INTRODUCTION

Volumetric titrations are widely used for
routine analysis because of their rapidness, convenience
and accuracy. However, most weak acidic drugs are not
usually titrated in aqueous solvent because their disso-
ciation constants are so small that their reactions
are not sufficiently complete to yield satisfactory end
points. Another reason is their poor solubilities in
water. Thus, neutralization titrations of these weak
acidic drugs are usually conducted in non-aqueous system.
However, some extra precautions should be considered.
First, moisture is generally to be avoided in using non-
aqueous procedures. Water, being a weak acid, will
compete with the weak acid for the basic titrant. Hence,
the sharpness of the end point will be lost. Experi-
mentally, it has been found that the moisture content in non-
aqueous titrimetry should be held to less than 0.05% so as
not to have any appreciable effect on end point determina-
tion(1). Second, temperature must be strictly constant
throughout the titration because of the high coefficient
of expansion of organic solvent (2). Third, utilization
of indicators for determination of end points may not be
totally satisfactory. The color change may not be as

obvious as might be desired. Hence, the potentiometric end point determination with a glass electrode should be employed. However, it has been recommended that a glass electrode and a reference electrode should be used with glass frit diaphram tubes and an electrolyte and appropriate solvent such as a saturated alcoholic solution of LiCl is filled to ensure good conductivity. This is not practical for routine analysis.

According to the problems of the titration in non-aqueous solvent, the titration in aqueous solvent may become useful if we can avoid the problems of precipitation during the course of titration and difficulty in end point determination. Mixed solvent of organic solvent and water may be employed in order to increase the solubility of weak acidic drugs and potentiometry will be employed when a suitable indicator is not available (3, 4).

Various methods for the determination of end point volumes in potentiometric titration are classified into three main types according to Anfalt and Jagner (5).

1. Methods Based on the Sigmoid Form of a Titration Curve

The end point will be located on the steeply rising portion of the curve. Although the curve shows a very clearly marked steep portion at the equivalence region, an approximate value of end point will be given. Thus, a titration curve of weak acid, which has poorly

defined inflection point, will give an unreasonable end point value. These methods are, as followed :

1.1 Tubb's or Circle Fitting Method

In this method (6, 7), a thin rigid plastic sheet is needed on which is marked a series of circles or concentric arcs. One of the circles is constructed to partly coincide with the sigmoid part of the titration curve for V > Ve and the other circle is constructed in a similar way for V < Ve. The end point is evaluated as the V value where the line connecting the centers of two circles intersects the titration curve.

1.2 The Kohn-Zitko Method

In this method (5), a straight line which intersects the primary titration curve at three points is constructed so that the two areas formed between the titration curve and the straight line are equal. The end point is the point where the two areas meet.

1.3 The Method of Bisection

Each of straight lines is extended from the curve when it shows reasonably good straight lines before and after the steep part of the curve, the lower portion to the right and the upper portion to the left. Then at suitable points vertical lines are erected, one to the right of the steep part of the titration curve and one to the left. These vertical lines are then bisected, and

the mid points are joined. The line joining the mid points intersects the titration curve at the end point volume (7).

1.4   The Method of Parallel Tangents

A thin rigid plastic, on which is marked a central horizontal line, together with a number of pairs of parallel lines drawn on either side of the central line, is laid on the top of the titration curve in such a position that a given pair of parallel lines is tangential to the upper and lower parts of the titration curve. A pencil is marked through the central slot at the point where it cuts the steep part of the titration curve then indicates the end point (7).

2.   Differential Methods

These methods are concerned with differences in potential or pH between each new addition of titrant. Accuracy of measured potential or pH is important for end point evaluation because differentiation of error potentials or pHs will give a poor end point value. Several methods are described.

2.1   Method Based on $\triangle E/\triangle V$ Values

The ratios of $\triangle E/\triangle V = (E_{n+1} - E_n)/(V_{n+1} - V_n)$ are plotted against $(V_{n+1} + V_n)/2$ where the V_n denote the volumes of titrant and E_n denote potential values that correspond to the volumes of titrant in the nth titration

point. The maximum point of the curve is the end point.

