

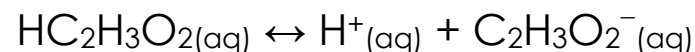
## 8.2 Weak Acids and Bases

- *Review approximation method to make calculations easier.*
- A weak acid is an acid that partially ionizes in solution but exists primarily in the form of molecules.
- A weak base is a base that has a weak attraction for protons.
- According to Brønsted-Lowry, a base must possess an atom with a lone pair of valence electrons capable of accepting a proton from water, which would produce the hydroxide ion.

### Percent Ionization of Weak Acids

- Most weak acids ionize less than 50%
- have a pH close to 7.
- Percent ionization:  $p = \frac{\text{concentration of acid ionized}}{\text{concentration of acid solute}} \times 100\%$

- For weak acids:  $[H^+_{(aq)}] = \frac{p}{100} \times [HA_{(aq)}]$
- where p is the percent ionization and  $[HA_{(aq)}]$  is the concentration of the acid.
- E.g. For a 0.10 mol/L solution of acetic acid, 1.3% ionizes:



$$[H^+_{(aq)}] = \frac{1.3}{100} \times [0.10 \text{ mol} / L]$$

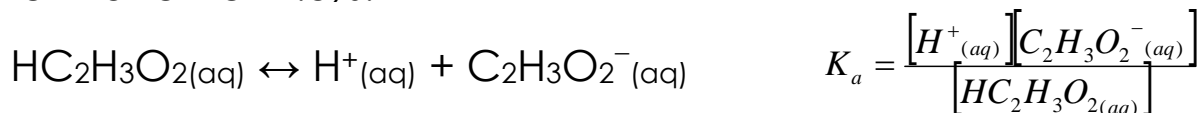
$$[H^+_{(aq)}] = 1.3 \times 10^{-3} \text{ mol/L}$$

### Ionization Constant for Weak Acids

- Acid ionization constant,  $K_a$  is the equilibrium constant for the ionization of an acid.
- For the reaction:  $HA_{(aq)} \leftrightarrow H^+_{(aq)} + A^-_{(aq)}$

$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$

- E.g. calculate the acid ionization constant of acetic acid if a 0.100 mol/L solution at equilibrium at SATP has a percent ionization of 1.3%.



	$\text{HC}_2\text{H}_3\text{O}_{2(aq)}$	$\leftrightarrow$	$\text{H}^+_{(aq)}$	+	$\text{C}_2\text{H}_3\text{O}_2^-_{(aq)}$
I	0.100		0		0
C	-x		+x		+x
E	0.100-x		x		x

$$x = 0.100 \text{ mol/L} \times 0.013 = 0.0013 \text{ mol/L}$$

$$\begin{aligned} \text{therefore: } [\text{HC}_2\text{H}_3\text{O}_{2(aq)}] &= 0.100 - 0.0013 = 0.0987 \text{ mol/L} \\ [\text{H}^+_{(aq)}] &= 0.0013 \text{ mol/L} \\ [\text{C}_2\text{H}_3\text{O}_2^-_{(aq)}] &= 0.0013 \text{ mol/L} \end{aligned}$$

$$K_a = \frac{[\text{H}^+_{(aq)}][\text{C}_2\text{H}_3\text{O}_2^-_{(aq)}]}{[\text{HC}_2\text{H}_3\text{O}_{2(aq)}]} = \frac{(0.0013)(0.0013)}{0.0987} = 1.7 \times 10^{-5}$$

## Percent Ionization and Concentration

- Percent ionization varies with the concentration of the solution. In other words, the more dilute the solution the greater the degree of ionization.

## Ionization constants for Weak Bases

- Base ionization constant,  $K_b$  is the equilibrium constant for the ionization of a base.
- For the reaction:  $\text{B}_{(aq)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{HB}^+_{(aq)} + \text{OH}^-_{(aq)}$

$$K_b = \frac{[\text{HB}^+_{(aq)}][\text{OH}^-_{(aq)}]}{[\text{B}_{(aq)}]}$$

- Problems are solved in a similar manner as acids (see above).

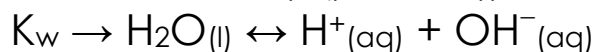
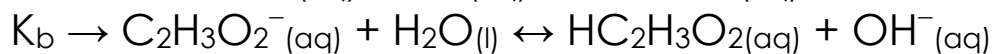
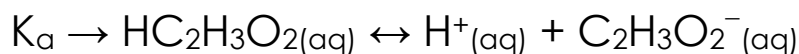
## Organic Bases

- Organic bases usually have a  $\text{-NH}_2$  group attached or N with a lone pair of electrons capable of accepting a proton.

