CHEM 2
Problem Set Ch.16

Key Begins on page 3.

1. A 0.0560 g quantity of acetic acid is dissolved in enough water to make 50.0 mL of solution. Calculate the concentrations of H^+, $C_2H_3O_2^-$, and $HC_2H_3O_2$ at equilibrium. (K_a for acetic acid = 1.8×10^{-5}.)

2. Use NH_3 and its conjugate acid NH_4^+ to derive the relationship between K_a and K_b.

3. Calculate the pH for a 0.050 *M* pyridine solution.

4. What is the original molarity of a solution of ammonia whose pH is 11.22?

5. Calculate the concentrations of H^+, HCO_3^-, and CO_3^{2-} in a 0.025 *M* H_2CO_3 solution.

6. Predict whether a water solution of each of the following salts will be acidic, basic, or neutral.

KF,	$NaNO_3$,
NH_4NO_2,	$MgSO_4$,
KCN,	$NaC_7H_5O_2$,
RbI,	Na_2CO_3,
$CaCl_2$,	$KHCO_2$

7. Calculate the pH of a 0.36 *M* $NaC_2H_3O_2$ solution.

8. Determine the hydrogen ion and acetate ion concentrations in a 0.100 *M* $HC_2H_3O_2$ solution and (b) the concentrations of the same ions in a solution that is 0.100 *M* in both $HC_2H_3O_2$ and HCl.

9. (a) Calculate the pH of the 0.20 *M* NH_3/0.20 *M* NH_4Cl buffer.

(b) What is the pH of the buffer after the addition of 10.0 mL of 0.10 *M* HCl to 65.0 mL of the buffer.

10. If 25.0 mL of 0.100 *M* $HC_2H_3O_2$ is titrated with 0.100 *M* NaOH, what is the pH
(a) after 2.00 mL of 0.100 *M* NaOH has been added?

(b) after 25.00 mL of 0.100 *M* NaOH has been added?

(c) after 40.00 mL of 0.100 *M* NaOH has been added?

1. THE INITIAL CONCENTRATION OF ACETIC ACID ($HC_2H_3O_2$) IS:

$$\frac{0.0560\,g\left(\frac{1\,mol}{60\,g}\right)}{0.050\,L} = 0.0187\,M$$

SO:

$$HC_2H_3O_2 \rightleftharpoons H^{+} + C_2H_3O_2^{-1}$$

	$HC_2H_3O_2$	H^+	$C_2H_3O_2^{-1}$
INITIAL	0.0187	0	0
CHANGE	$-x$	$+x$	$+x$
EQUIL.	$0.0187 - x$	x	x

$$K_a = \frac{[H^+][C_2H_3O_2^{-1}]}{[HC_2H_3O_2]}$$

$$1.8\times10^{-5} = \frac{x^2}{(0.0187-x)} \quad \text{(IGNORE)} \qquad x = 5.8\times10^{-4}\,M$$

$$[H^+] = [C_2H_3O_2^{-1}] = 5.8\times10^{-4}\,M$$
$$[HC_2H_3O_2] = 0.0187 - 5.8\times10^{-4} = 1.81\times10^{-2}\,M$$

2.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$
$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$K_a \times K_b = \frac{\cancel{[NH_3]}[H_3O^+]}{\cancel{[NH_4^+]}} \times \frac{\cancel{[NH_4^+]}[OH^-]}{\cancel{[NH_3]}} = [H_3O^+][OH^-] = K_w$$

SO

$$K_a \times K_b = K_w$$

(3.) $C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^{\oplus} + OH^{\ominus}$ $(K_b = 1.4 \times 10^{-9})$

	C_5H_5N		$C_5H_5NH^{\oplus}$	$OH^{\ominus}$
START	0.050		0	0
CHANGE	$-x$		$+x$	$+x$
EQUIL.	$0.050 - x$		x	x

$$1.4 \times 10^{-9} = \frac{(x)(x)}{(.050 - x)}$$ ← IGNORE

$x = [OH^-] = 8.4 \times 10^{-6}$ M

pOH = 5.08

pH = 8.92

(4.) IF pH = 11.22 THEN pOH = 2.78 $\Rightarrow$ $[OH^-] = 1.7 \times 10^{-3}$ M = "x"