.2.2 Cohen's Method

According to the $\triangle E/\triangle V$ plots, several values of $\triangle E/\triangle V$ and the corresponding volumes are selected from either curves. Let L for the volume taken from the left hand curve (before the end point) and R for the volume taken from the right hand curve (after end point). $M = \frac{1}{2}(L + R)$, the average of these two values is computed, and the difference between these two values is D (D = R − L). Plot M as a function of D, as illustrated in Figure 1, the extrapolation of D = 0 is the end point (8).

2.3 The Kolthoff-Hahn-Fortuin Methods

This group of methods exploits titration data around end point. Ratios between the corresponding E values are calculated. The end point is evaluated from parameters (ρ) which is obtained from Kolthoff (3), Hahn (5), or Fortuin nomograph (9). The end point is calculated from equation as followed :

$$Ve = V + \rho V$$

2.4 Second Derivatives

The plot of $\triangle^2 E/\triangle V^2$ and V locates the end point with the intersection on the volume axis. $\triangle^2 E/\triangle V^2 = (\triangle E_{n+1} - \triangle E_n)/(V_{n+1} - V_n)^2$ where $\triangle E_n$ denote the difference values of potential and V_n are the volumes in
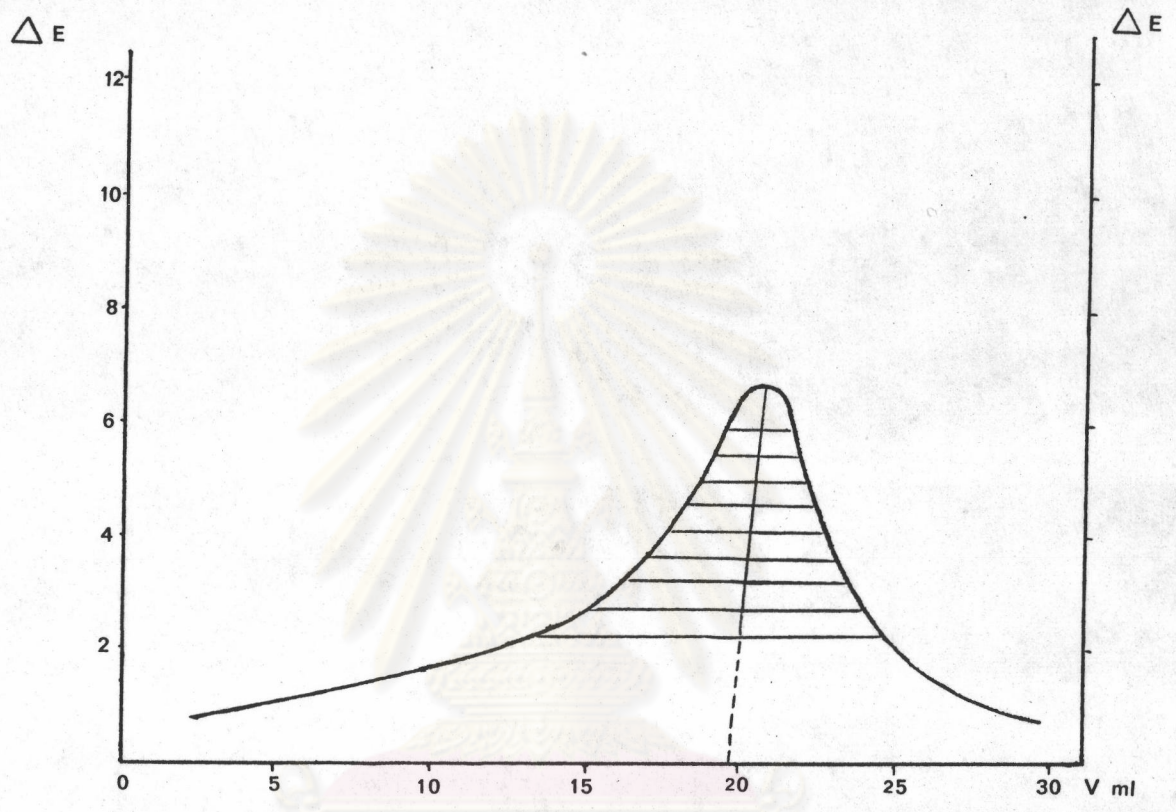
Figure 1   End point determination by Cohen's method

the nth titration point.

