Chem 1B Objective 8:
Apply equilibrium principles to acids and bases

Key Ideas: Many important acids and bases, e.g., H_2SO_4 in battery acid, CH_3COOH in vinegar, amino acids.

Acid (HA) dissociation reaction: HA --> $H^+ + A^-$
K_a is K_{eq} for this reaction. $K_a = [H^+] [A^-]/[HA]$

Base (A^-) hydrolysis reaction: $A^- + H_2O$ --> $HA + OH^-$
K_b is K_{eq} for this reaction. $K_b = [HA] [OH^-]/[A^-][H_2O]$

Water dissociation reaction: H_2O --> $H^+ + OH^-$
K_w is K_{eq} for this reaction. $K_w = [H^+] [OH^-] = 1 \times 10^{-14}$.

$K_w = K_a K_b$

Chemical reactions produce the ***COLOR*** and ***SMELL*** of

Grilled Meat, Roasted Coffee, Dark Beer, Toasted Bread

http://www.starkinsider.com/2009/07/steak-marinade-recipe-tender-juicy-bb.html

http://www.suite101.com/view_image.cfm/1464543

http://www.shutterstock.com/pic-9044662/stock-photo-side-view-of-a-blank-white-plate-with-a-inch-caramelized-sugar-cage-used-as-an-edible-prop-for-an.html

4 types of browning reactions in foods:

Maillard: sugar + amino cpd (protein) ---> aroma, flavor, color

Caramelization: sugar + heat ---> caramel flavor, color

ascorbic acid oxidation: Vitamin C

enzymatic browning (Lab 5): phenolics --- enzyme --> color, flavor

Enzyme is a protein --> amino acid --> acid/base http://cen.acs.org/articles/90/i11/Deciphering-Caramels-Deliciousness.html

3/12/12, CEN, p. 52 Caramel Composition determined

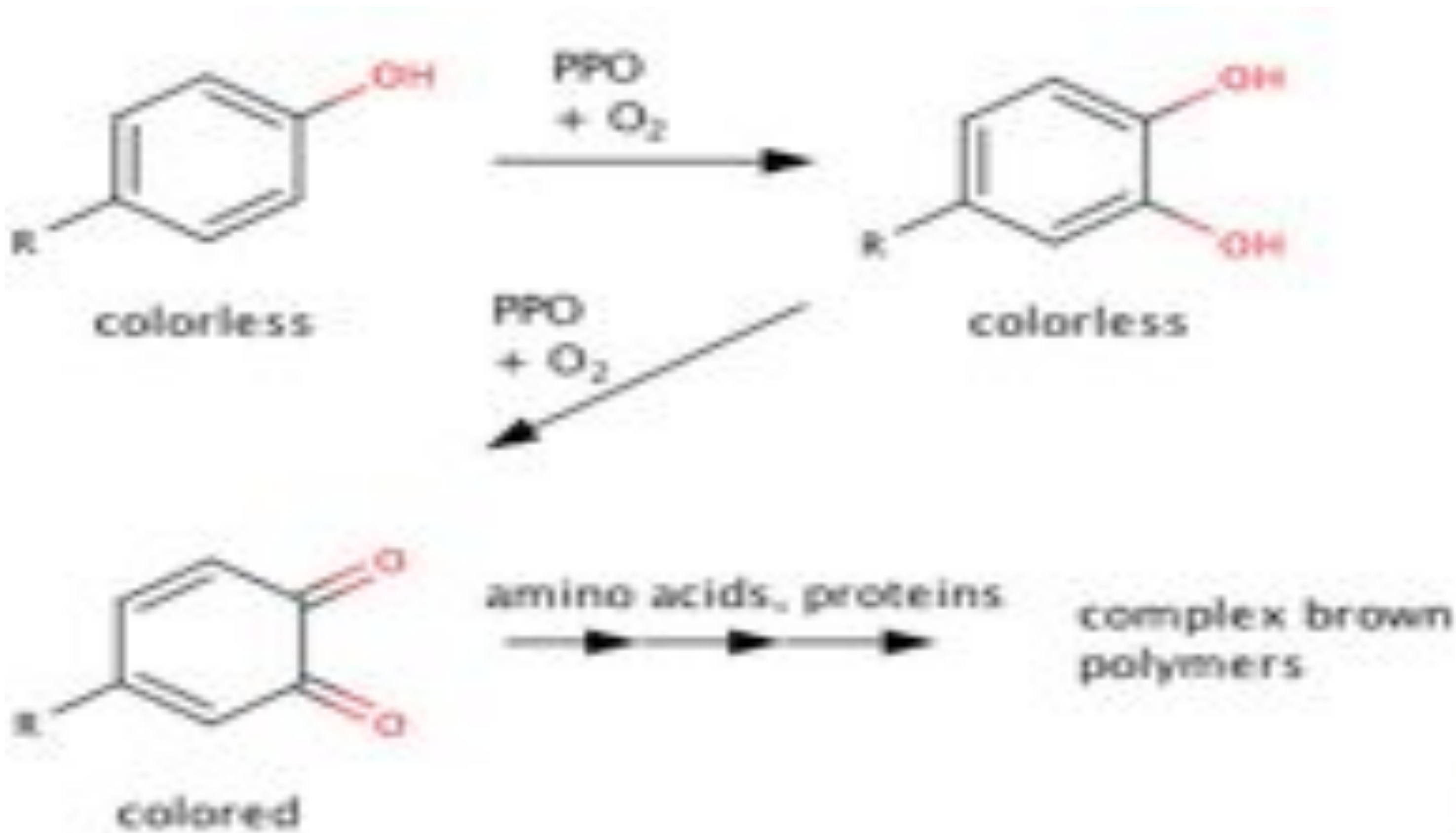
http://italiandish.squarespace.com/imported-20090913150324/2008/11/29/caramel-cake-daring-bakers-november-challenge.html

