CHAPTER 3

Acid-Base Titrations and pH

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3.1 THE LAW OF MASS ACTION

Many chemical reactions are known in which the change produced during the reaction is complete and irreversible; for example,

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$$

The reaction is quantitative and the extremely insoluble barium sulfate is formed from virtually all the barium originally present.

Reactions also occur in which the change is neither complete nor irreversible. Under one set of circumstances, the reaction will proceed in one direction but, under different circumstances, it will proceed in the opposite direction. Reactions of this type are said to be *reversible* or balanced. The double arrow symbol $\rightleftharpoons$ or $\rightleftarrows$ is used to denote a reversible reaction instead of the more usual unidirectional arrow or the equals sign.

When a reversible reaction proceeds to a certain point at which all the products remain together in the system, a state of *equilibrium* is said to have been attained.

Reversible Reactions. Cadmium chloride solution reacts with hydrogen sulfide gas to form cadmium sulfide and hydrogen chloride:

$$CdCl_2 + H_2S \rightarrow CdS + 2HCl$$

Hydrochloric acid acts upon cadmium sulfide to form cadmium chloride and hydrogen sulfide:

$$CdS + 2HCl \rightarrow CdCl_2 + H_2S$$

The factor that determines the predominating reaction is the concentration of hydrogen chloride and of hydrogen sulfide. If both are present in reasonable amounts, the cadmium will be present partly as chloride and partly as sulfide. The above two equations can therefore be combined into a single reversible equation:

$$CdCl_2 + H_2S \rightleftharpoons CdS + 2HCl$$

Equations of this type do not indicate where the equilibrium lies—we cannot tell from the equation what percentage of the cadmium is present as chloride and what percentage is sulfide.

Equilibrium should be regarded as a dynamic state and not a static condition. At the point of equilibrium, the forward and reverse reactions should be regarded as proceeding at equal rates and not as proceeding to a certain point and then ceasing to change further.

In the synthesis of hydrogen iodide from hydrogen and gaseous iodine, the reactant molecules are pictured as moving at high speed in random directions (kinetic theory). To form a molecule of hydrogen iodide, a hydrogen molecule must collide and unite with an iodine molecule:

$$H_2 + I_2 \rightarrow 2HI$$

As more and more molecules of hydrogen iodide are formed, there is a greater chance of collision between them to give the reverse reaction:

$$2HI \rightarrow H_2 + I_2$$

At equilibrium, the number of hydrogen/iodine collisions will equal the number of hydrogen iodide/hydrogen iodide collisions, and again we see the equilibrium as dynamic rather than static. The frequency of intermolecular collisions will depend upon the concentration of the molecules; this is another way of saying that the *rate* at which a reaction occurs will depend upon the concentration of the reacting molecules.

The Law of Mass Action

Definition. The rate of a reaction at constant temperature is proportional to the products of the concentrations of each reacting substance.

In the case of a homogeneous reaction,

$$A + B \rightleftharpoons C + D,$$

the rate at which A and B will react together is proportional to the product of their concentrations; therefore,

$$v_1 = k_1[A][B] \quad \text{and} \quad v_2 = k_2[C][D]$$

where v_1 is the velocity of the forward reaction, v_2 is the velocity of the reverse reaction, [ ] is concentration in gram molecules per liter, and k_1 and k_2 are proportionality constants.

At equilibrium $v_1 = v_2$, therefore,

$$k_1[A][B] = k_2[C][D]$$

$$\frac{[C][D]}{[A][B]} = \frac{k_2}{k_1} = K$$

K is the *equilibrium constant.*

The final expression may be expressed in words: At equilibrium, the product of the concentrations of the substances on the right side of the equation (the resultants) divided by the product of the concentrations of the substances on the left side of the equation (the reactants) is constant at constant temperature.

A further generalization can be made for any homogeneous reversible reaction:

$$xA + yB + zC + \cdots \rightleftharpoons pD + qE + rF + \cdots$$

$$K = \frac{[D]^p[E]^q[F]^r \cdots}{[A]^x[B]^y[C]^z \cdots}$$

3.2 APPLICATION OF THE LAW OF MASS ACTION TO IONIC EQUILIBRIA

Since the charge carried by the ion of an electrolyte is relatively high, in concentrated solutions we would expect forces of attraction and repulsion to

interfere with the random movement of molecules. It may be assumed that the attractive forces are much smaller in dilute solutions and can be neglected for most purposes. On this basis, much information can be obtained by application of the law of mass action to dilute solutions of electrolytes.

A. ACIDS AND BASES

Earlier attempts to define acids and bases were based on their properties. The ability of acids to change the color of vegetable dyes and their sour taste were advanced at one time as definitive. The later discovery that all acids contained hydrogen gave the definition that an acid was a compound containing hydrogen which could be partially or completely replaced by a metal. An alternative form of this latter definition was that an acid was a compound containing hydrogen which could be replaced with sodium by treatment with sodium hydroxide, forming a *salt* and water. The definition of a salt therefore follows directly from the definition of an acid—a salt is a compound formed by replacement of hydrogen in an acid with a metal.

Bases were originally defined in terms of their soapy feeling on the skin and by their action on vegetable dyes. The discovery that they neutralized acids led to the definition that a base was a compound which reacted with an acid to form a salt and water. There were some exceptions to this, particularly with respect to ammonia and amines, which form salts only (that is, no water is obtained) with anhydrous acids.

Acids, bases, and salts were thus defined in terms of each other, and it was not possible to define one without implying a knowledge of the others. The properties of acids as a group are largely interrelated with the properties of bases as a group. Acids and bases are said to exhibit a *conjugate* relationship.

B. THE IONIC THEORY OF ACIDS AND BASES

According to the ionic theory, the only property common to all acids is that in solution they give rise to hydrogen ions. When absolutely pure, they are covalent compounds, but moisture always promotes the formation of hydrogen ions.

A base is a compound containing a hydroxyl group which is set free in solution as a hydroxyl ion. Any compound which does not contain the hydroxyl group but which can give rise to hydroxyl ions in solution is also classed as a base. For example,

$$\text{acids:} \qquad HA \rightleftharpoons H^+ + A^-$$
$$\text{bases:} \qquad BOH \rightleftharpoons B^+ + OH^-$$
$$B + H_2O \rightleftharpoons BH^+ + OH^-$$
$$\text{neutralization:} \qquad HA + BOH \rightleftharpoons BA + H_2O$$
$$\text{(salt)}$$

C. THE LOWRY-BRÖNSTED THEORY OF ACIDS AND BASES

Definitions: An acid is any chemical species which has a tendency to lose (donate) a proton. A base is any chemical species which has a tendency to gain (accept) a proton.

We can immediately appreciate that these are much broader definitions than any previously mentioned. By this definition, an acid may be an electrically neutral molecule (HCl, CH_3COOH, H_2O), a negatively charged ion ($H_2PO_4^-$, HSO_4^-), or a positively charged ion ($CH_3CH_2NH_3^+$, NH_4^-). A base may be either an electrically neutral molecule (NH_3, H_2O) or a negatively charged ion (Cl^-, CH_3COO^-).

The relationship between an acid and a base may therefore be stated:

$$A \rightleftharpoons H^+ + B$$

acid   proton   base

B is called the *conjugate base* of A; A is the *conjugate acid* of B. See Table 3.1 for examples.

TABLE 3.1

Acids				Conjugate bases
HCl	$\rightleftharpoons$	H^+	$+$	Cl^-
H_3PO_4	$\rightleftharpoons$	H^+	$+$	$H_2PO_4^-$
$H_2PO_4^-$	$\rightleftharpoons$	H^+	$+$	HPO_4^-
CH_3COOH	$\rightleftharpoons$	H^+	$+$	CH_3COO^-
$C_6H_5NH_3^+$	$\rightleftharpoons$	H^+	$+$	$C_6H_5NH_2$
NH_4^+	$\rightleftharpoons$	H^+	$+$	NH_3
H_2O	$\rightleftharpoons$	H^+	$+$	OH^-
H_3O^+	$\rightleftharpoons$	H^+	$+$	H_2O

It will be seen that some species, for example, $H_2PO_4^-$ and H_2O, can act as both acids and bases, depending upon conditions. A corollary to the Lowry-Brönsted definitions of acids and bases is that an acid only shows the properties of an acid when a base is present to accept a proton, and a base only shows the properties of a base when an acid is present to donate a proton.

D. THE DISSOCIATION OF WATER

After 40 distillations, water was found to retain a specific conductivity of 0.0384×10^{-6} mho. (Ordinary single distilled water has a specific conductivity of 5 to 10×10^{-6} mho.) It was evident that the conductivity of the very pure water was a physical property of water and was not due to dissolved impurities. Some water molecules must dissociate into hydrogen and hydroxyl ions:

$$H_2O \rightleftharpoons H^+ + OH^- \tag{3.1}$$

Since a hydrogen ion is too highly active to remain a separate entity, it attaches itself to an undissociated molecule:

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

where H_3O^+ is *the hydroxonium or hydronium ion.* The dissociation of water is therefore more correctly shown as

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

The shorter form of Eq. (3.1) is easier to write and is usually adopted for all general purposes connected with the subject.

Since only a very small number of ions are formed relative to the number of undissociated water molecules, the ions are regarded as being present at infinite dilution.

$$\Lambda_{\infty,H_2O} = \Lambda_{\infty,H^+} + \Lambda_{\infty,OH^-} = \frac{\text{specific conductivity}}{c}$$

where c is expressed in gram ions per liter. Therefore,

$$\frac{0.0384 \times 10^{-6}}{c} = 318 + 174 \qquad \text{(at 18°C)}$$

Thus we have

$$c = \frac{0.0384 \times 10^{-6}}{492} = 0.78 \times 10^{-7}$$

that is, pure water contains 0.78×10^{-7} gram ion of dissociated water per liter at 18°C.

Applying the law of mass action to the dissociation of water,

$$K = \frac{[H^+][OH^-]}{[H_2O]} \tag{3.2}$$

Since the term $[H_2O]$ is virtually constant for all practical considerations, Eq. (3.2) can be shortened to its accepted form,

$$K_w = [H^+][OH^-] \tag{3.3}$$

where K_w is the *water constant* or the *ionic product of water.* Since $[H^+] = [OH^-]$,

$$K_w = (0.78 \times 10^{-7})(0.78 \times 10^{-7}) \qquad \text{(at 18°C)}$$
$$= 0.6 \times 10^{-14}$$

K_w increases rapidly with rise in temperature, for example,

$$\text{at } 0°C: \quad K_w = 0.116 \times 10^{-14}$$
$$24°C: \quad K_w = 1.000 \times 10^{-14}$$
$$40°C: \quad K_w = 2.919 \times 10^{-14}$$

Since 24°C is very close to room temperature at most times of the year, the round figure of 1×10^{-14} is used universally in analytical work.

At 24°C, $[H^-] = [OH^-] = 1 \times 10^{-7}$. A value of 1×10^{-7} gram ion per liter for hydrogen and hydroxyl ion concentration is very low, but it cannot be ignored, because it is these ions which determine the properties of many aqueous solutions. All aqueous solutions contain *both* hydrogen ions and hydroxyl ions, even in strongly acidic or strongly basic solution. If we know the concentation of one ion, we can calculate the concentration of the other.

EXAMPLE 1: In a completely dissociated normal solution of an acid, $[H^-] = 1$ (a normal solution is defined as containing 1 gram ion of hydrogen per liter):

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{K_w}{1}$$

$$= 1 \times 10^{-14}$$

EXAMPLE 2: In completely dissociated decinormal alkali solution, $[OH^-] = 0.1$. Therefore,

$$[H^+] = \frac{1 \times 10^{-14}}{0.1}$$

$$= 1 \times 10^{-13}$$

E. THE HYDROGEN ION EXPONENT

To avoid the mathematically ponderous values used to express the concentrations of hydrogen and hydroxyl ions, the Danish scientist Sörensen developed the system whereby these ionic concentrations are represented by their negative logarithm to the base of ten. The symbols used for these negative logarithms are p_H and p_{OH}, but these are much more commonly changed to pH and pOH largely because of the relative ease with which they can be written, typed, or printed.

$$pH = -\log_{10}[H^+] \quad \text{and} \quad pOH = -\log_{10}[OH^-]$$

Therefore,

$$pH = \log \frac{1}{[H^+]} \quad \text{and} \quad pOH = \log \frac{1}{[OH^-]}$$

In pure water at 24°C,

$$[H^-] = 1 \times 10^{-7} \text{ gram ion per liter}$$

$$= 1 \times 10^{-7}N$$

$$pH = -\log 10^{-7} = 7$$

that is, a neutral solution should have a pH value of 7.

The major advantage of this method of Sörensen's is that all degrees of hydrogen ion concentration from fully dissociated normal acid solutions to fully dissociated normal base solutions can be represented on a scale from 0 to 14. This is particularly convenient for graphic work.

EXAMPLE 3: In a completely dissociated normal solution of an acid, $[H^+] = 1$.
Therefore,
$$pH = -\log 1 = 0$$

EXAMPLE 4: In a completely dissociated normal solution of a base, $[OH^-] = 1$. Thus,
$$[H^-] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{1} = 1 \times 10^{-14}$$
$$pH = -\log [1 \times 10^{-14}]$$
$$= 14$$

Alternatively, $[OH^-] = 1$ and pOH $= 0$. Since $[H^+][OH^-] = K_w$, we have
$$\log [H^-] + \log [OH^-] = \log K_w$$
$$-\log [H^-] - \log [OH^-] = -\log K_w$$
$$pH + pOH = pK_w$$

(using Sörensen's device to express K_w as a positive integer analogous to pH
and pOH). Therefore, $$pH = pK_w - pOH$$

In our example, pOH $= 0$, and so
$$pH = 14 - 0 = 14$$

All solutions with a pH value less than 7 are acidic, and all solutions with a
pH greater than 7 are basic or alkaline. As we go from pH $= 0$ upwards, we
pass from strongly acidic through weakly acidic to neutral at pH $= 7$, then
through weakly basic to strongly basic.

