# 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 equivalent volume in potentiometric titration that may be classified into three main types according to Anfalt and Jagner ( 1971 ).

1. <u>Methods based on the sigmoid form of a titration curve.</u>

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 equivalent 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 parallel tangents ( Jeffery et al., 1989 )

2. Differential methods.

These methods can be used to determine the equivalent 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 I method (Gran, 1988 ).

3. Methods based on mass balance, charge balance and equilibrium equation or Gran method.

This method was studied by many scientists; e.g., Gran (1952), Rossotti and Rossotti (1965), Ingman and Still (1966), Arttamangkul, S. (1986) and Sukbuntherng,J. (1988).

The equivalent volume which can be determined by extrapolation of straight line before equivalent point (G plot) and after equivalent point (V plot). This method has several advantages comparing with potentiometric titration curves and differential plots. Since 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 equivalent point. The treated portions of the curve are before or after the equivalent point; thus, 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 equations for titration data prior to equivalent 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).

$$HA + NaOH \longrightarrow H_2O + NaA$$

Dissociation reaction of weak acid was

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

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

which Ka = the dissociation constant of weak acid

The solution must be electrically neutral, meaning that

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

and at the equivalent point

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

which Ve = volume of base equivalent to weak acid, called equivalent volume

N = normality of titrant

Vo = the initial volume of the solution

V = volume of titrant added.

$C_{HA}$ = concentration of weak acid

The concentration of sodium ion at any volumes of titrant was

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

and the fact that

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

Combining Eq.2 and Eq.4 gave

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

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

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

which might be rearranged to

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

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

$$Ka = \frac{[H^+]\{VN/(Vo+V)+[H^+]-[OH^-]\}}{VeN/(Vo+V)-\{VN/(Vo+V)+[H^+]-[OH^-]\}} \qquad \text{Eq.8}$$

and rearrangement gave

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

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

2. Ionized weak acid

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

$$HA^+X^- + NaOH \longrightarrow H_2O + A + NaX \qquad \text{Eq.11}$$

and the dissociation reaction of the ionized weak acid was

$$HA^+\,X^- \longrightarrow HA^+ + X^-$$

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

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

Charge balance of the titration solution was

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

At the equivalent point

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

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

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

Substitution Eq.4 into Eq.14 gave

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

and substitution of Eq.15 into Eq.17 gave

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

Eq.16 was substituted by Eq.18, yielded

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

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

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

and rearrangement gave

$$G[H^+] = KaVeN - KaG \qquad \text{Eq.21}$$

Although 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 was in the form of $HA^+X^-$ . It was found that Eq.9 and Eq.21 were identical. The slope of the linear equation was the dissociation constant (Ka) and the term of KaVeN was the intercept in which the equivalent volume (Ve) of the weak acidic compound could be obtained.

**Derivation of Gran equations for titration data after equivalent point**

1. Neutral weak acid

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

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

Which $[A^-]$ was the concentration of conjugated base of weak acid [HA].

The mass balance of weak acid was

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

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

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

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

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

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

$$\frac{Kw}{[H^+]} = \frac{VN}{(Vo+V)} - \frac{VeN}{(Vo+V)} \qquad \text{Eq.26}$$

which Kw = ionization constant of water.

Eq.26 could be rearranged to

$$\frac{KwVt}{[H^+]} = VN - VeN = (V-Ve)N \qquad \text{Eq.27}$$

which $Vt = Vo + V$

In this case, the plot of $KwVt/[H^+]$ versus V would give a linear relationship with slope N and Ve 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 equivalent point was

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

and the mass balance of weak acid was

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

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

As previously derived, Eq.28 and Eq.29 would give

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

Though the ionized weak acid was in the form of $K^+HA^-$, the derivation of Gran equation for the titration data after the equivalent point could be made in the same manner as for $HA^+X^-$; thus, the final equation was identical to Eq.30. As a consequence, either equations (Eq. 27 or Eq.30) was employed to determined the equivalent volume of weak acid for the titration data after equivalent point.

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

For the titration of the mixture of two weak acid compounds, both equivalent volumes could be determined by these methods if there was an appreciable difference in their acid strength, generally at 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 steep of slope of titration curve and a small displacement of the position of the first potential jump, which no longer represented the equivalent 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 acids lied very closely to each other, only one jump in the titration curve could be obtained.

Moreover, there were many scientists ,such as; McCullum and Midgley (1975), Boiani (1986), and Castillo and Alonso (1989) studied about the determination of the equivalent volumes in potentiometric titrations of acid mixtures which had the different in pKa values more than 4.

In 1986, Betti et. al. studied the potentiometric titrations of mixtures of two monobasic weak acids by using weighted non-linear regression analysis. The precisions of the concentrations obtained were dependent on the difference between the values of pKa ($\Delta$pKa), on the ratio of the initial concentrations, and on the standard errors of measurement of both pH and volume of strong base added. For any given values of the ratio of concentrations and the standard errors of measurement, the precision of the concentration depended on ΔpKa and was poorest when ΔpKa was approximately 1.5 and improved if ΔpKa was either larger or smaller. However, this method was a theoretical research, not confirmed by actual experiment.

In 1993, Chieawchanwattana modified the equation used for determination equivalent volume of two weak acid mixtures by using multiple linear regression analysis and the computer program, SPSS/PC$^+$, for the data analysis. Both theoretical and experimental researches were studied and compared. 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 equations for titration two neutral weak acid mixtures.**

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

$$HA + HB + 2\,NaOH \longrightarrow 2\,H_2O + NaA + NaB \qquad \text{Eq.31}$$

The dissociation reaction of two weak acid were

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

$$Ka_A = \frac{[H^+][A^-]}{[HA]} \qquad \text{Eq.32}$$

$$HB \rightleftarrows B^- + H^+$$

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

The mass balance of two weak acids were

$$\frac{C_AVo}{(Vo+V)} = [HA] + [A^-] \qquad \text{Eq.34}$$

$$\frac{C_BVo}{(Vo+V)} = [HB] + [B^-] \qquad \text{Eq.35}$$

and the charge balance of this titration solution was

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

The concentration of sodium ion at any volume of titrant was

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

Substitution of Eq.37 into Eq.36 gave

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

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

$$Ka_A = \frac{[H^+][A^-]}{\{C_AVo/(Vo+V) - [A^-]\}}$$

$$[A^-] = \frac{Ka_A Ve_A N}{(Vo+V)(Ka_A + [H^+])} \qquad \text{Eq.39}$$

$$Ka_B = \frac{[H^+][B^-]}{\{C_B Vo/(Vo+V) - [B^-]\}}$$

$$[B^-] = \frac{Ka_B Ve_B N}{(Vo+V)(Ka_B + [H^+])} \qquad \text{Eq.40}$$

which $C_A Vo$ = $Ve_A N$

$C_B Vo$ = $Ve_B N$

$Ve_A$ = equivalent volume of weak acid A

$Ve_B$ = equivalent volume of weak acid B

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

$$[H^+] + \frac{NV}{(Vo+V)} = [OH^-] + \frac{Ka_A Ve_A N}{(Vo+V)(Ka_A + [H^+])} + \frac{Ka_B Ve_B N}{(Vo+V)(Ka_B + [H^+])} \qquad \text{Eq.41}$$

