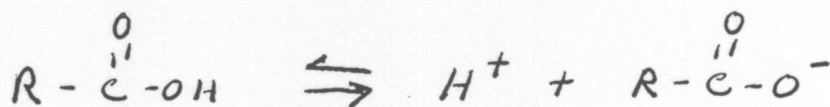


ACID-BASE EQUILIBRIA

THE CLASSIC WEAK ACID IS ACETIC ACID $\text{HC}_2\text{H}_3\text{O}_2$

LIKE ALL ORGANIC ACIDS IT CONTAINS THE

CARBOXYL GROUP COOH



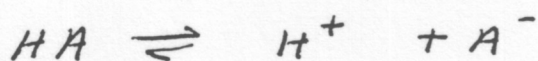
WHERE R STANDS
FOR ANY GROUP
OF ATOMS

A CARBOXYLIC ACID

CARBOXYLATE ANION

K FOR THE FORWARD REACTION IS 1.7×10^{-5}

THE GENERAL REACTION IS EXPRESSED THIS WAY



ACID \rightleftharpoons PROTON + ANION

ACID \rightleftharpoons PROTON + CONJUGATE BASE

K FOR THIS REACTION IS CALLED K_a , ACID-IONIZATION CONSTANT

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

K_a GIVES A MEASURE OF HOW MUCH IONIZATION OCCURS

CALLED THE DEGREE OF IONIZATION OR % IONIZATION

THE MAIN TYPE OF PROBLEM IN THIS CHAPTER IS CALCULATING

K_a , pH, DEGREE OF IONIZATION AND % IONIZATION

EXAMPLE:

A WEAK ACID IS DISSOLVED IN H_2O AT A CONCENTRATION OF 0.012 M. THE pH OF THE SOLUTION IS 3.39.

WHAT IS K_a ?

WHAT IS THE % IONIZATION OF THE ACID?

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

	[HA]	[H ⁺]	[A ⁻]
STARTING	0.012M	≈ 0	0
CHANGE	-x	+x	+x
EQUILIBRIUM	0.012-x	x	x

SUBSTITUTE IN THE EQUATION FOR K_a

$$K_a = \frac{x^2}{0.012-x}$$

THE pH IS GIVEN 3.39, WHAT IS [H⁺] (x)

$$[H^+] = \text{ANTILOG}^{-3.39} = 4.1 \times 10^{-4} \text{ OR } .00041$$

(SUBSTITUTE THIS VALUE

$$K_a = \frac{(4.1 \times 10^{-4})^2}{0.012 - 0.00041} = \frac{16.8 \times 10^{-8}}{0.01159} = 1.4 \times 10^{-5} = K_a$$

DEGREE OF IONIZATION IS DEFINED AS $\frac{[H^+]}{[HA]} = \frac{4 \times 10^{-4}}{1.2 \times 10^{-2}} =$

$$3.4 \times 10^{-2} \approx 3.4\%$$

A SIMPLIFYING ASSUMPTION

SINCE IONIZATION OF A WEAK ACID IS ONLY A PERCENT OR SO,

[HA] IS UNAFFECTED BY $HA \rightarrow H^+ + A^-$

SO, FOR A 0.1M WEAK ACID WITH $K_a = 1.4 \times 10^{-5}$ CALCULATE pH, % IONIZATION

	[HA]	[H ⁺]	[A ⁻]
INITIAL	0.1	0	0
CHANGE	0.1-x	x	x
EQUIL	0.1-x	x	x

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$1.4 \times 10^{-5} = \frac{x^2}{0.1-x} \quad \text{SIMPLIFY} \quad 1.4 \times 10^{-5} = \frac{x^2}{0.1} \quad x^2 = 1.4 \times 10^{-6} \quad x = 1.2 \times 10^{-3}$$

INITIAL [HA] 0.1M ...

AFTER SIMPLIFYING, YOU MUST CHECK IF IT WAS REASONABLE.