Note: (1) An increase in pH value means a decrease in the hydrogen ion
           concentration and hence a decrease in acidity (and vice versa).
       (2) A unit change in pH value means a tenfold change in hydrogen
           or hydroxyl ion concentration.

EXAMPLE 5: If the hydrogen ion concentration of an acid solution is 1×10^{-3},
calculate the pH:
$$[H^+] = 1 \times 10^{-3}$$
$$pH = -\log (1 \times 10^{-3}) = -(-3) = 3$$

EXAMPLE 6: Calculate the pH of a basic solution having a hydroxyl ion
concentration of 1×10^{-3}:
$$[OH^-] = 1 \times 10^{-3} \qquad pH = pK_w - pOH$$
$$pOH = 3 \qquad pH = 14 - 3 = 11$$

EXAMPLE 7: If the hydrogen ion concentration of a solution is 2×10^{-6},
calculate the pH:
$$pH = -\log (2 \times 10^{-6})$$
$$= -\log 2 - \log 10^{-6}$$
$$= -0.30 - (-6)$$
$$= 6 - 0.30$$
$$= 5.70$$

EXAMPLE 8: Calculate the pH of an acidic solution of hydrogen ion concentration 4.71×10^{-4}:

$$pH = -\log 4.71 \times 10^{-4}$$
$$= 4 - \log 4.71$$
$$= 4 - 0.67$$
$$= 3.33$$

EXAMPLE 9: A solution of sodium hydroxide has a hydroxyl ion concentration of 1.05×10^{-3}. Calculate the pH of the solution:

$$[OH^-] = 1.05 \times 10^{-3}$$
$$pOH = -\log 1.05 \times 10^{-3}$$
$$= 3 - \log 1.05$$
$$= 2.98$$
$$pH = 14 - 2.98$$
$$= 11.02$$

When the pH of a solution is given and we are asked to calculate the hydrogen ion concentration, the reverse process is applied.

EXAMPLE 10: If the pH of a solution is 5.3, calculate the hydrogen ion concentration:

$$pH = -\log [H^+]$$
$$5.3 = -\log [H^+]$$
$$\log [H^+] = -5.3$$
$$[H^+] = \text{the antilog of } -5.3$$
$$= \text{the antilog of } \bar{6}.7$$
$$= 5.01 \times 10^{-6}$$

EXAMPLE 11: Calculate the hydrogen ion concentration of a solution of pH 3.8:

$$[H^+] = \text{the antilog of } -3.8$$
$$= \text{the antilog of } \bar{4}.2$$
$$= 1.59 \times 10^{-4}$$

EXAMPLE 12: What is the hydroxyl ion concentration of a solution of pH 10.75? If pH = 10.75, pOH = 3.25, then

$$[OH^-] = \text{the antilog of } -3.25$$
$$= \text{the antilog of } \bar{4}.75$$
$$= 5.62 \times 10^{-4}$$

THE DISSOCIATION CONSTANTS OF ACIDS AND BASES

When a molecule of an acid dissociates in solution, it yields a hydrogen ion and an anion. The extent to which a given acid dissociates is governed by

temperature and by concentration. At a fixed temperature, the degree of dissociation will depend only upon concentration, and we can apply the law of mass action to the equilibrium.

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (3.4)$$

In this equilibrium, K_a is known as the *dissociation constant* of the acid HA. The dissociation constant of a base BOH can be found in the same manner:

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad (3.5)$$

The law of mass action can also be applied to dibasic acids and diacidic bases, where the hydrogen and hydroxyl ions are released in successive steps. For a dibasic acid H_2A,

$$H_2A \rightleftharpoons H^+ + HA^-$$
$$HA^- \rightleftharpoons H^+ + A^-$$

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} \quad \text{and} \quad K_2 = \frac{[H^+][A^-]}{[HA^-]}$$

For example, for oxalic acid, $K_1 = 5.90 \times 10^{-2}$ and $K_2 = 6.40 \times 10^{-5}$. For o-phthalic acid, $K_1 = 1.3 \times 10^{-3}$ and $K_2 = 3.9 \times 10^{-5}$.

The same principles can be applied to polybasic acids and polyacidic bases to obtain the requisite number of dissociation constants. For example, for citric acid, $K_1 = 8.4 \times 10^{-4}$, $K_2 = 1.8 \times 10^{-5}$, and $K_3 = 4.0 \times 10^{-4}$. For pyrophosphoric acid, $K_1 = 1.4 \times 10^{-1}$, $K_2 = 3.2 \times 10^{-2}$, $K_3 = 1.7 \times 10^{-6}$, and $K_4 = 6 \times 10^{-9}$. Since these dissociation constants do change with temperature, the temperature at which the values were determined is usually quoted.

The relationship between the dissociation constant of an acid HA and the dissociation constant of its conjugate base A^- is frequently required, and it can be deduced from the equations

$$HA \rightleftharpoons H^+ + A^- \qquad \text{(HA an acid)}$$
$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad \text{(A^- its conjugate base)}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{and} \quad K_b = \frac{[HA][OH^-]}{[A^-][H_2O]}$$

Since the concentration of water in the expression for K_b is vastly in excess of any of the other quantities and since it will remain virtually constant, it is usually omitted. Therefore,

$$K_a K_b = \frac{[H^+][A^-]}{[HA]} \cdot \frac{[HA][OH^-]}{[A^-]}$$
$$= [H^+][OH^-]$$
$$= K_w$$

It follows that the weaker the acid, the stronger the conjugate base and vice versa.

Also, since $K_a K_b = K_w$,

$$\log K_a + \log K_b = \log K_w$$
$$-\log K_a - \log K_b = -\log K_w$$

or

$$pK_a + pK_b = pK_w \tag{3.6}$$

Once again, Sörensen's notation is used to express dissociation constants of acids and bases as exponents:

$$pK_a = -\log_{10} K_a \quad \text{and} \quad pK_b = -\log_{10} K_b$$

EXAMPLE 13: If the dissociation constant of pyridine is 1.71×10^{-9}, calculate the dissociation constant of the conjugate acid. (The conjugate acid is $C_6H_5NH^+$.)

$$K_b = 1.71 \times 10^{-9}$$
$$K_a = \frac{K_w}{1.71 \times 10^{-9}} = \frac{1 \times 10^{-14}}{1.71 \times 10^{-9}} = 5.85 \times 10^{-6}$$

EXAMPLE 14: The pK_b value of strychnine is 6.00. Calculate the pK_a of strychnine hydrochloride:

$$pK_a + pK_b = pK_w \tag{3.6}$$
$$pK_a = 14 - 6 = 8$$

We frequently speak of *weak* and *strong* acids and *weak* and *strong* bases, and the meaning of these terms must now be defined. The relative strengths of acids can be obtained by application of the simple rule that the stronger of two acids will displace the weaker from its salts. For example, if hydrochloric acid is added to a solution of an acetate, we can smell acetic acid. This indicates that hydrochloric acid has displaced acetic acid from a salt; hydrochloric acid is therefore the stronger acid. Similarly, since acetic acid causes evolution of carbon dioxide from sodium carbonate, it must be stronger than carbonic acid ($H_2O + CO_2$). Phenol is acidic but it will not evolve carbon dioxide from sodium carbonate. The four acids can therefore be arranged in decreasing order of "strength" on the basis of the above observations:

$$HCl > CH_3COOH > H_2CO_3 > C_6H_5OH$$

Examination of the dissociation constants of these acids shows that they are in the same order—the larger the dissociation constant, the stronger the acid. The expression used to obtain K_a from the application of the law of mass action to the dissociation equilibrium shows that the larger the value of K_a, the greater the degree of dissociation and the more hydrogen ions produced. The fundamental definition of "strength" of an acid is therefore based on the fact that the properties of an acid are those of the hydrogen ions it can

produce. The greater the concentration of hydrogen ions an acid can produce at a given dilution, the stronger is that acid. Or, simply:

strong acids dissociate to a large extent in solution,
weak acids dissociate to a small extent.

No other definition of "strength" is acceptable. Strength is synonomous with larger values for K_a (smaller values for pK_a).

The dissociation constant K_a can also be written in terms of degree of dissociation. Let α be the degree of dissociation of a solution containing c gram molecules of acid HA. At equilibrium,

$$HA \rightleftharpoons H^+ + A^-$$
$$[HA] = (1 - \alpha)c \quad . [H^+] = [A^-] = \alpha c$$
$$K_a = \frac{(\alpha c)(\alpha c)}{(1 - \alpha)c} = \frac{\alpha^2 c}{1 - \alpha}$$

The value of α can be found by conductivity measurements and related directly to the dissociation constant. [Note: If $\alpha =$ degree of dissociation, then $100\alpha =$ percentage dissociation.]

Bases can be treated in the same manner, and they are designated as weak or strong depending upon their ability to produce hydroxyl ions in solution. The list of values of K_a and K_b in Table 3.2 for some of the common acids and bases is arranged in each case in alphabetical order.

There is a tendency in a few texts (for example, Ref. 10) to list only the acid dissociation constants (pK_a values of the conjugate acids). Pyridine, for example is listed as having a pK of about 5.23, meaning that the *conjugate acid* has a pK_a value of 5.23. If we wish to obtain the pK_b value or K_b value for pyridine, care must be observed in selecting the correct figure.

The relative strengths of acids and bases depend upon their degree of dissociation, but, since the degree of dissociation of any solute tends toward the maximum value at infinite dilution, the differences in relative strengths tend to disappear upon dilution.

For example, 1 N hydrochloric acid is 200 times stronger than 1 N acetic acid; but 0.0001 N hydrochloric acid is only $2\frac{1}{2}$ times stronger than 0.0001 N acetic acid. The degree of dissociation must obviously be taken into account when attempting to calculate the true hydrogen ion concentration of an acid or base.

EXAMPLE 15: Decinormal hydrochloric acid is about 91% dissociated. Calculate the pH of 0.1 N hydrochloric acid solution:

The hydrogen ion concentration of 0.1 N acid, ignoring the dissociation, is 0.1. Therefore,

$$\text{true } [H^+] = 0.1 \times \frac{91}{100} = 9.1 \times 10^{-2}$$

and the pH will be 1.04.

TABLE 3.2: Dissociation Constants and pK Values of Some Acids and Bases*

Acids

	K_a	pK_a	Ref.
Barbiturates			
Amobarbital	9.6×10^{-9}	8.02	2
Barbital	8.71×10^{-9}	8.06	2
Butabarbital	6.92×10^{-9}	8.16	2
Cyclobarbital	1.62×10^{-8}	7.79	2
Pentobarbital	6.76×10^{-9}	8.17	2
Phenobarbital	2.88×10^{-8}	7.54	2
Secobarbital	1.26×10^{-8}	7.9[f]	3
Sulfonamides			
Sulfacetamide	4.17×10^{-6}	5.38	4
Sulfadiazine	3.31×10^{-7}	6.48	4
Sulfadimethoxine	1.15×10^{-6}	5.94[c]	5
Sulfadimidine	4.27×10^{-8}	7.37	4
Sulfafurazole	1.0×10^{-5}	5.00[d]	5
Sulfamerazine	8.71×10^{-8}	7.06	4
Sulfamethizole	3.55×10^{-6}	5.45	9
Sulfamethoxypyridazine	2×10^{-7}	6.7[f]	9
Sulfanilamide	3.72×10^{-11}	10.43	4
Sulfaphenazole	1.95×10^{-6}	5.71[d]	5
Sulfapyridine	3.72×10^{-9}	8.43	4
Sulfasomidine	6.76×10^{-8}	7.17[d]	5
Sulfathiazole	7.59×10^{-8}	7.12	4
	1.0×10^{-7}	7.00[d]	5
Miscellaneous			
Acetic acid	1.76×10^{-5}	4.75	1
Acetylsalicylic acid	3.27×10^{-4}	3.49	6
p-Aminobenzoic acid	2.09×10^{-5}	4.68	4
Benzoic acid	6.30×10^{-5}	4.20	6
Benzylpenicillin	1.74×10^{-3}	2.76	6

	K_a	pK_a	Ref.
Miscellaneous			
Boric acid			
$\quad K_1$	7.3×10^{-10}	9.14[c]	1
$\quad K_2$	1.8×10^{-13}	12.74[c]	
$\quad K_3$	1.6×10^{-14}	13.80[c]	
Caffeine	1×10^{-14}	14.00	6
Formic acid	1.77×10^{-4}	3.75[c]	1
Hydrogen cyanide	4.93×10^{-10}	9.31	1
Hydrogen sulfide			
$\quad K_1$	9.1×10^{-8}	7.04	1
$\quad K_2$	1.2×10^{-15}	14.92	
Lactic acid	1.39×10^{-4}	3.86	6
Malonic acid			
$\quad K_1$	1.49×10^{-3}	2.83	1
$\quad K_2$	2.03×10^{-6}	5.69	
Oxalic acid			
$\quad K_1$	5.90×10^{-2}	1.23	1
$\quad K_2$	6.40×10^{-5}	4.19	
Phenol	1×10^{-10}	10.00	6
Phosphoric acid			
$\quad K_1$	7.52×10^{-3}	2.12	1
$\quad K_2$	6.23×10^{-8}	7.21	
$\quad K_3$	2.2×10^{-13}	12.67[c]	
Picric acid	4.2×10^{-1}	0.38	6
Saccharin	2.5×10^{-2}	1.60	6
Salicylic acid			
$\quad K_1$	1.07×10^{-3}	2.97[b]	1
$\quad K_2$	4×10^{-14}	13.40[a]	
Tartaric acid			
$\quad K_1$	9.6×10^{-4}	3.02	6
$\quad K_2$	4.4×10^{-5}	4.36	

TABLE 3.2 (continued)

