Differential Temperature Model (DTM): A New Thermodynamic Indicator for the Detection of the Number of Ionizable Protons in Strong Acids

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Short Research Article	

ABSTRACT

The chemistry of ionization of strong acids via oxonium route was examined in thermodynamics context. The research led to the establishment of a new chemical hypothesis which derivatives gave rise to a differential temperature model. The thermodynamic model has been applied to detect the number of ionizable protons in one molecule of any strong acid in solution.

Keywords: Thermodynamic indicator; protons; strong acids.

1. INTRODUCTION

One particular cation, the proton H^+ deserves special thermodynamic attention since, being a unique ion in having no electrons, its effective radius is far smaller than the radii of all other ions. Its unique properties have been studied to derive several properties of chemical species in solution through the application of thermodynamic and theoretical principles [1-4]. A charge spread over a relatively minute volume gives rise to a very high surface- change density, so that in solution the proton exerts a considerable attractive force towards the negative oxygen end of dipolar water molecules. One thus expects strong bonding between protons and water molecules and an aquated species in solution, $H^+_{(aq)}$, may be postulated.
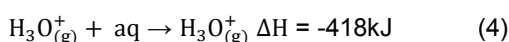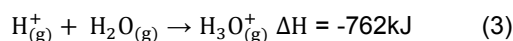
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Thermochemical evidence certainly supports this contention; there is a considerable quantity of energy liberated on aquation of a proton, far in excess of that for other ions in aqueous solution [5].

$$H_{(g)}^+ + aq \rightarrow H_{(aq)}^+ \qquad \Delta H = -1180 \text{ kJ} \qquad (1)$$

$$Na_{(g)}^+ + aq \rightarrow Na_{(g)}^+ \quad \Delta H = -396 \text{ kJ} \qquad (2)$$

It has been suggested that one water molecules in particular is closely bound to each proton, and the entity H_3O^+ has been postulated to represent the aquated proton in solution. A principal justification for this assertion is the proved existence of this ion H_3O^+ in certain solid hydrate crystals. Solid perchloric acid hydrate, at one time represented as $HClO_4.H_2O$, has been demonstrated to exist as H_3O^+ cation and ClO_4^- anion [6].

The three hydrogen atoms are equivalent, and each is bonded to the same oxygen. The substance is stable ionic crystal, with the same structure as ammonium perchlorate, $NH_4^+ClO_4^-$. Further evidence for the nature of the hydrated proton is obtained by considering the heat of hydration of the proton (-1180kJ) as made up of two parts.

$$H_{(g)}^+ + H_2O_{(g)} \rightarrow H_3O_{(g)}^+ \ \Delta H = -762\text{kJ} \qquad (3)$$

$$H_3O_{(g)}^+ + aq \rightarrow H_3O_{(g)}^+ \ \Delta H = -418\text{kJ} \qquad (4)$$

The heats of these individual reactions cannot be obtained by direct experiment, but can be calculated from the appropriate thermochemical cycles [7,8]. Thus the heat of hydration is considered to arise from the formation of the species $H_3O_{(g)}^+$, and its subsequent hydration. Through rigorous research into the thermodynamics of ionisation in acid solutions, the author and his team had proved the formation and existence of oxonium ion [9]. Consequently, the author has postulated oxonium hypothesis (oxonium law). The present publication is a report of the use of Differential Temperature Model (DTM) to determine the number of ionizable protons in all strong acids.

2. EXPERIMENTAL DETAILS

Three strong acids (monobasic, dibasic and tribasic) namely HCl, H_2SO_4 and H_3PO_4 were purchased from BDH Limited and dissolved as

purchased without further purification. The solvent was de-ionised water. The reaction (dissolution of the acid) was carried out in a well-insulated vessel, known as the colorimeter as described elsewhere [10]. Being perfectly insulated, it could effectively measure the heat energy transferred during the reaction.