http://www.thekitchn.com/good-question-how-do-i-make-ch-45160

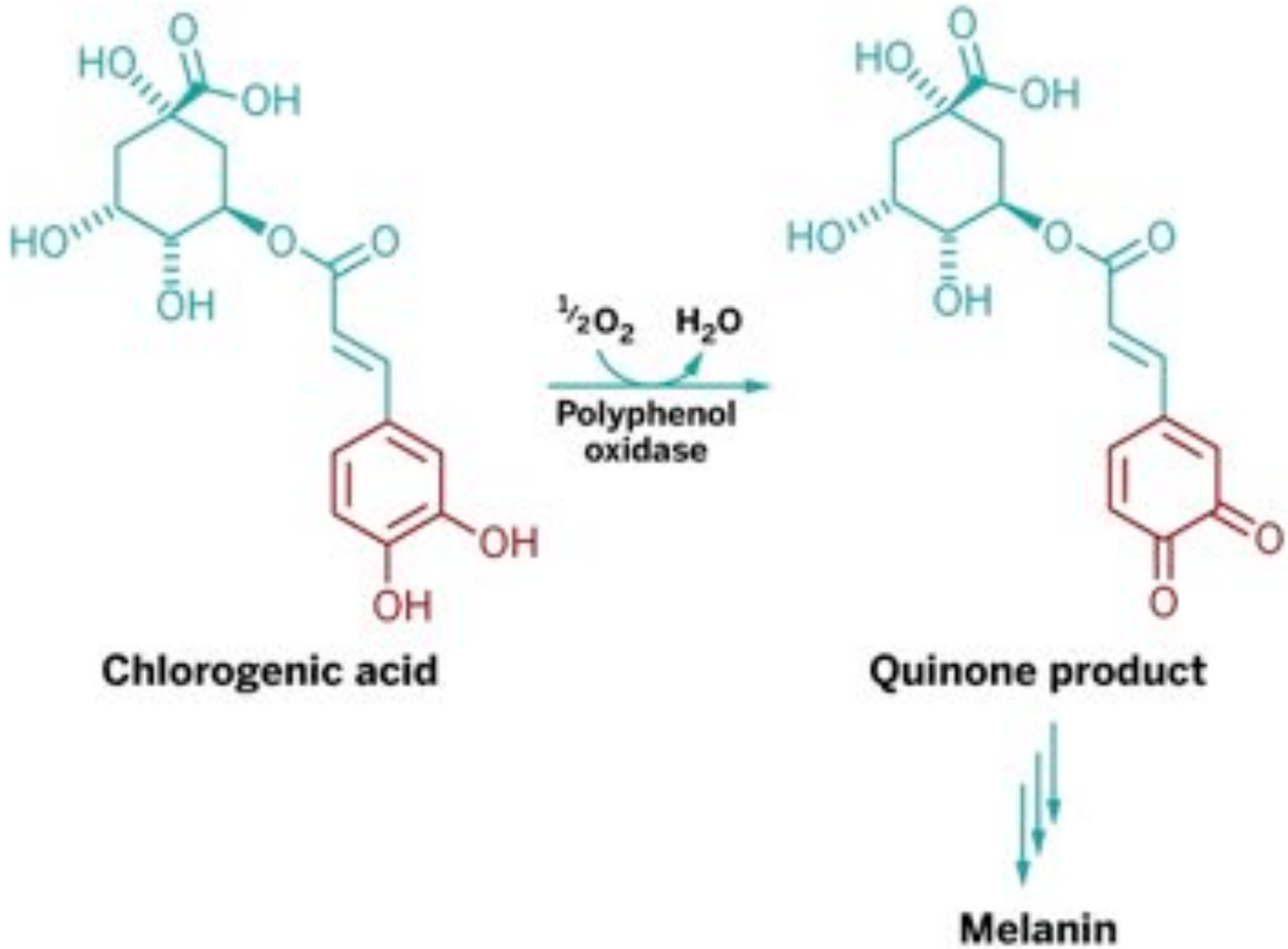
glucose, fructose, and saccharose ---heat---> caramel

Caramel consists of several thousand compounds.
These include oligomers with up to 12 carbohydrate units formed through unselective glycosidic bonding, dehydration products of oligomers that can lose up to eight water molecules, hydroxyfurfural derivatives, and colored aromatic products.

Lab 5: *Enzymatic Browning occurs when fruit tissue is cut or peeled.*
Polyphenol Oxidase (PPO) enzyme is released, which oxidizes Phenolic compounds.
Fruit turns **<u>Brown</u>**.



Chlorogenic acid, and other phenols are converted into melanin precursors with polyphenol oxidase (PPO), .



Fruit can be prevented from browning with preservatives or BUFFERS

a. What is the pH of an apple? Banana?
http://www.engineeringtoolbox.com/food-ph-d_403.html
b. At what pH is the fruit browning enzyme active?
http://www.worthington-biochem.com/TY/default.html
Polyphenol oxidase in mushroom
c. If the fruit browning enzyme is active at the same pH as the apple, what color will the apple be?
d. Do fruits/vegetables that contain Vitamin C turn brown? Give reasons. (see https://appliedphlogiston.wordpress.com/2010/07/06/the-science-of-cooking-why-guacamole-turns-brown/)

References:

