



## Thermochemical Studies on Partial Molar Gibbs Free Energy and Entropy of Tetraoxosulphate (VI) Acid in Binary Solution

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**Abstract** Partial molar free energy, entropy and heat of solution of  $\text{H}_2\text{SO}_4$  as solute in a fixed volume of water have been studied in a non-ideal solution through thermodynamic provisions for ideal system. The behaviour of the binary solution have been explained using the values of the measured potentials. Other thermal quantities measured have been used to calculate the molecular mass of the  $\text{H}_2\text{SO}_4$  completely ionized

**Keywords** Partial Molar, Free Energy, Entropy, Tetraoxosulphate (VI) acid

### Introduction

Thermodynamic potentials function as indicators as they respond to changes in solute concentrations in binary and multicomponent systems [1]. Yet, the various changes they exhibit remain “thermodynamic dreams” in need of interpretation usually called inferences in research and laboratory experiments.

In real practice, most of the materials we come across are mixtures and they participate in reaction still as mixtures [2]. In every solution, we have the solvent and solute(s) as the system in which reactions take place. The presence of each material will affect the thermodynamic behaviour of the other [3, 4]. We must therefore devise a method of modifying our thermodynamics treatment of the single component systems to reflect the changes in composition that is encountered in mixtures. By so doing, we will discover an amazing area of physical chemical interest known as thermodynamic remediations.

### Ideal Mixtures

The change in Free energy  $\Delta G$  with pressure may be calculated for a reaction involving ideal systems as shown below [5]. If we choose  $P_1 = 1$  atm., defined as the standard state, then:

$$\Delta G = G - G^0 = nRT \ln P \quad \dots \quad \dots \quad \dots \quad 1$$

where  $P$  is the final pressure. For 1 mole we write

$$G = G^0 + RT \ln P \quad \dots \quad \dots \quad \dots \quad 2$$

We can translate Eqn. 2 for partial molar free energy due to component 1 as follows

$$G_1^- = G_1^0 + RT \ln P \quad \text{or} \quad \mu_1 = \mu_1^0 + RT \ln P \quad \dots \quad \dots \quad \dots \quad 3$$

$\mu_1^0$  represents the value of  $\mu_1$  at a given temperature at the standard state of  $P = 1$  atm.

Gibbs-Duhem equation for partial molar free energy or chemical potential provides that

$$dG = \sum \mu_i dn_i \quad \text{which by integration yields} \quad G = \sum \mu_i n_i \quad \dots \quad \dots \quad \dots \quad 4$$

For a binary solution (components 1 and 2), we can use Eqn. 4 to describe the total free energy of such a solution [6]

$$G = n_1 \mu_1 + n_2 \mu_2 \quad \dots \quad \dots \quad \dots \quad 5$$

From Eqns. 3 and 5,  $G_1 = n_1(\mu_1^0 + RT \ln P_1)$  and  $G_2 = n_2(\mu_2^0 + RT \ln P_2)$

The free energy of the mixture will be  $G_1 + G_2$ . Thus

$$G_{mix} = n_1(\mu_1^0 + RT \ln P_1) + n_2(\mu_2^0 + RT \ln P_2) \quad \dots \quad \dots \quad \dots \quad 6$$



In Eqn. 6,  $P_1$  and  $P_2$  represent the partial pressure of 1 and 2 in the mixture. Since  $P_1 = X_1P$  and  $P_2 = X_2P$ , ( $X_i$  = mole fraction of  $i$ ).

$$\begin{aligned} G_{mix} &= n_1(\mu_1^0 + RT\ln X_1 P) + n_2(\mu_2^0 + RT\ln X_2 P) \\ &= n_1(\mu_1^0 + RT\ln X_1 + RT\ln P) + n_2(\mu_2^0 + RT\ln X_2 + RT\ln P) \quad \dots \quad 7 \end{aligned}$$

The change in free energy of mixing  $\Delta G_{mix} = G_{mix} - G_1 - G_2$  where at mixing  $P_1 = P_2 = P$ , the total pressure [7].

$$\Delta G_{mix} = n_1 RT \ln X_1 + n_2 RT \ln X_2 \quad \dots \quad 8$$

On division of Eqn 8 by  $(n_1 + n_2)$ , the total number of moles of the components, the Free energy per mole or partial molar free energy  $G_{mix}$  is obtained

$$\overline{\Delta G}_{mix} = X_1 RT \ln X_1 + X_2 RT \ln X_2 \quad \dots \quad 9$$

Equations 8 and 9 are alternative forms of the same equation known as Gibbs Duhem equation for total free energy of mixing and partial molar free energy of mixing respectively for ideal systems.

An extension to derive an expression for partial molar entropy change of mixing for ideal systems follows the relation [8].

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \quad \dots \quad 10$$

For ideal mixture,  $\Delta H_{mix} = 0$  and  $\Delta S_{mix} = \frac{-\Delta G_{mix}}{T}$  or

$$\Delta S_{mix} = -n_1 R \ln X_1 - n_2 R \ln X_2 \quad \dots \quad 11$$

On division of Eqn 11 by  $(n_1 + n_2)$  provides that

$$\overline{\Delta S}_{mix} = X_1 R \ln X_1 + X_2 R \ln X_2 \quad \dots \quad 12$$

where the parameters have the normal meanings previously explained.