Eq.41 could be rearranged to

$$[H^+] + \frac{NV}{(Vo+V)} - [OH^-] = \frac{Ka_A Ve_A N}{(Vo+V)(Ka_A + [H^+])}$$

$$+ \frac{Ka_B Ve_B N}{(Vo+V)(Ka_B + [H^+])} \qquad \text{Eq.42}$$

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

$$y = a_1 x_1 + a_2 x_2 \qquad \text{Eq.43}$$

which

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

$$x_1 = \frac{1}{(Vo+V)(Ka_A + [H^+])} \qquad \text{Eq.45}$$

$$x_2 = \frac{1}{(Vo+V)(Ka_B + [H^+])} \qquad \text{Eq.46}$$

$$a_1 = Ka_A Ve_A N \qquad \text{Eq.47}$$

$$a_2 = Ka_B Ve_B N \qquad \text{Eq.48}$$

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 equivalent volumes of weak acids, $Ve_A$ and $Ve_B$ could be determined satisfactorily if ΔpKa of the acid mixtures was more than 2. The dissociation constant of each weak acid could be obtained from the slope of Gran plots of titration data of single weak acid solution. (as shown in Eq.9 and Eq.21)

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 $HB^+X^-$, could be performed in the same manner as the mixture of two neutral weak acids.

In 1996, Prachasitthisak modified Chiewcharnwatana's equation by using thermodynamic dissociation constant instead of concentration dissociation constant and studied potentiometric titrations of mixtures of two weak acids which had ΔpKa values less than 2.

Earlier methods used to determine the equivalent volume of the mixtures of two weak acids by multiple linear regression analysis above, (Chiewcharnwatana, 1993; Prachasitthisak, 1996) involved the samples which initial concentration ratios of the two weak acids were fixed at 1; therefore, it was interesting to investigate whether the modified equation could fit with other concentration ratios or not.

Since the accuracy and precision of the equivalent volumes obtained depended on various factors such as ΔpKa value, initial concentration ratios, titration data range being interpreted, changes of ionic strength of solution during the course of titration, experimental conditions and standard errors of pH measurement and volume of base, precisely and carefully examine these parameters were necessary and important.

Since the ionic strength of the solution might be changed during the titration, to reduce such a problem the thermodynamic dissociation constant ($Ka^o$) was used instead of the concentration dissociation constant (Ka). The thermodynamic dissociation constant was obtained by extrapolating the dissociation constant to zero concentration. (Butler, 1964)

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

$$Ka^o = \frac{\{H^+\}\{A^-\}}{\{HA\}} \qquad \text{Eq. 49}$$

$$Ka^o = \frac{(\gamma_{H^+})[H^+]\,(\gamma_{A^-})[A^-]}{\gamma_{HA}[HA]} \qquad \text{Eq. 50}$$

which $\gamma_{\pm}$ = the activity coefficient

$\{A^-\}$ = activity of ion $A^-$

and $\{A^-\} = (\gamma_{A^-})[A^-]$

$$Ka^o = (\gamma_{H^+}\gamma_{A^-})\,Ka \qquad \text{Eq. 51}$$

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

Eq. 51 could be rearranged to

$$Ka = \frac{Ka^o}{\gamma_{H^+}\gamma_{A^-}} \qquad \text{Eq. 52}$$

The activity coefficient was dependent on total ionic strength (I) of the solution, defined to be

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

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 Davies' equation (Bulter, 1964).

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

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

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

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

$$\varepsilon = \varepsilon_{H_2O} - (\delta^{+} + \delta^{-})C \qquad \text{Eq. 56}$$

where $\varepsilon_{H_2O}$ = static dielectric constant of water

$C$ = concentration in mole per litre

$\delta^+, \delta^-$ = 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 varied by the volume of titrant added during the titration, according to Eq. 52.

Thus, the modified equation in which the thermodynamic dissociation constant was used instead of the concentration dissociation constant could be derived on the basis of mass balance, charge balance and equilibrium equation in the following way.

**Derivation of modified Gran equations for titration of the single weak acid for titration data prior to equivalent 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).

$$HA + NaOH \rightarrow H_2O + NaA$$

Dissociation reaction of weak acid was

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

$$Ka^o = \frac{\{H^+\}\{A^-\}}{\{HA\}} \qquad \text{Eq.57}$$

$$Ka^o = \frac{\{H^+\}\,\gamma_{A^-}[A^-]}{\gamma_{HA}[HA]} \qquad \text{Eq.58}$$

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

$$Ka^o = \frac{\{H^+\}\,\gamma_{A^-}[A^-]}{[HA]} \qquad \text{Eq.59}$$

The solution must be electrically neutral, meaning that

$$[A^-] + [OH^-] = [Na^+] + [H^+] \qquad \text{Eq.60}$$

and at the equivalent point

$$VeN = (Vo + V)C_{HA} \qquad \text{Eq.61}$$

The concentration of sodium ion at any volumes of titrant was

$$[Na^+] = \frac{VN}{(Vo + V)} \qquad \text{Eq.62}$$

and the fact that

$$C_{HA} = [HA] + [A^-] \qquad \text{Eq.63}$$

Combining equation 60 and 62 gave

$$[A^-] = \frac{VN}{(Vo + V)} + [H^+] - [OH^-] \qquad \text{Eq.64}$$

Substitution of Eq. 64 into Eq.63 and combine it with Eq.61 gave

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

which might be rearranged to

$$[HA] = \frac{VeN}{(Vo + V)} - \left\{ \frac{VN}{(Vo + V)} + [H^+] - [OH^-] \right\} \qquad \text{Eq.65}$$

Substitution of Eq. 64 and Eq.65 into Eq.59 gave

$$Ka^o = \frac{\{H^+\} \{VN/Vo+V)+[H^+]-[OH^-]\} \gamma_{A^-}}{VeN/(Vo+V) - \{VN/(Vo+V)+[H^+]-[OH^-]\}} \qquad \text{Eq.66}$$

and rearrangement gave

$$G\{H^+\} \gamma_{A^-} = Ka^oVeN - Ka^oG \qquad \text{Eq.67}$$

$$\text{where } G = VN + (Vo + V)([H^+] - [OH^-]) \qquad \text{Eq.68}$$

2. <u>Ionized weak acid whose conjugate base has lower charge than its acid</u>

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

$$HA^+X^- + NaOH \rightarrow H_2O + A + NaX$$

and the dissociation reaction of the ionized weak acid was

$$HA^+ \rightleftarrows H^+ + A$$

$$Ka^o = \frac{\{H^+\}\{A\}}{\{HA^+\}} \qquad \text{Eq.69}$$

$$Ka^o = \frac{\{H^+\}\,\gamma_A[\,A]}{\gamma_{HA^+}[HA^+]} \qquad \text{Eq.70}$$

in dilute solution $\gamma_A \approx 1$

$$Ka^o = \frac{\{H^+\}\,[A]}{\gamma_{HA^+}[HA^+]} \qquad \text{Eq.71}$$

Charge balance of the titration solution was

$$[H^+] + [Na^+] + [HA^+] = [OH^-] + [X^-] \qquad \text{Eq.72}$$

At the equivalent point

$$C_{HA^+} = [X^-] = \frac{VeN}{(Vo + V)} \qquad \text{Eq.73}$$

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

$$C_{HA^+} = \frac{VeN}{(Vo + V)} = [HA^+] + [A] \qquad \text{Eq.74}$$

Substitution Eq.62 into Eq. 72 gave

$$[H^+] + \frac{VN}{(Vo + V)} + [HA^+] = [OH^-] + [X^-] \qquad \text{Eq.75}$$

and substitution of Eq. 73 into Eq. 75 gave

$$[HA^+] = \frac{VeN}{(Vo + V)} - \{\frac{VN}{(Vo + V)} - [H^+] - [OH^-]\} \qquad \text{Eq.76}$$