Bases

Alkaloids	K_b	pK_b	Ref.
Apomorphine	1.0×10^{-7}	7.00	6
Atropine	4.5×10^{-5}	4.35	6
Caffeine	4.1×10^{-14}	13.39ᵃ	6
Cocaine	2.6×10^{-6}	5.59	6
Codeine	9×10^{-7}	6.1	6
Ephedrine	2.3×10^{-5}	4.64	6
Morphine	7.4×10^{-7}	6.13	6
Papaverine	8×10^{-9}	8.1	6
Physostigmine			
K_1	7.6×10^{-7}	6.12	6
K_2	5.7×10^{-13}	12.24	
Pilocarpine			
K_1	7×10^{-8}	7.2	6
K_2	2×10^{-13}	12.7	
Quinine			
K_1	1.0×10^{-6}	6.00	6
K_2	1.3×10^{-10}	9.89	
Reserpine	4×10^{-8}	7.4	6
Strychnine			
K_1	1×10^{-6}	6.0	6
K_2	2×10^{-12}	11.7	
Theobromine	4.8×10^{-14}	13.32ᵃ	6
Antihistamines			
Antazoline	2.4×10^{-6}	5.62	7

	K_b	pK_b	Ref.
Thiopropazate			
K_1	1.4×10^{-7}	6.85	8
K_2	1.6×10^{-11}	10.80	
Thioridazine	1.45×10^{-5}	4.84	8
Trifluoperazine			
K_1	2.5×10^{-6}	5.60	8
K_2	7.9×10^{-11}	10.10	
Trifluopromazine	2.57×10^{-5}	4.59	8
Sulfonamides			
Sulfadiazine	1×10^{-12}	12.00	4
Sulfadimidine	2.3×10^{-12}	11.64	4
Sulfaguanidine			
K_1	5.6×10^{-12}	11.25	4
K_2	3.0×10^{-14}	13.52	4
Sulfamerazine	1.2×10^{-12}	11.92	4
Sulfanilamide	2.3×10^{-12}	11.64	4
Sulfapyridine			
K_1	3.8×10^{-12}	11.42	4
K_2	1×10^{-13}	13.00	4
Sulfathiazole	2.3×10^{-12}	11.64	4
Sympathomimetic Amines			
2-Aminoheptane	3.0×10^{-4}	3.52	8
dl-Amphetamine	5.9×10^{-5}	4.23	8
Cyclopentamine	2.95×10^{-4}	3.53	8

Compound	K	pK	Ref.
Chlorpheniramine	9.8×10^{-8}	5.01	7
Diphenhydramine	3.2×10^{-7}	6.50	7
Methapyrilene			
$\quad K_1$	5.4×10^{-7}	6.27	7
$\quad K_2$	4.7×10^{-11}	10.33	
Pheniramine	1.9×10^{-6}	4.73	7
Pyrilamine			
$\quad K_1$	2.6×10^{-7}	6.58	7
$\quad K_2$	3.4×10^{-11}	10.47	
Thonzylamine			
$\quad K_1$	9.1×10^{-6}	5.04	7
$\quad K_2$	1.45×10^{-12}	11.84	
Tripelennamine			
$\quad K_1$	5.1×10^{-6}	5.29	7
$\quad K_2$	1.6×10^{-10}	9.80	
Phenothiazines			
Chlorpromazine	1.66×10^{-5}	4.78	8
Levomepromazine	1.4×10^{-5}	4.85	8
Pipamazine	4.0×10^{-6}	5.40	8
Prochlorperazine			
$\quad K_1$	3.5×10^{-7}	6.46	8
$\quad K_2$	4.0×10^{-11}	10.40	
Promethazine	1.26×10^{-5}	4.90	8
Pyrathiazine	8.1×10^{-6}	5.09	8
Ephedrine	3.8×10^{-5}	4.42	8
Mephentermine	2.4×10^{-4}	3.62	8
d-Methamphetamine	1.6×10^{-4}	3.80	8
Methoxamine	1.5×10^{-5}	4.82	8
Methylhexaneamine	3.5×10^{-4}	3.46	8
Naphthazoline	1.38×10^{-4}	3.86	8
Propylhexedrine	3.3×10^{-4}	3.48	8
Miscellaneous			
Acetanilide	4.1×10^{-14}	13.39*	6
p-Aminobenzoic acid	2.6×10^{-12}	11.58	4
Ammonia	1.79×10^{-5}	4.75	1
Aniline	3.82×10^{-10}	9.42	6
Benzocaine			
$\quad K_1$	6.0×10^{-12}	11.22	
Dapsone			
$\quad K_1$	3.1×10^{-12}	11.31	
$\quad K_2$	2.0×10^{-13}	12.70	4
Dimethylamine	5.2×10^{-4}	3.28	1
Hydrazine	3×10^{-6}	5.52	1
Piperazine			
$\quad K_1$	6.4×10^{-5}	4.19	1
$\quad K_2$	3.7×10^{-9}	8.43	
Procaine	7×10^{-6}	5.2	6
Pyridine	1.71×10^{-9}	8.77	1
Trimethylamine	5.45×10^{-5}	4.26	1
Urea	1.5×10^{-14}	13.82	1

* All values of K_a and K_b were determined at 25°C except: a, 18°C; b, 19°C; c, 20°C; d, 28°C; e, 40°C; f, unspecified.

EXAMPLE 16: Calculate the pH of a decinormal solution of acetic acid, if the degree of dissociation is 1.34%:

$$[H^+] = 0.1 \times \frac{1.34}{100} = 1.34 \times 10^{-3}$$

$$pH = 2.87$$

This does not mean that equal volumes of 0.1 N acetic acid and 0.1 N hydrochloric acid will require different volumes of the same alkali for neutralization. As the titration of an acid proceeds, the hydrogen ions already formed will be taken up by the added base. More undissociated acid molecules will then dissociate in an effort to maintain equilibrium between dissociated and undissociated molecules. Eventually, all acid molecules (whether acetic or hydrochloric or any acid) will yield their hydrogen ions, and the same volume of alkali will be recorded for neutralization.

Since

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

then

$$[H^+][A^-] = K_a[HA]$$

Let c be the initial concentration of acid in gram equivalents per liter. For a weak acid, the concentration of undissociated acid at equilibrium will be almost the same as the initial concentration. For example,

$$c = [HA]$$

or very nearly so. Also,

$$[H^-] = [A^-]$$
$$[H^-]^2 = K_a c$$
$$[H^-] = \sqrt{K_a c}$$
$$\log[H^-] = \tfrac{1}{2}\log K_a + \tfrac{1}{2}\log c$$
$$-\log[H^-] = -\tfrac{1}{2}\log K_a - \tfrac{1}{2}\log c$$
$$pH = \tfrac{1}{2}pK_a - \tfrac{1}{2}\log c \qquad (3.7)$$

From Eq. (3.7), if the concentration and the dissociation constant are known, the pH of the solution can be calculated directly.

EXAMPLE 17: Calculate the pH of a decinormal solution of acetic acid ($pK_a = 4.75$):

$$pH = \tfrac{1}{2}pK_a - \tfrac{1}{2}\log c$$
$$= 2.38 - \tfrac{1}{2}(\log 0.1)$$
$$= 2.38 - (-0.5)$$
$$= 2.88$$

(see also Example 16). Similarly for bases,

$$BOH \rightleftharpoons B^+ + OH^-$$
$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

Let $c = [BOH]$. Since

$$[B^+] = [OH^-]$$
$$[OH^-]^2 = K_b c$$
$$[OH^-] = \sqrt{K_b c}$$
$$pOH = \tfrac{1}{2}pK_b - \tfrac{1}{2}\log c \qquad (3.8)$$

It is possible to substitute for pOH in Eq. (3.8) to get

$$pK_w - pH = \tfrac{1}{2}pK_b - \tfrac{1}{2}\log c$$
$$pH = pK_w - \tfrac{1}{2}pK_b + \tfrac{1}{2}\log c \qquad (3.9)$$

EXAMPLE 18: Calculate the pH of a 0.1 N solution of ammonia ($pK_b = 4.75$):

Using Eq. (3.9),

$$pH = 14 - 2.38 + \tfrac{1}{2}(\log 0.1)$$
$$= 11.62 - 0.5$$
$$= 11.12$$

G. THE HYDROLYSIS OF SALTS

The dissociation of salts in dilute solution may be regarded as complete. Since some water molecules are ionized into hydrogen and hydroxyl ions, there is a possibility of interaction between these ions and the ions of a dissolved salt; for example, ferric chloride yields ferric and chloride ions in solution.

$$FeCl_3 \rightleftharpoons Fe^{3+} + 3Cl^-$$
$$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3 \quad \text{(only slightly dissociated)}$$
$$3Cl^- + 3H^+ \rightleftharpoons 3HCl \quad \text{(completely dissociated)}$$

These partial equations may be combined in a single form:

$$Fe^{3+} + 3Cl^- + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ + 3Cl^-$$

The free hydroxyl ions of water are thus "fixed." Since the ionic product of water K_w must remain constant, there will be a preponderance of hydrogen ions, and a solution of ferric chloride is therefore acidic.

In dilute solutions of sodium carbonate, the sodium ions form strongly dissociated sodium hydroxide with hydroxyl ions, whereas the carbonate ions form the very poorly dissociated carbonic acid with the water hydrogen ions. Such solutions are basic. Potassium cyanide is another common example of a salt that forms basic solutions for the same reasons.

Any salt which interacts with ions from water in either way described above is said to be hydrolyzed.

1. Salts Formed from a Strong Acid and a Strong Base

Sodium chloride is the outstanding example of a salt formed by a strong acid and strong base. Theoretically, it is derived by neutralization of

hydrochloric acid with sodium hydroxide, although it can be obtained in practice in many other ways.

In solution, sodium chloride yields sodium ions and chloride ions, which interact with hydroxyl and hydrogen ions to yield sodium hydroxide and hydrochloric acid. Both products are fully dissociated in reasonably dilute solutions, there is no imbalance of ions in the water, and the solution remains neutral.

2. Salts Formed from a Weak Acid and a Strong Base

Consider a salt BA, where HA is a weak acid and BOH is a strong base, for example, potassium cyanide. In dilute solution,

$$BA \rightleftharpoons B^+ + A^-$$

$$B^+ + A^- + H_2O \rightleftharpoons HA + B^+ + OH^-$$

The acid HA, being a weak acid, is relatively undissociated. Applying the law of mass action, we have

$$K_\lambda = \frac{[HA][OH^-]}{[A^-]}$$

where K_λ is known as the *hydrolysis constant*. The $[H_2O]$ is omitted because it is virtually constant and $[B^+]$ is common to both sides of the equation. Since $K_w = [H^+][OH^-]$ and since, for the weak acid HA,

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

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

$$= K_\lambda$$

that is, $K_\lambda = K_w/K_a$.

Normally, the dissociation constant of the weak-acid component of the salt will be known, and the hydrolysis constant can be calculated directly. The expression

$$K_w/K_a = \frac{[HA][OH^-]}{[A^-]}$$

can now be used to derive an equation from which the pH of a solution of a salt of this type can be calculated.

Let the initial concentration of the salt be c gram molecules per liter and let $[HA] = [OH^-] = x$ gram molecules at equilibrium. Thus,

$$K_w/K_a = \frac{x^2}{c - x}$$

So long as the solution is not too dilute (c very small) or K_a is not too small

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(handwritten notes at top left) NaCl / Act / NaCl — Na, Cl   H   Cl

(HA a very weak acid), x will be much smaller than c and can be ignored in the denominator:

$$K_w/K_a = \frac{x^2}{c}$$

$$x = [OH^-] = \sqrt{K_w c/K_a}$$

$$\log [OH^-] = \tfrac{1}{2}\log K_w + \tfrac{1}{2}\log c - \tfrac{1}{2}\log K_a$$

$$- \log [OH^-] = -\tfrac{1}{2}\log K_w + \tfrac{1}{2}\log K_a - \tfrac{1}{2}\log c$$

$$pOH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_a - \tfrac{1}{2}\log c$$

$$pOH = pK_w - pH$$

$$pH = pK_w - \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a + \tfrac{1}{2}\log c$$

$$= \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a + \tfrac{1}{2}\log c. \qquad (3.10$$

The *degree of hydrolysis*, h, of a salt equals x/c. The *percentage* of the salt hydrolyzed is $100x/c$.

By using the term h, an alternative equation for K_h can be obtained. If h is the degree of hydrolysis and c is the initial concentration of the salt in gram molecules per liter,

$$K_h = \frac{[HA][OH^-]}{[A^-]} = \frac{hc \cdot hc}{(1-h)c} = \frac{h^2 c}{1-h}$$

EXAMPLE 19: Calculate the pH of an $0.1\ N$ solution of potassium cyanide (pK_a for HCN = 9.31):

$$pH = 7 + 4.66 + \tfrac{1}{2}(\log 0.1)$$
$$= 11.66 + (-0.5)$$
$$= 11.16$$

2. Salts Formed from a Weak Base and a Strong Acid

Consider a salt BA, where HA is a strong acid and BOH is a weak base, for example, ammonium chloride.

$$BA \rightleftharpoons B^+ + A^-$$
$$B^+ + A^- + H_2O \rightleftharpoons BOH + H^+ + A^-$$

The weak base BOH is relatively undissociated:

$$K_h = \frac{[BOH][H^+]}{[B^+]}$$

Since $K_w = [H^+][OH^-]$ and $K_b = [B^+][OH^-]/[BOH]$, we have

$$K_w/K_b = \frac{[H^+][OH^-]}{[B^+][OH^-]/[BOH]} = \frac{[H^+][BOH]}{[B^+]}$$
$$= K_h$$

that is, $K_h = K_w/K_b$.

Once again, a relationship has been deduced between the hydrolysis constant, the ionic product of water, and the dissociation constant of the weak component of the salt, in this case the base.