Dewar flask was used as calorimeter as shown in Fig. 1, because it has a large heat capacity. The inner surface of the vessel was silvered and a space between the inner and outer wall was evacuated in order to minimise exchange of heat energy with the surrounding. A cork stopper was fitted at the top of the mouth and it contained a thermometer. The heat was measured in calories and converted to Joules. The gram-calorie is the amount of heat required to raise the temperature of 1g of water through 1°C. The amount of heat evolved in the process was measured as, mass of the system multiplied by rise in temperature, multiplied by specific heat of the system. Thermal constants and other thermochemical properties were evaluated and recorded.
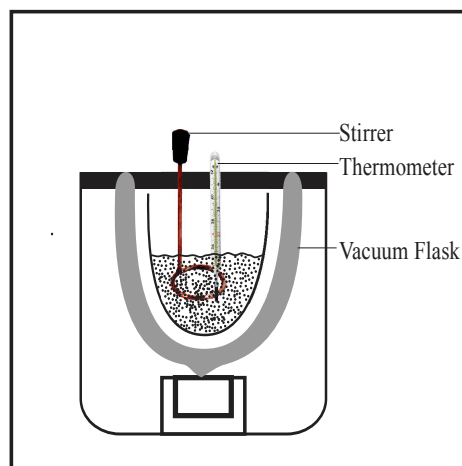

Fig. 1. Dewar flask for thermochemical measurements

3. RESULTS AND DISCUSSION

3.1 Results

The results obtained from thermochemical measurements of the dissolution of the selected acids are presented in Tables 1 to 3. The relationship between the differential temperature and thermal constants of the investigated acids are also presented in Figs. 2 to 4.

Table 1(a). Thermal constants for HCl at various dilutions

Percentage dilution (v/v%)	T_1(K)	T_2(K)	ΔT(K)	k (Kmolg^{-1})	b	k(M_{c^+} + M_{a^-}) (K)
15	303	309	6.00	0.11	1	6.0
20	303	311	8.00	0.15	1	8.2
25	303	312.5	9.50	0.17	1	9.3
30	303	315	12.00	0.22	1	12.0
35	303	316	13.00	0.24	1	13.1

Table 1(b). Values of basis constant, hydrobasic constant and thermohydrobasic constants of HCl at various dilutions

Percentage dilution (v/v%)	Basic constant kb^2 (mole)	Hydrobasic constant $18kb^2$(g)	Thermohydrobasic constant ΔT - $18kb^3$(g)
15	0.11	1.98	4.02
20	0.15	2.70	5.30
25	0.17	3.06	6.44
30	0.22	3.96	8.04
35	0.24	4.32	8.68

Table 2(a). Thermal constants for H_2SO_4 at various dilutions

Percentage dilution (v/v %)	T_1(K)	T_2(K)	ΔT(K)	k(Kmolg^{-1})	b	k(M_{c^+} + M_{a^-}) (K)
15	303	362	59	0.11	2	14.74
20	303	378	75	0.14	2	18.76
25	303	388.5	85.5	0.16	2	21.44
30	303	415.5	112.5	0.21	2	28.14
35	303	426.5	123.5	0.23	2	30.82

Table 2(b). Values of basis constant, hydrobasic constants and thermohydrobasic constants of H_2SO_4 at various dilutions

Percentage dilution (v/v%)	Basic constant kb^2 (mole)	Hydrobasic constant $18kb^2$ (g)	Thermohydrobasic constant ΔT-$18kb^3$ (g)
15	0.44	7.92	43.16
20	0.56	10.08	54.84
25	0.64	11.52	62.46
30	0.84	15.12	82.26
35	0.92	16.56	90.38

3.2 Discussion

3.2.1 Thermochemical postulates arising from the present study

The present study has led to the proposition of a new chemical hypothesis as well as oxonium formation hypothesis presented here by the author. Both hypotheses are novel report to generate chemical interests and provoke laboratory investigation on their validity.

"At constant temperature and pressure, the change in 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 the ionised species and the square of the basicity of the acid."

