

Chapter 16 – Acid-Base Equilibria

• 16.1 Acids & Bases: A Brief Review

- Arrhenius acids and bases:



- Brønsted-Lowry acids and bases:



• 16.2 Brønsted-Lowry Acids & Bases

- The H⁺ Ion in Water

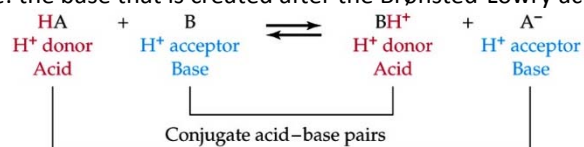
-- H₃O⁺ is called the hydronium ion and is what truly happens when H⁺ is in water

-- since all aqueous solution are in water we will use H₃O⁺ & H⁺ interchangeably

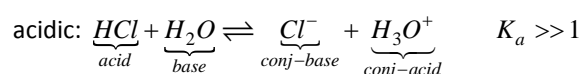
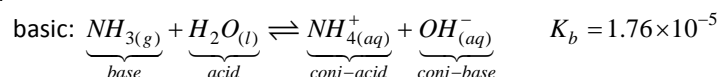
- Conjugate Acid-Base Pairs

-- conjugate acid: the acid that is created after the Brønsted-Lowry base has accepted the proton, BH⁺

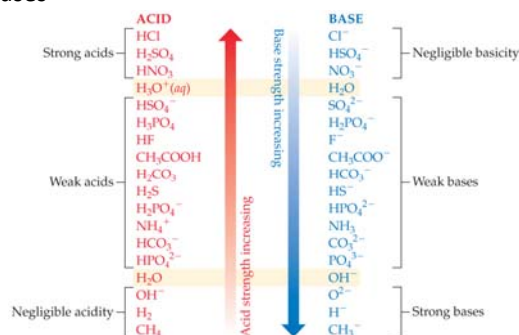
-- conjugate base: the base that is created after the Brønsted-Lowry acid has donated the proton, A⁻



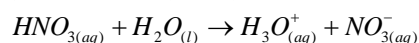
-- examples:



- Relative Strengths of Acids & Bases



-- a strong acid will completely dissociate/ionize in solution:



--- as soon as a strong acid is placed in water it will ionize completely

---- all the reactant goes to product

---- product is a very weak conjugate acid and base

--- other strong acids: HCl, HBr, H₂SO₄, HI, HClO₄, HClO₃, HNO₃

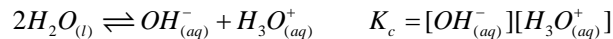
-- the same is the case for a strong base

- examples of strong bases: MOH (where M is alkali metal), NH_2^- , H^-
- a weak acid will only partially dissociate

$$\text{HNO}_{2(aq)}^- \rightleftharpoons \text{H}_{(aq)}^+ + \text{NO}_{2(aq)}^- \quad K_a = 4.0 \times 10^{-4}$$
- the eq constant is called K_a "a" for acid
- in this case some of the reactant is present at eq
- the larger the K_a the more an acid dissociates, the stronger the acid
 - e.g. for nitric acid $K_a \gg 1$
- we talk about K_a 's at length a little later

• 16.3 The Autoionization of Water

- as we will soon learn water may act as either an acid or a base - amphoteric
 - water as a base: $\text{HA}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}_{(aq)}^+ + \text{A}_{(aq)}^-$
 - water as an acid: $\text{B}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{BH}_{(aq)}^+ + \text{OH}_{(aq)}^-$
- Autoionization occurs when a species can ionize itself this occurs for water as shown below:



