

CHAPTER I



INTRODUCTION

Potentiometric titration is the method which involves measuring the potential or pH of solution by a suitable indicator electrode as a function of titrant volume (Christian , 1986). There are many methods for the determination of the equivalence volume in potentiometric titration. These methods can be classified into three main types according to Anfalt and Jagner (1971).

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 Tubb's or Circle fitting method (Tubbs , 1954) , the Kohn-Zitko method (Anfalt and Jagner, 1971) , the method of bisection and the method of parrallel tangents (Jeffery et al. , 1989)

2. Differential methods.

These methods can be used to determine the equivalence volume by plotting the difference in potential or pH between each of the addition of titrant as the function of average volume (Skoog ,West , and Holler , 1992). These methods involve the first derivative method , the second derivative method , the Liteanu-Cormos method (Liteanu and Cormos , 1960) , the Cohen's method (Cohen , 1966) , and the Gran's I method (Gran , 1988) .

3. Method based on mass balance , charge balance and equilibrium equation or Gran's method.

This method was studied by many scientists, such as : Gran (1952) , Rossotti and Rossotti (1965) , Ingman and Still (1966) , Seksiri Arttamangkul (1986) , and Juthamas Sukbuntherng (1988) .

The equivalence volume can be determined by the extrapolation of the straight lines before equivalence point called G plot and after equivalence point called V plot. This method has several advantages when compared to potentiometric titration curves and differential plots. The graphical analysis is a straight line rather than a curve , so fewer points are needed to define it and the points can be taken at regular intervals instead of being bunched in a narrow region around the equivalence point. The portion of the curve, which are used in this technique ,are before or after the equivalence point , so the linear extrapolation used in this method can provide more precise result than

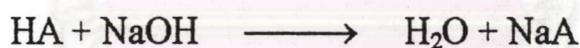
those obtained by the differential method, especially for asymmetrical titration curves.

Derivation of Gran equation for titration data prior to equivalence point.

The weak acidic compound could be classified into 2 types :
neutral and ionized weak acid.

1. Neutral weak acid

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



Dissociation reaction of weak acid was



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{Eq. 1}$$

which K_a = the dissociation constant of weak acid

The solution must be electrically neutral , meaning that

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

and at the equivalence point

$$V_e N = (V_0 + V) C_{HA} \quad \text{Eq. 3}$$

which V_e = volume of base equivalence to weak acid , called equivalence volume

N = normality of titrant

V_0 = the initial volume of the solution

V = volume of titrant added.

C_{HA} = the concentration of weak acid

The concentration of sodium ion at any volumes of titrant was

$$[Na^+] = \frac{VN}{(V_0 + V)} \quad \text{Eq. 4}$$

and the fact that

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

Combining equation 2 and 4 gave

$$[A^-] = \frac{VN}{(V_0 + V)} + [H^+] - [OH^-] \quad \text{Eq. 6}$$

Substitution of Eq.6 into Eq.5 and combine it with Eq.3 gave

$$\frac{VeN}{(V_0 + V)} = [HA] + \frac{VN}{(V_0 + V)} + [H^+] - [OH^-]$$

which might be rearranged to

$$[HA] = \frac{VeN}{(V_0 + V)} - \left\{ \frac{VN}{(V_0 + V)} + [H^+] - [OH^-] \right\} \quad \text{Eq. 7}$$

Substitution of Eq.6 and Eq.7 into Eq.1 gave

$$K_a = \frac{[H^+]\{VN/(V_0+V)+[H^+]-[OH^-]\}}{VeN/(V_0+V) - \{VN/(V_0+V)+[H^+]-[OH^-]\}} \quad \text{Eq. 8}$$

