USING GRAPHICS OF LOGARITHMIC CONCENTRATION (GLC) IN THE TITRATION OF BASES WITH STRONG ACIDS

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Abstract

In an acid – base titration reaction, it is important to have a suitable indicator which experiences a change in color (an end point) as close as possible to the equivalence point (EP) of the reaction. Due to the appearance of the titration jump on the titration curve, we can choose any acid–base indicator which has the pT value ranging within the titration jump with an allowable error [1, 2]. The graphics of logarithmic concentration method [3, 4] has been used to evaluate exactly the pH of the acid, base solutions [5, 6]; to determine the pH at the equivalence point (pH$_{EP}$) and the titration jump in the titration of acids with strong bases [7]. In this report, we study the applications of GLC in the titration of bases and mixture of bases with acids.

1. CONTENTS OF STUDY

The way to construct GLC and the steps in determining pH and equilibria components in solution (using GLC) are done similarly to the reference [5].

To estimate the pH$_{EP}$ value and titration jump, we consider some cases: titration of monoprotic base, mixture of strong and weak bases, mixture of monoprotic bases, polyprotic base, mixture of strong bases and polyprotic bases with strong acids using GLC.

$$[H^+] - [OH^-] - [NH_3] = C'_{HCl} = q.C_{NH_3} = q.\frac{C_0 V_0}{V + V_0} \approx q.\frac{CC_0}{C + C_0} \tag{1}$$

+ At the beginning of the titration jump: q = - 0.1%
$\rightarrow [H^+] + 10^{-4.30} = [OH^-] + [NH_3]$

From Fig. 1 we have: the lg[OH$^-$] line is underslung and far from the lg[NH$_3$] line; the lg[H$^+$] line is lower than the lg10$^{-4.30}$ line $\rightarrow$ [OH$^-$] << [NH$_3$] and [H$^+$] <<10$^{-4.30}$ $\rightarrow$ [NH$_3$] $\approx 10^{-4.30} \rightarrow$ the pH at the beginning of the titration jump (pH$_B$) is defined from the intersection of the lg[NH$_3$] line and the lg10$^{4.30}$ line $\rightarrow$ pH$_B$ = 6.23.

   +At the equivalence point, q = 0:

$$[H^+] = [OH^-] + [NH_3] \approx [NH_3]$$

$\rightarrow$ pH$_{EP}$ is determined from the crossing point of the lg[NH$_3$] line and the lg[H$^+$] line $\rightarrow$ pH$_{EP}$ = 5.27.

   + At the end of the titration jump, q = 0.1%:

$$[H^+] = [OH^-] + [NH_3] + 10^{-4.30}$$

Example 1: Titration of 0.10 M NH$_3$ (pK$_b$ = 4.76) with 0.10 M HCl. Estimate the pH at the equivalence point and the titration jump with the error q = ±0.1% (*system 1*).

The graphics of logarithmic concentration of *system 1* are expressed in Fig. 1.

Suppose we stop titrating after the equivalence point, the components at the end point are: NH$_4^+$, H$_2$O, excess HCl (C'_{HCl}). From the proton conservation law, we have:

Similarly we have: the lg[NH$_3$] line and the lg[OH$^-$] line is lower than the lg10$^{-4.30}$ line $\rightarrow$10$^{-4.30}$ $\approx$ [H$^+$] $\rightarrow$ the pH at the end of the titration jump (pH$_E$) is the junction of the lg10$^{-4.30}$ line and the lg[H$^+$] line $\rightarrow$ pH$_E$ = 4.30 $\rightarrow$ The titration jump is 6.23 - 4.30.

To check the studying result, we estimate the titration jump by the general method – solving an equation of higher degree with one variable. The comparison is shown in table 1.

Thus, there is the relative coherence between the obtained result from the GLC and the theory calculating.

Example 2: Titration the mixture of 0.010 M NaOH and 0.10 M CH$_3$COONa with the 0.10 M HCl. Choose an indicator for this titrymetry if the error is ±1% (system 2).

To choose the compatible indicator, we need to determine the pH at the equivalence point and the titration jump. The graphics of logarithmic concentration of this titrymetry are shown in Fig. 2.