- since water is in excess (it's the solvent) the concentration is constant

$$K_w = [\text{OH}_{(aq)}^-][\text{H}_3\text{O}_{(aq)}^+]$$

- relationship between $[\text{OH}_{(aq)}^-]$ and $[\text{H}_3\text{O}_{(aq)}^+]$

$$[\text{H}_3\text{O}_{(aq)}^+] > [\text{OH}_{(aq)}^-] \quad \text{acidic}$$

$$[\text{H}_3\text{O}_{(aq)}^+] = [\text{OH}_{(aq)}^-] \quad \text{neutral}$$

$$[\text{H}_3\text{O}_{(aq)}^+] < [\text{OH}_{(aq)}^-] \quad \text{basic}$$

- the value for both $[\text{OH}_{(aq)}^-]$ and $[\text{H}_3\text{O}_{(aq)}^+]$ in pure water are 1.0×10^{-7} at 298K

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- Example: Determine the hydroxide concentration in a solution with

$$[\text{H}_3\text{O}_{(aq)}^+] = 1.89 \times 10^{-4} \text{ M}$$

$$K_w = [\text{H}_3\text{O}_{(aq)}^+][\text{OH}_{(aq)}^-] \rightarrow [\text{OH}_{(aq)}^-] = \frac{K_w}{[\text{H}_3\text{O}_{(aq)}^+]} = \frac{1.0 \times 10^{-14}}{1.89 \times 10^{-4}} = 5.29 \times 10^{-11} \text{ M}$$

• 16.4 The pH Scale

- pH is a log scale which describes the "power of hydrogen"
- the pH is related to the $[\text{H}_3\text{O}_{(aq)}^+]$: $\text{pH} = -\log[\text{H}_3\text{O}_{(aq)}^+]$
 - for pure water: $\text{pH} = -\log[\text{H}_3\text{O}_{(aq)}^+] = -\log(1.0 \times 10^{-7}) = 7$ this is neutral pH
 - when a solution has a pH < 7.0 it is acidic
 - when a solution has a pH > 7.0 it is basic
- pOH & Other 'p' Scales
 - all 'p' scales mean '-log' of
 - pOH is exactly like pH except it is dependent upon $[\text{OH}_{(aq)}^-]$: $\text{pOH} = -\log[\text{OH}_{(aq)}^-]$
 - In Chapter 17 we will have $\text{p}K_a$ and $\text{p}K_b$ meaning the $-\log(K_a)$ etc.
 - the pH and pOH are related to K_w

$$K_w = [\text{OH}^-_{(aq)}][\text{H}_3\text{O}^+_{(aq)}]$$

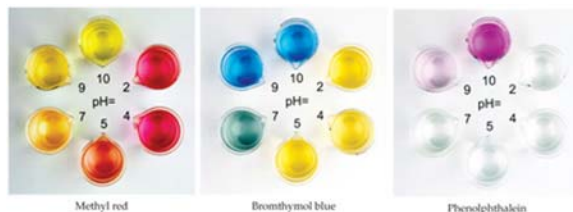
$$-\log K_w = -\log\{[\text{OH}^-_{(aq)}][\text{H}_3\text{O}^+_{(aq)}]\}$$

$$-\log K_w = -\log[\text{OH}^-_{(aq)}] - \log[\text{H}_3\text{O}^+_{(aq)}]$$

$$pK_w = pOH + pH = -\log(1.0 \times 10^{-14}) = 14$$

- Measuring pH

-- you may have used a litmus paper in GenChem I lab to see if something was more or less basic



--- phenolphthalein is pink in basic solution and appears clear in acidic as you can see above

-- This will become more relevant in Chapter 17 when we talk about titrations when we talk about color indicators

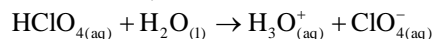
• 16.5 Strong Acids & Bases

- as we previously discussed strong acids and bases completely dissociate in water

-- therefore, whatever the concentration of our strong acid or base will be the concentration of the H^+ and OH^- , respectively

- Examples: Write the balanced equation for each of the following and determine the pH.