3.2.2 Mathematical implications of the hypothesis

$$\Delta T \ \propto b^2(M_{c^+} + M_{a^-}) \qquad (5)$$

Where M_{c^+} and M_{a^-} are the relative masses of the cation and anion species respectively and b, the basicity of the acid. ΔT is the change in

temperature between the maximum temperature attained after dilution and the initial temperature of the solvent (water) before dilution.

If a constant is introduced into the proportion in 5 above, we obtain

$$\Delta T = kb^2(M_{C^+} + M_{a^-}) \qquad (6)$$

Where k is the thermal constant of strong acids at equivalent dilution at constant temperature and pressure

From Eqn. 6,

$$k = \frac{\Delta T}{b^2(M_{c^+} + M_{a^-})} \qquad (7)$$

3.2.3 Determination of thermal constant k

The calculation of thermal constant k published elsewhere [11] is hereby represented for HCl, H_2SO_4 and H_3PO_4. The same procedures apply for other strong acids taking cognizance of the number of protons discharged (basicity).

3.2.3.1 HCl

The ionization and subsequent formation of oxonium for HCl in solution follows the mechanism.

$$H_2O_{(l)} + HCl_{(l)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \xrightarrow{H_2O} H_3O^+_{(aq)} + Cl^-_{(aq)} \quad \Delta H < O \qquad (8)$$
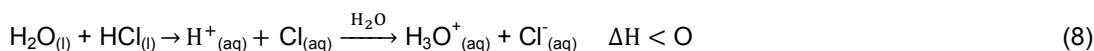
$$M_{C^+} = M_{H_3O^+} = 19; \quad M_{a^-} = M_{Cl^-} = 35.5$$
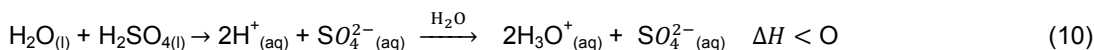
$$(M_{C^+} + M_{a^-}) = (19 + 35.5) = 54.5$$

For HCl,

$$k = \frac{\Delta T}{b^2(M_{c^+} + M_{a^-})} = \frac{\Delta T}{54.5} \qquad (9)$$

3.2.3.2 H_2SO_4

The ionization and subsequent formation of oxonium for H_2SO_4 in solution follows the mechanism.

$$H_2O_{(l)} + H_2SO_{4(l)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)} \xrightarrow{H_2O} 2H_3O^+_{(aq)} + SO_4^{2-}{}_{(aq)} \quad \Delta H < O \qquad (10)$$

$$M_{C^+} = 2M_{H_3O} = 38; \quad M_{a^-} = M_{SO_4^{2-}} = 96$$

$$(M_{C^+} + M_{a^-}) = (38 + 96) = 134$$

For H_2SO_4, $\quad k = \frac{\Delta T}{b^2(M_{c^+} + M_{a^-})} = \frac{\Delta T}{536} \qquad (11)$

3.2.3.3 H_3PO_4

The ionisation and subsequent formation of oxonium for H_3PO_4 in solution follows the mechanism:
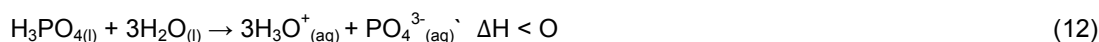
$$H_3PO_{4(l)} + 3H_2O_{(l)} \rightarrow 3H_3O^+_{(aq)} + PO_4^{3-}{}_{(aq)} \grave{} \quad \Delta H < O \qquad (12)$$

Table 3(a). Thermal constants for H_3PO_4 at various dilutions

Percentage dilution (v/v %)	$T_1(K)$	$T_2(K)$	$\Delta T(K)$	$k(Kmolg^{-1})$	b	$k(M_{c^+} + M_{a^-})$ (K)
10	301	305	4.0	0.002924	3	0.46
20	301	309	8.0	0.005848	3	0.91
30	301	313	12.0	0.008772	3	1.37
40	301	318	17.0	0.012427	3	1.89
50	301	319	18.0	0.013158	3	2.00
60	301	320	19.0	0.013889	3	2.11