Let the initial concentration of the salt be c gram molecules per liter and let $[BOH] = [H^-] = x$. Then

$$K_w/K_b = \frac{x^2}{c - x}$$

Again x can be neglected in the denominator, provided that K_b and c are not too small:

$$K_w/K_b = \frac{x^2}{c}$$

$$x = [H^+] = \sqrt{K_w c/K_b}$$

$$\log [H^+] = \tfrac{1}{2}\log K_w + \tfrac{1}{2}\log c - \tfrac{1}{2}\log K_b$$

$$-\log [H^+] = -\tfrac{1}{2}\log K_w - \tfrac{1}{2}\log c + \tfrac{1}{2}\log K_b$$

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b - \tfrac{1}{2}\log c. \tag{3.11}$$

The degree of hydrolysis h is x/c, and the percentage hydrolysis is $100x/c$. In terms of the degree of hydrolysis, and derived in a manner analogous to that used for salts of weak acids and strong bases,

$$K_h = \frac{h^2 c}{1 - h}$$

EXAMPLE 20: Calculate the pH of an 0.05 N solution of ammonium chloride (pK_b for ammonia $= 4.75$):

$$pH = 7 - 2.38 - \tfrac{1}{2}(\log 0.05)$$
$$= 4.62 - \tfrac{1}{2}(2.7)$$
$$= 4.62 + 0.65$$
$$= 5.27$$

4. Salts Formed from a Weak Acid and a Weak Base

Consider a salt BA, where HA and BOH are both weak; ammonium acetate is an example.

$$BA \rightleftharpoons B^+ + A^-$$
$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

Both BOH and HA are relatively undissociated:

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]}$$

In terms of degree of hydrolysis, this expression becomes

$$K_h = \frac{hc \cdot hc}{(1 - h)c \cdot (1 - h)c} = \frac{h^2}{(1 - h)^2}$$

Since this expression contains no term in concentration c, the degree of

hydrolysis of a salt of this type is independent of dilution. This was not the case with salts of type 2 or 3.

$$K_w = [H^+][OH^-] \qquad K_a = \frac{[H^+][A^-]}{[HA]} \qquad K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$K_w/K_aK_b = \frac{[H^+][OH^-]}{[H^+][A^-]/[HA] \cdot [B^+][OH^-]/[BOH]}$$

$$= \frac{[BOH][HA]}{[B^+][A^-]}$$

$$= K_\Lambda \tag{3.12}$$

that is, $K_\Lambda = K_w/K_aK_b$. Also, since

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

then

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

$$= K_a \frac{hc}{(1-h)c}$$

$$= K_a \frac{h}{1-h}$$

$$= K_a \sqrt{K_\Lambda} \tag{3.13}$$

Since K_a and K_Λ are constants, this means that the hydrogen ion concentration or pH of a solution of a salt of this type will be constant.

In the same way,

$$[OH^-] = K_b \sqrt{K_\Lambda}$$

$$= \text{a constant} \tag{3.14}$$

From Eq. (3.13) and (3.14), we know that the pH of a solution of a salt of this type will be constant at all dilutions. Finally, from Eq. (3.13)

$$[H^+] = K_a \sqrt{K_\Lambda}$$

$$= K_a \sqrt{K_w/K_aK_b} \qquad \text{[substitution for } K_\Lambda \text{ from Eq. (3.12)]}$$

$$\log[H^+] = \log K_a + \tfrac{1}{2}\log K_w - \tfrac{1}{2}\log K_a - \tfrac{1}{2}\log K_b$$

$$= \tfrac{1}{2}\log K_w + \tfrac{1}{2}\log K_a - \tfrac{1}{2}\log K_b$$

$$-\log[H^+] = -\tfrac{1}{2}\log K_w - \tfrac{1}{2}\log K_a + \tfrac{1}{2}\log K_b$$

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}pK_b \tag{3.15}$$

If the numerical values of K_a and K_b are approximately equal, then $\tfrac{1}{2}pK_a = \tfrac{1}{2}pK_b$ and pH $= \tfrac{1}{2}pK_w = 7$, that is, the solution of the salt will be neutral irrespective of the degree of hydrolysis or of the dilution factor. By definition, the salts of this class will be derived from acids and bases which have small dissociation constants, and it may be predicted that the solutions will have pH values in the vicinity of 7. The precise pH will depend upon slight differences in K_a and K_b.

3.3 NEUTRALIZATION CURVES FOR ACID/BASE TITRATIONS

A. A STRONG MONOBASIC ACID TITRATED WITH A STRONG BASE

The most common strong monobasic acid is hydrochloric acid. In analysis, hydrochloric acid is nearly always used as a normal, half-normal, or decinormal solution, although many other concentrations have more specific uses.
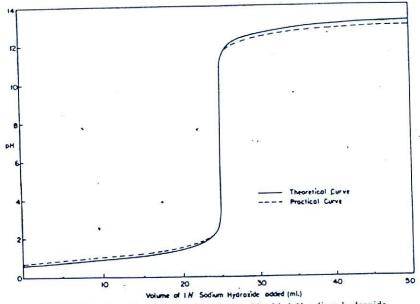
FIGURE 3.1: Titration of 1 N hydrochloric acid with 1 N sodium hydroxide.

It is generally assumed that normal solutions and more dilute solutions are completely dissociated. Although this is not absolutely accurate for normal or even decinormal solutions, theoretical curves for the titration of hydrochloric acid solutions, based on this premise, are almost identical with the curves obtained in practical experiments. Figure 3.1 combines the practical and theoretical curves for titration of 25 ml of 1 N hydrochloric acid with 1 N sodium hydroxide. The acid was diluted to 100 ml before commencing the titration, and all changes in volume were taken into account in calculating the theoretical curve.

Calculation of the Theoretical Curve. From the beginning of the titration until the equivalence point is reached, the hydrogen ion concentration is calculated from the remaining volume of 1 N acid. For example, before the addition of any alkali, 25 ml of 1 N hydrochloric acid are present, in a total volume of 100 ml. Assuming complete dissociation and expressing c as always in terms of gram equivalents per liter, we have

$$c = \frac{25 \times 1}{1000} \text{ gram equivalents in 100 ml}$$

$$= \frac{25 \times 1 \times 1000}{1000 \times 100} \text{ gram equivalents per liter}$$

$$= 0.25$$

(It will soon be realized that this figure may be reached more quickly by omitting the 1000 term in numerator and denominator.) In general,

$$c = \frac{\text{volume of acid (or base)} \times \text{normality}}{\text{total solution volume}}$$

It should be kept in mind that the initial volume of acid (or base) present can be obtained from the practical curve only. In practical experiments, the solutions used are rarely both exactly 1 N or 2 N or 0.1 N, etc. If the nominal volume pipetted is recorded as the initial volume of acid or base, the practical and theoretical curves will be laterally displaced by a volume corresponding to the difference between the true end-point volume and the volume pipetted. (In this example, for reasons of simplification an end-point volume of exactly 25 ml is assumed). Therefore,

$$pH = -\log 0.25$$
$$= 0.60$$

After the addition of 5 ml base,

$$pH = -\log \frac{20 \times 1}{105}$$

$$= 0.72$$

After the addition of 24.9 ml base,

$$pH = -\log \frac{0.1 \times 1}{124.9}$$

$$= 3.10$$

After the end point has been reached, it is assumed that the sodium hydroxide in excess is fully dissociated. For example, after 25.1 ml of base have been added,

$$pOH = -\log \frac{0.1 \times 1}{125.1}$$

$$= 3.10$$

$$pH = 10.90.$$

After the addition of 40.0 ml base,

$$pOH = -\log \frac{15 \times 1}{140}$$
$$= 0.97$$
$$pH = 13.03$$

The practical and theoretical curves are in excellent agreement until beyond the end point. The divergence between the two increases a little during the latter part of the titration, when the alkali is in large excess. This increasing (but still small) difference is probably partly due to the effect which a neutral salt has on the practical curve and partly to the fact that electrode systems are frequently slightly less accurate in strongly basic solutions.

The dilution of the acid or base at any point during the titration must be taken into account. Dilution will scarcely affect the almost vertical portion of the curve in the vicinity of the end point but it will markedly affect the "horizontal" portions. For example, if the 25 ml of 1 N hydrochloric acid had not been diluted prior to titration, the initial pH would be zero, that is

$$c = 1$$
$$pH = -\log 1 = 0$$

If the 25 ml of acid had been diluted to 200 ml instead of to 100, the initial pH would be 0.9. Thus the "horizontal" portions of the curves would be moved toward lower or higher pH values, respectively. When asked to calculate a theoretical curve to see how closely it matches the practical curve, the initial dilution (if any) must be known, at least approximately.

B. A WEAK MONOBASIC ACID TITRATED WITH A STRONG BASE

Figure 3.2 shows the general shape of curves resulting from titrations of a weak monobasic acid with a strong base. The individual shapes will vary within the group of weak acids. For the stronger acids, the initial inflection is less noticeable, whereas the end-point inflection is more accentuated. The initial inflection is larger for weaker members, but the end-point inflection is less marked.

Acetic acid is probably the most common member of the weak acid class, and it is nearly always used as the typical example. Since the dissociation of acetic acid in solution is far from complete, even at the weakest concentrations used in analysis, the calculation of theoretical curves is rather more complicated than for strong acids. There are certain equations available to us for the calculation of weak acid/strong base titration curves, but since these equations are based on certain assumptions, it is important that their derivations and limitations be fully understood.
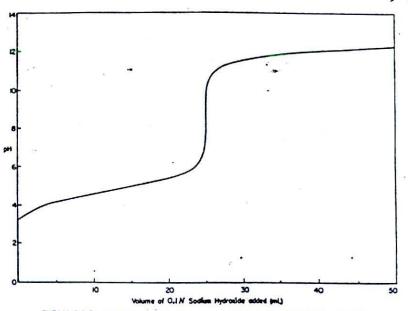
FIGURE 3.2: Titration of 0.1 N acetic acid with 0.1 N sodium hydroxide.

1. The Henderson Equation

Consider a system comprised of a weak acid in presence of its salt, which has been formed by interaction with a strong base; for example, acetic acid in the presence of sodium acetate.

The acetic acid will dissociate:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} \tag{3.16}$$

Let c be the total initial concentration of acetic acid and b be the concentration of strong base added. If the solutions are not too concentrated, we can assume that the sodium acetate is completely dissociated. Therefore,

$$b = [Na^+]$$

$$c = [CH_3COOH] + [CH_3COO^-]$$

since the acid is partly neutralized. We then have

$$[CH_3COOH] = c - [CH_3COO^-] \tag{3.17}$$

Since the solution is electrically neutral, the sum of the positive charges must

be equivalent to the sum of the negative charges:

$$[Na^+] + [H^+] = [CH_3COO^-] + [OH^-]$$
$$b + [H^-] = [CH_3COO^-] + [OH^-]$$
$$[CH_3COO^-] = b + [H^+] - [OH^-]$$

From Eq. (3.17),

$$[CH_3COOH] = c - [CH_3COO^-]$$
$$= c - b - [H^+] + [OH^-] \qquad (3.18)$$

Substituting for $[CH_3COOH]$ and $[CH_3COO^-]$ in Eq. (3.16), we have

$$[H^+] = K_a \frac{c - b - [H^+] + [OH^-]}{b + [H^+] - [OH^-]} \qquad (3.19)$$

This is the *Henderson equation* in its general form. It is valid for all pH calculations—acids and bases need not be considered separately. In deriving this equation, we have assumed (1) that sodium acetate is completely dissociated in solution, and (2) that activity coefficients may be neglected. As the concentration of the solution decreases, the validity of the assumptions increases.

Application of the Henderson Equation to the Titration of a Weak Acid

1. *To Calculate the* pH *before Addition of any Base.* At this point, $b = 0$ and $[OH^-]$ can be neglected, since it will be very much smaller than either K_a or $[H^+]$ or c. Equation (3.19) then becomes abbreviated to

$$[H^-] = K_a \frac{c - [H^+]}{[H^+]}$$
$$[H^+]^2 = K_a c - K_a[H^+]$$
$$[H^+] = \sqrt{K_a c - K_a[H^+]}$$

For most weak acids, including acetic acid, the term $K_a[H^-]$ will be much smaller than $K_a c$ at the usual concentrations employed, and this last equation can be simplified:

$$[H^+] = \sqrt{K_a c}$$
$$\log [H^-] = \tfrac{1}{2} \log K_a + \tfrac{1}{2} \log c$$
$$pH = \tfrac{1}{2} pK_a - \tfrac{1}{2} \log c \qquad (3.20)$$

This is the same equation derived in Section 3.2F, but by a different method.

2. *To Calculate the* pH *during Titration.* When c is greater than 0.01 (a stronger solution than 0.01 N) and the pH lies between 4 and 10, $[H^+]$ and $[OH^-]$ are very small in comparison and can be omitted from the general Henderson equation, which then becomes

$$[H^+] = K_a \frac{c - b}{b} \qquad (3.21)$$

This is the shortened or *approximate Henderson equation*, also known as the *Henderson-Hasselbach equation*.

Since $c - b = [CH_3COOH]$ and $b = [CH_3COO^-]$, we have

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

In equating $c - b$ to $[CH_3COOH]$, we are ignoring the small degree of dissociation of acetic acid, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. We are also ignoring the possible interaction between acetate ion and water:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Both factors will assume increasing importance as c becomes smaller. Thus,

$$-\log [H^+] = -\log K_a - \log \frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$pH = pK_a - \log \frac{[acid]}{[salt]}$$

or, as it is more commonly expressed,

$$pH = pK_a + \log \frac{[salt]}{[acid]} \tag{3.22}$$

The various assumptions and generalizations made in deriving this latter equation must be taken into consideration for-each case. Only in this way can a theoretical curve be obtained which will closely approximate the experimental curve. The accuracy desired in the theoretical graph must also be taken into consideration since Eq. (3.22) is intended to give only *approximate* values for a *general* case. When greater accuracy is desirable, each approximation must be closely examined for its validity in the case on hand.

