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:

$$HC_2H_3O_{2(aq)} \leftrightarrow H^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

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

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

Ionization Constant for Weak Acids

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

- 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%.

$HC_2H_3O_{2(aq)} \leftrightarrow H^+{}_{(aq)} + C_2H_3O_2^-{}_{(aq)}$

$$K_a = \frac{[H^+{}_{(aq)}][C_2H_3O_2^-{}_{(aq)}]}{[HC_2H_3O_{2(aq)}]}$$

	$HC_2H_3O_{2(aq)}$	$\leftrightarrow$	$H^+{}_{(aq)}$	+	$C_2H_3O_2^-{}_{(aq)}$
I	0.100		0	0	
C	–x		+x	+x	
E	0.100–x		x	x	

x = 0.100 mol/L × 0.013 = 0.0013 mol/L

therefore: $[HC_2H_3O_{2(aq)}]$ = 0.100 – 0.0013 = 0.0987 mol/L
$[H^+{}_{(aq)}]$ = 0.0013 mol/L
$[C_2H_3O_2^-{}_{(aq)}]$ = 0.0013 mol/L

$$K_a = \frac{[H^+{}_{(aq)}][C_2H_3O_2^-{}_{(aq)}]}{[HC_2H_3O_{2(aq)}]} = \frac{(0.0013)(0.0013)}{0.0987} = 1.7 \times 10^{-5}$$

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: $B_{(aq)} + H_2O_{(l)} \leftrightarrow HB^+{}_{(aq)} + OH^-{}_{(aq)}$

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

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

Organic Bases

- Organic bases usually have a $-NH_2$ 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:

  $K_a \rightarrow HC_2H_3O_{2(aq)} \leftrightarrow H^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$
  $K_b \rightarrow C_2H_3O_2^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HC_2H_3O_{2(aq)} + OH^-{}_{(aq)}$
  $K_w \rightarrow H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^-{}_{(aq)}$

  $K_w = 1.0 \times 10^{-14}$ (already known)
  $K_a = 1.8 \times 10^{-5}$ (look up K_a 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
$HC_2H_3O_{2(aq)} \leftrightarrow H^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$ $K_a = 1.8 \times 10^{-5}$ (look up K_a for acetic acid)
$H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^-{}_{(aq)}$ $K_w = 1.0 \times 10^{-14}$ (already known)

Sources of H^+ are acetic acid and water, but based on the K values, it is clear that almost all the 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 H^+ comes from acetic acid.

	$HC_2H_3O_{2(aq)}$	$\leftrightarrow$	$H^+_{(aq)}$	+	$C_2H_3O_2^-{}_{(aq)}$
I	0.10		0		0
C	–x		+x		+x
E	0.10–x		x		x

$$K_a = \frac{[H^+{}_{(aq)}][C_2H_3O_2^-{}_{(aq)}]}{[HC_2H_3O_{2(aq)}]} = \frac{[x][x]}{[0.10 - x]} = \frac{[x]^2}{[0.10 - x]} = 1.8 \times 10^{-5}$$

use quadratic or approximate using 100 rule

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

$$K_a = \frac{[H^+{}_{(aq)}][C_2H_3O_2^-{}_{(aq)}]}{[HC_2H_3O_{2(aq)}]} = \frac{[x][x]}{[0.10 - x]} = \frac{[x]^2}{[0.10]} = 1.8 \times 10^{-5}$$

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

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

x = $[H^+_{(aq)}]$ = 1.3×10^{-3} mol/L
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 hypochlorus acid solution and find it to be 4.23. What is the K_a for $HOCl_{(aq)}$?

pH = 4.23
$[H^+_{(aq)}] = 10^{-pH} = 10^{-4.23} = 5.9\times10^{-5}$ 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…

$HOCl_{(aq} \leftrightarrow H^+_{(aq)} + OCl^-_{(aq)}$

$$K_a = \frac{[H^+_{(aq)}][OCl^-_{(aq)}]}{[HOCl_{(aq)}]} = \frac{[5.9\times10^{-5}][5.9\times10^{-5}]}{[0.10]} = 3.5\times10^{-8}$$

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 1.7×10^{-6}

$N_2H_{4(aq)} + H_2O_{(l)} \leftrightarrow N_2H_5^+{}_{(aq)} + OH^-_{(aq)}$ $K_b=1.7\times10^{-6}$
$H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^-_{(aq)}$ $K_w = 1.0 \times 10^{-14}$

Most OH^- comes from hydrazine since the constant is so much bigger. We can ignore the OH^- from water. We can also ignore the influence of $N_2H_5^+$ since it is a weak conjugate acid.

$$K_b = \frac{[N_2H_5{}^+{}_{(aq)}][OH^-{}_{(aq)}]}{[N_2H_{4(aq)}]}$$ *we need concentrations*

	$N_2H_{4(aq)}$	+	$H_2O_{(l)}$	$\leftrightarrow$	$N_2H_5^+{}_{(aq)}$	+	$OH^-{}_{(aq)}$
I	0.100		*		0		0
C	-x		*		+x		+x
E	0.100-x		*		x		x

$$K_b = \frac{[N_2H_5{}^+{}_{(aq)}][OH^-{}_{(aq)}]}{[N_2H_{4(aq)}]} = \frac{x^2}{0.100 - x} = 1.7 \times 10^{-6}$$

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

$[OH^-{}_{(aq)}] = 4.11 \times 10^{-4}$ mol/L
pOH = $-\log[OH^+{}_{(aq)}] = -\log[4.11 \times 10^{-4}] = 3.38$
pH = pK_w – 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: $K_{a1} > K_{a2} > K_{a3} > \ldots$
- 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, $H_3PO_{4(aq)}$
  (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 H^+ comes from the first ionization.

  $H_3PO_{4(aq)} \leftrightarrow H^+_{(aq)} + H_2PO_4^-{}_{(aq)}$ $K_{a1} = 7.1 \times 10^{-3}$
  $H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^-{}_{(aq)}$ $K_w = 1.0 \times 10^{-14}$

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

	$H_3PO_{4(aq)}$	$\leftrightarrow$	$H^+_{(aq)}$	+	$H_2PO_4^-{}_{(aq)}$
I	1.00	0		0	
C	-x	+x		+x	
E	1.00-x	x		x	

$$K_{a1} = \frac{[H^+_{(aq)}][H_2PO_4^-{}_{(aq)}]}{[H_3PO_{4(aq)}]} = 7.1 \times 10^{-3} = \frac{(x)(x)}{(1.00 - x)} = \frac{x^2}{1.00 - x}$$

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

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

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

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

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

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E.g.

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