Since CH_3COO^- has $pK_b = 9.24 > 9$, we can only perform the individual titration of NaOH without titration of CH_3COO^- [1].

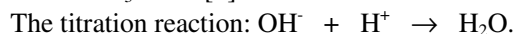The titration reaction: $OH^- + H^+ \rightarrow H_2O$.

Table 1: Comparing the result of defining the pH at the equivalence point and the titration jump in the titration of 0.10 M NH_3 with 0.10 M HCl, q = ±0.1% by the GLC and the general method theory calculating

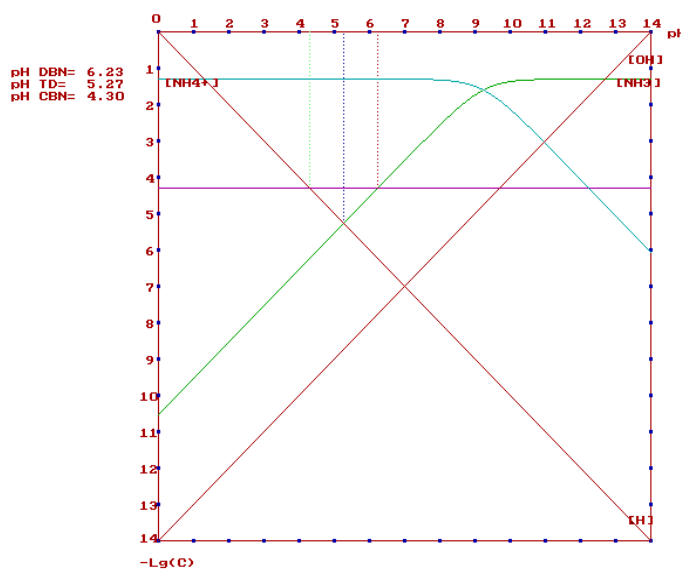| Method	GLC	The general
pH_{EP}	5.27	5.27
The titration jump	6.23 - 4.30	6.24 - 4.30

Fig. 1: The graphics of logarithmic concentration of the titration of 0.10 M NH_3 with 0.10 M HCl (q = ±0.1%)
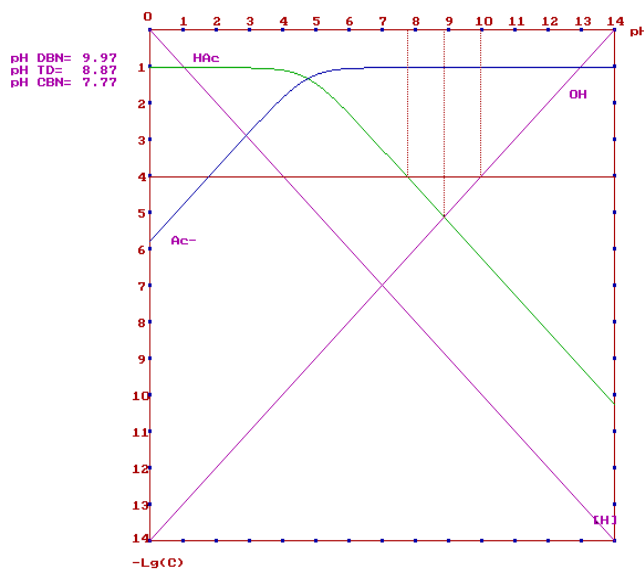

Fig. 2: The graphics of logarithmic concentration of the titration of 0.010 M NaOH and 0.10 M CH_3COONa with 0.10 M HCl (q = ±1%)

The difference between the components at the end point (H^+, OH^-, CH_3COOH) and at the equivalence point causes the titration error.

$$q = \frac{[H^+] - [OH^-] + [CH_3COOH]}{(C_{XOH})_c}$$

With $(C_{XOH})_c = \dfrac{C_{01}.V_0}{V + V_0} \approx \dfrac{C.C_{01}}{C + C_{01}} \rightarrow$

$$[H^+] = [OH^-] - [CH_3COOH] + q\frac{C.C_{01}}{C+C_{01}} \quad (4)$$

+ At the beginning of the titration jump, q = - 1%:

$$[H^+] + [CH_3COOH] + 10^{-4.03} = [OH^-]$$

From the graphics of logarithmic concentration, we can see the $\lg 10^{-4.03}$ line is much higher than the $\lg [H^+]$ line and the $\lg [CH_3COOH]$ line $\rightarrow$ $10^{-4.03} \gg [CH_3COOH]$, $10^{-4.03} \gg [H^+] \rightarrow [OH^-] = 10^{-4.03}$. Therefore, the pH at the beginning of the titration jump (pH_B) is defined from the intersection of the $\lg [OH^-]$ line and the $\lg 10^{-4.03}$ line $\rightarrow pH_B = 9.97$.