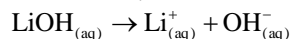
a.) 0.5000 M $\text{HClO}_{4(aq)}$



$$[\text{H}_3\text{O}^+_{(aq)}] = [\text{HClO}_{4(aq)}] = 0.5000 \text{ M}$$

$$\text{pH} = -\log(0.5000 \text{ M}) = 0.30$$

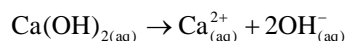
b.) 0.0256 M $\text{LiOH}_{(aq)}$



$$[\text{OH}^-_{(aq)}] = [\text{LiOH}_{(aq)}] = 0.0256 \text{ M}$$

$$\text{pH} = 14 - \text{pOH} = 14 - (-\log(0.0256 \text{ M})) = 12.41$$

- Example: Determine the hydronium ion concentration for a 0.01500 M $\text{Ca}(\text{OH})_2$.

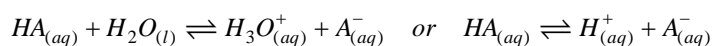


$$[\text{OH}^-_{(aq)}] = 2 \times [\text{Ca}(\text{OH})_{2(aq)}] = 2 \times 0.01500 \text{ M} = 0.03000 \text{ M}$$

$$[\text{H}_3\text{O}^+_{(aq)}] = \frac{K_w}{[\text{OH}^-_{(aq)}]} = \frac{1.0 \times 10^{-14}}{0.03000 \text{ M}} = 3.33 \times 10^{-13} \text{ M}$$

• 16.6 Weak Acids

- weak acids and bases do not completely dissociate in water - therefore at eq they are still present:



$$K_a = \frac{[\text{H}_3\text{O}^+_{(aq)}][\text{A}^-_{(aq)}]}{[\text{HA}]} = \frac{[\text{H}^+_{(aq)}][\text{A}^-_{(aq)}]}{[\text{HA}]}$$

- the K_a is called the acid-dissociation constant and gives us an idea of acid strength

- the larger the K_a the more strongly the equilibrium will lie toward product
- the more likely the acid is to dissociate and raise the acidity of the solution
- the stronger the acid

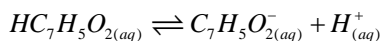
TABLE 15.2 Acid-Dissociation Constants at 25°C

Acid	Molecular Formula	Structural Formula*	K_a	$pK_a^†$
Stronger acid	Hydrochloric	HCl	2×10^6	-6.3
	Nitric	HNO_3	4.5×10^4	3.35
	Hydrofluoric	HF	3.5×10^3	3.46
	Acetylsalicylic (aspirin)	$\text{C}_9\text{H}_8\text{O}_4$		3.0×10^{-4}
	Formic	HCO_2H	1.8×10^{-4}	3.74
	Ascorbic (vitamin C)	$\text{C}_6\text{H}_8\text{O}_6$	8.0×10^{-5}	4.10
	Benzoic	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	6.5×10^{-5}	4.19
Weaker acid	Acetic	$\text{CH}_3\text{CO}_2\text{H}$	1.8×10^{-5}	4.74
	Hypochlorous	HOCl	3.5×10^{-8}	7.46
	Hydrocyanic	HCN	4.8×10^{-10}	9.31
	Methanol	CH_3OH	2.9×10^{-16}	15.54

* The proton that is transferred to water; when the acid dissociates is shown in color. † $pK_a = -\log K_a$.

- Calculating K_a from pH

- Similar to what we did last chapter with the %dissociation, we can get the K_a from the pH
- Example: What is the K_a of a 0.050 M solution of $\text{HC}_7\text{H}_5\text{O}_2$ if the pH of this solution is 2.75?