### The Relationship between $K_a$ and $K_b$

- See page 560 for proof.
- $K_a \times K_b = K_w$  or  $K_a = \frac{K_w}{K_b}$  or  $K_b = \frac{K_w}{K_a}$
- E.g. What is the value of the base ionization constant for the acetate ion at SATP? (*use the table in appendix C7*)

*Things to think about:*



$$K_w = 1.0 \times 10^{-14} \text{ (already known)}$$

$$K_a = 1.8 \times 10^{-5} \text{ (look up } K_a \text{ for acetic acid)}$$

$$K_b = ?$$

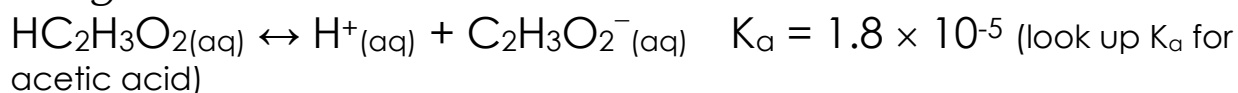
$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

- See figure 5 and the table on page 562 for the relationship between conjugate pairs.

## The pH of Weak Acid Solutions

- E.g. Calculate the hydrogen ion concentration and the pH of a 0.10 mol/L acetic acid solution.

*Things to think about*



*Sources of  $\text{H}^+$  are acetic acid and water, but based on the  $K$  values, it is clear that almost all the  $\text{H}^+$  comes from acetic acid. Also of note, the  $K_b$  value of acetate is also insignificant and has little effect. Therefore we can assume all the  $\text{H}^+$  comes from acetic acid.*

	$\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$	$\leftrightarrow$	$\text{H}^+(\text{aq})$	+	$\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$
I	0.10		0		0
C	-x		+x		+x
E	0.10-x		x		x

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})]}{[\text{HC}_2\text{H}_3\text{O}_2(\text{aq})]} = \frac{[x][x]}{[0.10-x]} = \frac{[x]^2}{[0.10-x]} = 1.8 \times 10^{-5}$$

*use quadratic or approximate using 100 rule*

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.10}{1.8 \times 10^{-5}} = 5.6 \times 10^3 \quad \text{since } 5.6 \times 10^3 > 100 \text{ we can}$$

assume  $0.10 - x = 0.10$

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})]}{[\text{HC}_2\text{H}_3\text{O}_2(\text{aq})]} = \frac{[x][x]}{[0.10-x]} = \frac{[x]^2}{[0.10]} = 1.8 \times 10^{-5}$$

$$x = 1.3 \times 10^{-3}$$

check assumption  $\frac{x}{[HA]_{aq}} \times 100\% < 5\%$  , which turns out to be 1.3%

$$x = [H^+_{(aq)}] = 1.3 \times 10^{-3} \text{ mol/L}$$

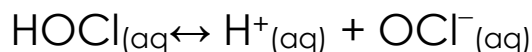
$$\text{pH} = -\log[H^+_{(aq)}] = -\log[1.3 \times 10^{-3}] = 2.89$$

- See summary for calculating the pH of a solution of weak monoprotic acid,  $HA_{(aq)}$  given the value of  $K_a$  on page 568
- E.g. You measure the pH of a 0.1 mol/L hypochlorous acid solution and find it to be 4.23. What is the  $K_a$  for  $HOCl_{(aq)}$ ?

$$\text{pH} = 4.23$$

$$[H^+_{(aq)}] = 10^{-\text{pH}} = 10^{-4.23} = 5.9 \times 10^{-5} \text{ mol/L} = [OCl^-_{(aq)}]$$

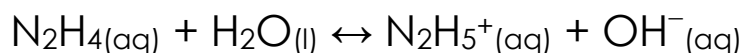
*The sources of  $H^+$  will primarily be the  $HOCl$  since there are so few given by water and the  $OCl^-$  is a weak conjugate base. Therefore...*



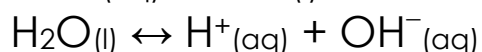
$$K_a = \frac{[H^+_{(aq)}][OCl^-_{(aq)}]}{[HOCl_{(aq)}]} = \frac{[5.9 \times 10^{-5}][5.9 \times 10^{-5}]}{[0.10]} = 3.5 \times 10^{-8}$$

## The pH of Weak Base Solutions

- Similar to acid problems.
- See summary on page 574
- E.g. Calculate the pH of a 0.100 mol/L aqueous solution of hydrazine, a weak base if the  $K_b$  for  $N_2H_{4(aq)}$  is  $1.7 \times 10^{-6}$



$$K_b = 1.7 \times 10^{-6}$$



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

Most  $\text{OH}^-$  comes from hydrazine since the constant is so much bigger. We can ignore the  $\text{OH}^-$  from water. We can also ignore the influence of  $\text{N}_2\text{H}_5^+$  since it is a weak conjugate acid.

$$K_b = \frac{[\text{N}_2\text{H}_5^+_{(aq)}][\text{OH}^-_{(aq)}]}{[\text{N}_2\text{H}_{4(aq)}]} \quad \text{we need concentrations}$$