Eq. 74 was substituted by Eq.76, yielded

$$[A] = \frac{VN}{(Vo + V)} + [H^+] - [OH^-] \qquad \text{Eq.77}$$

Substitution of Eq. 76 and Eq. 77 into Eq. 71 gave

$$Ka^{o} = \frac{\{H^+\}\ \{VN/Vo{+}V) + [H^+] - [OH^-]\}}{[VeN/(Vo{+}V) - \{VN/Vo{+}V) + [H^+] - [OH^-]\}]\gamma_{HA}{}^{+}} \qquad \text{Eq.78}$$

and rearrangement gave

$$\frac{G\{H^+\}}{\gamma_{HA}{}^{+}} = Ka^{o}VeN - Ka^{o}G \qquad \text{Eq.79}$$

3. <u>Ionized weak acid whose conjugate base has higher charge than its acid</u>

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

$$K^+HA^- + 2NaOH \longrightarrow H_2O + Na_2A + KOH$$

and the dissociation reaction of the ionized weak acid was

$$HA^- \rightleftarrows H^+ + A^{2-}$$

$$Ka^\circ = \frac{\{H^+\}\{A^{2-}\}}{\{HA^-\}} \qquad \text{Eq.80}$$

$$Ka^\circ = \frac{\{H^+\}\gamma_A^{2-}[A^{2-}]}{\gamma_{HA}^-[HA^-]} \qquad \text{Eq.81}$$

Charge balance of the titration solution was

$$[H^+] + [Na^+] + [K^+] = [OH^-] + [HA^-] + 2[A2^-] \qquad \text{Eq.82}$$

At the equivalent point

$$C_{HA}^- = [K^+] = \frac{VeN}{(Vo+V)} \qquad \text{Eq.83}$$

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

$$C_{HA}^- = \frac{VeN}{(Vo+V)} = [HA^-] + [A^{2-}] \qquad \text{Eq.84}$$

Substitution Eq.62 into Eq.82 gave

$$[H^+] + \frac{VN}{(Vo+V)} + [K^+] = [OH^-] + [HA^-] + 2[A^{2-}] \qquad \text{Eq.85}$$

and substitution of Eq.83 into Eq.85 gave

$$[HA^-] = \frac{VeN}{(Vo+V)} - \frac{VN}{(Vo+V)} - [H^+] + [OH^-] \qquad \text{Eq.86}$$

Eq.84 was substituted by Eq.86, yielded

$$[A^{2-}] = \frac{VN}{(Vo+V)} + [H^+] - [OH^-] \qquad \text{Eq.87}$$

Substitution Eq.86 and Eq.87 into Eq.81, gave

$$Ka^o = \frac{\{H^+\}\{VN/(Vo+V)+[H^+]-[OH^-]\}\gamma_A{}^{2-}}{[VeN/(Vo+V)-\{VN/(Vo+V)+[H^+]-[OH^-]\}\gamma_{HA}{}^{-}} \qquad \text{Eq.88}$$

and rearrangement gave

$$\frac{G[H]\gamma_A{}^{2-}}{\gamma_{HA}{}^{-}} = Ka^oVeN - Ka^oG \qquad \text{Eq.89}$$

The slope of these linear equations (Eq.67,79,89) was the thermodynamic dissociation constant ($Ka^o$) and the term $Ka^oVeN$ was the intercept of these equation which equivalent volume of the weak acidic compound could be obtained.

## Derivation of equations for titration of the mixture of two weak acids.

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

The mixture composed of two neutral weak acids, HA and HB which HA was the stronger one and titrant was strong base; e.g., sodium hydroxide.

$$HA + HB + 2\,NaOH \longrightarrow 2\,H_2O + NaA + NaB$$

The dissociation reaction of HA and HB were

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

$$Ka^o{}_A = \frac{\{H^+\}\{A^-\}}{\{HA\}} \qquad \text{Eq.90}$$

$$Ka^o{}_A = \frac{\{H^+\}\gamma_A{}^-[A^-]}{\gamma_{HA}[HA]} \qquad \text{Eq.91}$$

In dilute solution $\gamma_{HA} = 1$ Eq.91 could be rearranged to

$$Ka^o{}_A = \frac{\{H^+\}\,\gamma_A{}^-\,[A^-]}{[HA]} \qquad \text{Eq.92}$$

$$HB \rightleftarrows H + B$$

$$Ka^o{}_B = \frac{\{H^+\}\{B^-\}}{\{HB\}} \qquad \text{Eq.93}$$

$$Ka^{o}_{B} = \frac{\{H^{+}\}\gamma_{B^{-}}\ [B^{-}]}{\gamma_{HB}\ [HB]} \qquad \text{Eq.94}$$

In dilute solution $\gamma_{HB} \approx 1$ Eq.94 could be rearranged to

$$Ka^{o}_{B} = \frac{\{H^{+}\}\gamma_{B^{-}}\ [B^{-}]}{[HB]} \qquad \text{Eq.95}$$

The mass balance of two weak acids were

$$[HA] + [A^{-}] = C_{HA} = \frac{Ve_{A}N}{(Vo+V)} \qquad \text{Eq.96}$$

$$[HB] + [B^{-}] = C_{HB} = \frac{Ve_{B}N}{(Vo+V)} \qquad \text{Eq.97}$$

and the charge balance of this titration solution was

$$[H^{+}] + [Na^{+}] = [OH^{-}] + [A^{-}] + [B^{-}] \qquad \text{Eq.98}$$

The concentration of sodium ion at any volumes of titrant was

$$[Na^{+}] = \frac{VN}{(Vo+V)} \qquad \text{Eq.99}$$

Substitution of Eq.99 into Eq.98 gave

$$[H^{+}] + \frac{VN}{Vo+V} = [OH^{-}] + [A^{-}] + [B^{-}] \qquad \text{Eq.100}$$