3. *To Calculate the* pH *at the End Point.* At the end point (or equivalence point), the titration mixture is a solution of sodium acetate. $c = b$ and $[H^+]$ will be negligible in most cases; therefore Eq. (3.19) becomes abbreviated to

$$[H^+] = K_a \frac{[OH^-]}{b - [OH^-]} = K_a \frac{[OH^-]}{c - [OH^-]}$$

Also, since K_a and c will be considerably larger than $[OH^-]$ except in very dilute solutions of very weak acids, the equation can be further simplified to

$$[H^+] = K_a \frac{[OH^-]}{c}$$

(The term $[OH^-]$ in the numerator cannot be ignored.) Substituting $K_w/[H^+]$ for $[OH^-]$, we have

$$[H^+] = \frac{K_a \cdot K_w}{c \cdot [H^+]}$$

Therefore,

$$[H^+]^2 = K_a \cdot K_w/c$$

$$[H^+] = \sqrt{K_a K_w/c}$$

$$\log [H^+] = \tfrac{1}{2} \log K_a + \tfrac{1}{2} \log K_w - \tfrac{1}{2} \log c$$

$$-\log [H^+] = -\tfrac{1}{2} \log K_a - \tfrac{1}{2} \log K_w + \tfrac{1}{2} \log c$$

$$pH = \tfrac{1}{2} pK_a + \tfrac{1}{2} pK_w + \tfrac{1}{2} \log c \tag{3.23}$$

This equation was previously derived by a different method in Section 3.2G.

'4. *The Calculation of a Theoretical Curve from Eqs. (3.20), (3.22), and (3.23).* Twenty milliliters of approximately 0.1 N acetic acid are diluted to 100 ml and titrated with an 0.1002 N sodium hydroxide solution. If the end point occurs at 21.50 ml, calculate the theoretical curve.

Since the end point is at 21.50 ml of 0.1002 N sodium hydroxide, the initial concentration of acetic acid must be

$$\frac{21.50 \times 0.1002}{100} \text{ gram equivalents per liter}$$

$$= 0.02154$$

Using Eq. (3.20), we see that the pH before the addition of any titrant is

$$\begin{aligned}
pH &= \tfrac{1}{2}pK_a - \tfrac{1}{2}\log c \\
&= 2.38 - \tfrac{1}{2}(\log 0.02154) \\
&= 2.38 - \tfrac{1}{2}(2.3332) \\
&= 2.38 + 0.83 \\
&= 3.21
\end{aligned}$$

Equation (3.22) is now used to calculate the pH during the titration. It should be noted that the ratio [salt]/[acid] can be read directly in volume units, and the normality factor of the titrant may be neglected. This applies because the [salt] and [acid] factors are both expressed in the same normality terms and the normality cancels out, leaving the simple numerical volume ratio.

For example, after the addition of 1.00 ml of alkali,

$$\begin{aligned}
pH &= pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\
&= 4.75 + \log \frac{1}{21.50 - 1.00} \\
&= 4.75 + \log \frac{1}{20.50} \\
&= 4.75 + (-1.31) \\
&= 3.44
\end{aligned}$$

After 5 ml,

$$\begin{aligned}
pH &= 4.75 + \log \frac{5.00}{16.50} \\
&= 4.75 + (-0.52) \\
&= 4.23
\end{aligned}$$

After 20 ml,

$$\begin{aligned}
pH &= 4.75 + \log \frac{20.00}{1.50} \\
&= 4.75 + 1.12 \\
&= 5.87, \text{ etc.}
\end{aligned}$$

Since the expression [salt]'[acid] is a simple numerical ratio, it is possible to calculate values for the ratio at different points during the neutralization curve and apply them to all titrations of this type. The relationship between the percentage neutralization and the ratio [salt];[acid] is shown in Table 3.3. The values given for the log ratio are applicable to all weak acid/strong base titrations at the percentage neutralization quoted.

TABLE 3.3: The Relationship between % Neutralization and the [Salt]/[Acid] Ratio for a Weak Acid

Neutralization, %	Ratio $\frac{[salt]}{[acid]}$	$\log \frac{[salt]}{[acid]}$
10	10/90	−0.95
20	20/80	−0.60
30	30/70	−0.37
40	40/60	−0.18
50	50/50	0.0
60	60/40	0.18
70	70/30	0.37
80	80/20	0.60
90	90/10	0.95
99	99/1	1.996
99.9	99.9/0.1	2.999

The pH at the equivalence point is found from Eq. (3.23):

$$pH = \tfrac{1}{2}pK_a + \tfrac{1}{2}pK_w + \tfrac{1}{2}\log c$$

$$= 2.38 + 7 + \tfrac{1}{2}\left(\log \frac{21.50 \times 0.1002}{121.5}\right)$$

$$= 9.38 + (-0.88)$$

$$= 8.50$$

After the equivalence point has been reached, we assume that all hydroxyl ions are due to the excess of sodium hydroxide added. For example, after the addition of 25.00 ml of sodium hydroxide, the excess is 3.50 ml. Thus,

$$[OH^-] = \frac{3.50 \times 0.1002}{125.0}$$

$$= 0.002805$$

$$pOH = -\log 0.002805$$

$$= 2.55$$

$$pH = 11.45, \text{ etc.}$$

5. *Calculation of the Dissociation Constant of a Weak Acid.* The shortened form of the Henderson equation [Eq. (3.22)] can be used to calculate dissociation constants of weak acids from experimental titration curves. Neither

the initial concentration of acid present prior to commencement of the titration nor the exact strength of the titrant need be known. In Eq. (3.22), pH = pK_a + log ([salt]/[acid]), pK_a is the only unknown, since the pH of a partially neutralized solution of an acid can be determined and [salt] and [acid] are easily obtained at any point along the experimental titration curve.

Inspection of Table 3.3 shows that after 50% of the acid has been neutralized, [salt] = [acid]. Therefore,

$$pH = pK_a + \log \frac{1}{1}$$

$$= pK_a$$

that is, the pH at the midpoint of neutralization is the pK_a value of the acid. It is quite common to average several values of pK_a from a practical curve, at say, 40%, 50%, and 60% neutralization. At the 40% neutralization volume,

$$pK_a = pH_{obs} - \log \frac{40}{60}$$

At the 60% neutralization volume.

$$pK_a = pH_{obs} - \log \frac{60}{40}$$
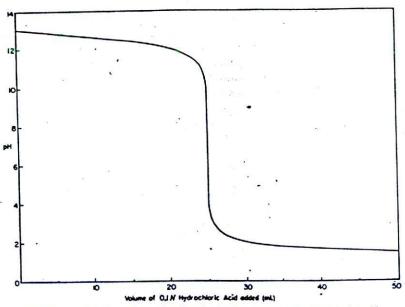
Any points along the almost horizontal portion of the practical curve can be chosen for calculation, but readings near the beginning or the end of the titration should be avoided. A simple experiment will illustrate these points. Take 100 ml of normal acetic acid and add 40 ml of normal sodium hydroxide solution. Read the pH on a pH meter. Add another 10 ml of the alkali and read the pH. Add another 10 ml and read the pH again. These three readings correspond to 40%, 50%, and 60% neutralization of the acetic acid. Calculation as shown will give an accurate figure for pK_a, from which K_a may be obtained.
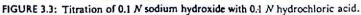
C. A STRONG MONOACIDIC BASE TITRATED WITH A STRONG ACID

Figure 3.3 shows the theoretical curve for titration of 25 ml of 0.1 N sodium hydroxide titrated (undiluted) with 0.1 N hydrochloric acid. Curves of this type are the mirror images of the titration of the corresponding strong acid solution with strong base. The calculations for this curve are made in exactly the same manner as illustrated in Section 3.3A. It is again assumed that base and acid are completely dissociated at the concentrations employed in ordinary titrations.
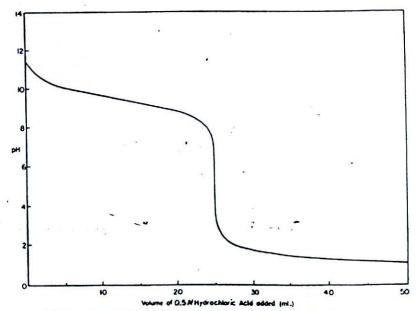
D. A WEAK MONOACIDIC BASE TITRATED WITH A STRONG ACID

Figure 3.4 shows the general shape of curves for titrations of this type. Once again we see that this curve is the mirror image of the curve obtained

FIGURE 3.3: Titration of 0.1 N sodium hydroxide with 0.1 N hydrochloric acid.

FIGURE 3.4: Titration of 0.5 N ethanolamine with 0.5 N hydrochloric acid.

for titration of a weak acid of comparable strength ($pK_a \doteq 4.5$) with a strong base (see Fig. 3.2).

As in the case of weak acids, three approximate equations can be deduced from a general Henderson equation, to completely delineate the theoretical curve up to and including the equivalence point.

Consider a base B. In aqueous solution, it dissociates:

$$B + H_2O = BH^- + OH^-$$

$$K_b = \frac{[BH^-][OH^-]}{[B]}.$$

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

By analogous reasoning, it is possible to deduce a *second* Henderson equation applicable to bases:

$$[OH^-] = K_b \frac{c - b, + [H^+] - [OH^-]}{b - [H^+] + [OH^-]} \tag{3.24}$$

where c is total initial concentration of base and b is the concentration of strong acid added.

Application of the Second Henderson Equation to the Titration of a Weak Base

1. *To Calculate the* pH *before Addition of Any Acid.* At this point, $b = 0$ and $[H^-]$ can be neglected. Equation (3.24) becomes

$$[OH^-] = K_b \frac{c - [OH^-]}{[OH^-]}$$

$$[OH^-]^2 = K_b c - K_b[OH^-]$$

$$[OH^-] = \sqrt{K_b c - K_b[OH^-]}$$

The term $K_b c$ will normally be much greater than $K_b[OH^-]$ and the above equation can be further simplified:

$$[OH^-] = \sqrt{K_b c}$$

$$-\log[OH^-] = -\tfrac{1}{2}\log K_b - \tfrac{1}{2}\log c$$

$$pOH = \tfrac{1}{2}pK_b - \tfrac{1}{2}\log c \tag{3.25}$$

Since $pOH = pK_w - pH$, then

$$pH = pK_w - \tfrac{1}{2}pK_b + \tfrac{1}{2}\log c \tag{3.26}$$

2. *To Calculate the* pH *during the Titration.* When c is greater than 0.01 and the pH lies between 4 and 10, $[H^-]$ and $[OH^-]$ are very small in comparison and can be omitted from the general equation [(3.24)], which then becomes

$$[OH^-] = K_b \frac{c - b}{b}$$

$$= K_b \frac{[base]}{[salt]}$$

Once again it is not strictly accurate to say that $c - b =$ [base], since some of the base will react with water:

$$-\log [OH^-] = -\log K_b - \log \frac{[base]}{[salt]}$$

$$pOH = pK_b - \log \frac{[base]}{[salt]}$$

or

$$pOH = pK_b + \log \frac{[salt]}{[base]} \checkmark \tag{3.27}$$

$$pH = pK_w - pK_b - \log \frac{[salt]}{[base]} \tag{3.28}$$

3. *To Calculate the* pH *at the End Point.* At the end point, the titration mixture is a solution of the salt of the base. $c = b$ and $[OH^-]$ will be negligible in most instances; therefore Eq. (3.24) can be abbreviated:

$$[OH^-] = K_b \frac{[H^+]}{c - [H^+]}$$

K_b and c will be considerably larger than $[H^+]$ except in very dilute solutions of very weak bases. The equation above can therefore be further simplified to

$$[OH^-] = K_b \frac{[H^+]}{c}$$

Since

$$[H^+] = \frac{K_w}{[OH^-]}$$

then

$$[OH^-] = \frac{K_b K_w}{c[OH^-]}$$

$$[OH^-]^2 = \frac{K_b K_w}{c}.$$

$$[OH^-] = \sqrt{K_b \cdot K_w/c}$$

$$-\log [OH^-] = -\tfrac{1}{2} \log K_b - \tfrac{1}{2} \log K_w + \tfrac{1}{2} \log c$$

$$pOH = \tfrac{1}{2}pK_b + \tfrac{1}{2}pK_w + \tfrac{1}{2} \log c \tag{3.29}$$

$$pH = pK_w - \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b - \tfrac{1}{2} \log c$$

$$= \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b - \tfrac{1}{2} \log c \tag{3.30}$$

Equation (3.30) is identical with Eq. (3.11).

Inspection will show that Eqs. (3.25), (3.27), and (3.29) are identical with (3.20), (3.22), and (3.23), respectively, except that pOH is substituted for pH and pK_b is substituted for pK_a. For convenience in calculations, Eqs. (3.25), (3.27), and (3.29) are translated into (3.26), (3.28), and (3.30), respectively, so that the pH can be calculated directly. Equations (3.26), (3.28), and (3.30) then appear to be quite different from Eqs. (3.20), (3.22), and (3.23) deduced from the first general Henderson equation for weak acids.

4. *The Calculation of a Theoretical Curve from Eqs.* (3.26), (3.28), and (3.30). Twenty milliliters of approximately 0.5 N ethylamine are diluted to

100 ml and titrated with 0.4903 N hydrochloric acid. If the end point occurs at 19.28 ml, calculate the theoretical curve for the experiment ($K_b = 5.6 \times 10^{-4}$ for ethylamine).

The initial concentration of ethylamine is equivalent to 19.28 ml of 0.4903 N solution, in a total volume of 100 ml. Therefore,

$$c = \frac{19.28 \times 0.4903}{100} = 0.09454.$$

$$K_b = 5.6 \times 10^{-4}$$

$$pK_b = 3.25$$

Substituting into Eq. (3.26),

$$pH = 14 - 1.63 + \tfrac{1}{2}(2.9756)$$
$$= 12.37 + \tfrac{1}{2}(-1.02)$$
$$= 12.37 - 0.51$$
$$= 11.86 \quad \text{(before adding titrant)}$$

$$pH = pK_w - pK_b - \log [\text{salt}]/[\text{base}] \quad \text{(during titration)} \quad (3.28)$$

Once again, the term [salt]/[base] is a simple numerical ratio (see also Section 3.3B and Table 3.3).

