of Magnesia ($Mg(OH)_2$) with orange juice, you get a 'Philips screw driver.') Hold the applause, it will only get worse.

Active metal oxides (ex. Na_2O or CaO) create OH- ions when they dissolve:

Write the equation here:

Hydrides and nitrides are also **strongly** basic anions, forming hydroxide ions on contact with water.

Ex. $NaH(s) + H_2O(l)$ --->

$Mg_3N_2(s) + 6H_2O(l)$ --->

16.6 Weak Acids

Weak acids form aqueous equilibria due to incomplete ___________________.

- $HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$ HX, HA or HB are common representations for a generic weak acid.

Ka = acid dissociation constant. Write the equilibrium expression for the rxn above:

Ka =

The weaker the acid the smaller the Ka value.

If Ka is known $[H^+]$ and pH can be calculated.

Notice that ICE tables are used extensively for weak acid and base problems.

There is an example problem on p. 580-85 in the textbook.

Weak acid solutions show much lower electrical conductivity than strong ones. They are classified as weak ___________________.

Polyprotic Acids

Ka for first, second and even third proton ionization is different.

Ex. $H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$ $\quad Ka_1 = 1.7 \times 10^{-2}$

$HSO_3^- \rightleftharpoons H^+ + SO_3^{-2}$ $\quad Ka_2 = 6.4 \times 10^{-8}$

Table 16.3 on p. 588 has the ionization constant values for several polyprotic acids.

With such acids, nearly all the hydrogen ion in solution comes from the **first ionization**.
For most polyprotic acids, Ka_1 is 10^3 or more times larger than Ka_2.
Because Ka_2 is usually so small, **pH can be calculated quite accurately from Ka_1**.

16.7 Weak Bases

Weak base + $H_2O \rightleftharpoons$ conjugate acid + OH^-

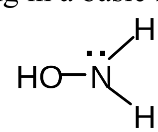
Ex. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Kc =

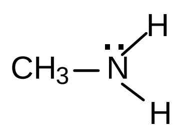
Once again, because water is a pure liquid, it is left out of the Kc expression. This is another 'special K.'

K_b = $\qquad$ K_b is called a **base dissociation constant.**

Many amines (--NH_2), HS^-, CO_3^{-2} and ClO^- ions cause this effect of ionizing water to form OH^- ions resulting in a basic solution.



hydroxylamine



methylamine

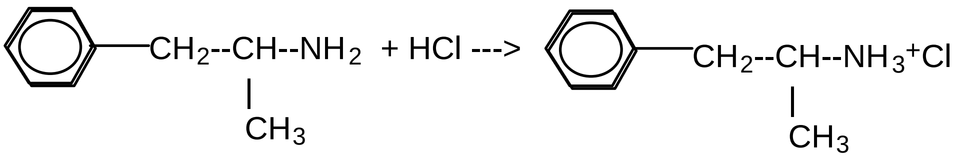
$CH_3\text{--}NH_2(aq) + H_2O(l) \rightleftharpoons CH_3\text{--}NH_3^+(aq) + OH^-(aq)$

Amines react readily with acids to form salts, much as ammonia does. If 'A' = amine,
A + HCl ---> AHCl: a 'hydrochloride' salt. Even without water, this is a type of acid/base reaction.

Many drugs are amines that are volatile, unstable and have a short shelf life. Stability and shelf life improve dramatically if the drug is converted to the hydrochloride salt. Effectiveness is largely unhampered.

There are several amine-based drugs: examples include quinine, codeine, caffeine and amphetamines.

Many amines have an unpleasant, fishy smell. They are what make dead fish and rotting meat smell rotten. One such compound is called 'cadaverine.' Others include indigestine, trash-cannine, and locker-roomine (just kiddine.)



Amphetamine Amphetamine hydrochloride

The salt is more stable than the straight amine.

A **second class of weak bases** are the anions (conjugate bases) of weak acids. Since weak acids have fairly strong conjugate bases, these anions act readily as hydrogen ion acceptors.

$C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons$

weaker side stronger side

When molecules or ions cause the ionization of water molecules, the process is called ___________________.

The **weaker side** of such equilibria (the molecular side vs. the ionic side) <u>is **always** favored</u>. That is, there will be more molecules in the system than ions.

Due to hydrolysis, salts with the anions of weak acids tend to form basic solutions with pH values _____________________.

Ex. of such salts include: ______________________________________.

Example problem: Find the pH of a 0.010M solution of NaClO, a common ingredient in most household bleaches and bleaching products (like Tilex®).

	$ClO^-(aq) + H_2O(l)$	$\rightleftharpoons$	$HClO(aq)$	$+ OH^-(aq)$
I	0.010M		0	0
C	-x		+x	+x
E	0.010-x		x	x

K_b = Table in book → K_b for $ClO^- = 3.3 \times 10^{-7}$ (p. 591)

Since K_b is very small, the value of x will also be very small and $0.010M - x \approx 0.010M$.

So, $K_b = x^2/0.010 = 3.3 \times 10^{-7}$ and $x^2 = 3.3 \times 10^{-9}$ $x = [OH^-] = 5.7 \times 10^{-5}$ M

$pOH = -\log [OH^-] = 4.2$ **pH = 14 - pOH = 14 - 4.2 = 9.8**

****Important note: if $K < 10^{-5}$ you may avoid the quadratic equation by making the assumption that compared to original concentrations, x is going to be very small and so the change in the original concentration will be small enough to be ignored.**

The solution of sodium hypochlorite in water is distinctly basic (although not strongly so.) If you have ever spilled bleach on your fingers, you know that it feels slippery. This is a characteristic of basic solutions. You may also have noticed that it does interesting things to colored clothing. Some years this is considered hip fashion, but usually not.