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

	NH_3	NH_4^+	OH^-
START	"y"	0	0
CHANGE	$-x$	$+x$	$+x$
EQUIL	$y - x$	x	x

LET "y" = ORIGINAL NH_3 CONC.

$$1.8 \times 10^{-5} = \frac{(1.7 \times 10^{-3})(1.7 \times 10^{-3})}{(y - 1.73 \times 10^{-3})}$$ ← IGNORE

↑ K_b FOR NH_3

y = 0.153 M

5. $H_2CO_3 \rightleftharpoons H^{\oplus} + HCO_3^{-1}$ $\quad Ka_1 = 4.3 \times 10^{-7}$

	H_2CO_3	$H^{\oplus}$	HCO_3^{-1}
START	0.025	0	0
CHANGE	$-x$	$+x$	$+x$
EQUIL	$0.025 - x$	x	x

$$4.3 \times 10^{-7} = \frac{(x)(x)}{(.025 - x)}$$ ← IGNORE

$x = 1.1 \times 10^{-4}$

SO

$$[H^+] = [HCO_3^-] = 1.1 \times 10^{-4} \text{ M}$$

NOW FOR THE 2nd H^+

$HCO_3^- \rightleftharpoons H^{\oplus} + CO_3^{-2}$ $\quad Ka_2 = 4.8 \times 10^{-11}$

	HCO_3^-	$H^{\oplus}$	CO_3^{-2}
START	1.1×10^{-4}	1.1×10^{-4}	0
CHANGE	$-x$	$+x$	$+x$
EQUIL.	$1.1 \times 10^{-4} - x$	$1.1 \times 10^{-4} + x$	x

$$4.8 \times 10^{-11} = \frac{(1.1 \times 10^{-4} + x)(x)}{(1.1 \times 10^{-4} - x)}$$ ← IGNORE (both)

$x = 4.8 \times 10^{-11}$

SO

$$[CO_3^{-2}] = 4.8 \times 10^{-11}$$

NOTE: FOR DIPROTIC ACIDS SUCH AS H_2A, $[A^{-2}]$ ALWAYS = Ka_2

6. KF (BASIC) $F^{-1} + H_2O \rightleftarrows HF + OH^{-1}$

NH_4NO_2 (ACIDIC) $NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$ $K_a = 5.5 \times 10^{-10}$

$NO_2^{-1} + H_2O \rightleftarrows HNO_2 + OH^{-1}$ $K_b = 2.2 \times 10^{-11}$

KCN (BASIC) $CN^{-1} + H_2O \rightleftarrows HCN + OH^{-1}$

RbI (NEUTRAL) BOTH ARE CONJUGATES OF STRONG electrolytes

$CaCl_2$ (NEUTRAL) EBBING & I DISAGREE ON WHETHER $Ca(OH)_2$ IS STRONG .... HE SAYS YES SO THIS SALT WOULD BE NEUTRAL.

$NaNO_3$ (NEUTRAL) BOTH IONS ARE CONJUGATES OF STRONG ELECTROLYTES

$MgSO_4$ (BASIC) $Mg^{+2} + 2H_2O \rightleftarrows Mg(OH)_2 + 2H^{\oplus}$

$SO_4^{-2} + H_2O \rightarrow$ N.R.

$NaC_7H_3O_2$ (BASIC) $Na^+ + H_2O \rightarrow$ N.R.

$C_7H_3O_2 + H_2O \rightarrow HC_7H_3O_2 + OH^-$

Na_2CO_3 (BASIC) $Na^+ + H_2O \rightarrow$ N.R.

$CO_3^{-2} + H_2O \rightarrow HCO_3^{-1} + OH^-$

$KHCO_3$ (BASIC) $K^+ + H_2O \rightarrow$ N.R.