For example, after the addition of 5 ml of the acid,

$$pH = 14 - 3.25 - \log \frac{5.00}{19.28 - 5.00}$$
$$= 10.75 - (-0.46)$$
$$= 11.21$$

After 15 ml have been added,

$$pH = 14 - 3.25 - \log \frac{15}{4.28}$$
$$= 10.75 - 0.54$$
$$= 10.21, \text{ etc.}$$

All the remarks in Section 3.3B concerning the general application of values of log [salt]/[acid] at various points during the titration of a weak acid are equally applicable to the log [salt]/[base] values during titration of a weak base. The same log values will be obtained as listed in Table 3.3 and can be directly applied at the corresponding point in the neutralization.

For example, after 20% neutralization of the ethylamine, (3.86 ml of the acid in the above example), we have

$$pH = 14 - 3.25 - (-0.60)$$
$$= 10.75 + 0.60$$
$$= 11.35$$

With other bases, the only difference at the 20% neutralization point will be the value of pK_b, thus permitting us to calculate the pH at any given point in a general manner.

The pH at the equivalence point is found with Eq. (3.30), that is,

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b - \tfrac{1}{2}\log c$$
$$c = [salt] = \frac{19.28 \times 0.4903}{119.28} = 0.07925$$
$$pH = 7 - 1.63 - \tfrac{1}{2}(-1.10)$$
$$= 5.37 + 0.55$$
$$= 5.92$$

After the end point, we assume that all hydrogen ions are due to the excess hydrochloric acid and that the acid is fully dissociated. For example, after the addition of 20 ml of the acid, the excess volume is 0.72 ml. Thus,

$$pH = -\log\frac{0.72 \times 0.4903}{120}$$
$$= -\log 0.002942$$
$$= -(3.4686)$$
$$= 2.53, \text{ etc.}$$

E. THE TITRATION OF MIXED ACIDS IN SOLUTION

Consider a mixture of 1 equivalent of each of two monobasic weak acids after 1 equivalent of a strong base has been added. The stronger acid will be neutralized first, but will it be completely or only partially neutralized? Can we obtain an expression which will indicate the percentage of each acid neutralized?

Neutralization begins when 0.1% of the stronger acid is present as its conjugate base (salt). Applying Eq. (3.22), we have

$$pH = pK_a + \log\frac{0.1}{99.9}$$
$$\doteqdot pK_a - 3$$

Neutralization is complete when 99.9% of the acid is in its conjugate form and

$$pH = pK_a + \log\frac{99.9}{0.1}$$
$$\doteqdot pK_a + 3$$

That is, effective neutralization of a monobasic weak acid is associated with a change of six pH units.

1. If the two acids in the mixture have pK_a values which differ by six or more units, the acids will titrate as separate entities, and the stronger acid will be completely neutralized at the first end point. The first end point also marks the commencement of neutralization of the weaker acid.

For example, if we have two acids, $pK_{a_1} = 2$ and $pK_{a_2} = 8$, the stronger acid will be 100% neutralized at $pH = 2 + 3 = 5$. Neutralization of the other acid will begin at $pH = 8 - 3 = 5$.

2. Examples of acids having pK_a values six or more units apart are relatively rare, and it is more common to have mixtures of acids with pK_a values much closer.

Consider a mixture of two acids HA_1 and HA_2 with pK_a values of 4.7 and 7.2,-respectively. The stronger-acid will theoretically be fully neutralized at pH 7.7, and the weaker acid should begin to titrate at pH 4.2. It is reasonable to assume that the second acid will already be partially neutralized at the first end-point inflection (this could be called the *apparent* first end point, since it does not represent the true first-end point).

Let the concentration of $HA_1 = a_1$ moles per liter, and let the concentration of $HA_2 = a_2$ moles per liter. Let the dissociation constants be k_1 and k_2, respectively, and suppose that b moles of a strong base BOH have been added:

$$k_1 = \frac{[H^+][A_1^-]}{[HA_1]} \tag{3.31}$$

$$k_2 = \frac{[H^+][A_2^-]}{[HA_2]} \tag{3.32}$$

$$[H^+] + [B^-] = [A_1^-] + [A_2^-] + [OH^-]$$

since the solution is electrically neutral. $[OH^-]$ can be neglected except in the vicinity of the end point. Thus

$$[H^+] = [A_1^-] + [A_2^-] - [B^+]$$
$$= [A_1^-] + [A_2^-] - b \tag{3.33}$$

(It is assumed that BOH is 100% dissociated in solution.)

$$a_1 = [HA_1] + [A_1^-] \quad \text{and} \quad a_2 = [HA_2] + [A_2^-]$$
$$[HA_1] = a_1 - [A_1^-] \quad \text{and} \quad [HA_2] = a_2 - [A_2^-]$$

Substituting into Eqs. (3.31) and (3.32), we have

$$k_1 = \frac{[H^+][A_1^-]}{a_1 - [A_1^-]} \quad \text{and} \quad k_2 = \frac{H^+[A_2^-]}{a_2 - [A_2^-]}$$

$$a_1 k_1 - [A_1^-]k_1 = [H^+][A_1^-]$$
$$a_2 k_2 - [A_2^-]k_2 = [H^-][A_2^-]$$

$$[A_1^-] = \frac{a_1 k_1}{[H^-] + k_1} \quad \text{and} \quad [A_2^-] = \frac{a_2 k_2}{[H^-] + k_2}$$

Substituting into Eq. (3.33), we obtain

$$[H^-] = \frac{a_1 k_1}{[H^-] + k_1} + \frac{a_2 k_2}{[H^-] + k_2} - b \tag{3.34}$$

This is a cubic equation. It can be greatly simplified by ignoring all terms in $[H^-]^3$, $[H^+]^2 k_1$, $[H^+]^2 k_2$, and $[H^-]k_1 k_2$, since these will be numerically very small. The remaining terms can be further simplified by substituting a_1 for b, since $b \doteq a_1$ at the first end point.

Equation (3.34) then becomes

$$a_1[H^+]^2 + k_2(a_1 - a_2)[H^+] - a_2k_1k_2 = 0 \qquad (3.35)$$

(This is an equation of type $ax^2 + bx + c = 0$.) We solve this quadratic equation for $[H^+]$, using the general formula

$$\left(x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \right)$$

and we obtain the solution

$$[H^+] = \frac{k_2(a_1 - a_2)}{2a_1} + \sqrt{\frac{k_2^2(a_1 - a_2)^2 + 4a_1a_2k_1k_2}{4a_1^2}}$$

If the molar concentrations of the two acids are equal or nearly so, then $a_1 = a_2$ and our solution becomes

$$[H^+] = \sqrt{\frac{4a_1a_2k_1k_2}{4a_1^2}} = \sqrt{k_1k_2}$$

$$pH = \tfrac{1}{2}pK_{a_1} + \tfrac{1}{2}pK_{a_2} \qquad (3.36)$$

In other words, the pH at the first end point will be midway between the two pK_a values, provided that the molar concentrations are approximately equal.

In the example where $pK_{a_1} = 4.7$ and $pK_{a_2} = 7.2$, the first end point will occur at pH 5.95. The percentage of acid HA_1 neutralized at this pH can now be calculated from the approximate Henderson equation [Eq. (3.22)]:

$$pH = pK_{a_1} + \log [salt]/[acid]$$

$$5.95 = 4.7 + \log \frac{b}{a_1 - b}$$

$$1.25 = \log \frac{b}{a_1 - b}$$

$$\frac{b}{a_1 - b} = \text{antilog of } 1.25 = 17.78$$

$$b = 17.78a_1 - 17.78b$$

$$18.78b = 17.78a_1$$

$$\frac{b}{a_1} = \frac{17.78}{18.78}$$

That is, % of acid HA_1 neutralized is $17.78 \times 100/18.78$ or 94.69%. Acid HA_2 must therefore be 5.31% neutralized.

In general, the smaller the difference between pK_{a_1} and pK_{a_2}, the greater will be the overlapping of neutralization of the two acids. Although the theoretical calculations of the equivalence points is still quite valid, the practical value is considerably reduced, since the inflection of the first end point does *not* correspond to the true stoichiometric neutralization of the first acid unless the difference in pK_a values is six or more.

The above remarks are of a general nature and could be applied to mixtures of any numbers of acids. If we have a mixture of three acids in approximately equivalent molar concentrations, and having pK_a values of 2, 5, and 8, the first end-point inflection will occur at pH 3.5 and the second at pH 6.5, etc.

᾿Construction of a theoretical curve for mixtures of acids gives useful information as to what type of experimental end-point detection must be used. If the end-point inflection is large enough, a suitable color indicator could be chosen. If the inflection is smaller, potentiometric determination must be employed, and if the inflection is very small, we could tell that even potentiometric measurements would not give a satisfactory end point (see Section 3.4A).

F. TITRATION CURVES OF POLYBASIC ACIDS

A polybasic acid may be treated as a mixture of acids, that is, each stage of dissociation is treated as a separate monobasic acid. For example, for a tribasic acid H_3A,

$$H_3A \rightleftharpoons H_2A^- + H^+ \qquad (k_1)$$
$$H_2A^- \rightleftharpoons HA^- + H^+ \qquad (k_2) \qquad (k_1 > k_2 > k_3)$$
$$HA^- \rightleftharpoons A^{3-} + H^+ \qquad (k_3)$$

The theoretical curve can be constructed by treating the solution of the tribasic acid as a mixture of three monobasic weak acids in equivalent concentrations. By using Eqs. (3.20), (3.22), and (3.23), the curve is calculated for the acid H_3A. The curves for the second and third components are individually calculated in the same way, and the three partial curves are drawn in sequence as shown in Fig. 3.5. When the separate units are joined by tangents, as shown in Fig. 3.6, the complete theoretical curve has been obtained for the tribasic acid.

The curves in Figs. 3.5 and 3.6 were based on titration, with 1 N sodium hydroxide, of 10 ml of 1 M phosphoric acid diluted to 50 ml. The three pK_a values for phosphoric acid are listed in Table 3.2. It should be noted that the first step is more akin to a strong acid than a weak acid, and the theoretical curve should be based on this assumption. The practical curve shows no inflection at the commencement of step one; this is further reason for treating the first step as titration of a strong acid. Step two corresponds to titration of a weak acid and step three to titration of a very weak acid.

Application of Eq. (3.36) shows that the first end point should occur at pH 4.65 and the second at pH 9.6, and these values are borne out in practice. Equation (3.23) shows that the third end point should occur at about pH 12.8 to 13.0. However, examination of both practical and theoretical curves shows that the third end point could not possibly be detected. This explains
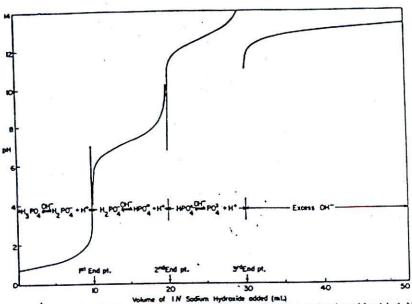
FIGURE 3.5: The partial theoretical curves for titration of 1 M phosphoric acid with 1 N sodium hydroxide.
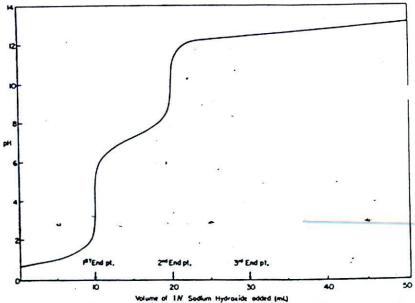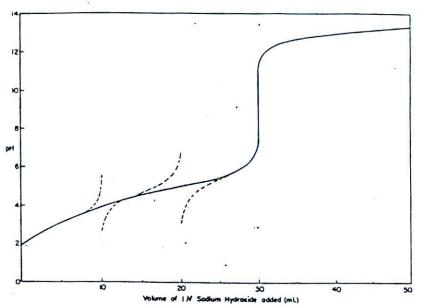
FIGURE 3.6: Theoretical curve for titration of 1 M phosphoric acid with 1 N sodium hydroxide.

why phosphoric acid titrations are carried out to the second end point only (see the 1963 edition of the *British Pharmacopoeia* and the XVII revision of the *United States Pharmacopeia.*)

Figure 3.7 shows the theoretical curve for titration of a molar solution of citric acid with normal sodium hydroxide solution. The first two end points are not detectable, but the third end point offers an excellent inflection which

FIGURE 3.7: Theoretical curve for titration of 1 *M* citric acid with 1 *N* sodium hydroxide.
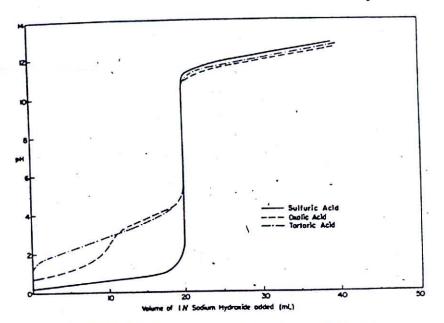
is readily detected by an appropriate indicator. Hence, as the theoretical curve predicts, assays of citric acid by titrimetric analysis are carried through to the third end point.

It should never be assumed that a dibasic acid will show two end points or that a tribasic acid will show three. Nor should it be assumed that any end point can be detected so long as the correct indicator for the appropriate pH range is available. Construction of theoretical curves usually gives a sufficiently accurate graph to allow decisions to be made as to which technique of end-point measurement to employ or whether a proposed acid/base titration can give an end point suitable for titrimetric analysis. In Fig. 3.8, curves have been drawn for the titration of various dibasic acids. These curves illustrate the dangers of unqualified assumptions. In each case, the theoretical curve will be found to match the experimental curve quite closely, and it could have been used to make any decisions about the method of assay, end-point detection, which end point to choose, etc.

FIGURE 3.8: Experimental curves for titration of some dibasic acids.