(AN ERROR OF LESS THAN 5% WILL OCCUR IF: $\frac{[HA]}{K_a} = 100$ OR MORE

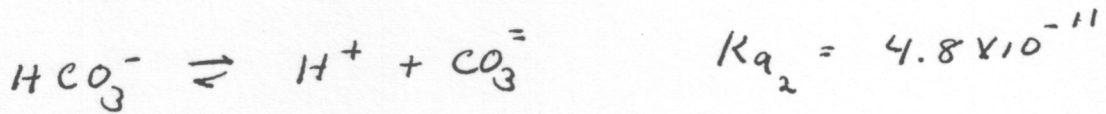
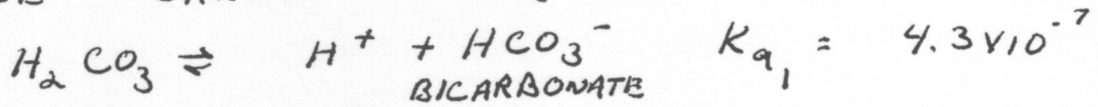
IF THE SIMPLIFYING ASSUMPTION IS NOT VALID

THE PROBLEM MUST BE SOLVED USING THE

QUADRATIC FORMULA

POLY PROTIC ACIDS HAVE MORE THAN ONE IONIZABLE H

FOR EXAMPLE CARBONIC ACID (FORMED FROM H_2O AND CO_2)



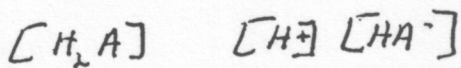
IN GENERAL, THE SECOND IONIZATION CONSTANT WILL BE MUCH SMALLER THAN THE FIRST. AND THE THIRD K_{a3} WILL BE MUCH SMALLER THAN THE SECOND.

CALCULATING CONCENTRATIONS WITH POLY PROTIC ACIDS

WHAT IS THE pH OF A 0.10M SOLUTION OF A POLY PROTIC ACID (DIPROTIC)? CALCULATE THE CONCENTRATIONS OF ALL SPECIES

IN THE SOLUTION. $K_{a1} = 7.9 \times 10^{-5}$ $K_{a2} = 1.6 \times 10^{-12}$

CONSIDERING THE FIRST IONIZATION



$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = 7.9 \times 10^{-5}$$

$$7.9 \times 10^{-5} = \frac{x^2}{0.10}$$

0.10 M

$2.8 \times 10^{-3} M$

$2.8 \times 10^{-3} M$

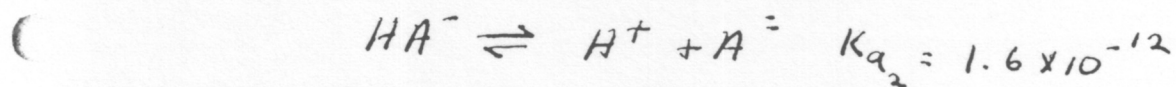
$$x^2 = 7.9 \times 10^{-6}$$

$$x = 2.8 \times 10^{-3}$$

$$pH = -\log [H^+] = -\log (2.8 \times 10^{-3}) = 2.55$$

DIPROTIC ACID CALCULATION CONTINUED

LOOKING AT THE SECOND IONIZATION



INITIAL 0.0028 0.0028 0

CHANGE $-x$ $+x$ $+x$ EQUILIBRIUM $0.0028-x$ $0.0028+x$ x

$$K_{a_2} = 1.6 \times 10^{-12} = \frac{(0.0028+x)x}{0.0028-x} \quad \text{Assume } x \ll 0.0028$$

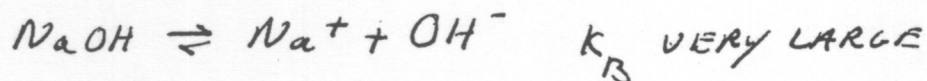
$$K_{a_2} = \frac{0.0028}{0.0028} x \quad x = K_{a_2} = 1.6 \times 10^{-12}$$