$HCO_3^{-1} + H_2O \rightarrow H_2CO_3 + OH^-$

(7.) K_b FOR $C_2H_3O_2^-$ $= \frac{K_w}{K_a\ HC_2H_3O_2} = \frac{1\times10^{-14}}{1.7\times10^{-5}} = 5.9\times10^{-10}$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

	$C_2H_3O_2^-$		$HC_2H_3O_2$	OH^-
START	0.36		0	0
CHANGE	$-x$		$+x$	$+x$
EQUIL	$0.36-x$		x	x

$$5.9\times10^{-10} = \frac{(x)(x)}{(0.36-x)}$$ ← IGNORE

$x = [OH^-] = 1.5\times10^{-5}\ M$

$pOH = 4.84$

$\boxed{pH = 9.16}$

(8.) a)

$$HC_2H_3O_2 \rightleftharpoons H^{\oplus} + C_2H_3O_2^{(-1)}$$

	$HC_2H_3O_2$	$H^{\oplus}$	$C_2H_3O_2^{(-1)}$
START	0.100	0	0
CHANGE	$-x$	$+x$	$+x$
EQUIL.	$0.100-x$	x	x

$$1.7\times10^{-5} = \frac{(x)(x)}{(0.100-x)}$$ ← IGNORE

$x = 1.3\times10^{-3}\ M$

$[H^+] = [C_2H_3O_2^{-1}] = 1.3\times10^{-3}\ M$

b)

$$HC_2H_3O_2 \rightleftharpoons H^{\oplus} + C_2H_3O_2^{(-1)}$$

	$HC_2H_3O_2$	$H^{\oplus}$	$C_2H_3O_2^{(-1)}$
START	0.100	0.100	0
CHANGE	$-x$	$+x$	$+x$
EQUIL.	$0.100-x$	$0.100+x$	x

$$1.7\times10^{-5} = \frac{(0.1+x)(x)}{(0.1-x)}$$ ← IGNORE (0.1+x), IGNORE (0.1−x)

$x = 1.7\times10^{-5}$

$[H^+] = 0.100 + 1.7\times10^{-5} \simeq 0.100\ M$

$[C_2H_3O_2^{-1}] = 1.7\times10^{-5}\ M$

(9.) a)

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

$$pH = -\log(5.6\times10^{-10}) + \log\left(\frac{0.20}{0.20}\right)$$

$$\boxed{pH = 9.26}$$

NOTE: K_a FOR NH_4^+

$$K_a = \frac{K_w}{K_b \text{ FOR } NH_3}$$

$$K_a = \frac{1\times10^{-14}}{1.8\times10^{-5}}$$

$$K_a = 5.6\times10^{-10}$$

b) ADDITION OF HCl WILL CONVERT NH_3 TO $NH_4^{\oplus}$

$(10.0\,mL)(0.10\,M) = 1$ mmol HCl

$(65.0\,mL)(0.20\,M) = 13.0$ mmol NH_3

$(65.0\,mL)(0.20\,M) = 13.0$ mmol NH_4^+

	NH_3	+ HCl	→ $NH_4^{\oplus}$	+ Cl^-	
START	13 mmol	1 mmol	13 mmol		
END	12 mmol	0	14 mmol	1 mmol	

NOW

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

$$pH = 9.26 + \log \frac{(0.160)}{(0.187)}$$

$$\boxed{pH = 9.19}$$

SO_3 NEW CONC.

$$[NH_3] = \frac{13\text{ mmol}}{75\,mL} = 0.160\,M$$

$$[NH_4^+] = \frac{14\text{ mmol}}{75\,mL} = 0.187\,\underline{M}$$

(10.) a) $(25.0\,mL)(0.1\,\underline{M}) = 2.5\,mmol\ HC_2H_3O_2$ INITIALLY.

