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Acid-Base Titration

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Abstract

Titration is an analytical method used in biomedical sciences and analytical chemistry laboratories to determine the quantity or the concentration of a known or unknown substance. There are many kinds of titrations, but this investigation is fundamentally based on acid-base titration, in which the development of a mathematical titration model is explained and determined. In a titration experiment, the concentration and volume of the base added is proportionally equal to those of the acid. The concentration of the substance is determined by following this principle. Moreover, these calculations are usually approximate. Thus, the construction of a titration model is done to minimize the percent errors, simultaneously describing the effect of titration, and also allowing the determination of the characteristics of the unknown substance used. Furthermore, the values generated by the titration model are compared to the theoretical ones. It allows the verification of the mathematical model constructed. Subsequently, the efficiency of titration model is further tested by using a theoretical problem to exclude the errors from the experiment. This verification displays the accuracy of the accepted titration model. The concentration of the unknown acid is found by using this mathematical model.

Keywords

titration model, titration experiment, acid, base

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PROBLEM STATEMENT

A mathematical titration model is constructed to display the effects of the titration which is also used to accurately determine the concentration of the unknown acid. The accurate determination of the concentration of the unknown substance will prevent confusion between two mislabeled substances that have different concentrations.

MOTIVATION

Titration is an analytical method used to quantify a substance from a solution. There are many kinds of titration, the most common ones are acid-base, reduction-oxidation, and precipitation as well as complexometric titrations. This inquiry is based on acid-base titration which is used in the determination of the unknown concentration of the considered substance. In acid-base titration, the data recorded are named as paired values (volume of base added and the pH of solution). Our intention is to construct a graph (volume of base added vs the pH of the solution) from the paired values (titration curve) which is used to calculate the unknown concentration of the substance. The usable part of this curve is restricted to the equivalence point; which is found by locating the region where the most rapid increase occurs. This determination is essentially done by observation, which means that the calculation is based on estimation *(Salem)*. Thus, if two substances having different concentrations are mislabeled then their dissociation constants are unknown; the variation between the concentrations allows the experimenter to identify them. So, the objective is to use more data to minimize the percent errors. The additional data allow the determination of the more accurate concentration. Having an accurate concentration prevents confusion between two substances even if they have close concentration values.

Furthermore, to facilitate the integration of the new data, a mathematical titration model is constructed to demonstrate the correlation between the volume of base added and the pH of the solution.

MATHEMATICAL DESCRIPTION AND SOLUTION APPROACH

Our objective is to create a mathematical model that represents the interaction between acid and base, and between the volume of the titrant added and pH of the solution. In this paper, a weak acid is used as solvent with a strong base.

In an acid-base reaction, the molecule of acid would react with the base to generate an anion of the acid and water molecule:

$$HA \text{ (acid)} + OH^- \text{ (base)} \rightleftharpoons A^- + H_2O \text{ (Salem)}$$

Therefore, the amount of mole of the acid prior the reaction occurs is equal to the volume times the concentration ($A \cdot a$) and the base also follows the same principle ($B \cdot b$). Moreover, the reaction reaches its equivalence point when enough base is added so $A \cdot a = B \cdot b$, and the solution is monitored by measuring the pH of every drop base added. However, a weak acid does not completely dissociate before reaching its equilibrium *(Salem)*,

$$\textit{Dissociation Reaction}: \quad HA \rightleftharpoons H^+ + A^- \textit{ (Salem)},$$
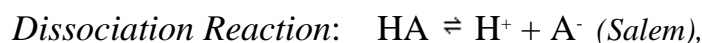
which means that the amount of moles of the acid present in this solution is equal to the amount of moles of hydrogen ion. Therefore, to keep track of the concentration of the substance, the amount of moles of each compound is divided by the total volume ($a+b$) used in this experiment *(Salem)*.