Substitution of Eq.96 into Eq.92 and Eq.97 into Eq.95 gave

$$Ka^{o}_{A} = \frac{\{H^{+}\}\ \gamma_{A^{-}}\ [A^{-}]}{\{Ve_{A}N/(Vo+V) - [A^{-}]\}} \qquad \text{Eq.101}$$

$$[A^{-}] = \frac{Ka^{o}_{A}Ve_{A}N}{(Vo+V)(Ka^{o}_{A} + \gamma_{A^{-}}\ \{H^{+}\}]} \qquad \text{Eq.102}$$

$$Ka^{o}_{B} = \frac{\{H+\}\ \gamma_{B^{-}}\ [B^{-}]}{\{Ve_{B}N/(Vo+V) - [B^{-}]\}} \qquad \text{Eq.103}$$

$$[B^{-}] = \frac{Ka^{o}_{B}Ve_{B}N}{(Vo+V)(Ka^{o}_{B} + \gamma_{B^{-}}\ \{H^{+}\})} \qquad \text{Eq.104}$$

Substitution of Eq.102 and Eq.103 into Eq.100 gave

$$[H^{+}] + \frac{VN}{(Vo+V)} = [OH^{-}] + \frac{Ka^{o}_{A}Ve_{A}N}{(Vo+V)(Ka^{o}_{A} + \gamma_{A^{-}}\{H^{+}\})} + \frac{Ka^{o}_{B}Ve_{B}N}{(Vo+V)(Ka^{o}_{B} + \gamma_{B^{-}}\{H^{+}\})} \qquad \text{Eq.105}$$

Eq.105 could be rearranged to

$$[H^{+}] + \frac{VN}{(Vo+V)} - [OH^{-}] = \frac{Ka^{o}_{A}Ve_{A}N}{(Vo+V)(Ka^{o}_{A} + \gamma_{A^{-}}\{H^{+}\})} + \frac{Ka^{o}_{B}Ve_{B}N}{(Vo+V)(Ka^{o}_{B} + \gamma_{B^{-}}\{H^{+}\})} \qquad \text{Eq.106}$$

Eq.106 could be written in term of variables : $y$, $x_1$, $x_2$

$$y = a_1x_1 + a_2x_2 \qquad \text{Eq.107}$$

which $$y = [H^+] + \frac{NV}{(Vo+V)} - [OH^-] \qquad \text{Eq.108}$$

$$x_1 = \frac{Ka^o{}_A N}{(Vo+V)(Ka^o{}_A + \{H^+\}\,\gamma_{A^-})} \qquad \text{Eq.109}$$

$$x_2 = \frac{Ka^o{}_B N}{(Vo+V)(Ka^o{}_B + \{H^+\}\,\gamma_{B^-})} \qquad \text{Eq.110}$$

$$a_1 = Ve_A \qquad \text{Eq.111}$$

$$a_2 = Ve_B \qquad \text{Eq.112}$$

The equuivalent volumes of each weak acid, $Ve_A$ and $Ve_B$ , could be obtained from partially regression coefficient, $a_1$ and $a_2$, which was achieved from solving the equation (Eq.106) by the multiple regression analysis and computer program, SPSS/PC$^+$ . The thermodynamic dissociation constant of each weak acid could be obtained from the slope of modified G plot of the titration data of the single weak acid solution as shown in Eq.67, Eq.79 and Eq.89.

## 2. Derivation of equations 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 calculated from Eq.90 and the dissociation constant of the ionized weak acid ($HB^+ X^-$ ) could be expressed as followed:

$$HB^+X^- \longrightarrow HB^+ + X^-$$

$$HB^+ \rightleftarrows H^+ + B$$

$$Ka^o_B = \frac{\{H^+\}\{B\}}{\{HB^+\}} \qquad \text{Eq.113}$$

$$Ka^o_B = \frac{\{H^+\}\,\gamma_B\,[B]}{\gamma_{HB^+}\,[HB^+]} \qquad \text{Eq.114}$$

In dilute solution $\gamma_B \approx 1$, Eq.114 could be rearranged to

$$Ka^o_B = \frac{\{H^+\}\,[B]}{\gamma_{HB^+}\,[HB^+]} \qquad \text{Eq.115}$$

The mass balance of two weak acids were

$$[HA] + [A^-] = C_{HA} = \frac{Ve_AN}{(Vo+V)} \qquad \text{Eq.116}$$

$$[HB^+] + [B] = C_{HB^+} = \frac{Ve_BN}{(Vo+V)} = [X^-] \qquad \text{Eq.117}$$

and the charge balance of this titration solution was

$$[H^+] + [Na^+] + [HB^+] = [OH^-] + [X^-] + [A^-] \qquad \text{Eq.118}$$

Substitution of Eq.117 into Eq.118 gave

$$[H^+] + [Na^+] = [OH^-] + [B] + [A^-] \qquad \text{Eq.119}$$

Substitution of Eq.117 into Eq.115 gave

$$Ka^o{}_B = \frac{\{H^+\}[B]}{\gamma_{HB^+}\left(\frac{Ve_BN}{Vo+V} - [B]\right)} \qquad \text{Eq.120}$$

$$[B] = \frac{\gamma_{HB^+} Ka_B\, Ve_BN}{(Vo+V)(\gamma_{HB^+} Ka^o{}_B + \{H^+\})} \qquad \text{Eq.121}$$

Substitution of Eq.99 , Eq.121 and Eq.102 into Eq.119 gave

$$[H^+] + \frac{VN}{Vo+V} = [OH^-] + \frac{Ka^o{}_A Ve_AN}{(Vo+V)(Ka^o{}_A + \gamma_{A^-}\{H^+\})} + \frac{\gamma_{HB^+} Ka^o{}_B Ve_BN}{(Vo+V)(\gamma_{HB^+} Ka^o{}_B + \{H^+\})} \qquad \text{Eq.122}$$

Eq.122 could be rearranged to

$$[H^+] + \frac{VN}{Vo+V} - [OH^-] = \frac{Ka^o{}_A Ve_AN}{(Vo+V)(Ka^o{}_A + \gamma_{A^-}\{H^+\})} + \frac{\gamma_{HB^+} Ka^o{}_B Ve_BN}{(Vo+V)(\gamma_{HB^+} Ka^o{}_B + \{H^+\})} \qquad \text{Eq.123}$$

Then $Ve_A$ and $Ve_B$ could be obtained as previously described in 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) calculated from Eq.90 and the dissociation constant of ionized weak acid ($K^+ HB^-$) could be expressed as followed.

$$K^+HB^- \longrightarrow K^+ + HB^-$$

$$HB^- \rightleftarrows H^+ + B^{2-}$$

$$Ka^\circ_B = \frac{\{H^+\}\{B^{2-}\}}{\{HB^-\}} \qquad \text{Eq.124}$$

$$Ka^\circ_B = \frac{\{H^+\}\,\gamma_{B^{2-}}\,[B^{2-}]}{\gamma_{HB^-}\,[HB^-]} \qquad \text{Eq.125}$$