+ At the equivalence point, q = 0: $[H^+] + [CH_3COOH] = [OH^-]$.

According to the graphics of logarithmic concentration, the $\lg [CH_3COOH]$ line is much higher than the $\lg [H^+]$ line $\rightarrow [CH_3COOH] \gg [H^+] \rightarrow [CH_3COOH] = [OH^-] \rightarrow$ The intersection of the $\lg[OH^-]$ line and the $\lg[CH_3COOH]$ gives us the pH_{EP} value (the pH at the equivalence point) $\rightarrow pH_{EP} = 8.87$.

+ At the end of the titration jump, q = +1%:

$$[H^+] + [CH_3COOH] = [OH^-] + 10^{-4.03}.$$

From the graphics of logarithmic concentration, we can see the $\lg 10^{-4.03}$ line is much higher than the $\lg[OH^-]$ line and the $\lg[CH_3COOH]$ line is much higher than the $\lg[H^+]$ line $\rightarrow [OH^-] \ll 10^{-4.03}$, $[H^+] \ll [CH_3COOH] \rightarrow 10^{-4.03} \approx [CH_3COOH] \rightarrow$ The pH at the end of the titration jump (pH_E) is detected from the junction of the $\lg[CH_3COOH]$ line and the $\lg 10^{-4.03}$ line $\rightarrow pH_E = 7.77$.

To check the studying result, we estimate the titration jump by the general method. From (4), after changing compatibly we obtain the error equation:

$$q = \left(h - \frac{Kw}{h}\right).\frac{C + C_{01}}{C.C_{01}} + \frac{C_{02}}{C_{01}}.\frac{h}{K_a + h}$$
$$\text{with } h = [H^+] \quad (5)$$

The comparison is shown in table 2.

Table 2: Comparing the result of defining the pH at the equivalence point and the titration jump in the titration of 0.010 M NaOH and 0.10 M CH₃COONa with 0.10 M HCl, q = ±0.1% by the GLC and the theory calculating

	pH_{EP}	The titration jump
GLC	8.87	9.97 – 7.77
The theory calculating	8.86	9.96 – 7.76

Thus, by two different methods the obtained results are approximate. From this result, we can choose the indicators of which pT is from 7.77 to 9.97 (7.77 ≤ pT ≤ 9.97). For example: Phenolphthalein (8 – 10): pT = 8, the color changes from red into colorless; α-naphtholphthalein has the pH range from 7.8 (pink) to 8.7 (greenish to blue) or thymol blue has the pH range from 8.0 (yellow) to 9.0 (blue) and others.

Example 3: Titrate the mixture of 0.10 M NaOH and 0.10 M NaClO ($pK_b = 6.47$) with the 0.10 M HCl (*system 3*). Evaluate the ability of the individual titration with each base in this mixture if the error is ±1%.

The graphics of logarithmic concentration of system 3 are expressed in the Fig. 3.

As ClO⁻ has $5 < pK_b = 6.47 < 9$, in this case we can perform the individual titration of each base [1].

Similarly to two cases mentioned above, from the difference between the components at the end point and at the equivalence point we can easily establish the error equation. Combining with GLC in Fig. 3 we will estimate pH_{EP} and titration jump quickly in two cases: individual titration of NaOH and total titration of NaOH and NaClO:

- First case: The individual titration of NaOH:

$$[H^+] = [OH^-] - [HClO] - q_I.\frac{C.C_{01}}{C + C_{01}} \quad (6)$$

$pH_{EP1} = 10.10$ and the titration jump: 10.70 – 9.53
- Second case: The total titration of NaOH and NaClO:

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$$[H^+]=[OH^-]+[ClO^-]+q_{II}\cdot\frac{C(C_{01}+C_{02})}{C+C_{01}+C_{02}} \quad (7)$$

$pH_{EP2} = 4.47$ and the titration jump: 5.77 - 3.13.