16.8 Relationship Between Ka and Kb.

$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$ $K_a = 5.6 \times 10^{-10}$

$\underline{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)}$ $K_b = 1.8 \times 10^{-5}$

Net Eq: $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ $K_w = 1.0 \times 10^{-14}$

Auto ionization of water.

***When 2 reactions are added together to give a third, the equilibrium constants of the third equation is the <u>product</u> of the equilibrium constants of the first 2 equations.**

If Reaction 1 + Reaction 2 = Reaction 3, then $K_1 \times K_2 = K_3$.

- From the above equations, $K_1 \times K_2 =$ = ________=______
- So, ****$K_a \times K_b$ always = _____ = __________**

If either K_a or K_b is known the ionization constant for the conjugate acid or base can be calculated easily.

16.8 Acid-Base Properties of Salt Solutions

Many ions that are the conjugate partners of weak acids or bases cause the hydrolysis of water.
Salts can be thought of as being formed by the neutralization of a parent _____________ and ____________.

- If both parents are strong, no hydrolysis will occur: Solution pH ________.
  Examples include ______________________.
- Salts of strong acid and weak base parents: pH ____________.
  Examples: NH_4Cl and $AlCl_3$
  Hydrolysis equations:
- Salts of weak acid and strong base parents: pH ____________.
  Examples: $NaC_2H_3O_2$, KF, $Ca(CN)_2$
  Hydrolysis equations:
- Weak acid and weak base parents: pH varies depending on which ion causes the greatest degree of hydrolysis.
  Examples: NH_4CN, $FeCO_3$
- To find pH we must compare K_a and K_b.
  NH_4^+; $K_a = 5.6 \times 10^{-10}$ CN^-; $K_b = 2.0 \times 10^{-5}$
  The cyanide ion causes more hydrolysis than ammonium, so the solution will be basic.

16.9 Acid-Base Properties of Salt Solutions

A couple of simple rules will help you predict whether a substance will be acidic, basic or neutral in a solvent.

- Ionization of H depends largely on _____________ and _______________.

- Ex. NH_4^+ and CH_4 are isoelectric, but N has the greater nuclear charge. The bonds are more polar and so the ammonium has a greater tendency to release H. Methane shows no acidic properties.
  - $NH_4^+ \rightleftharpoons H^+ + NH_3$ Ka = 5.6×10^{-10}
  - $CH_4 \rightleftharpoons CH_3^- + H^+$ No reaction
  - The more polar the bond character, the greater the value of Ka.
  - Or, the greater the electronegativity of the central atom, the greater the acidity.

This explains why HCl is such a strong acid. However, even though the electronegativity of HF is also very high, the short, strong bond present because of F's small radius, prevents the acid from being strong. HF does not ionize 100% and so is a weak acid.
We can make general predictions about any hydride. Metallic hydrides tend to be ______. Non-metallic hydrides tend to be _______. The closer the element is to the end of its row, the stronger acid or base it is likely to be.

Acidic character increases left to right across a row and as we go down a column.

16.10 Acid-Base Behavior and Chemical Structure
Hydroxides and Oxyacids
These compounds usually contain oxygen, hydrogen and one other element. If this other element is a metal that gives up electrons more easily than hydrogen, the hydroxide ion forms and the compound is a base.

If the 'other atom' is a nonmetal with higher electronegativity, the release of hydroxide becomes less likely. If the release of H is more likely, the compound is an acid.

Note that Oxygen gets an extra electron in either case. It just depends on whether the O lets go of the H or not.

For oxyacids with the same O and H structure but __________ central atoms, acid strength goes _______ as electronegativity goes up.

For oxyacid series with the ________ central atom, acid strength goes up as the number of _____________ goes up.
Examples include the sulfate and chlorate acid series.

16.11 Lewis Theory of Acids and Bases
Lewis acids and bases are defined in terms of electron pairs rather than protons.

To be a proton acceptor, a specie must have an **unshared electron pair.** Therefore, a Lewis base is referred to as an ____.

A Lewis acid is then described as an _____________________________.

The Lewis concept of acids and bases is broader than the Brønsted concept and includes many reactions that do not even involve H transfer.

Draw here the classic Lewis A/B example of NH_3 and BF_3 reacting.

Where aquatic systems and/or H^+ are involved, the B-L definition is most useful.

The Lewis system is not often used unless called for specifically in context.

BF_3 is not referred to as an acid normally, but it may be called an acid in the Lewis sense.

'Ragsdale definition'- any positive ion is an acid, and any negative ion is a base.
Fe^{+3} + 6:C□N:$^-$ ---> $[Fe(CN)_6{}^{-3}]$ ferricyanide ion
L. acid L. base
This reaction may also be classified as a complexation.

There are many complexing agents that will be attracted to these Lewis acid metal ions. Many are anions, but all must have at least one unbonded electron pair.

The number of complexing agents or **ligands** that surround the metal ion is called the **coordination number**.

Acid strength of metal ions depends on charge/size ratio. The larger the ratio, the stronger the hydrolytic effect.

- A large +1 ion has essentially no hydrolytic effect: Ex.
- A small +3 ion has a large hydrolytic effect: Ex.

The metal ion polarizes the water molecule, which then releases a H^+ ion while the OH- ion remains attracted to the metal ion.
General form: $M(H_2O)_n{}^{+z} \rightleftharpoons M(H_2O)_{n-1}(OH)^{+(z-1)} + H^+(aq)$
M = metal; n = #water molecules hydrating the ion; z = ionic charge

For most +3 ions, n = 6; for most +2 or +1 ions, n is probably 4.

Record the formation of aluminum hydroxide from aluminum hexahydrate ion:

K_h = 1 x 10-5 (pH = 5) K_h is an acid hydrolysis constant.