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 =  $H^+$  donor. Every acid has a partner (conjugate) base. Base =  $H^+$  acceptor. Every base has a partner (conjugate) acid.  $HCI + H_2O --> CI^-$ H<sub>3</sub>O E.g., Acid base conjugate base conjugate acid of HCI of H<sub>2</sub>O Shortcut: HCI (aq) --> Cl<sup>-</sup> (aq) H<sup>+</sup> (aq) + Important acid-base reactions and Keq: Acid (HA) dissociation reaction: HA -->  $H^+ + A^-$ .  $K_a$  is  $K_{eq}$  for this reaction.  $K_a = [H^+] [A^-]/[HA]$ Base (A<sup>-</sup>) hydrolysis reaction: A<sup>-</sup> + H<sub>2</sub>O --> HA + OH<sup>-</sup>. K<sub>b</sub> is K<sub>eq</sub> for this reaction. K<sub>b</sub> = [HA] [OH<sup>-</sup>]/[A<sub>1</sub>][H<sub>2</sub>O] Water dissociation reaction:  $H_2O \rightarrow H^+ + OH^-$ .  $K_w$  is  $K_{eq}$  for this reaction.  $K_w = [H^+][OH^-] = 1 \times 10^{-14}$ .  $K_w = K_a K_b$ Acids and bases are strong or weak. Strong acid easily donates its  $H^+$ . HCl --> Cl<sup>-</sup> (aq) +  $H^+$  (aq). Complete dissociation. K<sub>a</sub> is large. Weak acid does not easily donate its H<sup>+</sup>. CH<sub>3</sub>COOH --> CH<sub>3</sub>COO<sup>-</sup> (aq) + H<sup>+</sup> (aq). Partial dissociation. K<sub>a</sub> is small. Strong base easily accept H<sup>+</sup>. CH<sub>3</sub>COO<sup>-</sup> (aq) + H<sup>+</sup> (aq) --> CH<sub>3</sub>COOH. K<sub>eq</sub> is large. (Conjugate base of weak acid is strong.) Weak base does not easily accept H<sup>+</sup>. Cl<sup>-</sup> (aq) + H<sup>+</sup> (aq) --> HCl. K<sub>eq</sub> is small. (Conjugate base of strong acid is weak.) Quantify  $[H^{\dagger}]$  with pH. pH = - log  $[H^{\dagger}]$ . Strong acid: HCl (aq) completely dissociates into Cl<sup>-</sup> (aq) and H<sup>+</sup> (aq) so 0.1 M HCl = 0.1 M H<sup>+</sup> ==> pH = - log [0.1] = 1 Weak acid: CH<sub>3</sub>COOH partially dissociates into CH<sub>3</sub>COO<sup>-</sup> (aq) and H<sup>+</sup> (aq) so 0.1 M CH<sub>3</sub>COOH produces less than 0.1 M  $H^{+}$  so pH > 1. Calculate  $H^{+}$  and pH with an equilibrium calculation. CH<sub>3</sub>COOH --> CH<sub>3</sub>COO<sup>-</sup> (aq) +  $K_{eq} = 1.8 \times 10^{-5} = [CH_3COO^{-1}] [H^+]/[CH_3COOH]$ E.g., H<sup>+</sup> (aq) С 0 initial 0 reacts х х х  $K_{eq} = 1.8 \times 10^{-5} = [x] [x]/[C-x] = [x] [x]/[C]$ equilibrium C-x х х Note: Keq is very small so x is very small so assume C-x ≈ C  $p(something) = - \log(something)$  $pOH = - \log [OH^{-}]$  $pK = -\log K$ 

1. You have solutions of 0.01 M acetic acid and HCI.

a. Which solution, acetic acid and HCI, has a higher concentration of H<sup>+</sup>? Draw a picture of this solution to support your answer.

Answer: HCl has a higher concentration of H<sup>+</sup> than acetic acid because HCl is a strong acid and acetic acid is a weak acid. See Objective 8 Lecture Slide 13 Picture A.

b. Which solution is drinkable? Do these solutions have the same or different pH? Calculate the pH of each solution. Why does a weak acid have a higher pH than the same concentration of strong acid? Answer: acetic acid is drinkable because acetic acid is a weak acid and does not want to donate its proton to you. HCl has a different pH than acetic acid. HCl has a higher concentration of H<sup>+</sup> than acetic acid. pH of 0.01 M HCl = -log [H<sup>+</sup>] = - log (0.01) = 2

Do an equilibrium calculation to determine the pH of 0.01 M  $CH_3COOH$ .