2.5   The $\triangle V/\triangle E$ or Gran's I Method

$\triangle V/\triangle E$ is plotted against $(V_{n+1} + V_n)/2$ where $\triangle V = V_{n+1} - V_n$ and $\triangle E = E_{n+1} - E_n$. Two straight lines one before and one after the end point will intersect at the V value corresponding to the end point (10).   The use of linear line regression will improve the precission of the evaluation.   Johansson and Gran extended this method with the basis on the method of stepwise addition of equal volumes of titrant which showed better results (11, 12).

2.6   The Liteanu-Cormos Method

This method (13), $\triangle V/\triangle E$ values are used with a correction for the difference in slope at $V = V_{n+1}$ and $V = V_n$.   The linear lines before and after the end point are calculated by using the statistical formula for linear line regression.

2.7   The Cavanagh-Herringshaw Method

This method is partly based on mass balance condition (14, 15).   It is assumed that the reaction between the titrant and titrated solution is complete in all titrations except in the immediate vicinity of the equivalence point.   The volume at end point can be obtained from a few measurements at the beginning of the titration.   The differentiation in Nernst equation of two

successive titration points, V_n and V_{n+1}, predicts the end point according to

$$\frac{1}{[Ve - (V_n + V_{n+1})/2]} = \frac{FdE}{RTdV} - \frac{1}{[Vo + (V_n + V_{n+1})/2]}$$

where F is Faraday number, R is real gas constant and T is absolute temperature.

3. Methods Based on Mass Balance and Equillibrium Equation

3.1 Titration to Preselected EMF Value

A Titration is done by opposing the emf value in question with a known difference potential between the reference electrode and indicator electrode at the equivalence point. Titrant is added until no current flows. At this point the volume of titrant is the end point volume. This method is frequently applied in automatic titrators.

3.2 Multi-Parameter Refinement Method

This new technic of end point location was described by Barry and Meites (16). The multiparameter curve fitting is employed to combine data obtained during the titration with a theoretical equation to yield the best estimate of the parameters in that equation. There are three significant parameters in the equation. Those are the concentration of the titrated solution, an equillibrium constant and an apparent activity coefficient.

The function is expressed arithmatically by means of mass balance and equillibrium equations. A computer is necessary for execution.

3.3 Gran's Second Method

This method is based on an original idea of Sorensen (17), who plotted the antilogarithm of the pH as a function of the titrant volume which gave a straight line instead of sigmoid form of titration curve. Gran (18) had introduced a correction for the volume change during the course of titration, and he suggested that the correction made a better straight line than Sorensen's method. The end point volumes were determined by extrapolation of the straight lines before or after equivalence point.

From various method as described above, the optimal method for evaluating the end point of a particular potentiometric titration which respect to systematic error, precision and time required is the methods based on mass balance and equilibrium equations (5). However, the method of titration to a preselected emf value has a limit due to electrode reproducibility while multiparameter refinement method involves complicated equations so that it needs a programmable calculator for end point execution. Gran's second method, then seems to be the most suitable method for utilizing in routine works because of its accuracy, precision, rapidness and simplicity in

calculation (17, 18, 19). A semi-antilogarithmic paper (20, 21) and a Gran ruler (22) were suggested in Gran's second method in order to plot more easily.

The end point determination by Gran's second method is beneficially carried out by the technic of stepwise addition titration. A known volume of titrant is transfered to the titrated solution and measuring the pH values when equilibrium has reached (17, 23, 25).