The mass balance of two weak acids were

$$[HA] + [A^-] = C_{HA} = \frac{Ve_AN}{(Vo+V)} \qquad \text{Eq.126}$$

$$[HB^-] + [B^{2-}] = C_{HB^-} = [K^+] = \frac{Ve_BN}{(Vo+V)} \qquad \text{Eq.127}$$

and the charge balance of this titration solution was

$$[H^+] + [Na^+] + [K^+] = [OH^-] + [A^-] + [HB^-] + 2[B^{2-}] \qquad \text{Eq.128}$$

substitution of Eq.127 into Eq.128 gave

$$[H^+] + [Na^+] = [OH^-] + [A^-] + [B^{2-}] \qquad \text{Eq.129}$$

substitution of Eq.127 into Eq.125 gave

$$Ka^o_B = \frac{\{H^+\}\gamma_{B^{2-}}[B^{2-}]}{\gamma_{HB^-}\left(\frac{Ve_BN}{Vo+V} - [B^{2-}]\right)} \qquad \text{Eq.130}$$

$$[B2^-] = \frac{\gamma_{HB^-} Ka^o_B Ve_BN / \gamma_{B^{2-}}}{(Vo+V)(\gamma_{HB^-} Ka^o_B / \gamma_{B^{2-}} + \{H^+\})} \qquad \text{Eq.131}$$

$$[B^{2-}] = \frac{Ka^o_B Ve_BN}{(Vo+V)(Ka^o_B + \gamma_{B^{2-}}\{H^+\}/\gamma_{HB^-})} \qquad \text{Eq.132}$$

Substitution of Eq.99, Eq.102 and Eq.132 into Eq.128 gave

$$[H^+] + \frac{VN}{(Vo+V)} = [OH^-] + \frac{Ka^o_A Ve_AN}{(Vo+V)(Ka^o_A + \gamma_{A^-}\{H^+\})} + \frac{Ka^o_B Ve_BN}{(Vo+V)(Ka^o_B + \gamma_{B^{2-}}\{H^+\}/\gamma_{HB^-})} \qquad \text{Eq.133}$$

Eq.133 could be rearranged to

$$[H^+] + \frac{VN}{Vo+V} - [OH^-] = \frac{Ka^o_A Ve_A N}{(Vo+V)(Ka^o_A + \gamma_{A^-}\{H^+\})} + \frac{Ka^o_B Ve_B N}{(Vo+V)(Ka^o_B + \gamma_{B^{2-}}\{H^+\}/\gamma_{HB^-})} \quad \text{Eq.134}$$

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

## 3. Derivation of equations for titration of the mixture of two ionized weak acid.

### 3.1 Ionized weak acid ($HA^+X^-$) + Ionized weak acid ($HB^+Y^-$)

The dissociation constant of $HA^+X^-$ and $HB^+Y^-$ could be obtained from the equation derived as followed:

$$HA^+X^- \longrightarrow HA^+ + x^-$$

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

$$Ka^o_A = \frac{\{H^+\}\{A\}}{\{HA^+\}} \quad \text{Eq.135}$$

$$Ka^o_A = \frac{\{H^+\}[A]}{\gamma_{HA^+}[HA^+]} \quad \text{Eq.136}$$

$$HB^+Y^- \longrightarrow HB^+ + Y^-$$

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

$$Ka^o{}_B = \frac{\{H^+\}\{B\}}{\{HB^+\}} \qquad \text{Eq.137}$$

$$Ka^o{}_B = \frac{\{H^+\}\,[B]}{\gamma_{HB}{}^+\,[HB^+]} \qquad \text{Eq.138}$$

The mass balance of two weak acids were

$$[HA^+] + [A\ ] = C_{HA}{}^+ = \frac{Ve_AN}{(Vo+V)} = [X^-] \qquad \text{Eq.139}$$

$$[HB^+] + [B\ ] = C_{HB}{}^+ = \frac{Ve_BN}{(Vo+V)} = [Y^-] \qquad \text{Eq.140}$$

and the charge balance of this titration solution was

$$[H^+] + [Na^+] + [HA^+] + [HB^+] = [OH^-] + [X^-] + [Y^-] \qquad \text{Eq.141}$$

Substitution of Eq.139 and Eq.140 into Eq.141 gave

$$[H^+] + [Na^+] = [OH^-] + [A] + [B] \qquad \text{Eq.142}$$

Substitution of Eq.139 into Eq.136 gave

$$Ka^o{}_A = \frac{\{H^+\}[A]}{\gamma_{HA^+}\left(\frac{Ve_AN}{(Vo+V)} - [A]\right)} \qquad \text{Eq.143}$$

$$[A] = \frac{\gamma_{HA^+} + Ka^o{}_A\,Ve_AN}{(Vo+V)(\gamma_{HA}{}^+Ka^o{}_A + \{H^+\})} \qquad \text{Eq.144}$$

Substitution of Eq.140 into Eq.138 gave

$$Ka^{o}_{B} = \frac{\{H^{+}\}[B]}{\gamma_{HB^{-}}\left(\frac{Ve_{B}N}{Vo+V} - [B]\right)} \qquad \text{Eq.145}$$

$$[B] = \frac{\gamma_{HB^{+}}\, Ka^{o}_{B}\, Ve_{B}N}{(Vo+V)(\gamma_{HB^{+}}\, Ka^{o}_{B} + \{H^{+}\})} \qquad \text{Eq.146}$$

Substitution of Eq.99,Eq.144 and Eq.146 into Eq.142 gave

$$[H^{+}] + \frac{VN}{(Vo+V)} = [OH^{-}] + \frac{\gamma_{HA^{+}}\, Ka^{o}_{A} Ve_{A}N}{(Vo+V)(\gamma_{HA^{+}}\, Ka^{o}_{A} + \{H^{+}\})} + \frac{\gamma_{HB^{+}}\, Ka^{o}_{B} Ve_{B}N}{(Vo+V)(\gamma_{HB^{+}}\, Ka^{o}_{B} + \{H^{+}\})} \qquad \text{Eq.147}$$

Eq.147 could be rearranged to

$$[H^{+}] + \frac{VN}{(Vo+V)} - [OH^{-}] = \frac{\gamma_{HA^{+}}\, Ka^{o}_{A} Ve_{A}N}{(Vo+V)(\gamma_{HA^{+}}\, Ka^{o}_{A} + \{H^{+}\})} + \frac{\gamma_{HB^{+}}\, Ka^{o}_{B} Ve_{B}N}{(Vo+V)(\gamma_{HB^{+}}\, Ka^{o}_{B} + \{H^{+}\})} \qquad \text{Eq.148}$$

Thus, $Ve_{A}$ and $Ve_{B}$ could be obtained in the same manner as the mixture of two neutral weak acids.