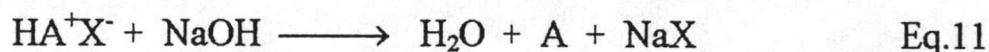
and rearrangement gave

$$G[H^+] = K_aVeN - K_aG \quad \text{Eq. 9}$$

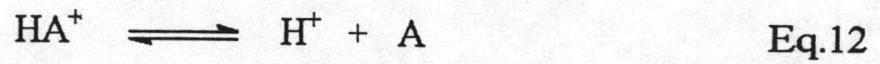
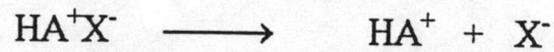
$$\text{where } G = VN + (V_0+V)([H^+]-[OH^-]) \quad \text{Eq.10}$$

2. Ionized weak acid

When an ionized weak acid , such as HA^+X^- was titrated , the reaction was



and the dissociation reaction of the ionized weak acid was



$$K_a = \frac{[\text{H}^+][\text{A}]}{[\text{HA}^+]} \quad \text{Eq.13}$$

Charge balance of the titration solution was

$$[\text{H}^+] + [\text{Na}^+] + [\text{HA}^+] = [\text{OH}^-] + [\text{X}^-] \quad \text{Eq.14}$$

At the equivalence point

$$C_{\text{HA}^+} = [\text{X}^-] = \frac{V_e N}{(V_0 + V)} \quad \text{Eq.15}$$

which C_{HA^+} = the concentration of ionized weak acid and

$$C_{\text{HA}^+} = \frac{V_e N}{(V_0 + V)} = [\text{HA}^+] + [\text{A}] \quad \text{Eq.16}$$

Substitution Eq.4 into Eq.14 gave

$$[\text{H}^+] + \frac{\text{VN}}{(\text{V}_0+\text{V})} + [\text{HA}^+] = [\text{OH}^-] + [\text{X}^-] \quad \text{Eq.17}$$

and substitution of Eq.15 into Eq.17 gave

$$[\text{HA}^+] = \frac{\text{VeN}}{(\text{V}_0+\text{V})} - \frac{\text{VN}}{(\text{V}_0+\text{V})} - [\text{H}^+] + [\text{OH}^-] \quad \text{Eq.18}$$

Eq.16 was substituted by Eq.18, yielded

$$[\text{A}] = \frac{\text{VN}}{(\text{V}_0+\text{V})} + [\text{H}^+] - [\text{OH}^-] \quad \text{Eq.19}$$

Substitution Eq.18 and Eq.19 into Eq.13, gave

$$\text{Ka} = \frac{[\text{H}^+] \{ \text{VN}/(\text{V}_0+\text{V}) + [\text{H}^+] - [\text{OH}^-] \}}{\text{VeN}/(\text{V}_0+\text{V}) - \{ \text{VN}/(\text{V}_0+\text{V}) + [\text{H}^+] - [\text{OH}^-] \}} \quad \text{Eq.20}$$

and rearrangement gave

$$G[H^+] = K_a V_e N - K_a G \quad \text{Eq.21}$$

Eventhough the ionized weak acid was in the form of K^+HA^- , the Gran equation could be obtained in the same manner as Eq.21 which it was in the form of HA^+X^- . It was found that Eq.9 and Eq.21 were identical. The slope of the equation was the dissociation constant (K_a) and the term of $K_a V_e N$ was the intercept of the equation. So, the equivalence volume of the weak acidic compound could be obtained from the intercept of the equation.

Derivation of Gran equation for titration data after equivalence point

1. Neutral weak acid

After equivalence point, the concentration of weak acid (HA) was negligible. The charge balance of the solution was

$$[Na^+] + [H^+] = [A^-] + [OH^-] \quad \text{Eq.22}$$

which $[A^-]$ was the concentration of conjugate base of weak acid(HA).

The mass balance of weak acid was

$$[A^-] = C_{HA} = \frac{VeN}{(V_0 + V)} \quad \text{Eq.23}$$

Eq.23 was substituted into Eq.22, and the rearrangement gave

$$[OH^-] - [H^+] = [Na^+] - \frac{VeN}{(V_0 + V)} \quad \text{Eq.24}$$

In the alkaline region, generally $[OH^-] \gg [H^+]$, Eq.24 could be reduced to

$$[OH^-] = [Na^+] - \frac{VeN}{(V_0 + V)} \quad \text{Eq.25}$$

Eq.4 was substituted into Eq.25 and $K_w = [H^+][OH^-]$, gave

$$\frac{K_w}{[H^+]} = \frac{VN}{(V_0 + V)} - \frac{V_e N}{(V_0 + V)} \quad \text{Eq.26}$$

which $K_w =$ the ionization constant of water.