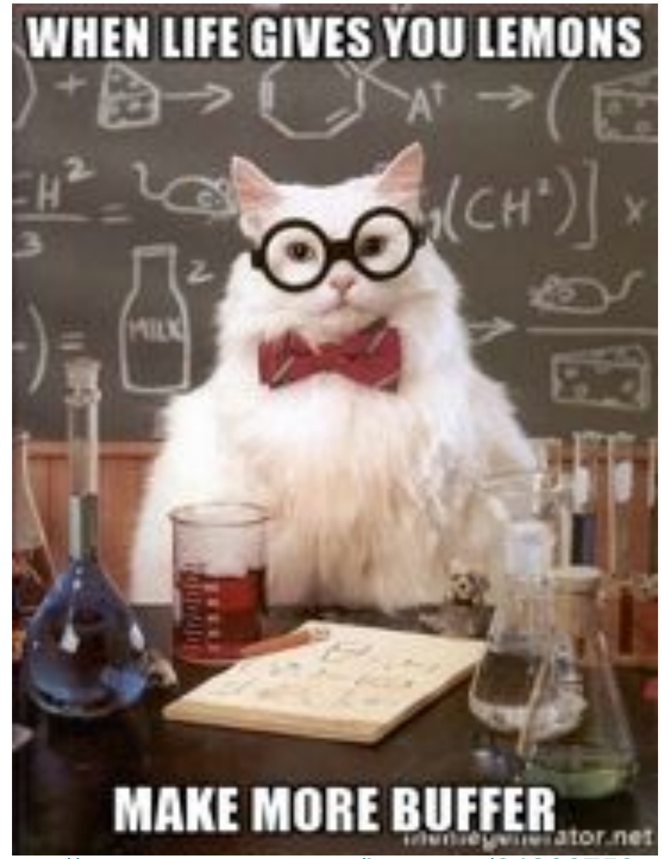
http://www.landfood.ubc.ca/courses/fnh/301/brown/brown_prin.htm
http://www.food-info.net/uk/colour/enzymaticbrowning.htm
http://www.5min.com/Video/Learn-about-the-Maillard-Reaction-83227082
http://www.cfs.purdue.edu/fn/fn453/ld_amino.html
http://www.math.unl.edu/~jump/Center1/BioChemLabs.html
http://www.exploratorium.edu/cooking/meat/INT-what-makes-flavor.html
http://class.fst.ohio-state.edu/fst605/605p/Maillard.pdf

Lab 5: Buffers are Used in Food Preservatives

Examples:

sodium benzoate (or benzoic acid) in salad dressing, carbonated drinks, jams, fruit juices

sodium citrate (or citric acid) in soft drinks, household cleaners, pharmaceuticals



https://memegenerator.net/instance/64266750

A Buffer is a substance that resists change in pH

A Buffer contains a weak ACID and its conjugate BASE (or weak base and its conjugate acid)

How does it work? Buffer de-activates enzyme by changing pH

Lab Report **<u>Objective</u>**: Communicate What You Did and What It Means

Table 1. (Descriptive title) Include your **<u>data</u>** and **<u>results</u>**.

	Apple time to turn brown, min	Banana time to turn brown, min	Apple reaction ranking	Banana reaction ranking
Control				
pH x				
pH y				
Vitamin C				
NaCl				

<u>Discussion</u>: Describe your <u>Data</u>. Convert <u>Data</u> to <u>Results</u>. Explain (interpret) what your <u>Results</u> mean.

"With _______, the time for the apple to turn brown was ___ min compared to ____ min for the control. .:. The effect of _____ on the fruit browning reaction is ____."

Fruit Fresh Keeps Fruit from Turning Brown
"Protect from browning up to 6 hours. All natural antioxidant."

Ingredients:
Dextrose,
Ascorbic Acid (Vitamin C),
Citric Acid,
Silicon Dioxide (Anti-caking).
Contains No Sulfites.

http://www.amazon.com/Jarden-24100-Fruit-Fresh-Produce-Protector/dp/B000KOSP6M/ref=pd_sbs_k_2/176-2250616-3954955?ie=UTF8&refRID=1XF2KHQ8K5ED71QC141G

How Else to Keep your Fruit Fresh?