We begin with an ICE Table

	$\text{HC}_7\text{H}_5\text{O}_2(aq)$	$\text{C}_7\text{H}_5\text{O}_2^-(aq)$	$\text{H}^+(aq)$
Initial	0.050	0.0	0.0
Change	-x	+x	+x
Eq	$0.050 - x$	+x	+x

Next, we write down symbolic representation of the equilibrium/acid dissociation expression:

$$K_a = \frac{[\text{C}_7\text{H}_5\text{O}_2^-(aq)][\text{H}^+(aq)]}{[\text{HC}_7\text{H}_5\text{O}_2(aq)]}$$

Now we remember we don't know K_a but need to find it which means we must know x:

$$[\text{H}^+(aq)] = 10^{-\text{pH}} = 10^{-2.75} = 1.77 \times 10^{-3} \text{ M}$$

Finally we plug in x for our equilibrium expression and solve

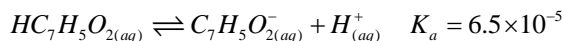
$$K_a = \frac{[\text{C}_7\text{H}_5\text{O}_2^-(aq)][\text{H}^+(aq)]}{[\text{HC}_7\text{H}_5\text{O}_2(aq)]} = \frac{x^2}{0.050 - x} = \frac{0.00177^2}{0.050 - 0.00177} = 6.5 \times 10^{-5}$$

- Percent Ionization

- degree of ionization/dissociation: percentage that an acid ionizes

$$\text{HA}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{A}^-_{(aq)} \quad \frac{[\text{H}^+]}{[\text{HA}]} \times 100\%$$

- Example: Determine the percent dissociation of 0.050M of benzoic acid.



We already will find $[\text{H}^+] = 1.77 \times 10^{-3} \text{ M}$ therefore

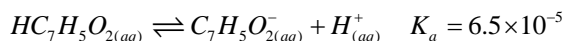
$$\frac{[\text{H}^+]}{[\text{HA}]} = \frac{1.77 \times 10^{-3} \text{ M}}{0.050 \text{ M}} \times 100\% = 3.54\%$$

It should be small since our K_a is so small

- Using K_a to Calculate pH/pOH

- we use ICE tables

-- Ex: Calculate $[H^+]$ and the pOH of 0.050M of benzoic acid.



	$HC_7H_5O_2(aq)$	$C_7H_5O_2^-(aq)$	$H^+(aq)$
Initial	0.050	0.0	0.0
Change	-x	+x	+x
Eq	0.050 - x	+x	+x

$$K_a = \frac{[C_7H_5O_2^-(aq)][H^+(aq)]}{[HC_7H_5O_2(aq)]} = \frac{x^2}{0.050 - x} = 6.5 \times 10^{-5}$$

$$x^2 = 3.25 \times 10^{-6} - 6.5 \times 10^{-5}x \rightarrow x^2 + 6.5 \times 10^{-5}x - 3.25 \times 10^{-6} = 0$$

$$x = \frac{-6.5 \times 10^{-5} \pm \sqrt{(6.5 \times 10^{-5})^2 - 4 \times 1 \times (-3.25 \times 10^{-6})}}{2}$$

$$x = \frac{-6.5 \times 10^{-5} \pm 3.61 \times 10^{-3}}{2} \rightarrow x = 1.77 \times 10^{-3} M$$

$$[H^+] = 1.77 \times 10^{-3} M$$

$$14 = pH + pOH \rightarrow pOH = 14 - pH = 14 + \log[H^+] = 11.25$$

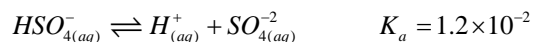
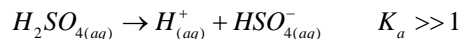
- Polyprotic Acids

-- for acids containing 1 proton we call them monoprotic

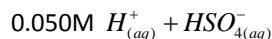
-- for two they are diprotic (e.g. H_2SO_4)

-- for three they are called triprotic (H_3PO_4)

-- Example: Calculate the $[H^+]$ of 0.050M of sulfuric acid.