THE CONCENTRATION OF THE A^{2-} ION = K_{a_2}

STRONG BASES

STRONG BASES ARE TREATED THE SAME AS STRONG ACIDS

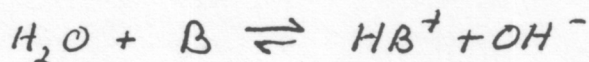
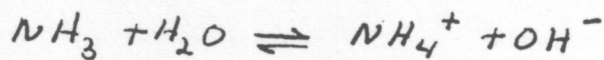
THAT IS, THEY IONIZE COMPLETELY



WEAK BASES

WEAK BASES ARE TREATED THE SAME AS WEAK ACIDS

$$K_B = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

THE CLASSIC WEAK BASE IS AMMONIA NH_3 

$$K_B = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

SO, WHAT IS THE pH OF A 0.1M NH_3 SOLUTION?

P_H OF A 0.10M NH₃ SOLUTION

	[NH ₃]	[NH ₄ ⁺]	[OH ⁻]
INITIAL	0.10	0	0
CHANGE	-x	+x	+x
EQUILIBRIUM	0.10-x	x	x

$$K_B = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.10-x} \quad \text{SIMPLIFY} \rightarrow = \frac{x^2}{0.1}$$

$$x^2 = 1.8 \times 10^{-6}$$

$$x = 1.3 \times 10^{-3} \quad \text{so } pOH = -\log 1.3 \times 10^{-3} = 2.89$$

$$pH + pOH = 14$$

$$pH = 14 - 2.89 = 11.11$$

ALTERNATIVELY

A 0.0015M SOLUTION OF A WEAK BASE GIVES A P_H OF 9.84. WHAT IS K_B

$$K_B = \frac{[BH^+][OH^-]}{[B]}$$

$$-\log [OH^-] = pOH \quad pOH = 14 - 9.84 = 4.16$$

$$-\log [OH^-] = 4.16$$

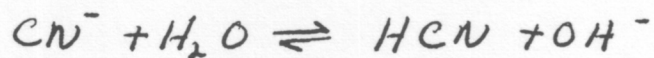
$$[OH^-] = 10^{-4.16} = 6.9 \times 10^{-5}$$

$$K_B = \frac{6.9 \times 10^{-5} \times 6.9 \times 10^{-5}}{1.5 \times 10^{-3}} = \frac{4.8 \times 10^{-9}}{1.5 \times 10^{-3}} = 3.2 \times 10^{-6} = K_B$$

ACID-BASE PROPERTIES OF SALT SOLUTIONS

SOME SALT IONS CAN ACT AS ACIDS OR BASES
 FOR EXAMPLE, A 0.1 M SOLUTION OF NaCN
 HAS A pH OF ABOUT 11

BECAUSE CN^- REACTS WITH H_2O TO PRODUCE OH^-

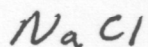


CN^- IS ACTING LIKE A BASE

THIS REACTION IS CALLED HYDROLYSIS

THERE ARE SIMPLE RULES FOR PREDICTING IF A SALT WILL
 BE ACIDIC OR BASIC

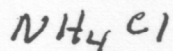
1) SALTS OF STRONG BASES AND STRONG ACIDS ARE NEUTRAL



2) SALTS OF STRONG BASE AND WEAK ACID ARE BASIC



3) SALTS OF WEAK BASE AND STRONG ACID ARE ACIDIC



4) SALTS OF WEAK BASE AND WEAK ACIDS:

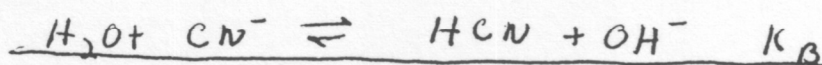
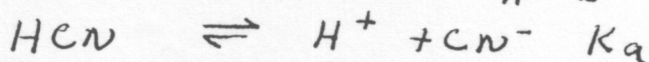
IF K_a IS LARGER THAN $K_b \rightarrow$ ACIDIC