Gran's second method can be applied, particulary when analyte concentration is too low to give well-defined end points. The advantages of utilizing low concentration of sample are the less problem will be obtained from precipitation of the unionized species and also ionic strength and the activity coefficient can be better controlled (25, 26, 27). Frazer and coworkers presented end point determination for the titration which was run on low concentration sample near the detection limited of the electrode by Gran's method which yielded excellent results (28).

In 1963, Ingman and Still (29) found that Gran's second method could not evaluate end point of a very weak acid ($Ka < 10^{-7}$) as Gran had not accounted for autoprotolysis of water. Therefore, the curvature near equivalence point would occur and the erroneous end point volume was obtained (29, 30).

The derivations for some weak acids and strong base titration which are modified from Ingman and Still's idea are shown as followed :

Derivations of Gran equations for titration data prior to equivalence point

1. Titration of monoprotic acid whose conjugate base has higher charge than its acid.

1.1 Neutral Weak Acid

When a weak acid, HA, is titrated with a strong base (sodium hydroxide),

$$HA \; + \; NaOH \; \longrightarrow \; H_2O \; + \; NaA$$
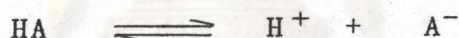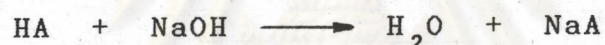
$$HA \; \rightleftharpoons \; H^+ \; + \; A^-$$

$$Ka \; = \; \frac{[H+][A-]}{[HA]} \qquad\qquad Eq. \; 1$$

The solution must be electrically neutral, meaning that

$$[A-] \; + \; [OH-] \; = \; [Na+] \; + \; [H+] \qquad\qquad Eq. \; 2$$

and at the equivalence point

$$VeN \; = \; (Vo \; + \; V)C_{HA} \qquad\qquad Eq. \; 3$$

The concentration of sodium ion at any volumes of titrant is

$$[Na+] \; = \; \frac{VN}{Vo \; + \; V} \qquad\qquad Eq. \; 4$$

and the fact that

$$C_{HA} = [HA] + [A-] \qquad \text{Eq. 5}$$

When combine equations 2 and 4 , give

$$[A-] = \frac{VN}{V_o + V} + [H+] - [OH-] \qquad \text{Eq. 6}$$

substitution of equation 6 into equation 5 and combining it with equation 3

$$\frac{VeN}{V_o + V} = [HA] + \frac{VN}{V_o + V} + [H+] - [OH-]$$

which may be rearranged to,

$$[HA] = \frac{VeN}{V_o + V} - \left(\frac{VN}{V_o + V} + [H+] - [OH-] \right) \text{Eq. 7}$$

subsititution of equation 6 and equation 7 into equation 1

$$Ka = \frac{[H+] \left(\dfrac{VN}{V_o + V} + [H+] - [OH-] \right)}{\dfrac{VeN}{V_o + V} - \left(\dfrac{VN}{V_o + V} + [H+] - [OH-] \right)} \quad \text{Eq. 8}$$
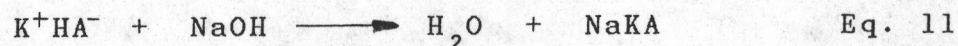
and rearrangement gives

$$G[H+] = KaVeN - KaG \qquad \text{Eq. 9}$$

where

$$G = VN + (V_o + V)\{[H+] - [OH-]\} \qquad \text{Eq. 10}$$

1.2 Ionized weak acid

When ionized weak acid, such as K^+HA^- is titrated, the reaction is

$$K^+HA^- + NaOH \longrightarrow H_2O + NaKA \qquad \text{Eq. 11}$$

and dissociation reaction of weak acid is

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad \text{Eq. 12}$$

$$Ka = \frac{[H+][A^{2-}]}{[HA^-]} \qquad \text{Eq. 13}$$

Charge balance of this titration solution is

$$[H+] + [Na+] + [K+] = [OH-] + 2[A^{2-}] + [HA-] \qquad \text{Eq. 14}$$

At the equivalence point

$$C_{HA^-} = [K+] = \frac{VeN}{Vo + V} \qquad \text{Eq. 15}$$

and

$$C_{HA^-} = \frac{VeN}{Vo + V} = [HA-] + [A^{2-}] \qquad \text{Eq. 16}$$

Substitution equation 15 and 4 in equation 14

$$[H+] + \frac{VN}{Vo + V} + \frac{VeN}{Vo + V} = [OH-] + 2[A^{2-}] + [HA-] \qquad \text{Eq. 17}$$

