

Differential Temperature Modelling (DTM) for the Determination of Molecular Masses of Strong Acids (Per Chloric and Sulphuric Acids)

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Abstract

The molecular masses of two (2) strong acids: per chloric (HClO_4) and sulphuric (H_2SO_4) have been determined using an experimental guided thermochemical model. The exothermic spree of strong acids was exploited at various percentage dilutions ranging from 10% to 50% using standard procedures. The differential temperature, ΔT and other thermochemical parameters (basic constants, kb^2 and thermohydrobasic constants, $\Delta T - 18kb^3$) were measured and theoretically manipulated. The $\Delta T_{(\text{HClO}_4)}/^\circ\text{C}$: 6.0, 11.0, 18.0, 22.0, 27.0 and $\Delta T_{(\text{H}_2\text{SO}_4)}/^\circ\text{C}$: 20.0, 48.5, 56.0, 72.0, 84.0 at constant pressure and volume, showed a steady increase in differential temperature within the percentage dilution range. The basic constants: 0.051, 0.093, 0.152, 0.185, 0.228 were obtained for per chloric acid and 0.149, 0.361, 0.417, 0.536, 0.625 were obtained for sulphuric acid at constant pressure and volume. The thermohydrobasic constants: 5.082, 9.326, 15.264, 18.670, 22.896 were obtained for per chloric acid and 14.643, 35.509, 41.001, 52.716, 61.501 were obtained for sulphuric acid at constant pressure and volume. The inverse of the gradient of the plot of basic constants, Kb^2 versus thermohydrobasic constants, $\Delta T - 18Kb^3$ affords the molecular masses of 101.00 ± 0.51 a.m.u and 98.04 ± 0.04 a.m.u for per chloric acid and sulphuric acid respectively.

Keywords: Differential Temperature Model (DTF), Thermochemical constants, Molecular masses, Strong acids

Introduction

The ability of a substance to dissociate completely in an aqueous medium is a characteristic function of strong acids. The system i.e. dissolution of strong acids, is known to witness evolution of heat (q) which could be an intrinsic feature. This interaction and associated observation is known as heat of solution. The heat of solution from a thermochemical point of view could be used in trailing inherent or unique nature of matter. One of such properties is the molecular weight. Some other properties include: boiling and melting points, refractive index e.t.c.

Exact molecular masses of substances are obtained conventionally by instrumental method (high resolution mass spectrometry) (Pleil and Isaac, 2016; Morentes and Grusak, 1998; Little *et al.*, (2012). They could as well be obtained classically from thermochemistry, by exploring the options of colligative properties of matter (Ibrahim, 2015; Ge and Wang, 2009; Atkins and de Paula; 2006; Ebbing, and

Gammon, 2009; Sharma, and Sharma, 1999). The molecular weight of a substance is usually expressed in atomic mass unit, a.m.u (Ebbing, and Gammon, 2009).

Temperature differential modeling (DTM) is a mathematical equation or expression relating thermochemical variables with the purpose of surveying the thermal characteristics of strong acids (Akpan, 2015). It takes into account atomic description of a molecular system. Modeling has been reported in vast fields of interest such as computational biochemistry, drug design, material science e.t.c (Parsons, 2005).

In-view of the economic implication of either acquiring or running instrumental methods of molecular weight determination, there is need to utilize an economical, fast and reliable quantitative thermochemical tools in evaluating molecular weight of strong acids. This approach could be used as a quality control measure in strong acids delivery.

Materials and Methods

Reagents (HClO_4 and H_2SO_4) used were of BDH and deionized water was collected from the Chemistry laboratory, Department of Chemistry, Federal University Otuoke, Bayelsa State, Nigeria. Glass wares, Lagged calorimeter with fitted mercury-in-glass thermometer and a stirrer.

The methodology for the study was based on the “Differential Temperature Model, DTM” hypothesis, as proposed and published by I. A. Akpan for chemical proof and theoretical consideration (Akpan, 2015). Percentage dilution ranging from 10% to 50% was carried out by transferring appropriate volumes of acid into calorimeters containing required volumes of deionised water.

PROPOSED HYPOTHESIS

“At constant temperature and pressure, the differential temperature ΔT of the dilution of equal volumes of strong acids in a fixed volume of water is directly proportional to the product of the sum of the relative masses of ionized species and the square of the basicity of acids” (Akpan, 2015).