The concentration of the compound prior to the dissociation is determined by formulas (1) and (2):

$$[HA] = \frac{A \cdot a - B \cdot b}{a + b} \qquad (1)$$

$$[A^-] = \frac{B \cdot b}{a + b} \qquad (2)$$

The titration model is created by using the dissociation constant formula:

$$K_a = \frac{[H^+] \cdot [A^-]}{[HA]} \qquad (3)$$

By equations (1), (2), and (3), the dissociation constant formula can be rewritten in terms of A, a, B, b, and $X = [H^+]$:

$$K_a = \frac{X \left(\frac{B \cdot b}{a + b} \right)}{\frac{A \cdot a - B \cdot b}{a + b}} = \frac{X \cdot B \cdot b}{A \cdot a - B \cdot b} \qquad (4)$$

By solving (4) for X we have:

$$X = \frac{K_a (A \cdot a - B \cdot b)}{B \cdot b} \qquad (5)$$

By knowing $X = [H^+]$, the pH of the solution (a measure of the molar concentration of hydrogen ions) is:

$$pH = -\log [H^+] \qquad (6)$$

and the pK_a of the solution is:

$$pK_a = -\log (K_a) \qquad (7)$$

By equations (5), (6), and (7), we obtain:

$$-\log X = -\log\left(\frac{K_a[A \cdot a - B \cdot b]}{[B \cdot b]}\right),$$

$$-\log[H^+] = -\log(K_a[A \cdot a - B \cdot b]) + \log(B \cdot b),$$

$$\text{pH} = \log(B \cdot b) - \log(A \cdot a - B \cdot b) + pK_a \qquad (8)$$

In titration, any data beyond the equivalence point are irrelevant and unusable; thus, the model is limited to $0 < b < \{b$ at the equivalence point$\}$, and the equation for P (b) represents the pH of the solution at the different volume of base added. Hence and by (8) the titration model is

$$P(b) = \log(B \cdot b) - \log(A \cdot a - B \cdot b) + pK_a, \qquad (9)$$

where $0 < \text{b} < \{$b at the equivalence point$\}$ and $A \cdot a > B \cdot b$.

Experimental Problem

In this inquiry, the titration of an unknown acid is done with NaOH (base) which has a concentration of 0.09141 M and the volume of solution before adding any base is 0.10 L *(Salem).*

Data :

Volume of Acid: 0.10 L

Volume total of Base added: 0 .05400 L

Concentration of Base: 0.09141 M

Concentration of Acid: Unknown

pK_a: Unknown

K_a: Unknown

Determination of the equivalence point

By observing the titration curve, a rapid increase between pH 6 and pH 10 is noticed, and the equivalence point is found around this area. Moreover, the estimation is done by searching the volume that is responsible for this increase. We obtain that the volume of NaOH at the equivalence point is 0.04L (see Appendix).

Determination of the dissociation constant

Determination of the dissociation constant K_a is done by knowing that at half-equivalence dissociation point the number of moles of base is equal to the number of moles of acid. Therefore, K_a is calculated at half-equivalence point, $[A^-] = [HA]$, $V=V$ (equiv.)/2 *(Reijenga Jetse)*.

pH at half-equivalence point:

$$V= 0.04L/2=0.02 \text{ L}$$

Hence the estimation for the pH at half-equivalence point is 5.40, where the volume is 0.02L or close to it (see Appendix).

Determination of dissociation constant of the unknown acid by assuming that the pH at half-equivalence point is 5.40

$$pK_a = -\log (K_a)$$

$$K_a = 10^{-pK_a}$$

$$K_a = 10^{-5.40} \approx 3.981 \times 10^{-6} M$$

Determination of the theoretical concentration of the unknown acid

$$C1 \times V1(M1) = C2(M2) \times V2$$

$$0.09141M \times 0.054L = C2 \times 0.1L$$

$$C2(M2) = 0.09141M \times \frac{0.054L}{0.1L} = 0.04936M$$

(C2: Theoretical concentration of the unknown acid)