IF K_b IS LARGER THAN $K_a \rightarrow$ BASIC

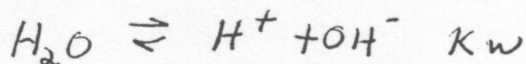
OBTAINING K_b FROM K_a OR VICE VERSA

FIND K_b FOR CN^- IF $K_a = (\text{FOR HCN}) = 4.9 \times 10^{-10}$

K_a and K_b ARE RELATED $K_a K_b = K_w$



SUM

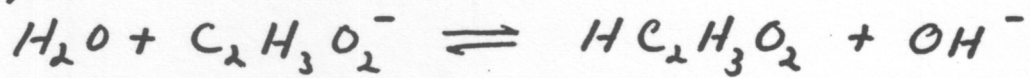


$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{4.9 \times 10^{-10}} = 2 \times 10^{-5}$$

SALT SOLUTIONS, HYDROLYSIS CONTINUED

WHAT IS THE pH OF A SOLUTION CONTAINING 0.01 M $\text{NaC}_2\text{H}_3\text{O}_2$ (SODIUM ACETATE)?

$\text{NaC}_2\text{H}_3\text{O}_2$ IS THE SALT OF A WEAK ACID. IN SOLUTION, Na^+ AND $\text{C}_2\text{H}_3\text{O}_2^-$ IONS ARE FORMED. Na^+ CAUSES NO HYDROLYSIS, BUT $\text{C}_2\text{H}_3\text{O}_2^-$ WILL HYDROLYSE H_2O



TO FIND THE pH, YOU NEED K_B FOR ACETATE ION

K_a FOR ACETIC ACID IS 1.7×10^{-5}

SINCE $K_a K_B = K_w$, $K_B = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.9 \times 10^{-10}$

NOW SUBSTITUTE:

$$K_B = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} \quad \text{SO } 5.9 \times 10^{-10} = \frac{x^2}{0.01 - x}$$

SIMPLIFYING, $x^2 = 5.9 \times 10^{-12}$
 $x = 2.4 \times 10^{-6} = [\text{OH}^-]$

AND $\text{pH} = 14.00 - \text{pOH}$

$$= 14.00 + \log 2.4 \times 10^{-6} = 14.00$$

$$\text{pH} = 8.38$$

$$\begin{array}{r} - 5.62 \\ \hline 8.38 \end{array}$$

CHECK THAT x CAN BE NEGLECTED IN THE $0.01 - x$ TERM

$$x = 2.4 \times 10^{-6} \quad 0.01 - 2.4 \times 10^{-6} = 0.01 \text{ TO WITHIN}$$

LESS THAN 1%

THE COMMON-ION EFFECT

AN EXAMPLE OF LECHATELIER'S PRINCIPLE

THE COMMON-ION EFFECT IS THE SHIFT IN AN IONIC EQUILIBRIUM CAUSED BY THE ADDITION OF A SOLUTE THAT PROVIDES AN ION THAT TAKES PART IN THE EQUILIBRIUM

FOR EXAMPLE, SUPPOSE WE ADD 0.01 M HCl TO A SOLUTION OF HA OF 0.10 M CONCENTRATION. IF HA HAS A K_a OF 1.7×10^{-5} ,

THIS SOLUTION IS ABOUT 1.3% IONIZED. WHAT WILL HAPPEN TO THE DEGREE OF IONIZATION AFTER THE ADDITION OF ENOUGH HCl TO MAKE [HCl] 0.01 M?