 $K_{eq} = 1.8 \times 10^{-5} = [CH_3COO^-] [H^+]/[CH_3COOH]$  $CH_3COOH --> CH_3COO^{-}(aq) +$  $H^{+}(aq)$ 0 initial C = 0.01 M0 reacts Х Х х  $K_{ea} = 1.8 \times 10^{-5} = [x] [x]/[0.01-x] = [x] [x]/[0.01]$ equilibrium 0.01-x х х Note:  $K_{eq}$  is very small so x is very small so assume 0.01-x  $\approx$  0.01 Solve for x =  $[(1.8 \times 10^{-5})(0.01)]^{0.5} = 4.2 \times 10^{-4} = [H^{+}]$  $pH = -\log[H^+] = -\log(4.2 \times 10^{-4}) = 3.4$ A weaker acid has a higher pH (lower  $[H^{\dagger}]$ ) than a stronger acid (higher  $[H^{\dagger}]$ ). Compare the  $[H^{\dagger}]$  of 0.01 M HCl and acetic acid solutions.

c. Every acid has a conjugate base. The conjugate base of a strong acid is weak. The conjugate base of a weak acid is

strong. (i) Consider the reaction:

HCI + H<sub>2</sub>O --> Cl H₂O<sup>†</sup> conjugate base Acid base conjugate acid of HCI of H<sub>2</sub>O This reaction is the acid dissociation reaction. A shortcut for this reaction is: HCI (aq) --> Cľ H<sup>+</sup> (aq) + The acid dissociation equilibrium constant,  $K_a$ , is:  $K_a = [CI] [H^{\dagger}]/[HCI]$ HCl is a strong acid. Is K<sub>a</sub> for HCl large or small? Answer: a strong acid, like HCI, has a large K<sub>a</sub>. Draw a picture of HCI (ag). Answer: see Objective 8 Lecture Slide 13 Picture A. Use your picture of HCI to explain why conjugate base of HCI is weak. In other words, why doesn't the above reaction go in the reverse direction? Answer: HCl is a strong acid and wants to donate its  $H^{+}$  and dissociate into  $H^{+}$  and Cl<sup>-</sup>. The conjugate base, Cl<sup>-</sup>, is a weak base and does not want to accept H<sup>+</sup> to reform HCI. (ii) H<sub>2</sub>O can behave like an acid or a base: OH  $H_3O^+$  (ag)  $H_2O + H_2O -->$ This reaction is the water dissociation reaction. A shortcut for this reaction is: H<sub>2</sub>O --> OH H<sup>+</sup> (aq) + The water dissociation equilibrium constant,  $K_w$ , is:  $K_w = [OH] [H^+] = 1 \times 10^{-14}$ . Draw a picture of H<sub>2</sub>O. Answer: see Objective 8 Lecture Slide 13 Picture B. Water consists of almost all H<sub>2</sub>O molecules with about 1 H<sup>+</sup> and 1 OH<sup>-</sup> for every 10 million H<sub>2</sub>O molecules. Use your picture of H<sub>2</sub>O to explain why the conjugate acid of H<sub>2</sub>O is strong. Answer:  $H_2O$  is a weak base and does not want to accept a H<sup>+</sup> to form  $H_3O^+$ . The conjugate acid,  $H_3O^+$ , is a strong acid and wants to donate  $H^{+}$  to reform  $H_{2}O$ . Use your picture of H<sub>2</sub>O to explain why the conjugate base of H<sub>2</sub>O is strong. Answer:  $H_2O$  is a weak acid and does not want to donate its  $H^+$  and dissociate into  $H^+$  and OH. The conjugate base, OH, is a strong base and wants to accept  $H^{\dagger}$  to reform H<sub>2</sub>O. (iii) Consider the reaction: CH<sub>3</sub>COOH + H<sub>2</sub>O --> CH<sub>3</sub>COO<sup>-</sup> H₃O⁺ Acid conjugate base conjugate acid base of CH<sub>3</sub>COOH of H<sub>2</sub>O This reaction is the acid dissociation reaction. A shortcut for this reaction is: CH<sub>3</sub>COOH (aq) --> CH<sub>3</sub>COO<sup>-</sup> H<sup>+</sup> (aq) Write the acid dissociation equilibrium constant, K<sub>a</sub>, for acetic acid. Answer:  $K_a = [CH_3COO^-] [H^+]/[CH_3COOH]$ CH<sub>3</sub>COOH is a weak acid. Is K<sub>a</sub> for CH<sub>3</sub>COOH large or small? Look up the K<sub>a</sub> of CH<sub>3</sub>COOH. You can find a table of K<sub>a</sub>'s for weak acids in the textbook or on the internet. Answer: a weak acid, like CH<sub>3</sub>COOH. has a small K<sub>a</sub>. For CH<sub>3</sub>COOH,  $K_a = 1.8 \times 10^{-1}$ (iv) When a base is dissolved in water, it reacts with water to form its conjugate acid and OH<sup>-</sup>. For example, sodium acetate (NaCH<sub>3</sub>COO) is a base. The CH<sub>3</sub>COO<sup>-</sup> part is the basic part of this compound. CH<sub>3</sub>COO<sup>-</sup> + H<sub>2</sub>O --> CH<sub>3</sub>COOH OH. + Base acid conjugate acid conjugate base of CH<sub>3</sub>COO<sup>-</sup> of H<sub>2</sub>O This reaction is the base hydrolysis reaction. The base hydrolysis equilibrium constant,  $K_b$ , is:  $K_b = [CH_3COOH] [OH]/[CH_3COO]$ . A table of K<sub>h</sub>'s for weak bases are not as easily found as for K<sub>a</sub>'s. But you can calculate K<sub>b</sub> as long as you know the K<sub>a</sub> of the conjugate acid using the formula:  $K_aK_b = K_w$ . What is the numerical value of K<sub>b</sub> for CH<sub>3</sub>COO<sup>-</sup>? Answer: For CH<sub>3</sub>COOH, K<sub>a</sub> =  $1.8 \times 10^{-5}$ For CH<sub>3</sub>COO<sup>-</sup>, K<sub>b</sub> = K<sub>w</sub>/ K<sub>a</sub> = 1 x  $10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$ 2. pH calculations for a weak acid – use K<sub>a</sub>. a. Aspirin has a pK<sub>a</sub> of 3.5; salicylic acid has a pK<sub>a</sub> of 2.98. Is aspirin a stronger or weaker acid than salicylic acid? To