	$\text{N}_2\text{H}_{4(aq)}$	+	$\text{H}_2\text{O}_{(l)}$	$\leftrightarrow$	$\text{N}_2\text{H}_5^+_{(aq)}$	+	$\text{OH}^-_{(aq)}$
I	0.100		*		0		0
C	-x		*		+x		+x
E	0.100-x		*		x		x

$$K_b = \frac{[\text{N}_2\text{H}_5^+_{(aq)}][\text{OH}^-_{(aq)}]}{[\text{N}_2\text{H}_{4(aq)}]} = \frac{x^2}{0.100 - x} = 1.7 \times 10^{-6}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 4.11 \times 10^{-4} \quad [\text{OR } 4.123 \times 10^{-4} \text{ by estimation}]$$

$$[\text{OH}^-_{(aq)}] = 4.11 \times 10^{-4} \text{ mol/L}$$

$$\text{pOH} = -\log[\text{OH}^-_{(aq)}] = -\log[4.11 \times 10^{-4}] = 3.38$$

$$\text{pH} = \text{pK}_w - \text{pOH} = 14 - 3.38 = 10.62$$

Therefore the pH of a 0.100 mol/L hydrazine solution is 10.62.

## Polyprotic Acids

- Acids with more than 1 proton to be released.
- In general:  $K_{a1} > K_{a2} > K_{a3} > \dots$
- You would assume these questions to be quite difficult but the first constant is usually so much bigger than the second that we can ignore all but the first constant.

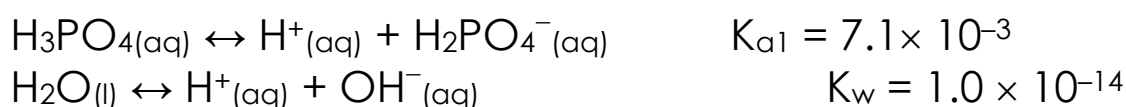
- E.g. Calculate the pH of 1.00 mol/L phosphoric acid,  $\text{H}_3\text{PO}_{4(\text{aq})}$   
(From textbook...textbook solution is incorrect)

From table 10 on page 575  $K_{a1} = 7.1 \times 10^{-3}$

$$K_{a2} = 6.3 \times 10^{-8}$$

$$K_{a3} = 4.2 \times 10^{-13}$$

Since  $K_{a1}$  is so much larger than the other 2 we can assume all the  $\text{H}^+$  comes from the first ionization.



Since phosphoric acid is a much stronger acid than water, we can assume all the  $\text{H}^+$  comes from the phosphoric acid.

	$\text{H}_3\text{PO}_{4(\text{aq})}$	$\leftrightarrow$	$\text{H}^+_{(\text{aq})}$	+	$\text{H}_2\text{PO}_4^-_{(\text{aq})}$
I	1.00		0		0
C	-x		+x		+x
E	1.00-x		x		x

$$K_{a1} = \frac{[\text{H}^+_{(\text{aq})}][\text{H}_2\text{PO}_4^-_{(\text{aq})}]}{[\text{H}_3\text{PO}_{4(\text{aq})}]} = 7.1 \times 10^{-3} = \frac{(x)(x)}{(1.00 - x)} = \frac{x^2}{1.00 - x}$$

$$7.1 \times 10^{-3} = \frac{x^2}{1.00 - x}$$

$$x^2 + 7.1 \times 10^{-3}x - 7.1 \times 10^{-3} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 8.079 \times 10^{-2}$$

$$x = [\text{H}^+_{(\text{aq})}] = 8.079 \times 10^{-2} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}^+_{(\text{aq})}] = -\log[8.079 \times 10^{-2}] = 1.09$$

## Homework

- Practice 1,2,3,4,5,6,7,8,9,10,12,13,14
- Questions 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18



## 8.2 Weak Acids and Bases

## STUDENT

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### Percent Ionization of Weak Acids

- Most weak acids ionize less than 50%
- have a pH close to 7.

Percent ionization:

- For weak acids:
- where  $p$  is the percent ionization and  $[HA_{(aq)}]$  is the concentration of the acid.

E.g.

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## **Percent Ionization and Concentration**

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## **Ionization constants for Weak Bases**

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For the reaction:
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## Organic Bases

- Organic bases usually have a  $\text{-NH}_2$  group attached or N with a lone pair of electrons capable of accepting a proton.

## The Relationship between $K_a$ and $K_b$

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- E.g. What is the value of the base ionization constant for the acetate ion at SATP? (*use the table in appendix C7*)

*Things to think about:*

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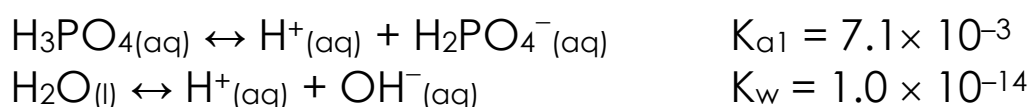
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