Eq.26 could be rearranged to

$$\frac{K_w V_t}{[H^+]} = VN - V_e N = (V - V_e)N \quad \text{Eq.27}$$

which $V_t = V_0 + V$

In this case, the plot of $K_w V_t / [H^+]$ & V would give a linear relationship of which N was slope and V_e could be obtained from intercept.

2. Ionized weak acid

If an ionized weak acid, such as HA^+X^- was titrated, the charge balance of the solution after equivalence point was

$$[X^-] + [OH^-] = [Na^+] + [H^+] \quad \text{Eq.28}$$

and the mass balance of weak acid was

$$C_{HA^+} = X^- = \frac{VeN}{(V_0 + V)} \quad \text{Eq.29}$$

which C_{HA^+} = the concentration of ionized weak acid.

In the similar way as derived early, Eq.28 and Eq.29 would give

$$\frac{K_w V_t}{[H^+]} = (V - Ve)N \quad \text{Eq.30}$$

Eventhough the ionized weak acid was in the form of K^+HA^- , the derivation of Gran equation for the titration data after the equivalence point could be made in the same manner as for HA^+X^- . So the final equation was identical to Eq.30. Eq.27 and Eq.30 were identical equations which were employed to determined the equivalence volume of weak acid for the titration data after equivalence point.

The various methods described above were the methods used to determine only the equivalence volume of the single weak acid titration.

For the titration of two acids mixture, the both equivalence volumes could be determined by these methods if there was an appreciable difference in their strength. There must generally be a difference in pKa value at least 4 (Skoog et al. , 1992). If the difference between the dissociation constant of the acids was not large enough, some of the weaker acid would have been titrated during the final stage of titration of the stronger acid. This resulted in a decrease in the height and a small displacement of the position of the first potential jump, which no longer represented the equivalence volume of the stronger acid alone. In a case like this, only the sum of the acid could be determined from the second potential jump. If the dissociation constant of the acid lied closed to each other, only one jump in the titration curve could be obtained.

Moreover, there were many scientists who studied about the determination of the equivalence volumes in potentiometric titrations of acid mixtures, such as; McCallum and Midgley (1975), Boiani (1986), and Castillo and Alonso (1989). Various methods studied by these scientists were used to determine the equivalence volumes of the mixture of strong and weak acid or the mixture of two acids which had a difference in their pKa values more than 4.

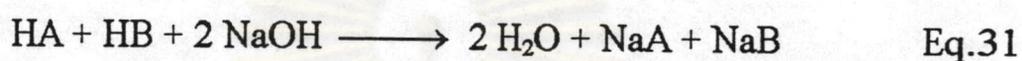
In 1986, Betti, Papoff, and Meites studied the potentiometric titrations in which mixtures of two monobasic weak acids were titrated with a strong base and in which weighted non-linear regression analysis was used to find the concentration for both acids. The precisions of the resulting values of the concentrations were depended on

the difference between the values of pK_a , on the ratio of the initial concentrations , and on the standard errors of measurement of both the pH and the volume of base. For any given values of the ratio of concentrations and the standard errors of measurement , the precision with which the concentration of the stronger acid could be evaluated was , in general , poorest when the difference between the pK_a value (ΔpK_a) was approximately 1.5 , and improved if ΔpK_a was either larger or smaller than that value. However , this method was only a theoretical research. There was no support by the actual experimentation and eventhough it was the method in theoretical, there was the error in determination, when the difference between pK_a values of two weak acids were about 1.5. It might be described that the fitting of the equation's model from the derivation was uncorrect.