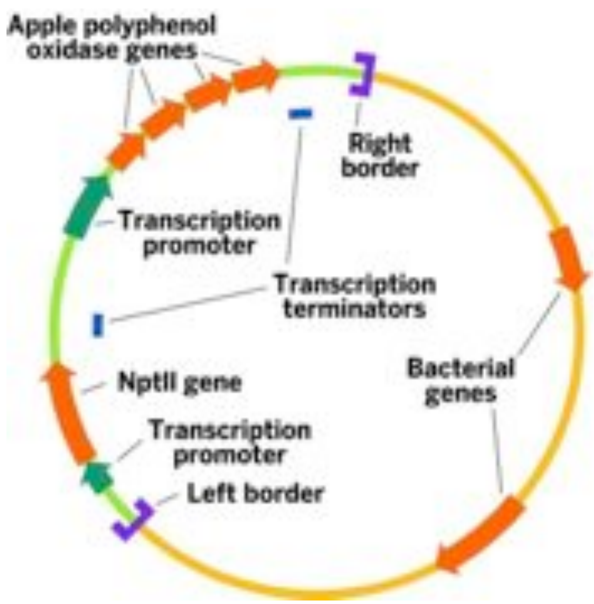
http://en.wikipedia.org/wiki/Lemon

Ingredients:
citric acid
Sodium citrate
Calcium ascorbate
Sea salt
glycerin

http://www.drvita.com/product/eat-cleaner-fruit-amp-vegetable-wash-8-oz/9331 http://cen.acs.org/articles/91/i14/Engineered-Apples-Near-Approval.html

4/8/13, CEN, p. 31 “Engineered Apples Near Approval”

Genetically engineered apples won’t turn brown. Okanagan Specialty Fruits (British Columbia) triggers a selective gene-silencing pathway and inserts a selection gene that is broadly recognized as harmless to humans.



Agrobacterium tumefaciens injects this plasmid, modified by Okanagan scientists, into infected cells. Only the genes between the border sequences of this plasmid are incorporated into the apple genome. The rest of the plasmid contains genes used by the bacterium (yellow).

in the U.S., 88% of corn, 93% of soybeans, and 94% of cotton is genetically engineered (Source: U.S. Department of Agriculture, 2012)

Water behaves like an Acid or a Base

Water dissociates into H^+ and OH^-: (equilibrium reaction)

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{H_2O} \Longleftrightarrow H_3O^+ + OH^-$$

SHORTCUT:

$$H_2O \Longleftrightarrow H^+(aq) + OH^- \qquad K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

$$H^+(aq) = H_3O^+$$

Why does water have a pH of 7? (do an equilibrium calculation)

Only 1 H_2O molecule in 10 million dissociates into H^+ and OH^-!

Why is pH = 7 considered neutral? (compare $[H^+]$ to $[OH^-]$)

Water behaves like an Acid or a Base

Water dissociates into H^+ and OH^-: (equilibrium reaction)

$$H_2O \Longleftrightarrow H^+ + OH^-$$

$$\boxed{K_w = [H^+][OH^-] = 1 \times 10^{-14}}$$

Why does water have a pH of 7? (do an equilibrium calculation)

$$[H^+] = 1 \times 10^{-7} \rightarrow \boxed{pH = -\log [H^+]}$$

Why is pH = 7 considered neutral? (compare $[H^+]$ to $[OH^-]$)

$$[H^+] = 1 \times 10^{-7} = [OH^-]$$

What is the pOH of water?

$$\boxed{\begin{array}{l} pOH = -\log [OH^-] \\ pH + pOH = 14 \end{array}}$$

Every Acid has a Partner (conjugate) Base (and vice versa).

HA +	H_2O <===>	H_3O^+	+	A^-
acid	base	conjugate acid		conjugate base
gives up its H^+		can give up its H^+		can accept a H^+

SHORTCUT:

HA <===> H^+ + A^-

acid	conjugate base
gives up its H^+	can accept a H^+

K_a = (See Chang, Table 16.3, 4)

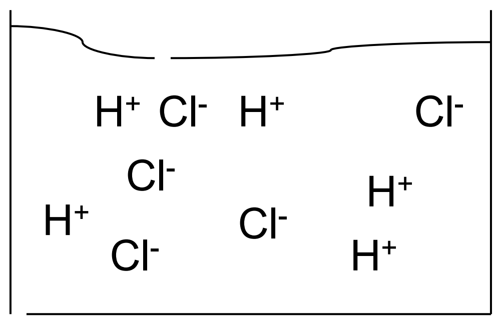
What is the conjugate base of sulfuric acid?