Determination of the concentration of the unknown acid at *pH* 5.50 using the titration model (see (9) and Appendix)

$$P(b) = \log(B \cdot b) - \log(A \cdot a - B \cdot b) + pK_a$$

$$5.50 = \log(0.09141M \times 0.02711L) - \log (A \times 0.1L - 0.09141M \times 0.02711L) + 5.40$$

$$Solved\ for\ A\ \text{(Concentration of acid)}$$

$$-5.50 + \log(0.09141M \times 0.02711L) + 5.40 = \log ((A \times 0.10L) - (0.09141M \times 0.02711L))$$

$$-2.705877\ moles = \log (0.1L\ A - 2.4781 \times 10^{-3} moles)$$

$$10^{-2.705877} moles = 0.1L\ A - 2.4781 \times 10^{-3} moles$$

$$0.1LA = 10^{-2.705877} moles + 2.4781 \times 10^{-3}\ moles$$

$$A = \frac{4.4465437 \times 10^{-3} moles}{0.1\ L} = 0.044465437\ \text{M (moles/L)}$$

VERIFICATION

Verification (Step 1) of the titration model (Experimental Problem)

Determination of percent error (Titration model deviation+ Experimental errors):

$$\left|\frac{Theorical\ value-Experimental\ Value}{Theorical\ Value}\right| \times 100\% = \left|\frac{0.04936M-0.044465M}{0.04936M}\right| \times 100\% \approx 9.92\%$$

Therefore, the percent of efficiency of titration model with the experimental errors is approximately 90.08%.

Verification (Step 2) of the titration model (Theorical Problem)

For the titration of 25.00 mL of CH_3CO_2H with 12.50 mL of 0.100 M NaOH:

$K_a = 1.8 \times 10^{-5}$ for CH_3CO_2H, pH =4.74. What is the concentration of the weak acid? *(B.C)*

Determination of the concentration of the acid (traditional method)

$$\text{pH} = pK_a + \log\frac{[Base]}{[Acid]} \quad (Bletry),$$

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.7447,$$

$$4.74 = 4.7447 + \log\frac{0.100M}{[CH3CO2H]},$$

$$[CH3CO2H] = 0.10109M$$

Determination of the concentration using the titration model (9)

$$P(b) = \log(B \cdot b) - \log(A \cdot a - B \cdot b) + pK_a$$

$$4.74 = \log(0.1M \times 0.0125L) - \log(A \times 0.025L - 0.1M \times 0.0125L) + 4.7447$$

$$2.898 = -\log(A \times 0.025\ L - 0.1 \times 0.0125\ moles)$$

$$-2.898 = \log(A \times 0.025\ L - 0.1 \times 0.0125\ moles)$$

$$10^{-2.898} + (0.1 \times 0.0125\ moles) = A \times 0.025L$$

$$A = \frac{2.515 \times 10^{-3}\ moles}{0.025\ L} = 0.10059\ M\ (moles/L)$$

The percent of efficiency (Theoretical Problem):

Determination of the (titration model) deviation:

$$\left|\frac{Theorical\ value - Experimental\ Value}{Theorical\ Value}\right| \times 100\% = \left|\frac{0.100M - 0.10059M}{0.100M}\right| \times 100\% = 0.59\%$$

Therefore, the percent of efficiency of the titration model with no experimental errors would be 99.41%.

<u>Determination of the experimental errors :</u>

$$\%\ Error = Deviation(\%) + Exp.Error(\%)$$

$$Exp.Error(\%) = 9.08\% - 0.59\% = 8.49\%$$

LIMITATION OF THE TITRATION MODEL

The volume of the base added in the titration model is restricted between 0 and the equivalence point. However, the amount of moles of base and acid also influences the titration model. The

titration model is constructed on weak acid /strong base reaction in which the concentration of the weak acid is lower than the base concentration. Moreover, what happens if the number of moles of the acid tends to be equal to those of the base in the titration model? :

$$A \cdot a \approx B \cdot b, \quad pK_a \approx \mathrm{P}\,(b),$$

$$P(b) = \log(B \cdot b) - \log(A \cdot a - B \cdot b) + pKa,$$

$$0 = \log(B \cdot b) - "\log(0\,+)" \rightarrow \log(B \cdot b) + "\infty"$$

Therefore, $P(b)$ *does not exist when* $A \cdot a \approx B \cdot b$.