confirm your answer, write the acid dissociation reaction for each acid, calculate the equilibrium constant,  $K_a$ , for each acid, and briefly discuss what the value of K means.

Answer: Aspirin is a weaker acid than salicylic acid.  $pK_a$  = - log  $K_a$  Solve for  $K_a = 10^{-pKa}$ Aspirin:  $K_a = 10^{-3.5} = 3.2 \times 10^{-4}$ Salicylic acid:  $K_a = 10^{-2.98} = 1.05 \times 10^{-3}$ Smaller  $K_a$  (or larger pK<sub>a</sub>) means weaker acid.

b. Acetic acid is the acid in vinegar. Write the acid dissociation reaction for this acid. Look up the  $K_a$  of acetic acid. Calculate the pH of a 0.1 M acetic acid solution. To calculate pH, do an equilibrium calculation:

i o oulouluto p	si i, ao an' oquiisn	ann baibaiation.		_
	CH₃COOH>	CH₃COO⁻ (aq) +	H⁺ (aq)	$K_a = 1.8 \times 10^{-5} = [CH_3COO^-] [H^+]/[CH_3COOH]$
initial	0.1	0	0	
reacts	х	Х	х	
equilibrium	0.1-x	Х	х	$K_a = 1.8 \times 10^{-5} = [x] [x]/[0.1-x] \approx [x] [x]/[0.1]$
				Note: K <sub>a</sub> is very small so x is very small so

Solve for  $x = [H^+] = 1.34 \times 10^{-3} M_{\odot}$ 

 $pH = -\log [H^+] = -\log (1.34 \times 10^{-3}) = 2.9$ 

The pH of a 0.1 M acetic acid solution is 2.9.

Vinegar is 0.9 M acetic acid. Does vinegar have a higher or lower pH than 0.1 M acetic acid? Calculate the pH of vinegar to confirm your answer.

assume 0.1 -x ≈ 0.1

Answer: vinegar has a lower pH than 0.1 M acetic acid. Same equilibrium calculation as above but C = 0.9 M instead of 0.1 M. So  $K_a = 1.8 \times 10^{-5} = [x] [x]/[0.1-x] \approx [x] [x]/[0.9]$ Solve for x = [(1.8 x 10<sup>-5</sup>)(0.9)]^0.5 = 4.0x10<sup>-3</sup> = [H<sup>+</sup>]