The studying result from GLC is in good agreement with the one obtained from general method-solving 6 equations of higher degree with one variable (table 3).
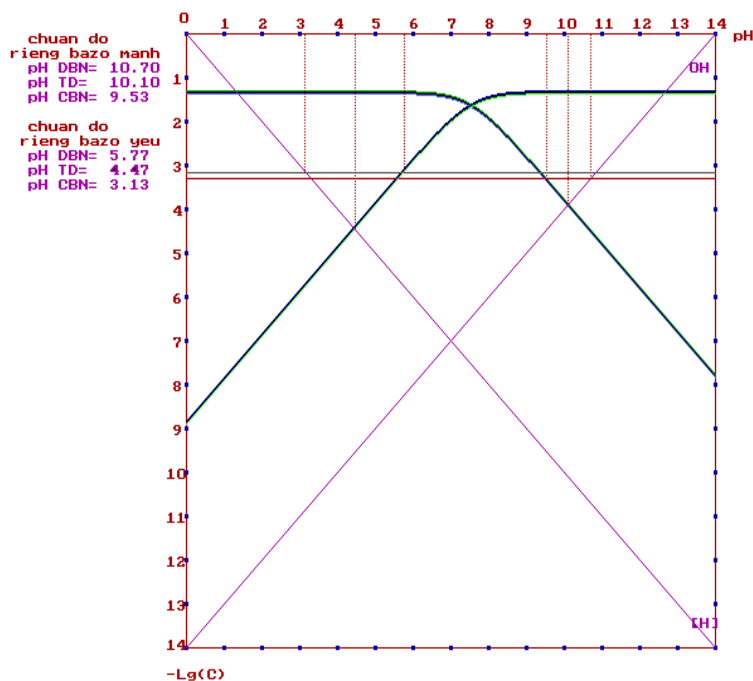

Fig. 3: The graphics of logarithmic concentration of the titration of 0.10 M NaOH and 0.10 M NaClO ($pK_b = 6.47$) with 0.10 M HCl (q = ±1%)

Table 3: Comparing the result of defining the pH at the equivalence point and the titration jump in the titration of 0.10 M NaOH and 0.10 M NaClO with 0.10 M HCl, q = ±1% by the different methods

	Method	pH_{EP}	The titration jump
The individual titration of the strong base	GLC	10.10	10.70 – 9.53
	The general method	10.11	10.72 – 9.50
The total titration of the two bases	GLC	4.47	5.77 – 3.13
	The general method	4.50	5.84 – 3.17

The results obtained from the graphics of logarithmic concentration show the ability of the individual titration of each base in the *system 3*. We can use thymolphthalein (9.40 – 10.60), the color changes from blue into colorless (pT = 9.40) or alizarine yellow (10.10 – 12.00), the color changes from violet into yellow (pT = 10.10) for defining NaOH. With the second step, we can use methyl red (4.40 – 6.20), the color changes from yellow into pink – orange (pT = 5.00), methyl orange (3.10 – 4.40), the color changes from yellow into pink – orange (pT = 4.00) or bromocresol green (3.80 - 5.40), the color changes from blue into yellow for the titration of two bases. Since then the amount of NaClO is determined.

Through the titration of the mixture of a strong and a weak monoprotic base, we can infer that the ability in individual titration of A⁻ in the mixture of two weak monoprotic base A⁻ ($K_{b,A}$, C_{01}) and B⁻ ($K_{b,B}$, C_{02}) depends on the relationship between two base equilibrium constants (assume that $K_{b,A} > K_{b,B}$) and the concentration of two bases. It was shown in the textbook that the base A⁻ can be titrated individually if $pK_{b,B} - pK_{b,A} > 6$ with q ≤ 0.1% and $pK_{b,B} - pK_{b,A} > 4$ with q ≤ 1% [2] (with $C_{01} \approx C_{02}$).

Example 4: Titrate the mixture of 0.010 M NH₃ and 0.010 M NaOCl with the 0.010 M HCl (system 4) if the error is ±1% and $pK_{b,NH_3} = 4.76$; $pK_{b,ClO^-} = 6.47$.