What is the conjugate acid of NaOH?

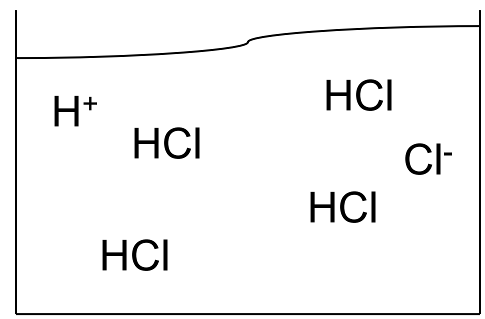
Acids can be <u>Strong</u> or <u>Weak</u>

Strong acids have large K_a. (easily donates H^+, many H^+ in soln)
Weak acids have K_a < 1. (wants to keep its H^+, low $[H^+]$)

Which picture best represents HCl?



A

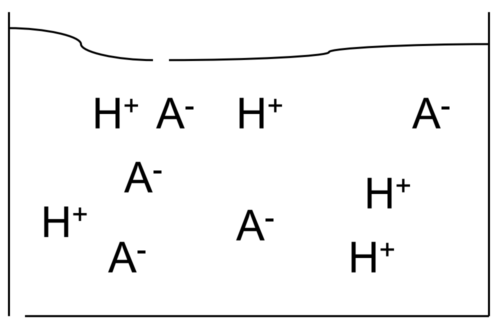


B

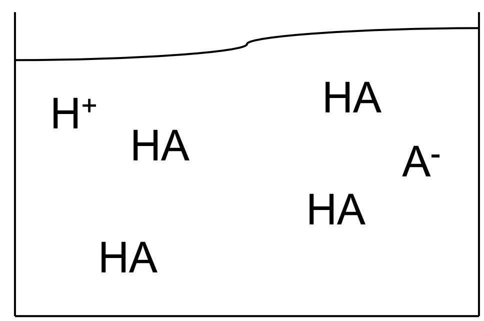
Acids can be <u>Strong</u> or <u>Weak</u>

Strong acids have large K_a. (easily donates H^+, many H^+ in soln)
Weak acids have $K_a < 1$. (wants to keep its H^+, low $[H^+]$)

Which picture best represents CH_3COOH (HA)?



C

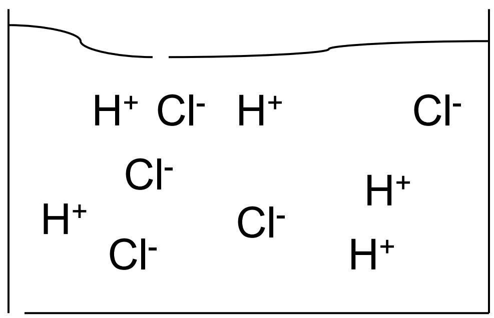


D

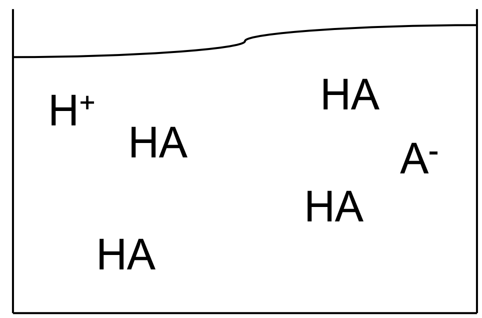
Acids can be Strong or Weak

Strong acids have large K_a. (easily donates H^+, many H^+ in soln)

Weak acids have K_a < 1. (wants to keep its H^+, low $[H^+]$)



A



D

Which statement is true?

(i) 0.1 M HCl has a higher $[H^+]$ than 0.1 M acetic acid.

(ii) 0.1 M HCl has a higher pH than 0.1 M acetic acid.

Objective: Calculate the pH of a weak acid

0.1 M HCl (strong acid) has a pH of 1. Why?

However, 0.1 M acetic acid (weak acid) has a pH greater than 1.
Calculate the pH of 0.1 M acetic acid.