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

The dissociation constant of $HA^+X^-$ and $K^+HB^-$ could be obtained from the equation, derived as followed:

$$HA^+X^- \longrightarrow HA^+ + X^-$$

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

$$Ka^o_A = \frac{\{H^+\}\{A\}}{\{HA^+\}} \qquad \text{Eq.149}$$

$$Ka^o_A = \frac{\{H^+\}[A]}{\gamma_{HA^+}[HA^+]} \qquad \text{Eq.150}$$

$$K^+HB^- \longrightarrow HB^- + K^+$$

$$HB^- \rightleftharpoons H+ + B^{2-}$$

$$Ka^o_B = \frac{\{H^+\}\{B^{2-}\}}{\{HB^-\}} \qquad \text{Eq.151}$$

$$K^oa_B = \frac{\{H^+\}\gamma_{B^{2-}}[B^{2-}]}{\gamma_{HB^-}[HB^-]} \qquad \text{Eq.152}$$

The mass balance of two weak acids were

$$[HA^+] + [A] = C_{HA^+} = \frac{Ve_AN}{Vo+V} = [X^-] \qquad \text{Eq.153}$$

$$[HB^-] + [B^{2-}] = C_{HB^-} = \frac{Ve_B N}{Vo+V} = [K^+] \qquad \text{Eq.154}$$

and the charge balance of this titration solution was

$$[H^+] + [Na^+] + [HA^+] + [K^+] = [OH^-] + [X^-] + [HB^-] + 2[B^{2-}] \qquad \text{Eq.155}$$

Substitution of Eq.153 and Eq.154 into Eq.155 gave

$$[H^+] + [Na^+] = [OH^-] + [A] + [B^{2-}] \qquad \text{Eq.156}$$

Introduction of Eq.99, Eq.132 and Eq.144 into Eq.156 gave

$$[H^+] + \frac{VN}{(Vo+V)} = [OH^-] + \frac{\gamma_{HA^+} Ka^o_A Ve_A N}{(Vo+V)(\gamma_{HA^+} Ka^o_A + \{H^+\})} + \frac{Ka^o_B Ve_B N}{(Vo+V)(Ka^o_B + \gamma_{B^{2-}} \{H^+\}/\gamma_{HB^-})} \qquad \text{Eq.157}$$

Eq.157 could be rearranged to

$$[H^+] + \frac{VN}{(Vo+V)} - [OH^-] = \frac{\gamma_{HA^+} Ka^o_A Ve_A N}{(Vo+V)(\gamma_{HA^+} Ka^o_A + \{H^+\})} + \frac{Ka^o_B Ve_B N}{(Vo+V)(Ka^o_B + \gamma_{B^{2-}} \{H^+\}/\gamma_{HB^-})} \qquad \text{Eq.158}$$

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

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

The dissociation constant of $K^+HA^-$ and $K^+HB^-$ could be obtained from the equation derived in the same manner as Eq.151. Therefore, the multiple linear equation could be obtained as followed.

$$\frac{[H^+] + VN - [OH^-]}{(Vo+V)} = \frac{Ka^o_A Ve_A N}{(Vo+V)\,(Ka^o_A + \gamma_A{}^{2-}\{H^+\}/\gamma_{HA^-})} + \frac{Ka^o_B Ve_B N}{(Vo+V)\,(Ka^o_B + \gamma_B{}^{2-}\{H^+\}/\gamma_{HB^-})} \qquad \text{Eq.159}$$

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

All of the equations used to find the equivalent volumes of both acids in the titration of mixtures of two weak acids above could be expressed in term of the function

$$y = f(x, V_1, V_2, ..., V_j) \quad \text{or}$$

$$F(\xi,\eta,\alpha,\beta,\gamma) \qquad \text{Eq.160}$$

where $V_i$ denotes the ith one of a total of j numerical parameters involved

$y,\xi$ denotes dependent variable

$x,\eta$ denotes independent variable

$\alpha,\beta,\gamma$ denotes numerical parameters involved this equation was called "condition equation" or "model equation"

All quantities in these equations would be classified into three categories : parameters, constants, and variables. The parameters were the unknown values which were searched for such as equivalent volumes in the titration ($Ve_A$, $Ve_B$). The constants were both experimental(normality of sodium hydroxide) and semi-empirical ( Kw, $Ka_A$ ,$Ka_B$ and Vo). The variables were the remaining quantities whose values changed during the course of the experiment; e.g., volume of titrant and pH observed.

The condition equation in principle could be written down by combining all the model equations together, followed by substituting and eliminating all the variables together in favor of pH and V. In practice , these equations could not be reduced to a single equation relating pH, V. They could, however, be solved numerically and since the "condition equation" needed not be so reduced, the full set of model equations are identified as Deming's "condition equation". This entity $F(x, y; V_1, V_2) = 0$ was interpreted as followed.

1. Identify y with pH and x with V.
2. Identify the parameters $V_1$, $V_2$ with $Ve_A$, $Ve_B$
3. Let the numerical solution of the model equations for a given values of parameters, constants, and pH be denoted by $y = f(x; V_1, V_2)$. The condition equation is $F(x, y; V_1, V_2) = 0$ and least-squares "best" values of these parameters ($Ve_A$, $Ve_B$) could be calculated by multiple linear regression.

## Basis for Least Squares Adjustment of Data

Assume that the errors of each of the observations of a given quantity belonged to a Gaussian distribution, commonly expressed as

$$f(r_x) = \frac{1}{\sqrt{2\sigma_x}} e^{-r_x^2/2\sigma_x^2} \qquad \text{Eq.161}$$

where $\sigma_x$ = standard error (also called standard deviation or root mean square error), $\sigma_x^2$ = variance, $r_x$ = true residual of x = absolute of (observed value- true value). The probability of observing the ith residual in the region $r_{x_i}$ to $r_{x_i} + dr_{x_i}$ was

$$P_i = \frac{1}{\sqrt{2\sigma_x}} e^{-r_x^2/2\sigma_x^2} dr_x \qquad \text{Eq.162}$$

Since the probability of obtaining a given set of n observations was simply the product of the probabilities of each of the ith measurements,

$$P = \prod_{i=1}^{n} P_i = \left(\frac{dr_x}{\sqrt{2\sigma_x}}\right)^n e^{-(1/2\sigma_x^2)\sum r_{x_i}^2} \qquad \text{Eq.163}$$

Now, based upon the principle of maximum likelihood, the probability became a maximum when the sum of the squared residuals became a minimum.

$$\sum r_{x_i}{}^2 = \text{min imum} \qquad \text{Eq.164}$$

Hence, the origin of the term least squares was apparent.

In the above discussion it was assumed that all measurements arised from the same distribution. However, in the more general situation where this was not true, Eq.162 should be written as

$$P_i = \frac{1}{\sqrt{2\sigma_{x_i}}} e^{-r_{x_i}{}^2/2\sigma_{x_i}{}^2}\, dr_x \qquad \text{Eq.165}$$

Equation 163 then became

$$P = \prod_{i=1}^{n} P_i = \left(\frac{dr_x}{\sqrt{2}}\right)^n \frac{1}{\sigma_{x_1}\sigma_{x_2}\ldots\sigma_{x_n}}\, e^{-\frac{1}{2}\sum(r_{x_i}{}^2/\sigma_{x_i}{}^2)} \qquad \text{Eq.166}$$

and the least squares principle then became

$$\sum \frac{r_{x_i}{}^2}{\sigma_{x_i}{}^2} = \text{min imum} \qquad \text{Eq.167}$$

If the weight of an observation was defined as a quantity inversely proportional to the variance,

$$W_{x_i} = \frac{\sigma_0{}^2}{\sigma_{x_i}{}^2} \qquad \text{Eq.168}$$

where $\sigma_0{}^2$ = variance of unit weight (an arbitrary constant), then the principle of least squares was

$$\sum W_{x_i} r_{x_i}^{\ 2} = \text{min imum} \qquad \text{Eq.169}$$

i.e., the sum of the weighted squares of the residuals was made a minimum.