Equation 17 is substracted by equation 16, yields

$$[H+] + \frac{VN}{Vo + V} = [OH-] + [A^{2-}]$$

and rearrangement

$$[A^{2-}] = \frac{VN}{Vo + V} + [H+] - [OH-] \qquad \text{Eq. 18}$$

Substitution equation 18 in equation 16 and rearrangement

$$[HA-] = \frac{VeN}{Vo + V} - \left(\frac{VN}{Vo + V} + [H+] - [OH-] \right) \qquad Eq. \ 19$$
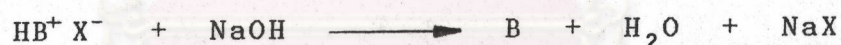
Substitution equations 18 and 19 in equation 13, gives

$$Ka = \frac{[H+] \left(\dfrac{VN}{Vo + V} + [H+] - [OH-] \right)}{\dfrac{VeN}{Vo + V} - \left(\dfrac{VN}{Vo + V} + [H+] - [OH-] \right)} \qquad Eq. \ 20$$
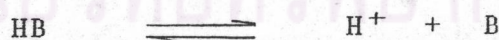
Equation 20 is transformed by G and rearranged

$$G[H+] = KaVeN - KaG \qquad Eq. \ 21$$

2. Titration of monoprotic acid whose conjugate base has lower charge than its acid.

When an acid salt (HB^+X^-) is titrated with sodium hydroxide. The reaction is

$$HB^+ X^- + NaOH \longrightarrow B + H_2O + NaX$$

The dissociation of weak acid is

$$HB \rightleftharpoons H^+ + B$$

$$Ka = \frac{[H+][B]}{[HB+]} \qquad Eq. \ 22$$

and charge balance of the solution ,

$$[HB+] + [H+] + [Na+] = [OH-] + [X-] \qquad Eq. \ 23$$

At the equivalence point,

$$VeN = C_{HB^+}(Vo + V) \qquad \text{Eq. 24}$$

During titration, mass balance of weak acid is

$$C_{HB^+} = [X-] = [HB+] + [B] \qquad \text{Eq. 25}$$

combining equations 23, 24, and 4 gives

$$[HB+] = \frac{VeN}{Vo + V} - \left(\frac{VN}{Vo + V} + [H+] - [OH-] \right) \qquad \text{Eq. 26}$$

substitution equation 26 into equation 25, combining with equation 24 and rearrange to

$$[B] = \frac{VN}{Vo + V} + [H+] - [OH-] \qquad \text{Eq. 27}$$

substitution equations 26 and 27 into equation 22 , gives

$$Ka = \frac{[H+]\left(\dfrac{VN}{Vo + V} + [H+] - [OH-] \right)}{\dfrac{VeN}{Vo + V} - \left(\dfrac{VN}{Vo + V} + [H+] - [OH-] \right)} \qquad \text{Eq. 28}$$

equation 28 is transfromed by G and rearranged

$$G[H+] = KaVeN - KaG \qquad \text{Eq. 29}$$

It is found that equations 9, 21 and 29 are identical linear equations which are corrected for the change of volumes during the course of titration and the autoprotolysis constant of water. If,

$$\frac{VN}{Vo + V} \gg [H+] - [OH-] \qquad \text{Eq. 30}$$

equations 9, 21 and 29 will be reduced to

$$V[H+] = KaVe - KaV \qquad \text{Eq. 31}$$

Equation 31 is similar to Gran's second plot which is corrected only for the change of volumes during the course of titration.
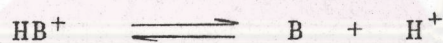
3. Titration of diprotic acid whose conjugate base has lower charge than its acid.