ADDITION OF $(2.0\,mL)(0.100\,\underline{M}\ NaOH) = 0.20\,mmol\ OH^-$

SO,

$$HC_2H_3O_2 + NaOH \longrightarrow NaC_2H_3O_2 + H_2O$$

	$HC_2H_3O_2$	$NaOH$	$NaC_2H_3O_2$	H_2O
START	2.5 mmol	0.2 mmol	0	0
END	2.3 mmol	0	0.2 mmol	0.2 mmol

SO, NEW INITIAL CONCENTRATIONS

$$[HC_2H_3O_2] = \frac{2.3\,mmol}{27\,mL} = 0.085\,\underline{M}\ HC_2H_3O_2$$

$$[C_2H_3O_2^{-1}] = \frac{0.2\,mmol}{27\,mL} = 0.0074\,M\ C_2H_3O_2^{-1}$$

$$pH = pKa + \log\frac{[C_2H_3O_2^{-1}]}{[HC_2H_3O_2]}$$

$$pH = -\log(1.7\times10^{-5}) + \log\frac{(0.0074)}{(.085)}$$

$$pH = 3.71.$$

b) $25\,mL$ OF $0.1\,\underline{M}\ NaOH = 2.5\,mmol\ OH^-$

SO, $HC_2H_3O_2 + OH^- \longrightarrow C_2H_3O_2^{-1} + H_2O$

	$HC_2H_3O_2$	OH^-	$C_2H_3O_2^{-1}$	H_2O
START	2.5 mmol	2.5 mmol	0	0
END	0	0	2.5 mmol	2.5 mmol

SO ALL THAT'S LEFT HERE AT EQ.PT IS $[C_2H_3O_2^{-1}] = \frac{2.5\,mmol}{50\,mL} = 0.05\,\underline{M}$

$$C_2H_3O_2^{-1} + H_2O \longrightarrow HC_2H_3O_2 + OH^{-1} \qquad K_b = 5.9\times10^{-10}$$

	$C_2H_3O_2^{-1}$		$HC_2H_3O_2$	OH^{-1}	
START	0.05		0	0	$5.9\times10^{-10} = \frac{(x)(x)}{(.05-x)}$
CHANGE	$-x$		$+x$	$+x$	
EQUIL	$0.05-x$		x	x	$x = [OH^-] = 5.4\times10^{-6}$

$pOH = 5.27$ $\quad pH = 8.73$

c) ONCE 40.0 mL OF NaOH IS ADDED, YOU'RE PAST THE EQUIV. POINT AND HAVE ONLY EXCESS NaOH AND $C_2H_3O_2^{-1}$.

	$HC_2H_3O_2$	+ OH^-	⟶ $C_2H_3O_2^{-1}$	+ H_2O
START	2.5 mmol	4.0 mmoles	0	0
END	0	1.5 mmoles	2.5 mmoles (0.038 M)	2.5 mmoles

$$[OH^-] = \frac{1.5 \text{ mmoles}}{65 \text{ mL}} = 0.023 \text{ M } OH^- \qquad pOH = 1.04$$

$$\boxed{pH = 12.36}$$

WHAT ABOUT ANY EXTRA OH^- PRODUCED BY THE HYDROLYSIS OF $C_2H_3O_2^{-1}$? LET'S CHECK.

$$C_2H_3O_2^{-1} + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \quad (K_b = 5.9 \times 10^{-10})$$

	$C_2H_3O_2^{-1}$	$HC_2H_3O_2$	OH^-
START	0.038 M	0	0.023
CHANGE	−X	+X	+X
EQUIL.	0.038 − X	X	0.023 + X

$$5.9 \times 10^{-10} = \frac{(X)(0.023 + X)}{(0.038 - X)} \simeq \frac{(X)(0.023)}{(0.038)}$$

(0.023 + X: IGNORE; 0.038 − X: IGNORE)

$$X = 9.7 \times 10^{-10} \quad (\text{CONTRIBUTION TO } OH^- \text{ FROM HYDROLYSIS OF } C_2H_3O_2^{-1})$$

$$\text{SO } [OH^-] = 0.023 + 9.7 \times 10^{-10} \simeq 0.023 \text{ M}$$ SAME AS ABOVE

$$\boxed{pH = 12.36}$$