The graphics of logarithmic concentration of system 4 are expressed in the Fig. 4.

Since $\Delta pK_b = pK_{b,ClO^-} - pK_{b,NH_3} = 6.47 - 4.76 = 1.71 < 4$

and $pK_{b,ClO^-} < 9$, we can't perform the titration of each individual base, so we must titrate the total bases NH_3 and ClO^-. The error equation is established from the proton conservation law with the starting material is the end point's component or from the difference between the components at the end point and at the equivalence point:

$$[H^+] = [OH^-] + [ClO^-] + [NH_3] + q_{II} \cdot \frac{C \cdot (C_{01} + C_{02})}{C + C_{01} + C_{02}}$$

(8)

Combine (8) with GLC in Fig. 4, it's easily to determine the value of the titration jump of *system 4*: 5.83 - 4.17 and $pH_{EP} = 5.00$.
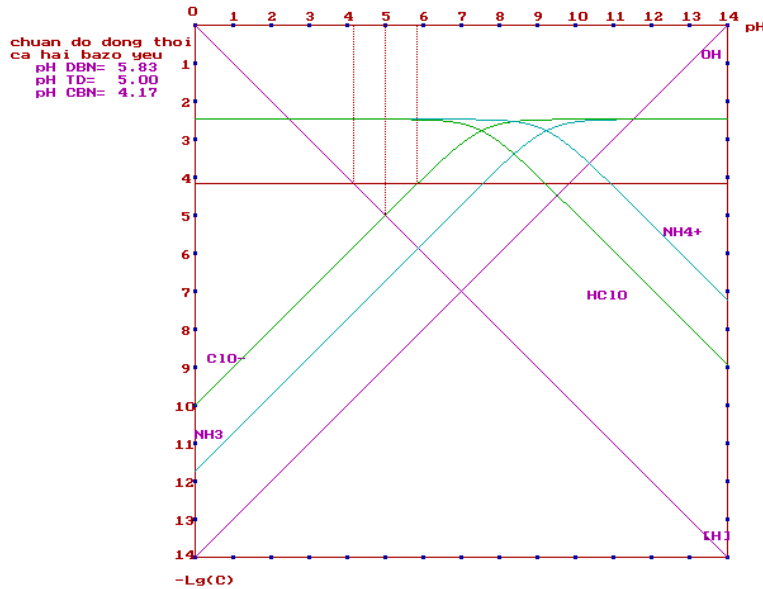

Fig. 4: The graphics of logarithmic concentration of the titration of 0.01 M NH_3 ($pK_{b,NH_3} = 4.76$) and

0.01 M NaOCl ($pK_{b,ClO^-} = 6.47$) with 0.01 M HCl (q = ± 1%)

By the graphics of logarithmic concentration, the pH at the equivalence point and the titration jump are in agreement with those by the general method. In which, solving the cubic equations, we get the pH_{EP}, pH_B and pH_E values:

$pH_{EP} = 5.00$ and the titration jump: 5.84-4.17.

From these results, we can select the indicator of which titration number (pT) is from 4.17 to 5.84 (such as methyl red: the color changes from yellow into pink) for this titrymetry.

Example 5: Define the titration jump of the titration of 0.10 M NH_2-CH_2–CH_2–NH_2 (A^{2-}) with 0.10 M HCl (system 5) if the error is ±1%; $pK_{bi} = 4.072$ and 7.152.

The graphics of logarithmic concentration of system 5 are expressed in Fig. 5.

Since $pK_{b2} < 9$, $\Delta pK_b = pK_{b2} - pK_{b1} = 7.152 - 4.072 < 4$, we have to perform the total titration of two steps of ethylenediamine with the error equation (9).

From the graphics of logarithmic concentration,

the following values are defined quickly:

$pH_{EP} = 4.17$; the titration jump: 5.17 - 3.17.

These results correspond with those from general method by solving equations of higher degree with one variable h = $[H^+]$ which are combined from the error equations (10), α_{HA^-} and $\alpha_{A^{2-}}$ are the concentration ratio of HA^- and A^{2-}, respectively.