G. TITRATION CURVES OF POLYACIDIC BASES AND MIXED BASES

The general theories discussed in Sections 3.3E and 3.3F are applicable to mixed bases and polyacidic bases, with the appropriate changes in the choice of equations. The base with the smallest pK_b is the strongest base (and has the weakest conjugate acid). Once again the theoretical curves are drawn for each individual species of base present, and then the individual portions are joined by tangents to obtain the complete continuous theoretical curve. Inspection of these curves will show the feasibility of using any specific equivalence point in titration of a mixture or of a polyacidic base for analytical purposes.

H. AIDS TO THE MEMORIZATION OF EQUATIONS

A number of fundamental equations have been propounded in the foregoing sections to enable us to calculate theoretical curves for various types of titrations. Some of these are rather similar, and it is easy to make an error with one or other of the components of an equation or with a sign. There are a few simple rules which help to avoid these errors.

1. Dissociation Constants

K_a and K_b (hence also pK_a and pK_b) always refer to the weak acid or base being titrated and never to the titrant.

2. The Sign of pK

If the wrong sign is used, the answer will be less than pH 0, greater than pH 14, or on the wrong side of pH 7. The error should be easily discovered by inspection of the answer.

For example, Eq. (3.28) states that

$$pH = pK_w - pK_b - \log [salt]/[base]$$

If we accidentally change this to $pH = pK_w + pK_b - \log [salt]/[base]$ in the titration of 25 ml of 0.1 N ammonia solution when 5 ml of 0.1 N hydrochloric acid have been added, we calculate

$$pH = 14 + 4.75 - \log\frac{5}{20}$$
$$= 18.75 - (-0.6)$$
$$= 19.35$$

Since this is obviously wrong, the equation should immediately be checked for the correct signs of the terms.

3. Sign of log c

If any doubt arises concerning the correct sign of $\log c$ in an equation, calculate two values. (Two of the simplest are when $c = 0.1$ and $c = 1.0$.) Substitute the two values in the equation in use and note the direction in which the pH moves as c decreases (that is, as the solution becomes more dilute). The more dilute solution should always have a pH value closer to 7.

For example in Eq. (3.26),

$$pH = pK_w - \tfrac{1}{2}pK_b + \tfrac{1}{2}\log c$$

For a base where $pK_b = 4$ and $c = 0.1$,

$$pH = 14 - 2 + \tfrac{1}{2}(-1)$$
$$= 11.5$$

When $c = 1.0$,

$$pH = 14 - 2 + \tfrac{1}{2}(0)$$
$$= 12$$

that is, the more dilute solution has a pH closer to 7 and the sign of $\log c$ is therefore correct. If we change Eq. (3.26) to $pH = pK_w - \tfrac{1}{2}pK_b - \tfrac{1}{2}\log c$, when $c = 0.1$

$$pH = 14 - 2 - \tfrac{1}{2}(-1)$$
$$= 12.5$$

When $c = 1.0$, $$pH = 14 - 2 - \tfrac{1}{2}(0)$$
$$= 12$$

Since the more concentrated solution has a pH closer to 7, the sign of $\log c$ is incorrect, and the equation should be carefully checked.

3.4 CHOICE OF METHOD FOR DETERMINATION OF THE END POINT

A. GENERAL COMMENTS

An end-point inflection in an acid/base titration curve may be detected potentiometrically or by a color indicator method. It is generally accepted that the stoichiometric end point can be detected within ± 0.1 pH unit potentiometrically and to within ± 0.5 pH unit with an indicator. The choice of method will therefore depend upon the slope of the pH/volume curve at the end point and upon the precision required in the determination. For the majority of assays, the end-point inflection is steep enough that the relatively accurate potentiometric method has no practical advantages over the less precise indicator method. All the strong acid/strong base, weak acid/strong base, and weak base/strong acid titrations in common use give excellent indicator end points.

In the titration of highly colored solutions or where the end-point inflection is less than about 1.5 to 2.0 pH units, the potentiometric method has much more utility. However, hand plotting of pH readings can be tedious and time-consuming; thus indicator methods are used wherever possible in manual titrations.

There are several "automatic" titration units available in which a titration is carried out to a predetermined end-point pH. The instrument adds titrant continuously until this pH is reached, when the burette is closed off and the end-point volume is read off or printed out. In such instruments, a high degree of accuracy should be attainable, even when the slope of the curve at the end point is not too great, because slight deviations between the preset pH and the exact solution end-point pH will represent a very small volume of titrant. Some recording instruments are available that produce a pen-drawn curve during the titration. These instruments have the enormous advantage of permitting careful study of a complete experimental curve without the necessity of hand plotting. The first derivative of a pen-drawn pH/volume curve is very smooth and free from the irregularities of a first derivative of a manual titration curve (see Section 3.4C).

B. DETERMINATION OF THE END POINT FROM A GRAPH

When a strong acid/strong base titration curve is obtained potentiometrically, the end-point volume is very obvious, because the portion of the curve
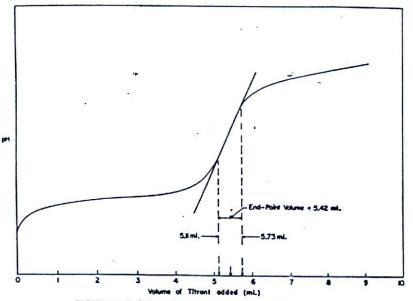
FIGURE 3.9: Determination of the end point from a graph.

near the end point is almost vertical. In titration of weak acids/strong bases and weak bases/strong acids, the end points are not always so obvious, and a "mechanical" approach may be helpful in locating them. The method is very simple: draw a straight line with a ruler along the steepest portion of the curve. Mark the volumes at which this line leaves the curve. The volume midway between these two volumes is the end point (see Fig. 3.9).

C. DERIVATIVE CURVES

If pH is plotted against volume of titrant added during an experiment, the familiar S-shaped curve is obtained. If we construct a graph of change in pH/change in volume of titrant added against the volume of titrant added, we obtain the first-derivative curve. Mathematically, if $x =$ pH and $y =$ volume of titrant, the first derivative is a plot of dx/dy against y. This curve will have the shape shown in Fig. 3.10, where the peak marks the end point. The peak value is the volume at which a maximum value is reached for the increase in pH with change in volume. When a manual titration is done potentiometrically, it is difficult to add the titrant in equal increments and, as a result, the first-derivative curve is usually rather irregular. It will frequently be necessary to extrapolate the two halves of the derivative curve to obtain the true maximum value of ΔpH/ΔV and hence the true end-point volume.
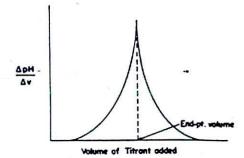
FIGURE 3.10: First-derivative curve.
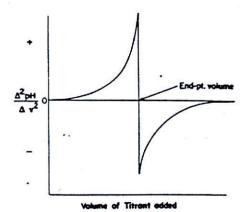
FIGURE 3.11: Second-derivative curve.

A second-derivative curve may also be considered. If $x = $ pH and $y = $ volume of titrant added, the second derivative will be a plot of d^2x/dy^2 against y, and a curve of the type shown in Fig. 3.11 will be obtained. It should be pointed out that the time and trouble involved in the additional calculations and graphs for second-derivative curves is *not* repaid by increased accuracy.

D. COLOR INDICATORS

A color indicator is a compound which shows a well-defined change in color over a definite pH range. This pH range is usually limited to one narrow part of the scale, although some indicators show multiple color changes at more than one part of the scale. For example, the useful pH range of methyl orange is 2.9 to 4.0.

Color indicators are mainly weak organic acids, although a few are weak bases. The color change is associated with a change from un-ionized to

ionized forms (or vice versa) of the weak acid or base. In solution, these indicators will exist as an equilibrium mixture of the two forms according to the usual reversible reaction equations.

For a weak acid indicator HIn,

$$HIn \rightleftharpoons H^+ + In^- \tag{3.37}$$

Un-ionized   Ionized
(color A)   (color B)

In a few cases, the un-ionized form is colorless, and we then have a *one-color indicator*. The majority of common indicators are *two-color indicators*.

From Eq. (3.37), it can be seen that, if a solution of an indicator is added to a titration mixture, its pH will cause the indicator equilibrium to reach a new value, which might be represented by a percentage ionization. As titrant is added to the titration mixture, change in pH will occur, and the indicator equilibrium will be displaced to a new value, represented by a new percentage ionization. As more titrant is added, a point will eventually be reached when the solution will show a definite color change associated with change in the percentage ionization of the indicator. Indicators are powerful dyes, and since small volumes of weak solutions are sufficient for a distinct color change, the acid-base equilibrium under study is not affected by addition of weak acid or weak base indicators.

$$K_I = \frac{[H^+][In^-]}{[HIn]}$$

where K_I is the dissociation constant of the indicator. Thus

$$[H^+] = K_I \frac{[HIn]}{[In^-]}$$

$$pH = pK_I + \log \frac{[In^-]}{[HIn]} \tag{3.38}$$

$$= pK_I + \log \frac{\cdot [\text{ionized form}]}{[\text{un-ionized form}]}$$

$$= pK_I + \log \frac{[\text{color B}]}{[\text{color A}]}$$

Equation (3.38) is really a variety of Eq. (3.22). Equation (3.28) holds for weak base indicators.

When $[In^-] = [HIn]$, then pH $= pK_I$, that is, pH $= pK_I$, at 50% ionization of the indicator.

Another constant, pK_T is occasionally used—it is called the *titration exponent* of the indicator. It is the pH at which the indicator shows the end-point color and usually lies within 0.5 of a pH unit of pK_I. The constants quoted in tables of indicators are pK_I.

When 10% of the indicator has changed from color A to color B, the average

human eye can detect the first discernible color change. At this point,

$$pH = pK_I + \log\frac{10}{90}$$
$$\doteqdot pK_I - 1$$

The last discernible color change occurs when there remains only 10% color A. At this point

$$pH = pK_I + \log\frac{90}{10}$$
$$\doteqdot pK_I + 1$$

This means that the pH range between the first and last color changes discernible to the eye is 2 units or a little less. Since the useful range for any indicator depends upon the value of the ratio [ionized form]/[un-ionized form] and since this will give rise to a constant shade of color at constant hydrogen ion concentration, it follows that the concentration of indicator used is not critical.

The one-color indicators are the only exception to this general rule. For these indicators, the color associated with the ionized form will become discernible when the ratio [ionized form]/[un-ionized form] produces color sufficient for the eye to detect. This limiting color level will depend upon the pH of the solution *and* upon the concentration of indicator used.

When the range of an indicator is quoted, for example, 2.9 to 4.0, at pH 2.9, the indicator is entirely in the "acid" form (and color) and, at pH 4.0, it is entirely in the "alkaline" form (and color). Although the range may not pass from acid to alkaline values, as in the example given, these terms are retained and they indicate the lower and upper limits of the range only. Any two-color indicator will show graded hues between the range limits, but each hue will be characteristic of a definite hydrogen ion concentration. The determination of pH by addition of indicator to a series of standard buffer solutions and comparison with the color of unknown plus indicator is based on this fact.

1. Factors Affecting the Indicator Range

(a) Solvents can affect K_I just as solvents can alter the hydrogen ion concentration. In analysis, the presence of high concentrations of alcohol will affect the range of many indicators, and care should be exercised in the choice of an indicator in such titrations.

(b) Temperature can affect K_I.

(c) Depending upon the colors involved, the detection of 10% acid color in 90% alkaline color may be easier or more difficult than the detection of 10% alkaline color in 90% acid color. If so, the pH range of the indicator will not be symmetrical about pK_I.

2. The Selection of an Indicator

Since there can be great variation in the pH of a titration mixture at the end point, depending upon the acid and base in use, the choice of an indicator must be based upon sound theoretical principles. The pH at the equivalence point should be known and an indicator then chosen which has a pK_I value as close to it as possible. In the absence of a table of pK_I values, the center of the indicator range is an excellent guide. Since each indicator has a limited range, a series of color indicators is necessary to span the pH scale. Table 3.4 lists some common indicators, their ranges and the colors of their various forms. A number of reference volumes[1,11-16] give a more complete listing of indicators.

Table 3.4: Ranges and Color Changes of Common Indicators

Indicator	pH scale												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Dimethyl yellow	← red →		2.9–4.0 ←					yellow					→
Methyl orange	← red →		2.9–4.0 ←					yellow					→
Bromophenol blue	← yellow → 3.0–4.6 ←							blue-violet					→
Congo red	← blue → 3.0–5.0 ←							red					→
Bromocresol green	← yellow → 3.8–5.4 ←							blue					→
Methyl red	← red → 4.4–6.0 ←							yellow					→
Litmus	← red → 4.5–8.3 ←							blue					→
Bromothymol blue	← yellow → 6.0–7.6 ←							blue					→
Phenol red	← yellow → 6.8–8.4 ←							red					→
Phenolphthalein	← colorless → 8.3–10.0 ← red →									colorless →			

A few simple, general rules can be stated which are applicable to most common laboratory acid-base titrations.

(a) For titration of weak acids, the end-point pH for decinormal solutions will fall approximately between pH 8 and pH 9.50. (These are rough limits only, since the degree of dilution prior to titration and the strength of the titrant will cause variation.) Any indicator whose pK_I value is in this vicinity will be suitable, for example, phenolphthalein. If the titrant is a very strong base and if the acid solution is not too dilute, the inflection associated with the end point will be sufficiently large that even indicators with pK_I as low as 5 to 7 will give excellent results.

(b) For titration of strong acids, whether the titrant is a strong or a weak base, the end-point pH will be on the acid side of pH 7, and the indicator of choice is usually Methyl Orange, although Methyl Red is about equally good. Phenolphthalein will be satisfactory if the titrant is a strong base (see Fig. 3.1).

(c) For titration of any acid against carbonate or bicarbonate, Methyl Orange is preferred. Phenolphthalein is useless in titrations where carbon dioxide is evolved, because it is weaker than carbonic acid and becomes inactivated.