Initially all 0.050M of the H_2SO_4 dissociates completely into



	$HSO_4^-(aq)$	$H^+(aq)$	$SO_4^{2-}(aq)$
Initial	0.050	0.050	0.0
Change	-x	+x	+x
Eq	0.050 - x	0.050+x	+x

$$K_a = \frac{[H^+(aq)][SO_4^{2-}(aq)]}{[HSO_4^-(aq)]} = \frac{(0.050 + x)x}{(0.050 - x)} = 1.2 \times 10^{-2}$$

$$0.050x + x^2 = 6.0 \times 10^{-4} - 1.2 \times 10^{-2}x$$

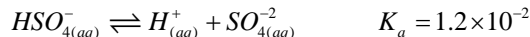
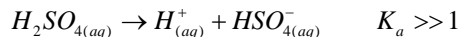
$$x^2 + 0.062x - 6.0 \times 10^{-4} = 0$$

$$x = \frac{-0.062 \pm \sqrt{(0.062)^2 - 4 \times 1 \times (-6.0 \times 10^{-4})}}{2}$$

$$x = \frac{-0.062 \pm 7.90 \times 10^{-2}}{2} \rightarrow x = 8.51 \times 10^{-3} M$$

$$[H^+] = 0.050 + 0.0085 = 0.059M$$

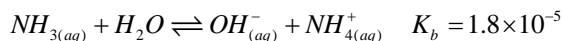
-- Why is $K_{a1} > K_{a2}$?



- electrostatically, it is more difficult to remove H+ from $SO_{4(aq)}^{-2}$ than $HSO_{4(aq)}^{-}$
- therefore, the second K_a is always smaller than the first

• 16.7 Weak Bases

- we handle them just like we do weak acids
- this time our eq const is the base dissociation constant or K_b
- Example: Calculate the pH of 0.050 M NH_3 .



	$NH_{3(aq)}$	$OH_{(aq)}^-$	$NH_{4(aq)}^+$
Initial	0.050	0.0	0.0
Change	-x	+x	+x
Eq	0.050 - x	+x	+x

$$K_b = \frac{[OH_{(aq)}^-][NH_{4(aq)}^+]}{[NH_{3(aq)}]} = \frac{x^2}{0.050 - x} = 1.8 \times 10^{-5}$$

$$x^2 = 9 \times 10^{-7} - 1.8 \times 10^{-5}x \rightarrow x^2 + 1.8 \times 10^{-5}x - 9 \times 10^{-7} = 0$$

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 - 4 \times 1 \times (-9 \times 10^{-7})}}{2}$$

$$x = 9.4 \times 10^{-4} M$$

$$[OH^-] = 9.4 \times 10^{-4} M$$

$$pH = 14 + \log[OH^-] = 14 - 3.03 = 10.97$$

• 16.8 Relationship Between K_a & K_b

- $K_w = K_a * K_b$
- falls out of the relationship that we have already discussed $K_{total} = K_1 * K_2 * \dots$
- Example: Determine the K_b of HCN if $K_a = 4.9 \times 10^{-10}$.

$$K_w = K_a \times K_b \rightarrow K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5}$$

• 16.9 Acid-Base Properties of Salt Solutions

- the stronger partner always dominates:
 - strong acid + strong base = neutral soln
 - strong acid + weak base = acidic soln
 - weak acid + strong base = basic soln

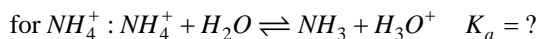
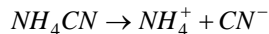
Example: Classify the following solutions as basic, acidic, or neutral.

a.) KBr b.) $NaNO_2$ c.) NH_4Cl

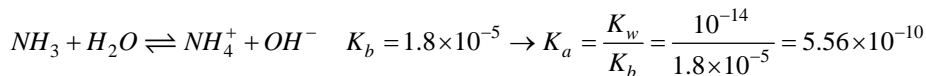
Answer:

a.) Neutral b.) basic c.) acidic

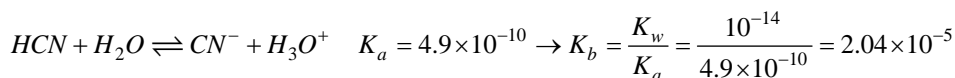
Example: Calculate the K_a for the cation & the K_b for the anion in an aqueous solution containing NH_4CN . Is the solution acidic, basic, or neutral?