$CH_3COOH <==> H^+ + CH_3COO^-$ $\qquad$ $K_a = 1.8 \times 10^{-5}$

Answer? (a) pH = 1

(b) pH = 2.4

(iii) pH = 2.9

(iv) pH = 7

Objective: Determine the amounts of reactants and products at *Equilibrium*

Calculate the pH of 0.1 M acetic acid.

$CH_3COOH \Longleftrightarrow H^+ + CH_3COO^-$ $K_a = 1.8 \times 10^{-5}$

Solution:

	CH_3COOH <==>	H^+ +	CH_3COO^-
Initial [ ]	0.1	0	0
Amount reacts	x	x	x
Amount at equilibrium	0.1-x	x	x

$$K_a = 1.8 \times 10^{-5} = \frac{(x)^2}{(0.1 - x)} = \frac{(x)^2}{0.1}$$

Keep it Simple: Since K_a is very small → assume $0.1 - x \approx 0.1$

Solve for x! $x = [H^+] = 0.0013$ M

$pH = -\log(0.0013) = 2.9$

How Does Concentration Affect pH?

http://www.foodsubs.com/Vinegars.html

Acetic acid has a K_a of 1.8×10^{-5}.

Vinegar is 0.9 M acetic acid with a pH of 2.4

0.1 M acetic acid has a pH of 2.9.

Using equilibrium principles, explain why the pH of vinegar is lower than the pH of 0.1 M acetic acid.

Do Weak Acids Have the Same Weakness?

Aspirin ($C_9H_8O_4$) has a K_a of 3.0×10^{-4}.

http://markfuscomd.com/blog/2012/05/should-aspirin-be-stopped-prior-to-laparoscopic-abdominal-surgery/

Which acid is stronger? Why?

Acetic acid has a K_a of 1.8×10^{-5}.

http://www.foodsubs.com/Vinegars.html

Draw the structure of aspirin. Which H is acidic?
Calculate the pH of 0.1 M aspirin solution.

Bases undergo hydrolysis

$$A^- + H_2O \Longleftrightarrow HA + OH^- \qquad K_b = K_w/K_a$$

Bases can be <u>strong</u> or <u>weak</u>.

Which statement is true?

(i) Weak bases accept H^+ more easily than strong bases.

(ii) Weak bases have a lower K_b than strong bases.

(iii) NaOH is a weaker base than $NaC_2H_3O_2$.

(iv) 0.1 M NaOH has the same pH as 0.1 M $NaC_2H_3O_2$.

(v) 0.1 M NaOH has a lower [OH-] than 0.1 M $NaC_2H_3O_2$.

Add Equations (1) and (2).
What do you get?

$HA <===> H^+ + A^-$	K_a	acid dissociation (1)
$A^- + H_2O <===> HA + OH^-$	K_b	base hydrolysis (2)
	$K_3 =$	(3)

How is K_3 related to K_a and K_b?

Objective: Calculate the pH of a weak base

What is the pH of a 0.1 M $NaCH_3COO$ solution?

To calculate the pH of a weak base, e.g., $NaC_2H_3O_2$:

- write base hydrolysis reaction
- calculate K_b. Look up K_a of acid.
- do an equilibrium calculation to calculate $[OH^-]$
- calculate pOH (= - log $[OH^-]$)
- calculate pH (using pH + pOH = 14)

Objective: Calculate the pH of a weak base

What is the pH of a 0.1 M $NaCH_3COO$ solution?

write base hydrolysis reaction

$$CH_3COO^- + H_2O <===> CH_3COOH + OH^-$$

calculate K_b. Look up K_a of acid.

$$K_b = K_w/K_a = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}.$$

do an equilibrium calculation to calculate $[OH^-]$

	CH_3COO^-	+ H_2O <===>	CH_3COOH	+ OH^-
Initial	0.1		0	0
Reacts	x		x	x
Equilibrium	0.1 – x		x	x

$K_b = 5.6 \times 10^{-10} = x^2/(0.1 - x) \approx x^2/(0.1)$ $\quad x = [OH^-] = 7.5 \times 10^{-6}$

calculate $pOH = - \log [OH^-] = - \log (7.5 \times 10^{-6}) = 5.1$

calculate $pH = 14 - pOH = 14 - 5.1 = 8.9$

https://thechronicleflask.wordpress.com/tag/sodium-benzoate/

Sodium Benzoate (NaC_6H_5COO) is used as a food preservative.