Mathematically,

$$\Delta T \propto b^2(M_{c+} + M_{a-}) \quad (1)$$

Introducing a constant, equation 1 is transformed into:

$$\Delta T = Kb^2(M_{c+} + M_{a-}) \quad (2)$$

Where:

ΔT - differential temperature

K- thermal constant

b^2 – square of basicity(b)

M_{c+} - mass of hydrated proton (hydronium)

M_{a-} - mass of anionic acidic residue

Manipulating equation 2, expression for K, Kb^2 and $\Delta T = 18Kb^3$ can be explored and presented as:

$$K = \Delta T / b^2 (M_{c^+} + M_{a^-}) \quad (3)$$

$$Kb^2 = \Delta T / (M_{c^+} + M_{a^-}) \quad (4)$$

$$\Delta T - 18Kb^3 = Kb^2 (Mc^+ - M_{H2O} + Ma^-) = Kb^2 M_{mass} \quad (5)$$

Where: M_{mass} – molecular mass of strong acid

Making kb^2 the subject of formula from equation 5:

$$Kb^2 = \frac{1}{M_{mass}} (\Delta T - 18Kb^3)$$

Thus, the inverse of the gradient of the plot of basic constant, kb^2 against the thermohydrobasic constant, $(\Delta T - 18Kb^3)$ will theoretically validate the molecular mass of strong acids.

Results and Discussions

Tables 1-4 show the results obtained from the exploration of the proposed hypothesis while the plots are presented in figures 1 - 3.

Table 1. Differential temperature, ΔT and thermal constant, k for per chloric acid at various dilutions, at constant pressure and volume

Percentage (v/v%)	dilution	T_f °C	ΔT °C	K
10		32.0	6.0	0.051
20		37.0	11.0	0.093
30		44.0	18.0	0.152
40		48.0	22.0	0.185
50		53.0	27.0	0.228

*initial temperature : 26 °C; T_f : final temperature

Table 2. Differential temperature, ΔT and thermal constant, K for sulphuric acid at various dilutions, at constant pressure and volume

Percentage (v/v%)	dilution	T_f °C	ΔT °C	K
10		46.0	20.0	0.037
20		74.5	48.5	0.090
30		82.0	46.0	0.104
40		98.0	72.0	0.134
50		110.0	84.0	0.156

*initial temperature : 26 °C; T_f : final temperature

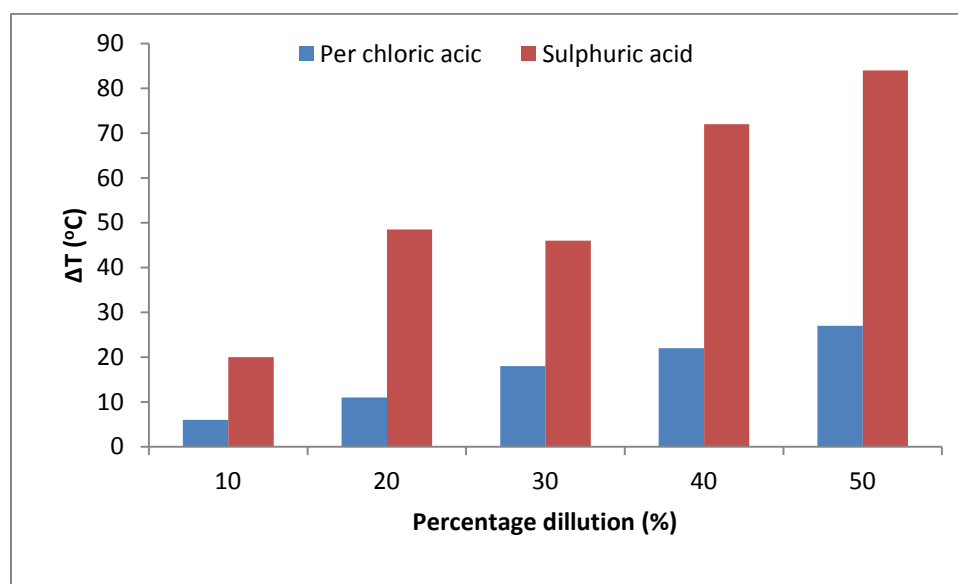


Fig. 1. Differential temperature of per chloric and sulphuric acids at constant pressure and volume

Table 3. Basic constants, Kb^2 , hydrobasic constants, $18Kb^3$ and thermohydrobasic constants, $\Delta T - 18Kb^3$ for per chloric acid at various dilutions, at constant pressure and volume \