Table 3(b). Values of basis constant, hydrobasic constants and thermohydrobasic constants of H_3PO_4 at various dilutions

Percentage dilution (v/v%)	Basic constant kb^2 (mole)	Hydrobasic constant $18kb^2$ (g)	Thermohydrobasic constant $\Delta T\text{-}18kb^3$ (g)
10	0.02632	0.47376	2.5789
20	0.05263	0.94734	5.1579
30	0.07895	1.42110	7.7368
40	0.01118	0.20124	10.9605
50	0.01184	0.21315	11.2505
60	0.12500	2.25000	12.2499
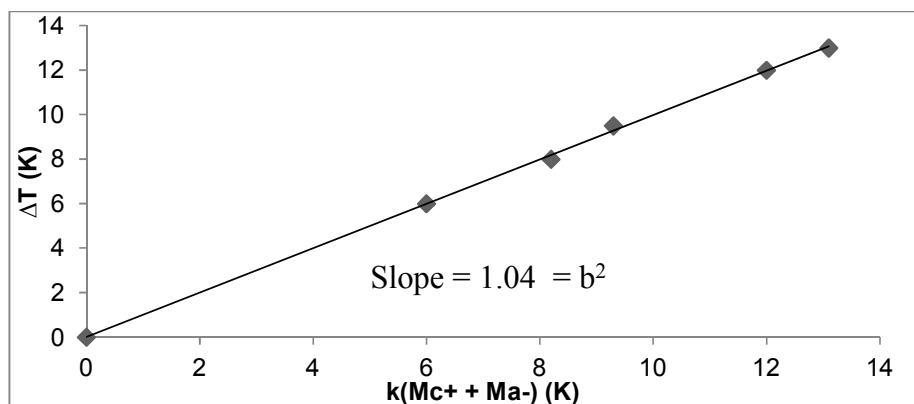
Fig. 2. Plot of Differential Temperature (ΔT) versus k($M_{c^+} + M_{a^-}$) for the determination of ionizable protons in HCl
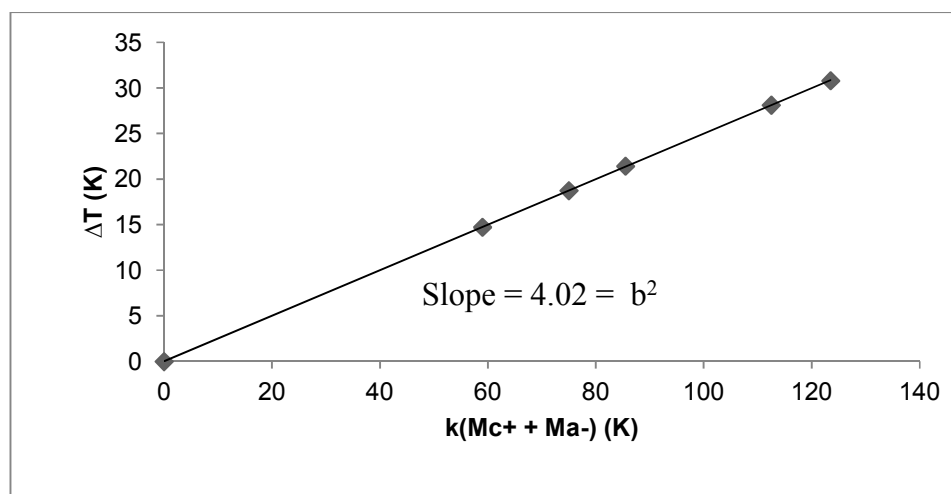