	$[HA]$	\rightleftharpoons	$[H^+] + [A^-]$
INITIAL	0.10		0.010 0
CHANGE	-x		+x +x
EQUILIBRIUM	0.10 - x		0.010 + x x

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(0.01 + x)(x)}{0.10 - x} = 1.7 \times 10^{-5}$$

ASSUME x IS SMALL COMPARED TO 0.01

$$\text{SO } 0.01 - x = 0.01$$

$$0.10 - x = 0.10$$

$$\text{THEN } \frac{0.01x}{0.10} = 1.7 \times 10^{-5} \rightarrow x = 1.7 \times 10^{-5} \left(\frac{0.10}{0.01} \right)$$

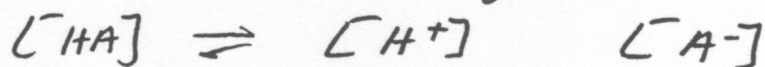
$$x = 1.7 \times 10^{-4} \quad \text{AND DEGREE OF IONIZATION} \\ = \frac{x}{0.10} = 0.17\%$$

% IONIZATION IS MUCH LESS BECAUSE ADDITION OF HCl REPPRESSES IONIZATION OFF HA

SOLUTIONS OF AN ACID AND ITS CONJUGATE BASE

A SOLUTION IS PREPARED TO BE 0.10 M HA AND 0.20 M A^- . WHAT IS THE pH OF THIS SOLUTION IF $K_a = 5 \times 10^{-4}$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$



INITIAL	0.10	0	0.20
CHANGE	-x	+x	+x
EQUILIBRIUM	0.10-x	x	0.20+x

$$5 \times 10^{-4} = \frac{(0.20+x)x}{0.10-x} \quad \text{ASSUME } x \text{ IS SMALL}$$

$$5 \times 10^{-4} = \frac{x(.20)}{.10} \rightarrow x = 5 \times 10^{-4} \times \frac{0.10}{0.20} = 2.5 \times 10^{-4}$$

$$[H^+] = 2.5 \times 10^{-4} \quad \text{pH} = -\log(2.5 \times 10^{-4}) = 4 - 0.398 = 3.6$$

FOR COMPARISON, THE pH OF 0.10 M HA = 2.15

THE pH OF THE PURE HA SOLUTION (0.10 M) IS LOWER BECAUSE THE A^- ION REPRESSES THE IONIZATION OF HA IN THE OTHER SOLUTION (0.2 M A^-) BY THE COMMON ION EFFECT THIS IS AN EXAMPLE OF A BUFFER SOLUTION

BUFFERS

A BUFFER IS A SOLUTION WITH AN ABILITY TO RESIST pH CHANGE WHEN ACID OR BASE IS ADDED
 BUFFERS ARE MOST IMPORTANT IN BIOLOGICAL FLUIDS SUCH AS BLOOD, CYTOPLASM, LYMPH, ETC BECAUSE MOST BIOCHEMICAL REACTIONS REQUIRE pH CONTROL

BUFFERS ARE CHARACTERIZED BY A pH AND A BUFFER CAPACITY

A BUFFER IS USUALLY MADE FROM A WEAK ACID AND ITS CONJUGATE BASE - OR A WEAK BASE AND ITS CONJUGATE ACID. OFTEN IN A 1:1 RATIO

THE pH OF A BUFFER

A BUFFER IS PREPARED BY ADDING 60.0 mL OF 0.100 M NH₃ TO 40 mL OF 0.100 M NH₄Cl. WHAT IS THE pH

1) CALCULATE [B] [HB⁺]

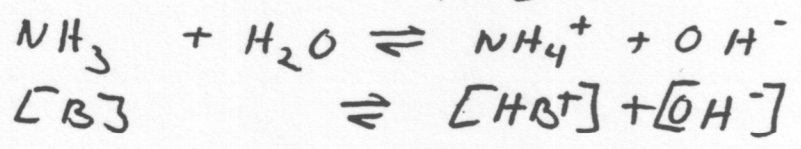
FOR NH₃ 0.060 L x 0.100 mol/L = 0.0060 moles NH₃