When a dibasic acid, such as salt of weak base, $H_2B^{2+}X^{2-}$ is titrated. The dissociation of this acid is
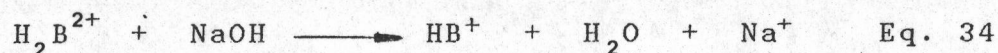
$$H_2B^{2+} \rightleftharpoons HB^+ + H^+$$
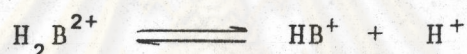
$$Ka_1 = \frac{[HB+][H+]}{[H_2B^{2+}]} \qquad \text{Eq. 32}$$

and

$$HB^+ \rightleftharpoons B + H^+$$

$$Ka_2 = \frac{[B][H+]}{[HB+]} \qquad \text{Eq. 33}$$

If $Ka_1 \gg Ka_2$, such that neutralization of the first acidic function is completed prior to neutralization of the second acidic function, the reaction before first equivalence point is

$$H_2B^{2+} + NaOH \longrightarrow HB^+ + H_2O + Na^+ \qquad \text{Eq. 34}$$

The charge balance equation for the solution is

$$[H+] + [HB+] + 2[H_2B^{2+}] + [Na+] = [OH-] + 2[X^{2-}] \qquad \text{Eq. 35}$$

The mass balance of weak acid gives

$$C_{H_2B^{2+}} = [X^{2-}] = [HB+] + [H_2B^{2+}] \qquad \text{Eq. 36}$$

substracting equation 35 with 36 yields

$$[H+] + [H_2B^{2+}] + [Na+] = [OH-] + [X^{2-}] \qquad \text{Eq. 37}$$

If,

$$[X^{2-}] = C_{H_2B^{2+}} = \frac{V_{e_1}N}{V_0 + V} \qquad \text{Eq. 38}$$

substitution equations 4 and 38 into equation 37

$$[H_2B^{2+}] = \frac{V_{e_1}N}{V_0 + V} - \left(\frac{VN}{V_0 + V} + [H+] - [OH-] \right) \qquad \text{Eq. 39}$$

substitution equation 39 into equation 36 and combining with equation 38 which may be rearranged to

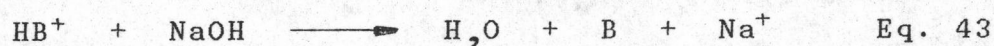$$[HB+] = \frac{VN}{V_0 + V} + [H+] - [OH-] \qquad \text{Eq. 40}$$

substitution equations 39 and 40 in equation 32

$$Ka_1 = \frac{[H+]\left(\dfrac{VN}{V_0 + V} + [H+] - [OH-] \right)}{\dfrac{V_{e_1}N}{V_0 + V} - \left(\dfrac{VN}{V_0 + V} + [H+] - [OH-] \right)} \qquad \text{Eq. 41}$$

substitution G in equation 41 and rearrange

$$[H+]G = Ka_1 V_{e_1} N - Ka_1 G \qquad \text{Eq. 42}$$

Before second equivalence point, it is assumed that $[H_2B^{2+}]$ is approximately zero. The reaction is

$$HB^+ + NaOH \longrightarrow H_2O + B + Na^+ \qquad \text{Eq. 43}$$

and charge balance

$$[H+] + [HB+] + [Na+] = [OH-] + 2[X^{2-}] \qquad \text{Eq. 44}$$

The mass balance of weak acid is

$$C_{HB^+} = 2[X^{2-}] = [HB+]_t + [B] \qquad \text{Eq. 45}$$

where

$$C_{HB^+} = 2[X^{2-}] = \frac{Ve_2 N}{Vo + V} \qquad \text{Eq. 46}$$

and

$$[HB+]_t = \frac{Ve_1 N}{Vo + V} + [HB+] \qquad \text{Eq. 47}$$

substitution equations 46 and 4 in equation 44, give

$$[HB+] = \frac{Ve_2 N}{Vo + V} - \left(\frac{VN}{Vo + V} + [H+] - [OH-] \right) \qquad \text{Eq. 48}$$