What is the conjugate acid of benzoate, $C_6H_5COO^-$?

What is the pH of a 0.1 M Sodium Benzoate solution?

K_a of benzoic acid = 6.5×10^{-5}.
K_b of benzoate =
$[OH^-] = 3.9 \times 10^{-6}$ M

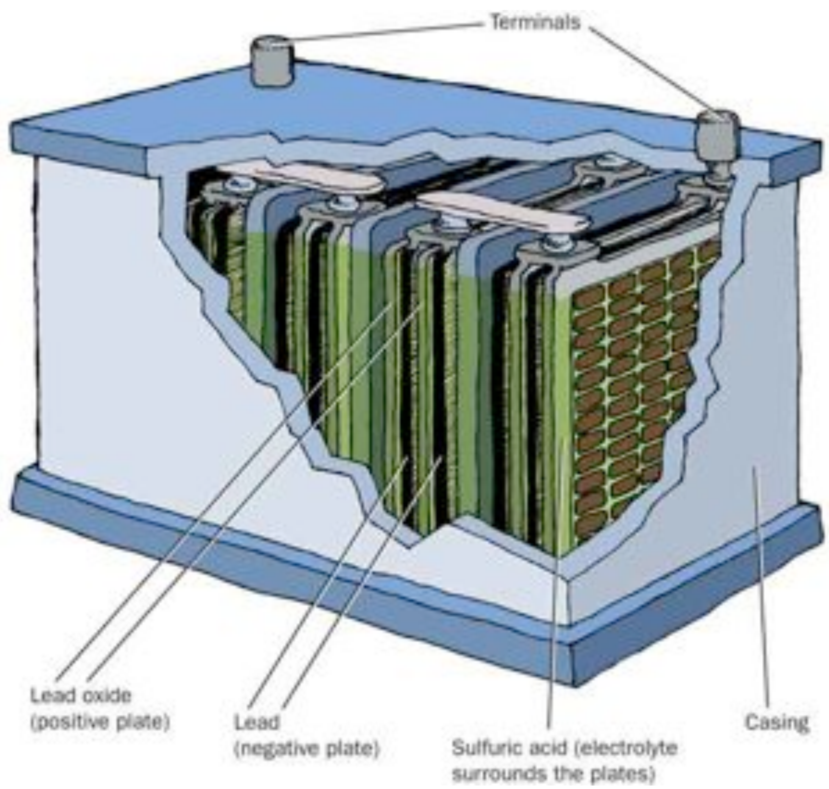
Baking Soda ($NaHCO_3$) is a ____.

Calculate the pH of a 0.1 M baking soda solution.

http://www.armandhammer.com/solutions/solution-53/antacid.aspx

H_2CO_3 $pK_a = 6.4$
$[OH^-] = 5.0 \times 10^{-5}$ M
pH = 9.7

Sulfuric acid is the acid found in car batteries. What is/are the major sulfur containing substance(s) in this solution?
http://www.propertiesofmatter.si.edu/carbattery.html



Decomposition of $CaCO_3$:

$$CaCO_3 \Longleftrightarrow CaO + CO_2.$$

At 1000^oC, K = 9.75

At 848^oC, K = 1.

http://www.tums.com/products.html

$CaCO_3$ is the active ingredient in Tums and Rolaids.
Is this reaction exothermic or endothermic?

Is K greater than 1 or less than 1 at room temperature?
(Note: we will calculate K at room temperature later.)

Is it safe to store Tums at room temperature?