In 1993 , Supawadee Chieawchanwattana proposed the new method used for the determination of two weak acid mixtures. The equation was developed and modified in order to determine the equivalence volume of two weak acid mixtures. The statistical procedures, the multiple linear regression analysis, and the computer program, SPSS/PC⁺ , was used for the data analysis. The both theoretical and experimental research were studied. The modified equation was based on the basic principle of mass balance , charge balance and equilibrium equation , which could be derived , as followed.

Derivation of equation for titration of two neutral weak acids mixture.

When two neutral weak acids, HA and HB, were titrated with a strong base, NaOH.



The dissociation reaction of two weak acid were



$$K_{aA} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{Eq.32}$$



$$K_{aB} = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} \quad \text{Eq.33}$$

The mass balance of two weak acids were

$$\frac{C_A V_0}{(V_0 + V)} = [\text{HA}] + [\text{A}^-] \quad \text{Eq.34}$$

$$\frac{C_B V_0}{(V_0 + V)} = [\text{HB}] + [\text{B}^-] \quad \text{Eq.35}$$

and the charge balance of this titration solution was

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{A}^-] + [\text{B}^-] \quad \text{Eq.36}$$

The concentration of sodium ion at any volumes of titrant was

$$[\text{Na}^+] = \frac{NV}{(V_0 + V)} \quad \text{Eq.37}$$

Substitution of Eq.37 into Eq.36 gave

$$[\text{H}^+] + \frac{NV}{(V_0+V)} = [\text{OH}^-] + [\text{A}^-] + [\text{B}^-] \quad \text{Eq.38}$$

Substitution of Eq.34 into Eq.32 and Eq.35 into Eq.33 gave

$$K_{aA} = \frac{[\text{H}^+][\text{A}^-]}{\{C_A V_0 / (V_0+V) - [\text{A}^-]\}}$$

$$[\text{A}^-] = \frac{K_{aA} V e_{AN}}{(V_0+V)(K_{aA} + [\text{H}^+])} \quad \text{Eq.39}$$

$$K_{aB} = \frac{[\text{H}^+][\text{B}^-]}{\{C_B V_0 / (V_0+V) - [\text{B}^-]\}}$$

$$[\text{B}^-] = \frac{K_{aB} V e_{BN}}{(V_0+V)(K_{aB} + [\text{H}^+])} \quad \text{Eq.40}$$

$$\text{which } C_A V_0 = V_{e_A} N$$

$$C_B V_0 = V_{e_B} N$$

$$V_{e_A} = \text{the equivalence volume of weak acid A}$$

$$V_{e_B} = \text{the equivalence volume of weak acid B}$$

Substitution of Eq.39 and Eq.40 into Eq.38 gave

$$\begin{aligned}
 [H^+] + \frac{NV}{(V_0+V)} &= [OH^-] + \frac{K_{a_A} V_{e_A} N}{(V_0+V)(K_{a_A}+[H^+])} \\
 &+ \frac{K_{a_B} V_{e_B} N}{(V_0+V)(K_{a_B}+[H^+])} \quad \text{Eq.41}
 \end{aligned}$$

Eq.41 could be rearranged to

$$\begin{aligned}
 [H^+] + \frac{NV}{(V_0+V)} - [OH^-] &= \frac{K_{a_A} V_{e_A} N}{(V_0+V)(K_{a_A}+[H^+])} + \\
 &\frac{K_{a_B} V_{e_B} N}{(V_0+V)(K_{a_B}+[H^+])} \quad \text{Eq.42}
 \end{aligned}$$