DISCUSSION

The purpose of this experiment is to create a mathematical model that determines an accurate concentration of an unknown substance. By using the titration model, the result is approximately 0.044465 M which is close to the theoretical value (0.04936 M) of the substance. The percent error of the titration model is approximately 9.1 % which is acceptable. However, the percent error of the titration model also includes the experimental errors. Thus, by applying the titration model in a theoretical problem, the deviation of the titration model is ~0.6% (as predicted), because the titration model is created by considering any elements that can impact the result. If the titration model has ~0.6% deviation in the theoretical problem, the deviation of titration should be about the same under any circumstances. Therefore, the experiment errors were calculated by using this equation: %Error = Deviation (%) + Exp. Errors (%).

So, the acid-base titration contains ~8.5 % of experimental errors and the titration model has ~0.6% deviation. A mathematical model with no deviation would likely generate accurate

values, and there will be no confusion between two substances that have close concentration values. However, the deviation of the titration model is independent to the experimental errors, which means the titration model cannot influence the experimental errors, but the experimental errors can alter the result. Therefore, an accurate concentration is guaranteed if the experimental error is low. Furthermore, the identification of the unknown substance would be easily done.

Thus, the titration model has accomplished its objective because the concentration of the unknown substance (weak acid) is determined with a low percent error and the correlation between pH and the volume of base added is demonstrated. However, the titration model has its limitations which are:

1. The volume used should be between 0 and the volume of the base at the equivalence point.

2. The amount of moles of acid and base present should not be equal.

CONCLUSION AND RECOMMENDATION

The mathematical model is based on acid-base titration and its development allows the determination of the concentration of the acid used. The model is constructed by following the dissociation constant rules and the amount of moles present. Its purpose is to minimize the percent error as low as possible (<1%) which is achieved. By comparing the values generated by the titration model to theoretical one, the percent efficiency is ~99.4% which is remarkable. However, the titration model cannot minimize the experimental errors, which means the titration model cannot erase any errors made during the experiment. The percent error in this experiment is ~9%, which means the calculation, or the determination of the equivalence point is slightly off.

Therefore, to minimize the experimental errors, the use of computer algebra system is needed to lower the percent error in the dissociation constant; and the acid-base titration should be repeated several times. Besides, the titration model has an efficiency of ~99.4%, which means that any value generated would be accurate. Moreover, the titration model displays a correlation between pH, pK_a, volumes, and concentrations. This correlation allows the determination of any one of those four elements. Therefore, this mathematical model also describes the different characteristics (pH, pK_a, volume, concentration) of the substances used (acid or base).

In conclusion, the accurate concentration of the acid is found by using this model, see (9).

And any other characteristics (pH, pKa, volume) of the substances used could be also determined.

Hypothetically, if two acidic substances are mislabeled they have different concentration values, and the constant of dissociation are unknown. Those two substances could be easily identified by using the titration model constructed in this paper, and the confusion between those two substances would be elucidated.

NOMENCLATURE(S)

Table 1. List of symbols used in this paper:

Symbols	Descriptions	Units
H^+	Hydrogen Ion	moles
A^-	Base	moles
HA	Acid	moles
NaOH	Sodium hydroxide	moles
A	Concentration of acid used	M = moles/liter
B	Concentration of base used	M = moles/liter
a	Initial volume of acid solution	L=liter
b	Total volume of base added	L=liter
H_2O	Water molecule	moles
Aa	# of moles of the acid	moles
Bb	# of moles of the base	moles
a+b	Total volume of the system	L=liter
pH	-log[H^+]	none

[H⁺]	Concentration of the Hydrogen Ion	M = moles/liter
pK_a	-log[K_a]	none
[Base] or **[A⁻]**	Concentration of the base used	M = moles/liter
[Acid] or **[HA]**	Concentration of the acid used	M = moles/liter
K_a	Dissociation constant of acid	M = moles/liter
V(equiv.)	Volume at equivalence point	L=liter
V(equiv.)/2	Volume at half-equivalence point	L=liter
P(b)	pH of the solution at different volume of base added	None
	This table describes the symbols used in our experiment with their units (SI)	