(d) For titration of ammonia and other weak bases with strong acids, Methyl Red is the indicator normally chosen, since it gives a better end point than Methyl Orange (see Fig. 3.4)..
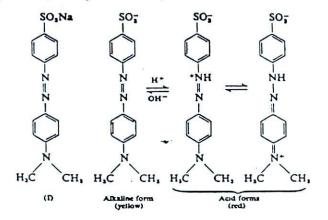
(e) For strongly alcoholic solution (for example, the determination of ketones in volatile oils) Dimethyl Yellow is one of the better indicators. It gives a sharper end point under these conditions than the more common indicators. For titration of weaker acids in aqueous alcohol, Phenol Red is very useful. It is probably the indicator of choice in titrations such as in the determination of the equivalent weight of a water-insoluble weak acid.
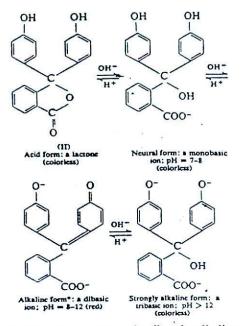
3. Color/Structure Relationships

It is not strictly accurate to state that the behavior of color indicators can be explained by ionic equilibria, the dissociation of weak acids and bases etc. The color is due to transformation of benzenoid to quinonoid systems or vice versa, within the molecule by rearrangement of the electronic structures. The rearrangements cause the formation of chromophores with different light absorption (and hence color) characteristics.

The common synthetic indicators can be divided into three principal chemical types.

a. The Azo Dyes. Examples in this class are Congo Red, Methyl Orange, Dimethyl Yellow, Methyl Red.

(I)   Alkaline form (yellow)   Acid forms (red)

(II)
Acid form: a lactone
(colorless)

Neutral form: a monobasic
ion; pH = 7–8
(colorless)

Alkaline form*: a dibasic
ion; pH = 8–12 (red)

Strongly alkaline form: a
tribasic ion; pH > 12
(colorless)
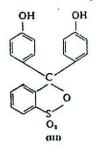
Methyl Orange (I) is red in acid and yellow in alkaline solution. This color change is associated with a rearrangement involving the azo link.

b. The Phthalein Compounds. Examples are phenolphthalein and thymolphthalein. Phenolphthalein (II) is colorless in acid solution, red in alkaline solution, and colorless in strongly alkaline solution.

c. The Sulfonphthalein Compounds. This type of compound and the parent phthalein indicators are also classed together as part of the large variety of triphenylmethane dyes. Examples are Bromocresol Green, Bromophenol Blue, Bromothymol Blue, and Phenol Red.

As the name suggests this class is identical with the phthalein compounds except that they are sulfonic acid not carboxylic acid derivatives [see, for

(III)

. * The deep red of the alkaline form is due to resonance among a variety of possible structures.

example, Phenol Red (III)]. Indicators in this class go through a series of changes similar to those outlined for phenolphthalein.

3.5 BUFFER SOLUTIONS

When acid or base is added to water, the hydrogen ion concentration changes markedly. If 1 ml of 0.1 N hydrochloric acid is added to 100 ml of water, the pH will drop from about 6 to 7 down to 3. If 1 ml of 0.1 N sodium hydroxide is added to 100 ml of water, the pH will rise to about 11.

When acid or base is added to certain other solutions, little change is observed in the hydrogen ion concentration or pH. Solutions which exert a resistance to change in hydrogen ion concentration are called *buffer* solutions. Strong acids and strong bases in solution can act as buffers in the low and high pH regions, but they are quite unsuitable in the intermediate pH range. The commonest buffer solutions contain mixtures of a weak acid and its salt and some contain a weak base and its salt. Weak acids or weak bases alone are poor buffering agents, as examination of the first portion of the titration curves in Figs. 3.2 and 3.4 will show.

A. WEAK ACID/SALT MIXTURES

The most common salts used to prepare buffer solutions are acetates, borates, citrates, phosphates, and phthalates.[1]

If a solution contains a mixture of acetic acid and sodium acetate for example, the acid will be even less dissociated than if it were alone because the acetate ion from the salt will depress the dissociation of the acid:

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+ \quad \text{(highly dissociated)}$$
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^- \quad \text{(slightly dissociated only)}$$

If acid is added to such a mixture, the hydrogen ions will be removed by the acetate ions from the salt:

$$CH_3COO^- + H^- \rightleftharpoons CH_3COOH$$

More of the weak acid is formed, but very little difference will occur in the hydrogen ion concentration because of the very low degree of dissociation of the acid under these conditions.

If base is added to such a mixture, the hydroxyl ions will be removed by the weak acid to form strongly dissociated salt; again, little change is found in the hydrogen ion concentration:

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

The acid is said to be in reserve—unable to increase the hydrogen ion concentration but available to neutralize added base. Similarly, the acetate ion

(a base) is unable to contribute to the hydroxyl ion concentration but is available to neutralize added acid.

The Henderson-Hasselbach equation (3.22) expresses the relationship between hydrogen ion concentration, the concentration of weak acid and its salt, and the dissociation constant of the acid:

$$pH = pK_a + \log \frac{[salt]}{[acid]} \qquad (3.22)$$

The *buffering capacity* of a solution is defined as the number of gram equivalents of strong acid or strong base required to cause a change of 1 pH unit in 1 liter of the solution. It should be clear from Eq. (3.22) that the buffering capacity will be dependent upon the ratio [salt]/[acid] and upon the absolute concentrations of the salt and the acid. Maximum buffering capacity will be exhibited when [salt] = [acid], and it will increase with increase in salt and acid concentrations.

EXAMPLE 21: Calculate the change in pH on adding 10 ml of 0.1 N sodium hydroxide to a solution containing 0.1 gram equivalent of sodium acetate and acetic acid.

The pH before addition of base is found from Eq. (3.22):

$$pH = 4.75 + \log \frac{0.1}{0.1}$$
$$= 4.75$$

After addition of the base,

$$pH = 4.75 + \log \frac{0.1 + 0.001}{0.1 - 0.001}$$
$$= 4.75 + \log \frac{0.101}{0.099}$$
$$= 4.759$$

The pH is changed by less than 0.01 pH unit.

EXAMPLE 22: Calculate the change in pH on adding 10 ml of 0.1 N sodium hydroxide to a solution containing 0.1 gram equivalent of acetic acid and 0.01 gram equivalent of sodium acetate.

For the pH before addition of the base, we have

$$pH = 4.75 + \log \frac{0.01}{0.1}$$
$$= 3.75$$

After addition of the base,

$$pH = 4.75 + \log \frac{0.01 + 0.001}{0.1 - 0.001}$$
$$= 3.80$$

Therefore, the change in pH is 0.05 units or about five times the change in Example 21.

Similarly, alteration of the solution to contain 0.1 gram equivalent of sodium acetate and 0.01 gram equivalent of acetic acid gives a change of 0.05 pH unit on addition of 10 ml of 0.1 N sodium hydroxide.

EXAMPLE 23: Calculate the buffering capacity of a solution containing 0.1 gram equivalent of sodium acetate and acetic acid.

The pH of this buffer is 4.75. To increase (or decrease) the pH by 1 unit, the ratio [salt]/[acid] will have to alter by a factor of 10:

$$5.75 = 4.75 + \log \frac{[salt]}{[acid]}$$

$$\log \frac{[salt]}{[acid]} = 1$$

Therefore,

$$\frac{[salt]}{[acid]} = 10$$

To reach pH 5.75, [salt] will have to increase to a concentration of about 0.182 gram equivalent and the acid decrease to about 0.018. The buffering capacity of the buffer mixture is therefore 0.082 gram equivalent.

The buffering capacities of some other common solution strengths are listed in Table 3.5.

TABLE 3.5: Buffering Capacities of Some Weak Acid/Salt Mixtures

Concentration of acid and salt	Buffering Capacity, gram equivalents
0.01	0.008
0.02	0.016
0.05	0.041
0.10	0.082
0.20	0.164
0.50	0.410
1.00	0.820

In analytical work, fairly high buffering capacities may be required, but it should be kept in mind that pharmaceutical formulations for injections and eye drops should contain low-capacity buffers to avoid straining the buffering resources of the body, resulting in possible tissue damage.

Most buffers range from 0.05 to about 0.5 N with respect to the acid and salt. Each individual buffer can be safely used over a range of 1 pH unit on either side of the pK_a value of the acid. When choosing a buffer system,

choose an acid with a pK_a value as close as possible to the desired pH. After preparation, the pH of a buffer should always be checked, especially if the salt concentrations are high.

B. WEAK BASE/SALT MIXTURES

A mixture of a weak base B and its salt BH^+ acts as a buffer in a manner analogous to the weak acid/salt mixture. If acid is added, the base removes the hydrogen ions as the fully dissociated salt BH^+, with little or no accompanying change in hydrogen or hydroxyl ion concentration. The base is so slightly dissociated that removal of some scarcely alters the level of hydroxyl ions:

$$B + H^+ \rightleftharpoons BH^+$$

If base is added to the mixture, the salt removes hydroxyl ions and forms more of the very poorly dissociated base B:

$$BH^+ + OH^- \rightleftharpoons B + H_2O$$

Equation (3.27) has already been derived to express the relationship between hydroxyl ion concentration, the concentration of the weak base and its salt, and the dissociation constant of the base:

$$pOH = pK_b + \log \frac{[salt]}{[base]} \qquad (3.27)$$

or

$$pH = pK_w - pK_b - \log \frac{[salt]}{[base]} \qquad (3.28)$$

Once again, it can be shown that maximum buffering capacity is obtained when [salt] = [base]. Equation (3.28) can be used to calculate the pH of any such buffer solution and to determine the change in pH on addition of acid or base.

PROBLEMS

P3.1. (a) Calculate the pH of a fully dissociated 0.02 N solution of sulfuric acid.

    (b) Calculate the pH of an 0.05 N solution of hydrochloric acid, if it is 98% dissociated.

    (c) Calculate the pH of an 0.6% w/v solution of acetic acid which is completely dissociated. What will be the pH of the solution if it is only 50% dissociated?

    (d) What is the hydrogen ion concentration of a solution of pH 1.40?

P3.2. (a) Calculate the hydroxyl ion concentrations of 0.5 N, 0.066 N, 0.02 N, and 0.01 N solutions of a strong base. Assume 100% dissociation in each case.

    (b) Calculate the pH of the solutions in part (a) of this question.

    (c) Calculate the pH of solutions of hydroxyl ion concentration 1×10^{-4}, 7.2×10^{-4}, 2.35×10^{-3}.

    (d) If an 0.2% w/v solution of sodium hydroxide is 93% dissociated, what is the pH of the solution?

P3.3. Calculate the hydrogen ion concentration and the pH of the following solutions:

(a) 0.05 N acetic acid $(K_a = 1.76 \times 10^{-5})$.

(b) 0.15 N tartaric acid $(K_a = 9.6 \times 10^{-4})$.

(c) 0.1 N hydrogen cyanide $(K_a = 4.93 \times 10^{-10})$.

P3.4. Calculate the hydroxyl ion concentration and the pH of the following solutions:

(a) 0.5 N ammonia $(K_b = 1.79 \times 10^{-5})$.

(b) 1 N pyridine $(K_b = 1.71 \times 10^{-9})$.

(c) 0.01 N dimethylamine $(K_b = 5.2 \times 10^{-4})$.

P3.5. Calculate the pH of a decinormal solution of ammonium chloride at 24°C. $(K_b$ for ammonia $= 1.79 \times 10^{-5}.)$

P3.6. What molar ratio of sodium acetate to acetic acid is required to prepare an acetate buffer of pH 5.00? $(K_a$ for acetic acid is $1.76 \times 10^{-5}.)$

P3.7. The dissociation constant of acetic acid at 25°C is 1.76×10^{-5}. Calculate (a) percentage dissociation in an 0.2 N solution, (b) the hydrogen ion concentration, and (c) the pH.

(*Hint*: in part (a), use the shortened equation $K_a = x^2 c$ instead of $K_a = [x^2 c/(1 - x)]$; this avoids a quadratic equation.)

P3.8. Calculate the three values (a), (b), and (c) in Problem P3.7 for an 0.2 N solution of acetic acid which contains ⅓ gram molecule of sodium acetate per liter. Assume 100% dissociation of the salt.

P3.9. Ephedrine is a monoacidic base, mw = 165. Calculate the degree of dissociation of ephedrine in a 1% w/v aqueous solution

Calculate the answer using (a) the full equation and (b) the abbreviated form suggested in Problem P3.7. Compare your answers and also the time required to arrive at each. $(K_b = 2.3 \times 10^{-5}.)$

P3.10. Calculate what must be the concentration of lactic acid so that when it is mixed with 0.02 N acetic acid, no change occurs in the ionization of either acid. $(K_a$ for lactic acid $= 1.39 \times 10^{-4}$; K_a for acetic acid $= 1.76 \times 10^{-5}.)$

P3.11. How many grams of ammonium chloride must be added to a liter of 0.1 N ammonium hydroxide to yield a solution of pH 9.3? $(K_b$ for ammonia $= 1.79 \times 10^{-5}.)$

P3.12. (a) Show how the Henderson-Hasselbach equation may be derived.

(b) On suitable graph paper, plot the theoretical curve for neutralization of 10 ml of 0.5 N pyridine with 0.5 N hydrochloric acid after the addition of 0, 2, 4, 6, 8, 9, 9.5, 9.9, 9.99, 10, 10.01, 10.1, 10.5, 11, 12, 14, 16, 18, and 20 ml of acid. Assume that the 10 ml pyridine were diluted to 100 ml with distilled water prior to commencement of the titration. Plot pH as the ordinate and the volume of acid added as the abscissa.

(c) Explain how you would choose an indicator for this titration on a theoretical basis.

P3.13. Two monobasic acids A and B are mixed in equal molar concentrations. The pK_a values of the two acids are, respectively, 3.25 and 6.31. Calculate the percentage of the stronger acid A, which is actually neutralized at the first end point.

P3.14. Calculate the theoretical curve for titration of (a) 25 ml of 1 N tartaric acid and (b) 25 ml of 1 N oxalic acid, assuming the acid solutions to be diluted to 50 ml prior to titration.

Compare the graphs obtained with those found in Fig. 3.8.

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