Eq.42 could be written in the term of the variables : y , x_1 , x_2

$$y = a_1x_1 + a_2x_2 \quad \text{Eq.43}$$

$$\text{which } y = \frac{[\text{H}^+] + \text{NV} - [\text{OH}^-]}{(\text{V}_0 + \text{V})} \quad \text{Eq.44}$$

$$x_1 = \frac{1}{(\text{V}_0 + \text{V})(\text{Ka}_A + [\text{H}^+])} \quad \text{Eq.45}$$

$$x_2 = \frac{1}{(\text{V}_0 + \text{V})(\text{Ka}_B + [\text{H}^+])} \quad \text{Eq.46}$$

$$a_1 = \text{Ka}_A \text{Ve}_A \text{N} \quad \text{Eq.47}$$

$$a_2 = \text{Ka}_B \text{Ve}_B \text{N} \quad \text{Eq.48}$$

From the partially regression coefficients , a_1 and a_2 , which obtained from solving the equation (Eq.42) by the multiple regression

analysis and computer program , SPSS/PC⁺ , the equivalence volumes of weak acids , V_{eA} and V_{eB} could be determined . The dissociation constant of each weak acid could be obtained from the slope of G plot of the titration data of the single weak acid solution.(as shown in Eq.9 and Eq.21)

For the derivation of equation for titration of the mixture of neutral and ionized weak acids, such as: HA and K^+HB^- or the mixture of two ionized weak acids, such as : K^+HA^- and HB^+X^- , it could be derived in the same manner as for the equation of two neutral weak acids. Thus, the equation were the same character as equation 42 and the volume of titrant which equivalence to the two weak acids were obtained from the value of partial regression coefficients (a_1 and a_2), as shown in Eq.47 and Eq.48.

The satisfying results of the equivalence volumes determination were obtained from the modified equation (Eq.42) with the aid of multiple linear regression analysis and SPSS/PC⁺ programme if ΔpK_a of the acid mixtures were > 2 . Equation 42 was also found to be incapable of accurately determining equivalence points for each weak acid in the mixture when ΔpK_a were < 2 . Moreover , this research did not include the samples which their ΔpK_a were between 1.3 and 1.9 .

In this paper, a potentiometric titrations of mixtures of two weak acids which had the difference between pK_a values less than 2 were studied. Since the ionic strength of the solution would be changed during the titration, the activity dissociation constant (K_a^0) was used instead of the concentration dissociation constant (K_a). The activity dissociation

constant is obtained by extrapolating the dissociation constant to zero concentration . (Butler, 1964)



$$K_a^0 = \frac{\{\text{H}^+\}\{\text{A}^-\}}{\{\text{HA}\}} \quad \text{Eq.49}$$

$$K_a^0 = \frac{(\gamma_{\text{H}^+})[\text{H}^+] (\gamma_{\text{A}^-})[\text{A}^-]}{\gamma_{\text{HA}}[\text{HA}]} \quad \text{Eq.50}$$

which γ_{\pm} = the activity coefficient

$$K_a^0 = (\gamma_{\text{H}^+}\gamma_{\text{A}^-}) K_a \quad \text{Eq.51}$$

$\gamma_{\text{HA}} \approx 1$ in dilute solution.

Eq.51 could be rearranged to

$$K_a = \frac{K_a^0}{\gamma_{H^+} \gamma_{A^-}} \quad \text{Eq.52}$$

where the braces indicated the activity of the species within the braces. The activity of the ion was set equal to its concentration times an activity coefficient (γ_{\pm}). The activity coefficient was found to depend on the total ionic strength (I) of the solution, defined to be

$$I = \frac{1}{2} \sum_{i=1} C_i Z_i^2 \quad \text{Eq.53}$$

which C_i = the concentration of ion i

Z_i = the charge of ion i

During the course of titration, the ionic strength of the solution could be calculated at each volume of titrant added. The activity coefficient of each ion could be obtained from the equation below which proposed by Davies. (Bulter, 1964)

$$-\log \gamma_{\pm} = A Z_{\pm}^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2 I \right) \quad \text{Eq.54}$$

A = the constant depend on absolute temperature (T)
and the dielectric constant (ϵ) of the solution ,
according to the relation

$$A = 1.825 \times 10^6 (\epsilon T)^{-3/2} \quad \text{Eq.55}$$

The dielectric constant of solution of electrolyte could be determined by the equation below. (Herbert and Benton , 1957)

$$\epsilon = \epsilon_{\text{H}_2\text{O}} - (\delta^+ + \delta^-)C \quad \text{Eq.56}$$

where $\epsilon_{\text{H}_2\text{O}}$ = the static dielectric constant of water

C = the concentration in mole per litre

δ^+ , δ^- = the contributions of the cation and anion ,

respectively.