equations 45, 47 and 48 give

$$[B] = \left(\frac{VN}{Vo + V} + [H+] - [OH-] \right) - \frac{Ve_1 N}{Vo + V} \qquad \text{Eq. 49}$$

substitution equations 48 and 49 in equation 33

$$Ka_2 = \frac{[H+]\left[\left(\frac{VN}{Vo + V} + [H+] - [OH-] \right) - \frac{Ve_1 N}{Vo + V} \right]}{\frac{Ve_2 N}{Vo + V} - \left(\frac{VN}{Vo + V} + [H+] - [OH-] \right)} \qquad \text{Eq. 50}$$

and substitution G in equation 39 and rearrangement gives

$$[H+](G - Ve_1 N) = Ka_2 Ve_2 N - Ka_2 G \qquad \text{Eq. 51}$$

If it is assumed that

$$\frac{VN}{Vo + V} \quad >> \quad [H+] - [OH-]$$

equations 42 and 51 are reduced to, respectively

$$V[H+] \quad = \quad Ka_1 Ve_1 - Ka_1 V \qquad \text{Eq. 52}$$

$$[H+](V - Ve_1) \quad = \quad Ka_2 Ve_2 - Ka_2 V \qquad \text{Eq. 53}$$

For the titration of ionized dibasic acid, equations 42 and 52 are linear equation. Equation 42 involves the autoprotolysis of water and the change of volumes during the course of titration while equation 52 corrects only the change of titration volumes. Both equations 42 and 52 are employed for first end point determination. Equations 51 and 53 are non-linear equation, however, they will be reduced to a simple linear equation once Ve_1 is known and second end point determination also obtained from extrapolation of linear line.

If a mixture of two monoprotic acids whose conjugate base has lower charge than its acid and the difference of dissociation constants is high enough that overlapping of each neutralization reaction will not occur, equations 42, 51, 52 and 53 can also be employed in the same way as the titration of ionized dibasic acid.

4. Titration of monoprotic weak acid whose unionized conjugate base precipitate during the course of titration.

Titration of some weak acids which their unionized cojugate base has limit solubility, precipitation may occur during the course of titration.

$$HB^+ \ + \ NaOH \longrightarrow B \ + \ Na^+ \ + \ H_2O$$

where B is the unionized form of weak acid, HB^+X^- The dissociation of HB^+ is
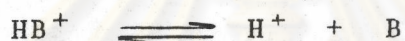
$$HB^+ \rightleftharpoons H^+ \ + \ B$$

$$Ka \ = \ \frac{[H+][B]}{[HB]} \qquad\qquad Eq. \ 54$$

Concentration of the unionized form, B, will increase during the course of titration. Once concentration of B in the solution exceeds its solubility, the excess B will precipitate out and the concentration of the dissolved B will remain constant throughout the rest of titration. When this phenomenon occurs, equation 54 describes the dissociation process only upto the point at which B starts to precipitate. Beyond this point, the dissociation is described (31, 32) by :

$$Ka \ = \ \frac{[H+][B]_c}{[HB+]} \qquad\qquad Eq. \ 55$$

where $[B]_c$ is the concentration of dissolved B on

saturation, charge balance for this solution is

$$[HB+] + [Na+] + [H+] = [OH-] + [X-] \qquad \text{Eq. 56}$$

and the fact that

$$C_{HB^+} = [X-] = \frac{VeN}{Vo + V} \qquad \text{Eq. 57}$$

Substitution of equations 4 and 57 gives

$$[HB+] = \frac{VeN}{Vo + V} - \left(\frac{VN}{Vo + V} + [H+] - [OH-] \right) \qquad \text{Eq. 58}$$