Fig. 3. Plot of differential temperature (ΔT) versus k($M_{c^+} + M_{a^-}$) for the determination of ionizable protons in H_2SO_4
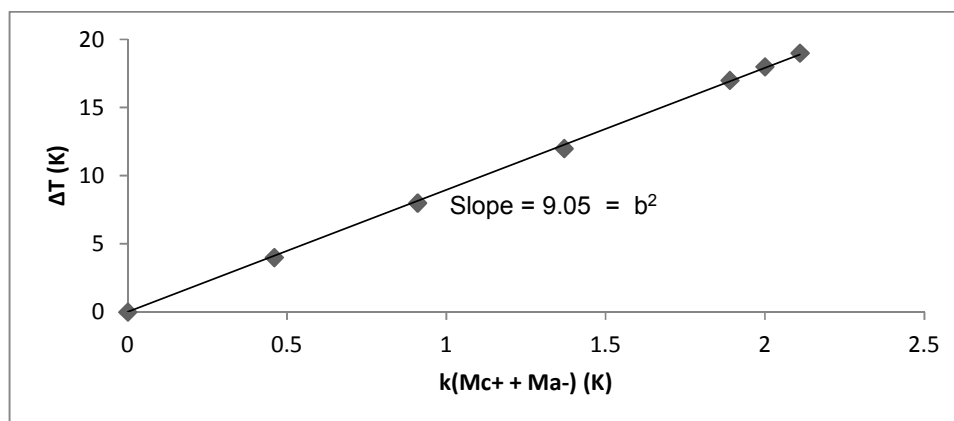
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Fig. 4. Plot of differential temperature (∆T) versus k(M_{c^+} + M_{a^-}) for the determination of ionizable protons in H_3PO_4

The thermal constant following the ionisation process is evaluated as follows:

Mass of solvated cation $M_{3H_3O^+}$ = 57, Mass of anion = $M_{PO_4^{3-}}$ = 95

$$(M_{3H_3O^+} + M_{PO_4^-}) = (57+95) = 152$$

For H_3PO_4, k = $\dfrac{\Delta T}{b^2(M_{3H_3O^+} + M_{PO_4^-})} = \dfrac{\Delta T}{1368}$ (13)

Where b = 3 because the acid is tribasic.

3.2.4 The oxonium hypothesis

The study has given rise to oxonium hypothesis hereby presented.

"At constant temperature and pressure, the thermal constants of all strong acids are equal at equivalent dilutions".

Thus; $k_1 = k_2 = k_3$ = a constant (14)

Where 1, 2, 3 ….. represent different strong acids. The expanded form of

Eqn. 14 is given below:

$$\frac{\Delta T_1}{b^2(M_{c^+} + M_{a^-})} = \frac{\Delta T_2}{b^2(M_{c^+} + M_{a^-})}$$ (15)

3.2.5 Application of the Differential Temperature Model (DTM) for the determination of the number of ionizable proton in solution

The analytical implications of the hypothesis provides that $\Delta T = kb^2(M_{c^+} + M_{a^-})$ where the parameters have been explained in the text. The quantity b gives the number of ionizable protons in solution.

Graphically, a plot of ∆T versus k(M_{c^+} + M_{a^-}) at various dilutions should produce a straight line from the origin with the slope equal to the square of the number of ionizable protons (b^2). Hence the square root of b^2 indicates the basicity of the experimental acid.

4. CONCLUSION

The research has established a valid chemical proof for the existence of oxonium ion, such that if oxonium ion exists in solution, the thermal constants of two or more strong acids must be equal. In this work, a counterpart thermodynamic hypothesis for ionization of strong acids is proposed. Like Bronsted and Lowry, the present work and discovery has added a new chapter for numerous calculations of molecular properties of strong acids such as the calculation of molecular mass by Differential Temperature Model (DTM); calculation of thermal constants, basic constant, hydrobasic constant and thermohydrobasic constants of strong acids in solution.

5. RECOMMENDATION

The author believes that, the hypothesis and the Differential Temperature Model (DTM) arising from the present research will generate chemical interests among the various National and International Chemical Societies such that the new chemical hypothesis would be adopted and upgraded to theory status for their application and further advancement of chemical studies.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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