In actual practice, of course, the true value of the quantity x was not known. However, the principle of least squares attempted to adjust the estimate of the parameter such that

$$\sum W_{x_i} V_{x_i}^{\ 2} = \text{min imum} \qquad \text{Eq .170}$$

where $v_{X_i}$ was defined as the residual in X; i. e.,

$$V_{x_i} = (X_i - \overline{X}) \qquad \text{Eq.171}$$

where $\overline{x}$ was the least squares estimate of the true parameter.

## General Least Squares Adjustment to a Single Function with Uncorrelated Data

The general problem of least squares adjustment data with uncorrelated errors was thoroughly presented by Deming. One section of this text was concerned with the specific problem of curve fitting to a single function containing parameters. In physical chemistry and generally in chemistry as a whole, the adjustment was frequently concerned with a single function containing one or more parameters to be determined (or system of equations which could be reduced to a single function). Under this restriction, Deming's treatment could be simplified considerably.

It would be assumed that pairs of observations ($x_i$, $y_i$) or ($V_d$,$pH_d$) in the titration experiment where $pH_d$ = observed pH, $V_d$ = volume of titrant used at any point of titration were obtained from the variables ( $\xi$, $\eta$ ) with a single function (F) relating these variables with additional three parameters ( $\alpha$, $\beta$, $\gamma$ ) or ($Ve_A$, $Ve_B$, ...) in the titration condition. The extension to more than two variable and more than three parameters would be obvious when the normal equations were developed. The treatment of the problem considering a varying number of variable (e.g., x,y,z) and a variable number of parameters could be facilitated by the use of matrix algebra. For reasons of clarity and simplicity this treatment would be concerned with a fixed number of variables and parameters.

Suppose a function related two variables $\xi$, $\eta$ and three parameters $\alpha$, $\beta$, $\gamma$

$$F(\xi,\eta,\alpha,\beta,\gamma) \qquad \text{Eq.172}$$

Furthermore, assumed that n pairs of observations made of the variables which would be designated ($x_i$, $y_i$) i = 1,2 ...n. Since n was a finite number, it was not possible to evaluate the true variables ( $\xi$, $\eta$ ) and the true parameters ( $\alpha$, $\beta$, $\gamma$ ).

However, an estimate of these parameters might be determined which would be designated by (a, b, c) based up the criteria of least squares of the observations ($x_i$, $y_i$). Designate the adjusted or calculated values the variables by ($x_i$, $y_i$) where i = 1,2, ...n and residuals of the observations by

$$\begin{Bmatrix} V_{x_i} = (x_i - \overline{x_i}) \\ V_{x_i} = (y_i - \overline{y_i}) \end{Bmatrix} \qquad \text{Eq.173}$$

The least squares problem could now be stated mathematically as a desire to obtain a minimization of sum of the squares of the weighted residuals

$$S = \Sigma(W_{x_i} V_{x_i}{}^2 + W_{y_i} V_{y_i}{}^2) = \min\text{imum} \qquad \text{Eq.174}$$

under the restriction that the condition equations

$$F_i(\overline{x_i}, \overline{y_i}, a, b, c) = 0 \qquad i = 1, 2, \ldots n \qquad \text{Eq.175}$$

be satisfied. The weights $w_{x_i}$, $w_{y_i}$ were defined Eq.168 and.$\sigma_0{}^2$ was generally selected so that magnitude of the weight was convenient.

The solution of this problem was simplified considerably if the condition equations were linear with respond to the $x_i$, $y_i$, a, b, c. This could be accomplished very simply by expanding the function in a Taylor 's Series about the point ($x_i$, $y_i$, $a_o$, $b_o$, $c_o$) and truncating the series after the first order terms. It was assumed satisfactory that first approximations to the parameters could be obtained by graphical means or a numerical solution of a system of equations (three equations in this case) with a selected set of the observations (three sets of in this case). Represented the difference between this first approximation to the parameters and the least squares estimate of these parameters by

$$\begin{aligned} \Delta a &= (a^0 - a) \\ \Delta b &= (b^0 - b) \qquad \text{Eq .176} \\ \Delta c &= (c^0 - c) \end{aligned}$$

The Taylor's Series expansion of the condition equation 175 then became

$$F_i(\overline{x_i},\overline{y_i},a,b,c) = F_i^0(x_i,y_i,a^0,b^0,c^0) - F_{x_i}V_{x_i} - F_{y_i}V_{y_i} - F_{a_i}\Delta a - F_{b_i}\Delta b - F_{c_i}\Delta c = 0$$

$i = 1, 2,\ldots,n$ Eq .177

The usual nomenclature for the partial derivatives had been employed

$$F_{x_i} = \left(\frac{\partial F_i}{\partial x}\right)\bigg|_{(x_i,\, y_i,\, a^0,\, b^0, c^0)}, \text{ etc.} \qquad \text{Eq.178}$$

$$F_{a_i} = \left(\frac{\partial F_i}{\partial a}\right)\bigg|_{(x_i,\, y_i,\, a^0,\, b^0, c^0)}, \text{ etc.}$$

Rearranging equations Eq.177, then

$$F_{x_i}V_{x_i} + F_{y_i}V_{y_i} + F_{a_i}\Delta a + F_{b_i}\Delta b + F_{c_i}\Delta c = F_i^0 \qquad i = 1, 2, 3, \ldots n$$

Eq.179

Now in order for S in equation Eq.174 to be a minimum it was necessary that the differential of S with respect to the residuals be zero.

$$\frac{1}{2}dS = \Sigma(W_{x_i} V_{x_i} dV_{x_i} + W_{y_i} V_{y_i} dV_{y_i}) = 0 \qquad \text{Eq.180}$$

The variations in the residuals, $dv_{x_i}$ and $dv_{y_i}$ had to also satisfy the condition equations Eq.179 or actually the differential of these expressions

$$F_{x_i} dV_{x_i} + F_{y_i} dV_{y_i} + F_{a_i} d\Delta a + F_{b_i} d\Delta b + F_{c_i} d\Delta c = 0 \quad i = 1,2,\ldots,n \quad \text{Eq.181}$$

This was not a simple minimization problem as encountered in elementary calculus, but it could conveniently be solved by the method of Lagrange multipliers. Equation Eq.181 had 2n + 3 differentials and n equations. Therefore, all the differentials were not arbitrary since in theory n of these differentials could be specified by the n linear equations Eq.181 and only 2n + 3 - n or n + 3 were arbitrary. Introduce n arbitrary multipliers designated by $-\lambda_1, -\lambda_2, \ldots\ldots -\lambda_n$ and multiplied each of these terms the Eq.181, i. E.