$pH_{EP} = 4.16$; the titration jump: 5.16-3.17.

$$q \cdot \frac{2 \cdot C \cdot C_0}{C + 2C_0} = [H^+] - [OH^-] - [HA^-] - 2[A^{2-}]$$

(9)

$$q = (h - \frac{K_w}{h}) \frac{C + 2C_0}{2C \cdot C_0} - \frac{1}{2}(a_{HA^-} + 2a_{A^{2-}})$$

(10)

We can choose the acid – base indicators which have 3.17 < pT < 5.17 for the titrymetry in *system 5* (for example: methyl orange, pT = 4.00, the color changes into yellow into pink - orange; bromocresol green, (3.8 < pT < 5.4), the color changes from blue into yellow, etc.

Example 6: Define the titration jump of the titration of 0.10 M Na_3PO_4 with 0.10 M HCl (system 6) if the error is ± 1% and pK_{bi} = 1.68; 6.79; 11.77.

GLC and the sum-lines of system 6 are shown in Fig. 6.

Since $\Delta pK_1 = pK_{b2} - pK_{b1} = 6.79 - 1.68 > 4$ and $pK_{b3} > 9$, we can carry out the individual titration of the first and second steps, the third step isn't titrated.

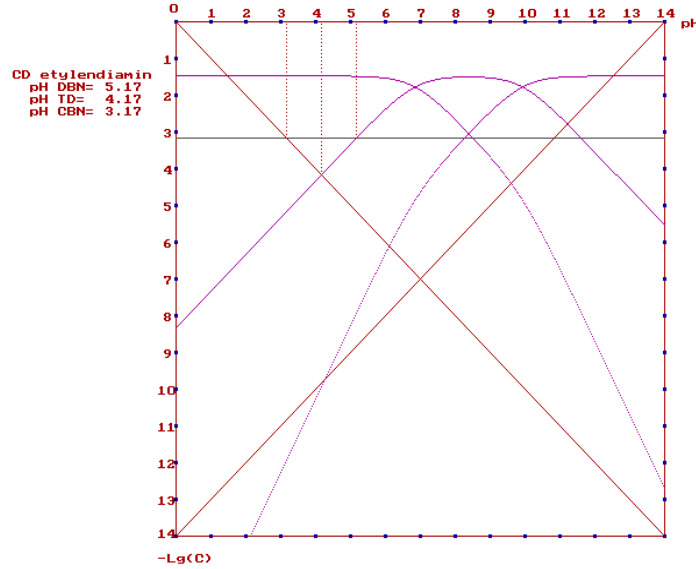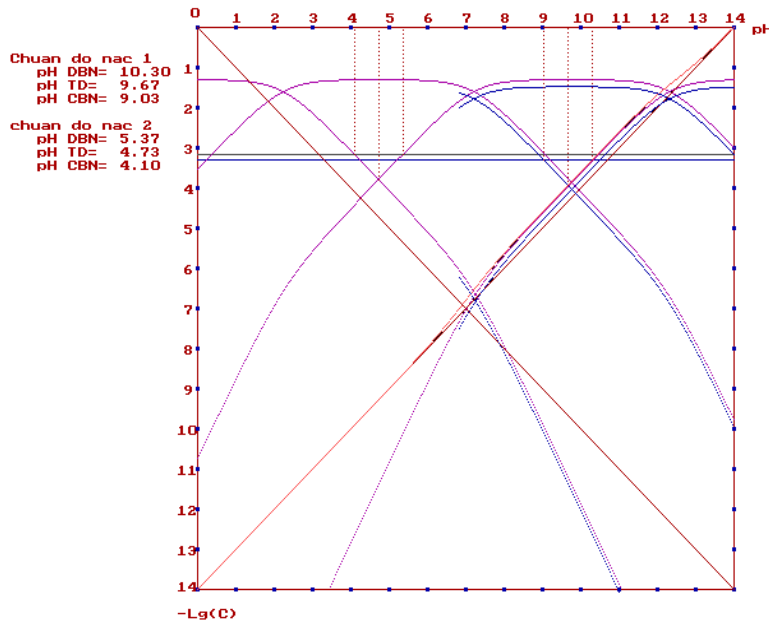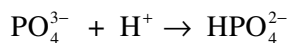*Fig. 5*: The graphics of logarithmic concentration of the titration of 0.10 M NH_2-CH_2–CH_2–NH_2 with 0.10 M HCl (q = ±1%)