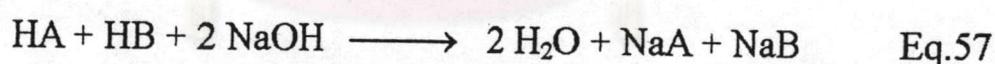
From the calculated value of the activity coefficient of any ion in the solution at each volume of titrant added, the dissociation constant of

the acid could be obtained at each ionic strength which vary by the volume of titrant added during the titration, according to Eq.52 .

Thus , the modified equation which the activity dissociation constant was used instead of the concentration dissociation constant and with the basic of mass balance , charge balance and equilibrium equation, could be derived as followed .

1. Derivation of equation for titration of the mixture of two neutral weak acids

The weak acids to be titrated were denoted by HA and HB. HA was the stronger. The titration was performed with a strong base , eg. sodium hydroxide.



The dissociation reaction of HA and HB were



$$K_{aA} = \frac{\{\text{H}^+\}[\text{A}^-]}{[\text{HA}]} \quad \text{Eq.58}$$



$$K_{aB} = \frac{\{\text{H}^+\}[\text{B}^-]}{[\text{HB}]} \quad \text{Eq.59}$$

Hydrogen ion activity was used instead of concentration. The relationship between activity and concentration was expressed by

$$\{\text{H}^+\} = \gamma_{\text{H}^+} [\text{H}^+] \quad \text{Eq.60}$$

The dissociation constant of acids HA and HB at zero ionic strength (K_{aA}^0 and K_{aB}^0) could be expressed as followed.

$$K_{aA}^0 = \frac{\{\text{H}^+\}\{\text{A}^-\}}{\{\text{HA}\}} \quad \text{Eq.61}$$

$$K_{aA}^0 = \frac{\{\text{H}^+\} \gamma_{\text{A}^-} [\text{A}^-]}{\gamma_{\text{HA}} [\text{HA}]} \quad \text{Eq.62}$$

$$K_{aA}^0 = (\gamma_{A^-}) K_{aA} \quad \text{Eq.63}$$

Eq.63 could be rearranged to

$$K_{aA} = \frac{K_{aA}^0}{\gamma_{A^-}} \quad \text{Eq.64}$$

$$K_{aB}^0 = \frac{\{H^+\}\{B^-\}}{\{HB\}} \quad \text{Eq.65}$$

$$K_{aB}^0 = \frac{\{H^+\} \gamma_{B^-} [B^-]}{\gamma_{HB} [HB]} \quad \text{Eq.66}$$

$$K_{aB}^0 = (\gamma_{B^-}) K_{aB} \quad \text{Eq.67}$$

Eq.67 could be rearranged to

$$K_{aB} = \frac{K_{aB}^0}{\gamma_{B^-}} \quad \text{Eq.68}$$

Introduction of Eq.64 and Eq.68 into Eq.42 and rearrangement gave the equation

$$\begin{aligned}
 NV + (V_0+V)([H^+]- [OH^-]) &= \frac{(K_{aA}^0/\gamma_{A^-})V_{eA}N}{(K_{aA}^0/\gamma_{A^-}) + \{H^+\}} + \\
 &\frac{(K_{aB}^0/\gamma_{B^-})V_{eB}N}{(K_{aB}^0/\gamma_{B^-}) + \{H^+\}} \quad \text{Eq.69}
 \end{aligned}$$