Combining of equations 55 and 58 yields

$$Ka = \frac{[H+][B]_c}{\frac{VeN}{Vo + V} - \left(\frac{VN}{Vo + V} + (Vo+V)\{[H+]-[OH-]\} \right)} \qquad \text{Eq. 59}$$

If, $\quad G = VN + (Vo + V)\{[H+] - [OH-]\}$

equation **59** may be rearranged

$$Ka = \frac{[H+][B]_c(Vo + V)}{VeN - G} \qquad \text{Eq. 60}$$

and

$$[H+](Vo + V) = \frac{KaVeN}{[B]_c} - \frac{KaG}{[B]_c} \qquad \text{Eq. 61}$$

as $[B]_c$ is constant, equation 61 can be rewritten

$$[H+](Vo + V) = K'VeN - K'G \qquad \text{Eq. 62}$$

and if,

$$\frac{VN}{Vo + V} \gg [H+] - [OH-]$$

equation 62 is reduced to

$$[H+](Vo + V) = K'VeN - K'VN \qquad Eq. 63$$

Derivation for titration data after equivalence point

1. Titration of monoprotic acid whose conjugate base has higher charge than its acid.

After equivalence point, concentration of HA is neglegible. Charge balance of the solution is

$$[A-] + [OH-] = [Na+] + [H+] \qquad Eq. 64$$

where [A-] is the concentration of conjugate base of a weak acid (HA). The mass balance of weak acid is

$$[A-] = C_{HA} = \frac{VeN}{Vo + V} \qquad Eq. 65$$

Substitution equation 65 in equation 64, and rearrange

$$[OH-] - [H+] = [Na+] + \frac{VeN}{Vo + V} \qquad Eq. 66$$

In the alkaline region, generally [OH-] >> [H+], equation 66 can be reduced to

$$[OH-] = [Na+] + \frac{VeN}{Vo + V} \qquad Eq. 67$$

Sustitution equation 4 in equation 67 and Kw = [H+][OH-] give,

$$\frac{Kw}{[H+]} = \frac{VN}{Vo + V} + \frac{VeN}{Vo + V} \qquad Eq. 68$$

which can be rearranged to

$$\frac{K_w V_t}{[H+]} = (V + V_e)N \qquad\qquad \text{Eq. 69}$$

where

$$V_t = (V_o + V)$$

In this case plot of $K_w V_t$ vs V will give a linear relationship of which N is slope and from intercept, V_e can be obtained.

2. **Titration of monoprotic acid whose conjugate base has lower charge than its acid.**

If an acid salt ($HB^+ X^-$) is titrated, charge balance of the solution after equivalence point is

$$[X-] + [OH-] = [Na+] + [H+] \qquad\qquad \text{Eq. 70}$$

and the mass balance of the weak acid is

$$[X-] = C_{HB^+} = \frac{V_e N}{V_o + V} \qquad\qquad \text{Eq. 71}$$

In the similar way as derived early, equations 70 and 71 will give

$$\frac{K_w V_t}{[H+]} = (V + V_e)N \qquad\qquad \text{Eq. 72}$$

3. **Titration of diprotic acid whose conjugate base has lower charge than its acid.**

Ionized dibasic weak acid ($H_2 B^{2+} X^{2-}$), the charge balance of the solution in alkaline region is

$$2[X^{2-}] + [OH-] \quad = \quad [Na+] + [H+] \qquad \text{Eq. 73}$$

and mass balance of this weak acid is

$$2[X^{2-}] \quad = \quad C_{H_2B^{2+}} \quad = \quad \frac{VeN}{Vo + V} \qquad \text{Eq. 74}$$

substitute equations 74 and 4 in equation 73

$$\frac{VeN}{Vo + V} + [OH-] \quad = \quad \frac{VN}{Vo + V} + [H+] \qquad \text{Eq. 75}$$

and in the similar way as derived early

$$\frac{KwV_t}{[H+]} \quad = \quad (V + Ve)N \qquad \text{Eq. 76}$$

Equations 69, 72, and 76 are identical equations which are employed in determination end point volumes of weak acids for titration data after equivalence point.

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