 $pH = -log[H^+] = -log(4.0x10^{-3}) = 2.4$ 

c. Carbonic acid is found in soda. Write the acid dissociation reaction for this acid. Look up the K<sub>a</sub> of carbonic acid. Calculate the pH of a 0.1 M carbonic acid solution. (Answer: pH between 3 and 4) Answer: carbonic acid = H<sub>2</sub>CO<sub>3</sub> acid dissociation reaction: H<sub>2</sub>CO<sub>3</sub> <==> H<sup>+</sup> + HCO<sub>3</sub><sup>-</sup> K<sub>a</sub> = 4.2x10<sup>-7</sup> Same equilibrium calculation as above but use K<sub>a</sub> for carbonic acid and C = 0.1 M. K<sub>a</sub> = 4.2x10<sup>-7</sup> = [X] [X]/[0.1-X] ≈ [X] [X]/[0.1] Solve for x = [(4.2x10<sup>-7</sup>)(0.1)]^0.5 = 2.0x10<sup>-4</sup> = [H<sup>+</sup>] pH = - log[H<sup>+</sup>] = -log(2.0x10<sup>-4</sup>) = 3.7

d. Benzoic acid is found in food preservatives. Write the acid dissociation reaction for this acid. Look up the  $K_a$  of benzoic acid. Calculate the pH of a 0.1 M benzoic acid solution. (Answer: pH between 2 and 3)

Answer: benzoic acid =  $C_6H_5COOH$ acid dissociation reaction:  $C_6H_5COOH <==> H^+ + C_6H_5COO^ K_a = 6.5x10^{-5}$ Same equilibrium calculation as above but use  $K_a$  for carbonic acid and C = 0.1 M.  $K_a = 6.5x10^{-5} = [x] [x]/[0.1-x] \approx [x] [x]/[0.1]$ Solve for  $x = [(6.5x10^{-5})(0.1)]^{0.5} = 2.5x10^{-3} = [H^+]$  $pH = - log[H^+] = -log(2.5x10^{-3}) = 2.6$ 

e. Vinegar contains acetic acid and has a pH of 2.4. Calculate the concentration of acetic acid in vinegar. (Answer: between 0.8 and 1 M)

Answer: equilibrium calculation as above but you know  $K_a$  and  $[H^{\dagger}]$  from pH.

 $K_a = 1.8 \times 10^{-5} = [CH_3COO^{-1}] [H^{+1}] [CH_3COOH]$  $CH_3COOH --> CH_3COO^{-}(aq) +$ H<sup>+</sup> (aq) initial С 0 0 reacts Х Х х equilibrium C-x x x =  $[H^+] = 10^{-pH} = 10^{-2.4} = 4.0 \times 10^{-3} M_{\odot}$  $K_a = 1.8 \times 10^{-5} = [x] [x]/[C-x] \approx [x] [x]/[C]$ х  $K_a = 1.8 \times 10^{-5} = [4.0 \times 10^{-3}] [4.0 \times 10^{-3}]/[C]$ Solve for C = 0.88 M

3. pH calculations for a weak base – use K<sub>b</sub>.

a. You have 0.1 M solutions of NaOH (strong base) and NaHCO<sub>3</sub> (weak base). Explain why the strong base has a higher pH than the weak base. Draw a picture of each solution to support your answer.

Answer:  $K_w = [H^+] [OH^-] = 1 \times 10^{-14} \text{ or } pH + pOH = 14$ 

```
Higher [OH] means lower [H^+].
```

NaOH dissociates into Na<sup>+</sup> and OH<sup>-</sup> so 0.1 M NaOH means [OH<sup>-</sup>] = 0.1 M.

NaHCO<sub>3</sub> is a weak base so HCO<sub>3</sub><sup>-</sup> reacts with H<sub>2</sub>O in a base hydrolysis reaction. HCO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O --> H<sub>2</sub>CO<sub>3</sub> + OH<sup>-</sup> Base acid conjugate acid conjugate base

of H<sub>2</sub>O

 $HCO_3^{-1}$  is a weak base so it does not want to accept H+ from H2O. At equilibrium, there is mostly reactants ( $HCO_3^{-1}$  and  $H_2O$ ) and hardly any products ( $H_2CO_3^{-1}$  and  $OH^{-1}$ ).

The [OH] in 0.1 M NaHCO<sub>3</sub> is much lower than the [OH] in 0.1 M NaOH.