Eq.69 could be written in term of variables : y , x_1 , x_2 as the Eq.43

$$\text{which } y = NV + (V_0+V)(\{H^+\}-\{OH^-\}) \quad \text{Eq.70}$$

$$x_1 = \frac{K_{aA}^0/\gamma_{A^-}}{(K_{aA}^0/\gamma_{A^-}) + \{H^+\}} \quad \text{Eq.71}$$

$$x_2 = \frac{K_{aB}^0 / \gamma_{B^-}}{(K_{aB}^0 / \gamma_{B^-}) + \{H^+\}} \quad \text{Eq.72}$$

$$a_1 = V_{eA}N \quad \text{Eq.73}$$

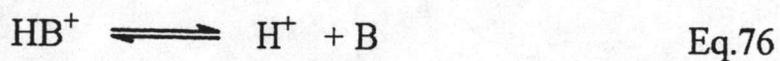
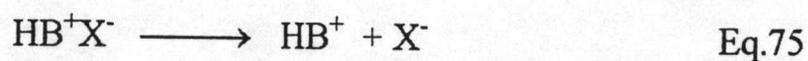
$$a_2 = V_{eB}N \quad \text{Eq.74}$$

From the partially regression coefficients a_1 and a_2 which obtained from solving the equation 69 by the multiple linear regression analysis and computer program, SPSS/PC⁺, the equivalence volumes of two weak acids, V_{eA} and V_{eB} could be determined. The dissociation constant of each weak acid could be obtained from slope of G plot of each single acid titrations (as shown in Eq.9).

2. Derivation of equation for titration of the mixture of neutral and ionized weak acid

2.1 Neutral weak acid (HA) + Ionized weak acid (HB⁺X⁻)

The dissociation constant of neutral weak acid (HA) was the same character as Eq.64 and the dissociation constant of the ionized weak acid (HB⁺X⁻) could be expressed as followed.



$$K_{\text{aB}} = \frac{\{\text{H}^+\}[\text{B}]}{[\text{HB}^+]} \quad \text{Eq.77}$$

$$K_{\text{aB}}^0 = \frac{\{\text{H}^+\}\{\text{B}\}}{\{\text{HB}^+\}} \quad \text{Eq.78}$$

$$K_{\text{aB}}^0 = \frac{K_{\text{aB}}}{\gamma_{\text{HB}^+}} \quad \text{Eq.79}$$

Eq.79 could be rearranged to

$$K_{\text{aB}} = (\gamma_{\text{HB}^+})K_{\text{aB}}^0 \quad \text{Eq.80}$$

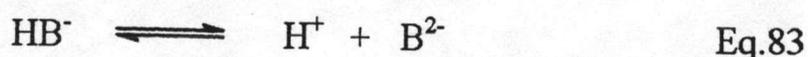
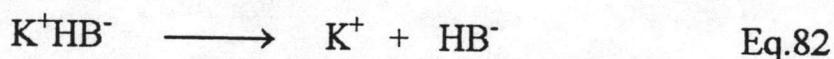
Introduction of Eq. 64 and Eq. 80 into Eq. 42 and rearrangement gave the equation

$$\begin{aligned}
 NV + (V_0 + V)([H^+] - [OH^-]) &= \frac{(K_{aA}^0 / \gamma_{A^-}) V_{eA} N}{(K_{aA}^0 / \gamma_{A^-}) + \{H^+\}} + \\
 &\frac{(\gamma_{HB^+}) K_{aB}^0 V_{eB} N}{(\gamma_{HB^+}) K_{aB}^0 + \{H^+\}} \quad \text{Eq.81}
 \end{aligned}$$

Then, V_{eA} and V_{eB} could be obtained in the same manner as the mixture of two neutral weak acids.

2.2 Neutral weak acid (HA) + Ionized weak acid (K^+HB^-)

The dissociation constant of neutral weak acid (HA) was the same character as Eq.64 and the dissociation constant of ionized weak acid (K^+HB^-) could be expressed as followed.