Percentage dilution (v/v%)	Kb^2	$18kb^3$	$\Delta T - 18kb^3$
10	0.051	0.918	5.082
20	0.093	1.674	9.326
30	0.152	2.736	15.264
40	0.185	3.330	18.670
50	0.228	4.104	22.896

*basicity, b = 1.0 w.r.t per chloric acid

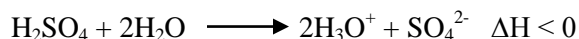
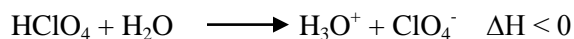
Table 4. Basic constants, Kb^2 , hydrobasic constants, $18Kb^3$ and thermohydrobasic constants, $\Delta T - 18Kb^3$ for sulphuric acid at various dilutions, at constant pressure and volume \ \

Percentage dilution (v/v%)	Kb^2	$18Kb^3$	$\Delta T - 18Kb^3$
10	0.149	5.357	14.643
20	0.361	12.990	35.509
30	0.417	14.999	41.001
40	0.536	19.284	52.716
50	0.625	22.499	61.501

*basicity, b = 2.0 w.r.t sulphuric acid

Per chloric acid is a monobasic substance which will furnish one mole of oxonium ion in solution. The process is exothermic and the associated differential temperature effect on the surrounding could be seen as reported in table 1. Sulphuric acid is a dibasic substance furnishing two moles of oxonium ions in solution. Its differential temperature effect is reported in table 2. Per chloric acid and sulphuric acid both showed a linear increase in differential temperature as percentage dilution increases as seen in fig. 1. It is

worthy to note that the dibasic acid has a higher differential temperature. This could be attributed to the greater amount energy involved in the solvation of two moles of protons as compared to the one mole of proton solvated in the monobasic (per chloric) acid.



The calculated values for hydrobasic constants, K_b^2 and thermohydrobasic constants, $\Delta T - 18K_b^3$ are presented in tables 3. and 4. for per chloric acid and sulphuric acid respectively. The monobasic acid from thermochemical expression contributes 18.0 unit mass to the solvated proton while the dibasic acid accounts for 36.0 unit mass. The plots of K_b^2 versus $\Delta T - 18K_b^3$ for the respective acids are presented in fig. 2. and fig. 3. The gradient of the straight line curve in fig. 2 gives 0.0099 whose inverse is 101.0, the theoretical molecular mass of per chloric within an estimated limit of ± 0.51 . Similarly, the gradient of the straight line curve in fig. 3. gives 0.0102 whose reciprocal is 98.04, the theoretical molecular mass of sulphuric acid within an estimated limit of ± 0.04 .