$$-\lambda_i F_{x_i} dV_{x_i} - \lambda_i F_{y_i} dV_{y_i} - \lambda_i F_{a_i} d\Delta a - \lambda_i F_{b_i} d\Delta b - \lambda_i F_{c_i} d\Delta c = 0 \qquad i = 1,2,\ldots,n \qquad \text{Eq .182}$$

Combine Eq.182 and Eq.180 together and collected coefficients of the differentials

$$\Sigma(W_{x_i}V_{x_i} - \lambda_i F_{x_i})dV_{x_i} + \Sigma(W_{y_i}V_{y_i} - \lambda_i F_{y_i})dV_{y_i} + \Sigma\lambda_i F_{a_i} d\Delta a + \Sigma\lambda_i F_{b_i} d\Delta b + \Sigma\lambda_i F_{c_i} d\Delta c = 0 \qquad \text{Eq.183}$$

the $\lambda_1, \lambda_2 \ldots \lambda_n$ were initially introduced as arbitrary multipliers, but now specify these multipliers so that n of the differentials in equation Eq.183 would disappear.

There were now n + 3 differentials remaining in equation Eq.183. However, it was previously decided that exactly this number, n + 3, of the differentials were arbitrary. Therefore it might be concluded that since the remaining n + 3 differentials in Eq.183 were arbitrary the only way in which equation Eq.183 could be specified was that the coefficient of each differential be equal to zero; i.e.,

$$\begin{Bmatrix} W_{x_i}V_{x_i} - \lambda_i F_{x_i} = 0, i = 1,2,\ldots,n \\ W_{y_i}V_{y_i} - \lambda_i F_{y_i} = 0, i = 1,2,\ldots,n \end{Bmatrix} \qquad \text{Eq .184}$$

$$\begin{Bmatrix} \Sigma\lambda_i F_{a_i} = 0 \\ \Sigma\lambda_i F_{b_i} = 0 \\ \Sigma\lambda_i F_{c_i} = 0 \end{Bmatrix} \qquad \text{Eq.185}$$

Eq.184 can be solved for the residuals

$$V_{x_i} = \frac{\lambda_i F_{x_i}}{W_{x_i}}, i = 1,2,\ldots,n$$

$$V_{y_i} = \frac{\lambda_i F_{y_i}}{W_{y_i}}, i = 1,2,\ldots,n \qquad \text{Eq.186}$$

The calculation procedure minimized the weighted sum-of-squares S of both residuals $V_{xi}$ and $V_{yi}$ over all n recorded points from Eq.174

$$S = \sum_{i}^{n}(w_{x_i} V_{x_i}{}^2 + w_{y_i} V_{y_i}{}^2) \qquad \text{Eq.187}$$

subject to the restraint imposed by the condition equation. The residuals were defined here as

$$V_x = pH_d - pH \text{ and } V_y = V_d - V \qquad \text{Eq.188}$$

and the weighting factors $W_x$ and $W_y$ were inversely proportional to $\sigma^2{}_x$ and $\sigma^2{}_y$, respectively. These latter quantities were the priori variance estimates of the x and y measurements.

The quality of the fit of this calculated curve to the data points was reflected in the sum S of Eq.187. This sum could be interpreted directly as the sum of squared deviations were. This sum was not for the weighting factors $W_x$ and Wy which were inversely proportional to $\sigma^2{}_x$ and $\sigma^2{}_y$ respectively, but otherwise arbitrary in magnitude.

Substituted Eq.186 in Eq.187 and collected coefficient of the results gave

$$S=\sum_{i}\left[\frac{\sigma_x^2}{\sigma_0^2}\left(\frac{\partial F}{\partial x}\right)_i^2+\frac{\sigma_y^2}{\sigma_0^2}\left(\frac{\partial F}{\partial y}\right)_i^2\right] \qquad \text{Eq.189}$$

By using the arbitrary multiplier $\sigma_o^2$ to normalize the Eq.189. With this normalization, the weighted sum of squared residuals became

$$S_m^2=\sum_{i=1}^{n}\left[\sigma_x^2\left(\frac{\partial F}{\partial x}\right)_i^2+\sigma_y^2\left(\frac{\partial F}{\partial y}\right)_i^2\right] \qquad \text{Eq.190}$$

This quantity should approximate the effective variance of the measurements of random error (lack-of-fit) and did not contribute to the deviation of the calculated curve from the data points.

However, because we had a priori estimates of the statistical uncertainties $\sigma^2_y$ and $\sigma^2_x$ of the $pH_d$ and $V_d$ measurements, respectively. $S^2_m$ was used as a means of estimating the priori effective variance of the measurements. These variances might serve as statistical uncertainty estimates of the parameters.

From the derivation above ,the condition equation which derived from mass balance, charge balance and equilibrium equation in the titration of two weak acid mixtures could be used to evaluate two parameters, the equivalent volume of stronger acid ($Ve_A$) and the equivalent volume of weaker acid ($Ve_B$), by using multiple linear regression analysis. The variance of the parameters were obtained from equations of the form

$$\sigma_{V_i} = \sum \left[\sigma_{pH}{}^2\left(\partial V_i/\partial_{pH}\right)^2 + \sigma_{Vb}{}^2\left(\partial V_i/\partial V_b\right)^2\right]^{1/2} \qquad \text{Eq.191}$$

Where $\sigma_{vi}$ = standard deviation of the parameter $V_i$

$\sigma_{pH}$ = standard deviation of pH measurement

$\sigma_{vb}$ = standard deviation of titrant volume

This equation used to predict the precisions of the parameters involved and had the orders of magnitude that were appropriate to careful work with modern apparatus with $\sigma_{pH}$ and $\sigma_{vb}$ . To permit prediction of what the standard deviation of the parameters would be for any other combination of the standard deviation of measurement, it was convenient to write the familiar equation 191 in the form

$$\sigma_{V_i} = 0.001F\sum \left[\left(\partial V_i/\partial_{pH}\right)^2 + (G/F)^2\left(\partial V_i/\partial V_b\right)^2\right]^{1/2} = F\sigma^*_{V_i} \quad \text{Eq.192}$$

where $F = \sigma_{pH}/0.001$, $G/F = \sigma_{Vb}/\sigma_{pH}$ and $\sigma^*_{Vi}$ was defined as quantity within square brackets in Eq.192.

As long as G/F was constant, the standard errors of the parameters were proportional to the changes of the experimental variables and conditions. These standard errors ($\sigma_{Vb}$ and $\sigma_{pH}$) affected the precisions of the parameters in ways that were different if the parameters were evaluated by multiple linear reqression analysis from the ways in which such changes affected precisions in the interpretations of titration curve data by classic techniques or from the ways in which the interpretation of titration data obtained by nonlinear regression analysis.

In studying the precision of the parameters ($Ve_A$, $Ve_B$), the applicability of SPSS/PC$^+$ program had to be studied so as to avoid errors owing to the efficiency and possibility of SPSS/PC$^+$ program in evaluating these parameters ($Ve_A$, $Ve_B$).