FOR NH₄Cl 0.040 L x 0.100 mol/L = 0.0040 moles NH₄Cl

TOTAL SOLUTION VOLUME IS 100 mL OR 0.1 L

SO [NH₃] = $\frac{0.0060 \text{ mol}}{0.100 \text{ L}}$ = 0.060 M NH₃

[NH₄Cl] = $\frac{0.0040 \text{ mol}}{0.100 \text{ L}}$ = 0.040 M NH₄Cl



INITIAL	0.060	0.040	0
CHANGE	-x	+x	+x
EQUILIBRIUM	0.060 - x	0.040 + x	x

$K_B = \frac{[HB^+][OH^-]}{[B]} = 1.8 \times 10^{-5}$ (TABLE 16.2)

$1.8 \times 10^{-5} = \frac{(0.040 + x)x}{0.060 - x}$ ASSUME X IS SMALL

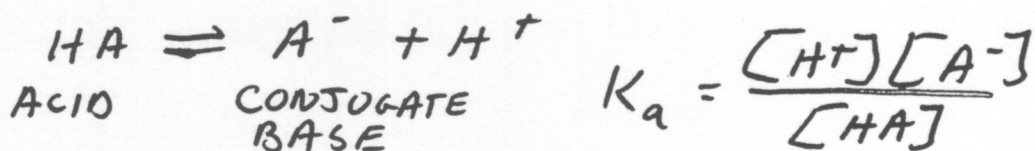
$1.8 \times 10^{-5} = \frac{0.040x}{0.060}$ $x = \frac{0.06}{0.04} \times 1.8 \times 10^{-5} = 2.7 \times 10^{-5}$

pH = 14.00 - log(2.7 x 10⁻⁵) = $\frac{14.00}{-4.57} = 9.43$ [OH⁻] = 2.7 x 10⁻⁵
[H⁺] = 3.7 x 10⁻¹⁰

THE HENDERSON-HASSELBALCH EQUATION

AN EQUATION WHICH RELATES THE pH OF A BUFFER TO THE CONCENTRATIONS OF CONJUGATE ACID AND BASE

FOR A WEAK ACID AND ITS CONJUGATE BASE



SOLVE FOR $[\text{H}^+]$

$$[\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

IF $[\text{HA}] = [\text{A}^-]$ (BUFFER PREPARED FROM EQUAL PARTS HA AND A^-)

$$[\text{H}^+] = K_a \times 1$$

NOW TAKE -LOG OF BOTH SIDES

$$-\text{Log} [\text{H}^+] = -\text{Log} K_a \times -\text{Log} \frac{[\text{HA}]}{[\text{A}^-]}$$

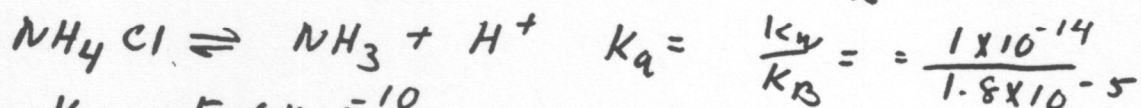
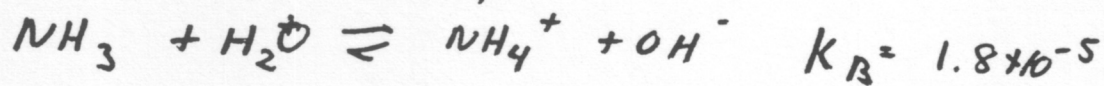
REWRITE

$$\text{pH} = \text{p}K_a - \text{Log} \frac{[\text{HA}]}{[\text{A}^-]}$$

THIS EQUATION REALLY SIMPLIFIES BUFFER CALCULATIONS.

CALCULATE THE pH OF A BUFFER CONTAINING

0.10 M NH_3 AND 0.20 M NH_4Cl



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

$$\text{p}K_a = 9.25$$

NOW USE H-H

$$\text{pH} = 9.25 + \text{Log} \frac{0.10}{0.20} = 8.95$$

NOTICE THAT $\text{pH} = \text{p}K_a$ WHEN $[\text{HA}] = [\text{A}^-]$...