we will not find this K_a in a table BUT we can find the K_b of NH_3 to it:



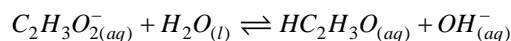
for CN^- we will have to use the K_a of HCN to get its K_b



$K_b(CN^-) > K_a(NH_4^+)$: the soln is basic

Example: Calculate the pH of a 0.25M $NaC_2H_3O_2$, $K_a = 1.76 \times 10^{-5}$.

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}$$



	$C_2H_3O_2^-(aq)$	$HC_2H_3O_2(aq)$	$OH^-(aq)$
Initial	0.250	0.0	0.0
Change	-x	+x	+x
Eq	0.250 - x	+x	+x

$$K_b = \frac{[HC_2H_3O_2(aq)][OH^-]}{[C_2H_3O_2^-(aq)]} = \frac{x^2}{0.250 - x} = 5.68 \times 10^{-10}$$

because we have a large concentration of acetate & a small K_b we will try and assume $0.250 \gg x$

$$\frac{x^2}{0.250 - x} \sim \frac{x^2}{0.250} = 5.68 \times 10^{-10} \rightarrow x = 1.19 \times 10^{-5} M$$

$$ck: \frac{1.19 \times 10^{-5}}{0.250} \times 100\% = 0.005\% < 5\%$$

therefore our assumption is valid and $[OH^-] = 4.77 \times 10^{-5} M$

$$pH = 14 - pOH$$

$$= 14 + \log[OH^-] = 9.08$$

• 16.10 Acid-Base Behavior & Chemical Structure

- electronegativity - **draw trend**

-- acid strength down a column in the periodic table

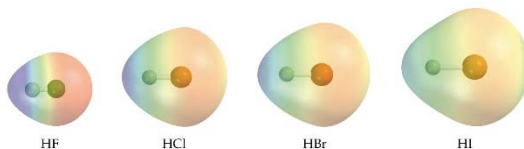
--- as we go down a column we decrease EN

--- a more EN atom will have a stronger bond to H^+

---- if the H-X bond is strong then it will be hard to dissociate HX

---- this will lead to a weaker acid in solution

--- acid strength: $HF < HCl < HBr < HI$



-- acid strength going across a row in the periodic table

- as we go across a row from left to right we increase EN
- we also increase polarity of the H-X bond
 - this means that if the H-X bond is broken it does not necessarily lead to H⁺ (e.g. CH₄)
 - if we don't have H⁺ then we have a weaker acid
- acid strength: CH₄ < NH₃ < H₂O < HF

- oxoacids: H_nXO_m

- electronegativity effects
 - for oxoacids of the halogens the trend is: HOI < HOBr < HOCl
 - this trend occurs because as we increase the EN of the halogen we are pulling electron-density away from the O-atom
 - if we take electron-density away from the O-atom we weaken the O-H bond
 - this will in turn allow H⁺ the freedom to break-away and go into soln
- number of oxygens in the acid (oxoacids)
 - if we increase the number of O-atoms in an acid then we increase its strength
 - this because we increase the oxidation number of the central atom
 - Example: Oxoacids of Chlorine

Acid	Oxidation State of Cl	K _a
HClO	+1	2.9 x 10 ⁻⁸
HClO ₂	+3	1.1 x 10 ⁻²
HClO ₃	+5	≈1
HClO ₄	+7	1 x 10 ⁸

• 16.11 Lewis Acids & Bases

- Definition:

- a base is a substance that donates pairs of electrons
- an acid is a substance that accepts pairs of electrons
- e.g. $NH_3 + BF_3 \rightarrow H_3NBF_3$ where NH₃ donates e⁻'s (base) and B is the acceptor (acid)