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APPENDIX

Graph 1- Titration Curve
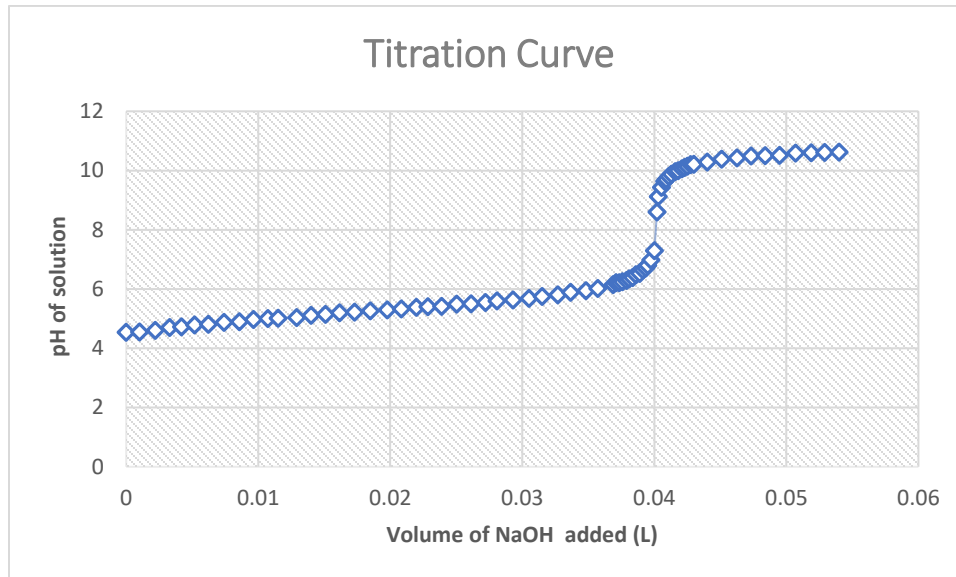
The titration curve is constructed by using data from Table 2 which shows the relation between

the pH of the solution and the volume NaOH added.

Table 2: Result collected

(*L* of base added)	*pH* of solution
0.00	4.54
0.00101	4.55
0.00220	4.61
0.00329	4.70
0.00419	4.72
0.00517	4.79
0.00623	4.81
0.00740	4.88
0.00858	4.90
0.00963	4.97
0.01074	5.00
0.01150	5.02
0.01290	5.04
0.01399	5.11

0.01510	5.15
0.01615	5.20
0.01730	5.22
0.01849	5.26
0.01978	5.30
0.01986	5.33
0.01990	5.40
0.02285	5.43
0.02389	5.46
0.02502	5.49
0.02711	5.50
0.02721	5.54
0.02809	5.60
0.02929	5.63
0.03051	5.69
0.03150	5.75
0.03270	5.80
0.03365	5.89
0.03483	5.95
0.03573	6.02
0.03689	6.15
0.03711	6.21
0.03734	6.22
0.03759	6.25
0.03789	6.29
0.03809	6.34
0.03835	6.39
0.03861	6.48
0.03890	6.53
0.03914	6.65
0.03935	6.71
0.03951	6.80
0.03975	6.98
0.04000	7.30
0.04021	8.60
0.04030	9.12
0.04053	9.43
0.04079	9.64
0.04091	9.71
0.04111	9.80
0.04130	9.88
0.04159	9.96
0.04180	10.00
0.04210	10.06
0.04229	10.10

0.04251	10.15
0.04275	10.20
0.04300	10.21
0.04401	10.29
0.04510	10.38
0.04625	10.43
0.04733	10.49
0.04839	10.50
0.04949	10.52
0.05069	10.59
0.05189	10.60
0.05289	10.61
0.05400	10.62

Determination of the dissociation constant using Table 2 (Observational Method)

The K_a is found by calculating the volume at half-equivalence point:

V= 0.04L/2=0.02,

■$pK_a \approx 5.40$ (observation from data),

$K_a = 10^{-5.40} \approx 3.981 \times 10^{-6} M$

Therefore, the dissociation constant of the acid is $\approx 3.981 \times 10^{-6} M$.

■Data used in the determination of the concentration of the unknown acid (using the titration model).

pH= 5.50 pK_a= 5.40

b= 0.02711 ≈0.03 L   B= 0.09141≈0.09 M

a= 0. 1L   A= ? M