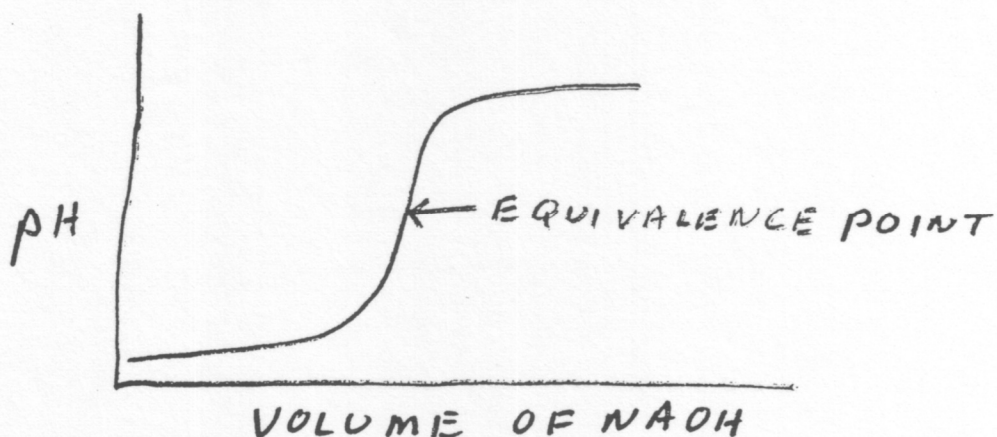
WE SAY THAT THE $\text{p}K_a$ IS THE pH AT HALF-TITRATION

TITRATION CURVES

ARE PLOTS OF THE pH OF A SOLUTION OF AN ACID (OR BASE) VS VOLUME OF ADDED BASE

THE pH OF THE SOLUTION RISES SLOWLY UNTIL NEAR THE EQUIVALENCE POINT. AT THIS POINT THE SOLUTION CONTAINS JUST AS MANY MOLES OF ACID AS IT DOES OF BASE

TITRATION CURVE



THE SPECIES PRESENT WILL BE THE CONJUGATE BASE IF AN ACID IS BEING TITRATED OR THE CONJUGATE ACID IF A BASE IS BEING TITRATED

SO THE EQUIVALENCE POINT WILL BE 7.0 IF A STRONG ACID TITRATES A STRONG BASE, BASIC IF A WEAK ACID IS TITRATED

(ONLY THE STRONG CONJUGATE BASE IS PRESENT) AND ACIDIC IF A WEAK ACID IS TITRATED

TITRATION CONTINUED

INDICATORS ARE SUBSTANCES WHICH CHANGE COLOR WITHIN A GIVEN pH RANGE

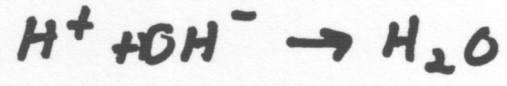
FIGURE 15.6 PG 655

THEY MAY BE USED TO INDICATE THE EQUIVALENCE POINT OR A pH METER MAY BE USED

EXAMPLE TITRATION CALCULATION

CALCULATE THE pH OF A SOLUTION IN WHICH 10.0 ML OF 0.100 M NaOH IS ADDED TO 25.00 ML OF 0.100 M HCl

THE REACTION OF A STRONG ACID WITH A STRONG BASE GOES TO COMPLETION



1) CALCULATE MOLAR AMOUNTS

MOLES OH- = 0.01 L x 0.10 M/L = 0.001 MOLES
MOLES H+ = 0.025 L x 0.10 M/L = 0.0025 MOLES

ALL THE OH- REACTS, LEAVING AN EXCESS OF H+

0.00250 MOLES H+
- 0.00100 MOLES OH-
0.0015 MOL H+ IN 0.035 L

0.0015 MOLE / 0.0350 L = 0.0429 M [H+]

pH = -log [H+] = 1.37