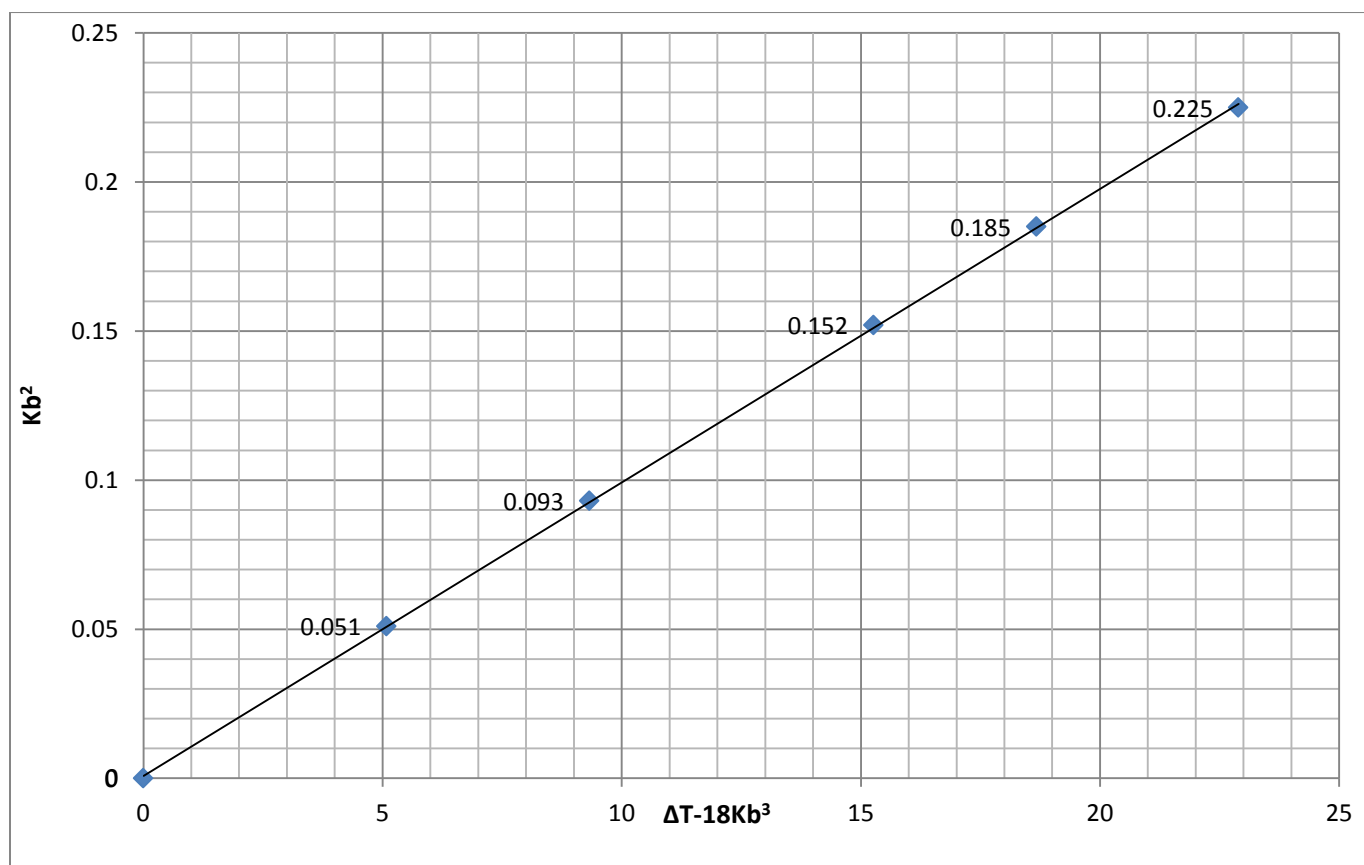


Fig. 2. The plot of basic constant (K_b^2) versus thermohydrobasic constant ($\Delta T - 18K_b^3$) for the determination of the molecular mass of per chloric acid (HOCl_4), at constant pressure and volume.