$$K_{aB} = \frac{\{H^+\}[B^{2-}]}{[HB^-]} \quad \text{Eq.84}$$

$$K_{aB}^0 = \frac{\{H^+\}\{B^{2-}\}}{\{HB^-\}} \quad \text{Eq.85}$$

$$K_{aB}^0 = \frac{(\gamma_{B^{2-}}) K_{aB}}{\gamma_{HB^-}} \quad \text{Eq.86}$$

Eq. 86 could be rearranged to

$$K_{aB} = \frac{(\gamma_{HB^-}) K_{aB}^0}{\gamma_{B^{2-}}} \quad \text{Eq.87}$$

Introduction of Eq.64 and Eq.87 into Eq.42 and rearrangement gave the equation

$$\begin{aligned}
 NV + (V_0+V)([H^+]-[OH^-]) &= \frac{(K_{aA}^0/\gamma_{A^-})V_{eA}N}{(K_{aA}^0/\gamma_{A^-}) + \{H^+\}} + \\
 &\frac{(\gamma_{HB^-}/\gamma_{B^{2-}})K_{aB}^0V_{eB}N}{(\gamma_{HB^-}/\gamma_{B^{2-}})K_{aB}^0 + \{H^+\}} \quad \text{Eq.88}
 \end{aligned}$$

V_{eA} and V_{eB} could be obtained in the same manner as the mixture of two neutral weak acids.

3. Derivation of equation for titration of the mixture of two ionized weak acids

3.1 Ionized weak acid (HA^+X^-) + ionized weak acid (HB^+X^-)

The dissociation constants of HA^+X^- and HB^+X^- could be obtained from the equation derived in the same manner as Eq.80 .

$$K_{aA} = (\gamma_{HA^+})K_{aA}^0 \quad \text{Eq.89}$$

$$K_{aB} = (\gamma_{HB^+})K_{aB}^0 \quad \text{Eq.90}$$

Introduction of Eq.89 and Eq.90 into Eq.42 and rearrangement gave the equation

$$\begin{aligned}
 NV + (V_0+V)([H^+]-[OH^-]) &= \frac{(\gamma_{HA^+})Ka_A^0Ve_A N}{(\gamma_{HA^+})Ka_A^0 + \{H^+\}} + \\
 &\frac{(\gamma_{HB^+})Ka_B^0Ve_B N}{(\gamma_{HB^+})Ka_B^0 + \{H^+\}} \quad \text{Eq.91}
 \end{aligned}$$

3.2 Ionized weak acid (HA^+X^-) + ionized weak acid (K^+HB^-)

The dissociation constants of HA^+X^- and K^+HB^- could be obtained from the equation derived in the same manner as Eq.80 and Eq.87, respectively.

Introduction of Eq.89 and Eq.87 into Eq.42 and rearrangement gave the equation

$$\begin{aligned}
 NV + (V_0+V)([H^+]-[OH^-]) &= \frac{(\gamma_{HA^+})Ka_A^0Ve_A N}{(\gamma_{HA^+})Ka_A^0 + \{H^+\}} + \\
 &\frac{(\gamma_{HB^-} / \gamma_{B^{2-}})Ka_B^0Ve_B N}{(\gamma_{HB^-} / \gamma_{B^{2-}})Ka_B^0 + \{H^+\}} \quad \text{Eq.92}
 \end{aligned}$$

3.3 Ionized weak acid (K^+HA^-) + ionized weak acid (K^+HB^-)

The dissociation constants of K^+HA^- and K^+HB^- could be obtained from the equation derived in the same manner as Eq.87 . Thus, the multiple linear equation could be obtained as followed.

$$\begin{aligned}
 NV + (V_0+V)([H^+]+[OH^-]) &= \frac{(\gamma_{HA^-}/\gamma_{A^{2-}})Ka_A^0 Ve_A N}{(\gamma_{HA^-}/\gamma_{A^{2-}})Ka_A^0 + \{H^+\}} \\
 &\quad + \frac{(\gamma_{HB^-}/\gamma_{B^{2-}})Ka_B^0 Ve_B N}{(\gamma_{HB^-}/\gamma_{B^{2-}})Ka_B^0 + \{H^+\}} \quad \text{Eq.93}
 \end{aligned}$$

Then, Ve_A and Ve_B could be obtained in the same manner as the mixture of two neutral weak acids.