Fig. 6: The graphics of logarithmic concentration of the titration of 0.10 M Na_3PO_4 with 0.10 M HCl and q = ±1%

The first step*:*

$$PO_4^{3-} + H^+ \rightarrow HPO_4^{2-}$$

From the difference between the components at the end point (H_3PO_4, HPO_4^{2-}, PO_4^{3-}, H^+, OH^-) and at

the equivalence point (HPO_4^{2-}, H_2O) we can easily establish the error equation (11) at the first step.

The second step:

$$PO_4^{3-} + 2H^+ \rightarrow H_2PO_4^-$$

Similarly, the error equation for the second step is presented in equation (12).

$$q_I \cdot \frac{C.C_0}{C+C_0} = [H^+] - [OH^-] + [H_2PO_4^-] + 2[H_3PO_4] - [PO_4^{3-}]$$

(11)

$$q_{II} \cdot \frac{2.C.C_0}{C+2C_0} = [H^+] - [OH^-] + [H_3PO_4] - [HPO_4^{2-}] - 2[PO_4^{3-}]$$

(12)

Combine two error equations and GLC (Fig. 6) (use the sum-line $\log([OH^-] + [PO_4^{3-}])$) to define

pH_{B1}, pH_{EP1}) we can determine promptly and visually the following values: pH_{EP1}= 9.67; the first titration jump: 10.30 - 9.03 and pH_{EP2} = 4.73; the second titration jump: 5.37 - 4.10

To check the studying results, we estimate the titration jump by the general method – solving equations of higher degree with one variable which are united from the error equations (13) and (14).

$$q_I = (h - \frac{K_w}{h})\frac{C+C_0}{C.C_0} + a_{H_2A^-} + 2a_{H_3A} - a_{A^{3-}} \quad (13)$$

$$q_{II} = (h - \frac{K_w}{h})\frac{C+2C_0}{2C.C_0} - \frac{1}{2}(a_{HA^{2-}} + 2a_{A^{3-}} - a_{H_3A^-}) \quad (14)$$

The comparison is shown in table 4.

Table 4: Comparing the result of defining the pH at the equivalence point and the titration jump in the titration of 0.10 M Na₃PO₄ with 0.10 M HCl, q = ±1% by the different methods

	Method	pH_{EP}	The titration jump
The first step	GLC	9.67	10.30 - 9.03
	The general method	9.69	10.21 - 9.16
The second step	GLC	4.73	5.37 - 4.10
	The general method	4.75	5.53 - 3.98

The pH_{EP} and the titration jump defined promptly and visually in the titration of 0.10 M Na₃PO₄ with 0.10 M HCl by the graphics of logarithmic concentration which has the construction of the sum line correspond with those by the general method.

In the general method, to get the pH_{EP} and the titration jump in both functions, we have to combine the error equations into the quintic equation with the [H⁺] variable. After accepting some approximate conditions, we get the quartic equation in the first step and the cubic equation in the second step. Solving the quartic equation is difficult if we do not use the programs.

By the graphics of logarithmic concentration, the indicators can be chosen: $9.03 \leq pT \leq 10.30$, for the first step (such as thymolphthalein ($9.4 < pT < 10.6$), the color changes from blue into colorless) and use the indicators: $4.10 \leq pT \leq 5.37$ for the second step (such as methyl red, pT = 5.0, the color changes from yellow into red; bromocresol green , ($3.8 < pT < 5.4$), the color changes from blue into yellow).

In the titration of a mixture of strong base and polyprotic base, the values of pH_{EP} and the titration jump are defined similarly.

4. CONCLUSIONS

We constructed the general program to draw the Graphics of Logarithmic Concentration (GLC) with forming the "total line".

Although the Graphics of Logarithmic Concentration method is complicated, but it allows us to estimate the pH at the equivalence point and the titration jump in the titration of bases with strong acid promptly, visually and effectively, without combining and solving the equation of higher degree.

The results of defining the pH at the equivalence point and the titration jump by GLC are in good agreement with those by the general method. The program has been written with the PASCAL language.

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