Since higher [OH] means lower [H<sup>+</sup>], this means the [H<sup>+</sup>] in 0.1 M NaHCO<sub>3</sub> is much higher than the [H<sup>+</sup>] in 0.1 M NaOH. Higher [H<sup>+</sup>] means lower pH.

b. Baking soda is sodium bicarbonate. What is the conjugate acid of baking soda? Write the base hydrolysis reaction for this base. Calculate  $K_b$ . Calculate pOH. Calculate pH. (Answers: pOH between 4 and 5. pH between 9 and 10.) Answer: NaHCO<sub>3</sub> is a weak base so HCO<sub>3</sub><sup>-</sup> reacts with H<sub>2</sub>O in a base hydrolysis reaction. H<sub>2</sub>CO<sub>3</sub> is the conjugate acid of HCO<sub>3</sub><sup>-</sup>. K<sub>a</sub> of H<sub>2</sub>CO<sub>3</sub> = 4.2 x 10<sup>-7</sup>

 $K_{b} = K_{w}/K_{a} = 1 \times 10^{-14}/4.2 \times 10^{-7} = 2.4 \times 10^{-8}$  $HCO_3^{-}$  + H<sub>2</sub>O -->  $H_2CO_3 +$ OH initial C = 0.10 0 reacts Х х х equilibrium 0.1-x Х x  $K_{b} = 2.4 \times 10^{-8} = [x] [x]/[0.1-x] \approx [x] [x]/[0.1]$ Solve for x =  $[OH^{-1}] = 4.9 \times 10^{-5}$  $pOH = -\log [OH^{-}] = -\log (4.9 \times 10^{-5}) = 4.3$ pH + pOH = 14 OR pH = 14 - pOH = 14 - 4.3 = 9.7

c. Sodium salicylate is the conjugate base of salicylic acid. Write the base hydrolysis reaction for this base. Calculate  $K_b$ . Calculate pOH. Calculate pH. (Answer: pH between 7.5 and 8.5)

Answer: salicylate ion =  $C_7H_5O_3^{-1}$ . Salicylic acid,  $C_7H_6O_3$ , is the conjugate acid of  $C_7H_5O_3^{-1}$ . K<sub>a</sub> of  $C_7H_6O_3$  = 1.1 x 10<sup>-3</sup>

 $C_7H_5O_3$  is a weak base so  $C_7H_5O_3$  reacts with  $H_2O$  in a base hydrolysis reaction.

 $K_{b} = K_{w}/K_{a} = 1 \times 10^{-14}/1.1 \times 10^{-3} = 9.3 \times 10^{-12}$  $C_7 H_5 O_3^- +$ H<sub>2</sub>O -->  $C_7H_6O_3 +$ OH initial C = 0.10 0 reacts Х Х Х equilibrium 0.1-x х Х  $K_b = 9.3 \times 10^{-12} = [x] [x]/[0.1-x] \approx [x] [x]/[0.1]$ Solve for  $x = [OH^{-}] = 9.7 \times 10^{-7}$  $pOH = -\log [OH^{-}] = -\log (9.7 \times 10^{-7}) = 6.0$ pH + pOH = 14 OR pH = 14 - pOH = 14 - 6.0 = 8.0

4. Concentrated sulfuric acid (18 M) is used as the electrolyte in car batteries.

a. Calculate the pH of battery acid. (pH will be negative.)

 $pH = -log[H^{+}] = -log(18) =$ 

b. Sulfuric acid is a diprotic acid. However,  $H^*$  and  $HSO_4^-$  are the two ions predominantly present. Explain why the concentration of  $SO_4^{2^-}$  is very low in sulfuric acid.

$H_2SO_4 \rightarrow H^+ + HSO_4^-$	$K_a$ = large since H <sub>2</sub> SO <sub>4</sub> is a strong acid so solution consists of H <sup>+</sup> and HSO <sub>4</sub> <sup>-</sup> ions.
$HSO_4^> H^+ + SO_4^{-2}$	$K_a = 10^{-2}$ since HSO <sub>4</sub> is a weak acid so solution contains almost all HSO <sub>4</sub> ions and
	hardly any $SO_4^{-2}$ ions.

c. At what pH will  $HSO_4^-$  and  $SO_4^{-2-}$  be observed? Give reasons.

As solution gets more basic (less acidic),  $HSO_4^- -> H^+ + SO_4^{-2}$  reaction shifts to product side (LeChatelier's principle). We will learn in Objective 8 that at pH greater than 2, both  $HSO_4^-$  and  $SO_4^{-2}^-$  will be observed.