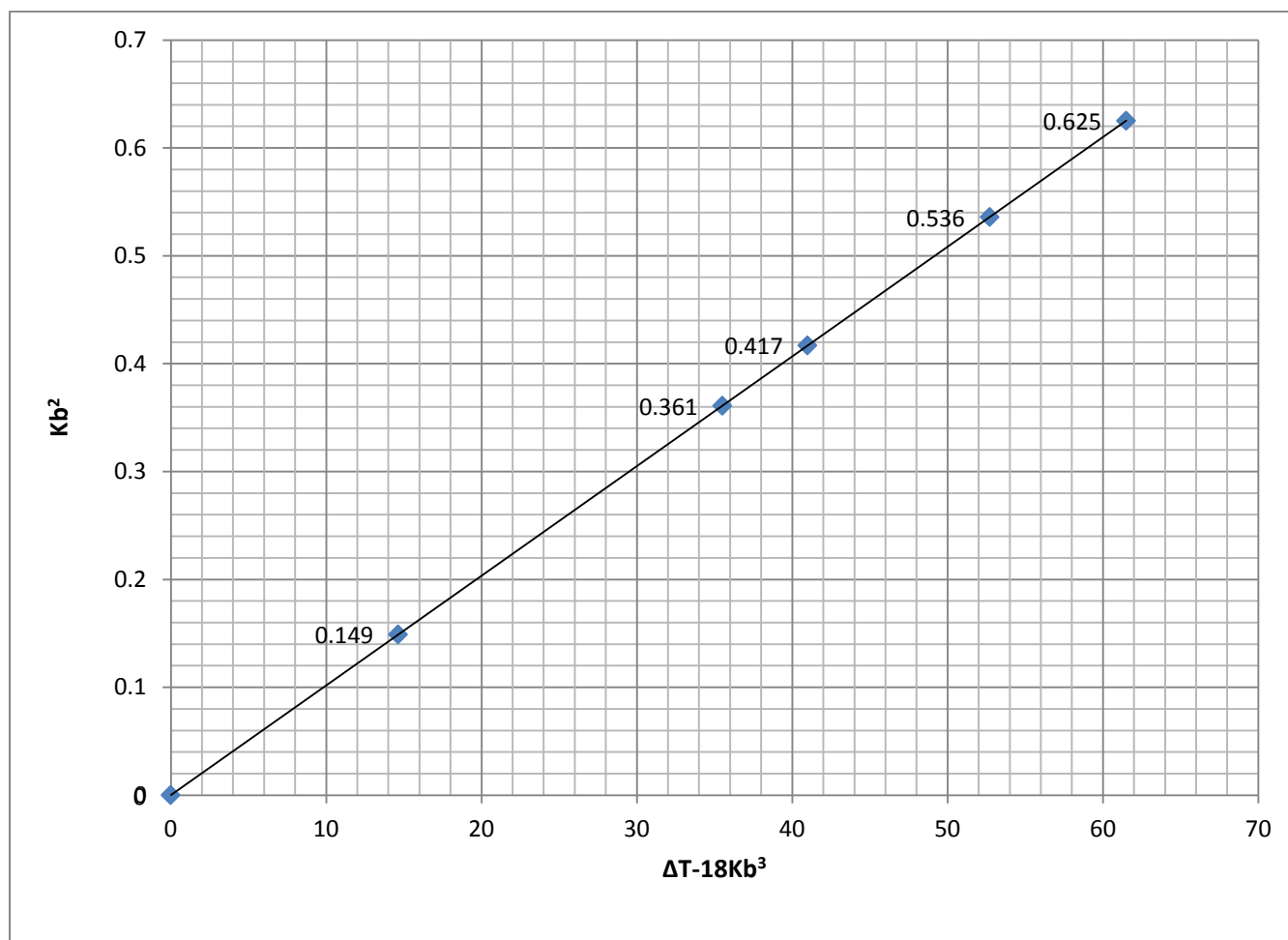


Fig. 3. The plot of basic constant (Kb^2) versus thermohydrobasic constant ($\Delta T - 18Kb^3$) for the determination of molecular mass of sulphuric acid (H_2SO_4), at constant pressure and volume.

Conclusion

The differential temperature model as proposed, is a justified tool for molecular mass determination of strong acids. The actual molecular mass of perchloric acid is 100.5 a.m.u while 98.079 a.m.u for sulphuric acid.

Acknowledgment

I wish to acknowledge the erudite contribution to knowledge by Dr. I.A.Akpan of the Department of Chemistry, University of Uyo, Akwa Ibom State, Nigeria. The DTM is indeed an optimizing tool for strong acids.

References

- Akpan, I. A. (2015). Determination of molecular mass of strong acids by Differential Temperature Model (DTM) using H_3PO_4 and HBF_4 for Classical Demonstration. *Journal of Material Science and Chemical Engineering*. 3, 41-47.
- Pleil, J.D. and Isaac, K.K. (2016). High-Resolution Mass Spectrometry: Basic Principles for Using Exact Mass and Mass Defect for Discovering Analysis of Organic Molecules in Blood, Breath, Urine and Environmental Media. *J. Breath Res.* 10, 1-11.
- Morentes, E. and Grusak, M.A. (1998). Mass Determination of Low-Molecular-Weight Protein Phloem Sap Using Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry. *Journal of Experimental Botany*. 49 (322), 903-911.
- Little, J.L., Williams, A.J., Pshenichnor, A. and Tkachenko, V. (2012) Identification of “Known and Unknowns” Utilizing Accurate Mass Data and Chemspider. *Journal of The American Society for Mass Spectrometry*. 23 (1), 179-185.
- Ibrahim, F.M. (2015). Determination of molecular weight of synthetic sugars by measuring the freezing point depression (colligative peoperties). *IJSR*, 6(9),1229-1231.
- Ge, X. and Wang, X. (2009). “ Estimation of Freezing Point Depression, Boiling Point Elevation And Vaporization Enthalpies Of Electrolyte Solutions”. *Industrial and Engineering Chemistry Research*. 48 (10), 5123-5123.
- Atkins, P and de Paula, J. (2006). *Physical Chemistry for the Life Sciences*. New York: W.H. Freeman Company.
- Ebbing, D.D. and Gammon, S.D. (2009). *General chemistry* (9th edition). Boston: Houghton Mifflin Company.
- Sharma, K.K. and Sharma, L.K. (1999). A Textbook of Physical Chemistry (4th Revised Edition). India: Vikas publishing House, PVT Ltd.
- Parsons, J., Holmes, J. B., Rojas, J. M., Tsai, J. and Strauss, C. E. (2005). Practical Conversion from torsion space to cartesian space for in Silico protein synthesis. *J Comput Chem*. 26, 1063-1068.