### Extension to Real Systems

An ideal system or solution is the one in which the activity of each constituent is equal to its mole fraction under all conditions of temperature, pressure and concentration [9].

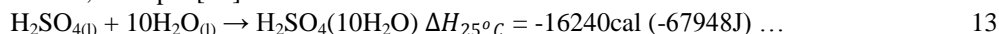
For such solution,  $\Delta H_{mix} = 0$ . Consequently, an ideal solution is formed without any evolution or absorption of heat. The  $\Delta S_{mix}$  predicts that for an ideal solution, the entropy of mixing is a function of only the concentration and quantity of constituents present [10].

In turn,  $\Delta G_{mix}$  indicates a function of these variables as well as of temperature. Neither of  $\Delta S_{mix}$  nor  $\Delta G_{mix}$  contains any factor specific of the nature of the substances involved [11].

For non ideal or real systems.  $\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$ ; where  $\Delta H_{mix} \neq 0$

Practically, the solution is accompanied by absorption or evolution of heat [12].

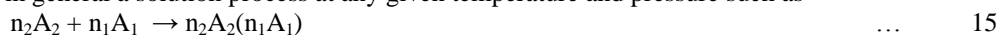
This thermal effect is termed the integral heat of solution of the substance. Per mole of substance, the integral heat of solution at any given temperature and pressure depends upon the amount of solvent in which the solution takes place. For this reason, it is essential to specify the number of moles of solvent per mole of solute in giving a heat of solution, example [13]:



At infinite dilution, when the amount of solvent per mole of substance is large, it is usually found that further dilution will produce no significant thermal effect [11]. Once this state of a dilute solution has been reached, the symbol "aq" is employed to indicate this fact. Thus the limiting value of the integral heats of solution would be represented theoretically for  $\text{H}_2\text{SO}_4$  as



Consider in general a solution process at any given temperature and pressure such as



The integral heat of solution,  $\Delta H$ , for this process is given by

$$\Delta H = H - (n_1 H_1^0 + n_2 H_2^0) \quad \dots \quad 16$$

where  $H$  is the enthalpy of the solution and  $H_1^0$  and  $H_2^0$  are the molar enthalpies of the two pure solution constituents. Since  $H$  is an extensive property, then Gibbs Duhem equation for partial molar quantities (in this case enthalpy) provides that  $H = n_1 \overline{H}_1 + n_2 \overline{H}_2$

Eqn 16 is redefined as =

$$\begin{aligned} \Delta H &= n_1 \overline{H}_1 + n_2 \overline{H}_2 - (n_1 H_1^0 + n_2 H_2^0) \\ &= n_1 (\overline{H}_1 - H_1^0) + n_2 (\overline{H}_2 - H_2^0) \\ &= n_1 \Delta \overline{H}_1 + n_2 \Delta \overline{H}_2 \quad \dots \quad 17 \end{aligned}$$

$$\text{where } \Delta \overline{H}_1 = (\overline{H}_1 - H_1^0) \text{ and } \Delta \overline{H}_2 = (\overline{H}_2 - H_2^0).$$

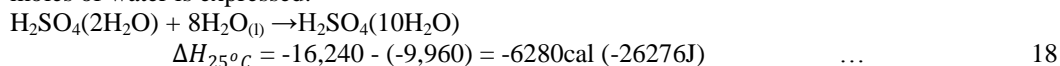
In Equation 17,  $\Delta \overline{H}_1$  and  $\Delta \overline{H}_2$  are the partial or differential molar heats of solution.

By employing methods already described,  $\Delta \overline{H}_1$  and  $\Delta \overline{H}_2$  can be evaluated from measured values of  $\Delta H$ .

The difference between any two integral heats of solution gives the heat involved in the dilution of a substance from the initial state to the final state and is termed the integral heat of dilution of the substance.

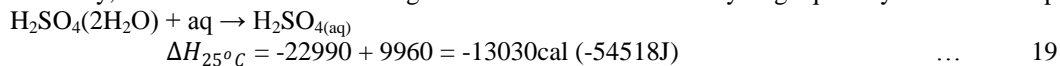


Theoretically, the heat recoverable on diluting with 8 moles of water a solution containing 1 mole of  $\text{H}_2\text{SO}_4$  in 2 moles of water is expressed:



-16240cal being heat evolved from 1 mole of acid in 10moles of water and -9960cal being heat evolved from 1 mole of acid in 2 moles of water.

Similarly, the heat evolved on diluting the same solution with a very large quantity of water is expressed thus:



22,990 cal being heat evolved at infinite dilution and -9960cal being heat evolved from 1mole of acid in 2 moles of water

The latter value represents the maximum heat obtainable from dilution of the given solution.

The corresponding author had published works on thermochemical properties of strong acids in binary solutions [15-17]. Similar studies have also been reported considering different perspectives [18, 19] The present work is in furtherance of observation of the direction of shift of the thermochemical properties as well as important thermodynamic potentials with respect to variations in solute concentrations.

The directions of shift of relevant potentials or partial molar quantities presents a new field of study in the area of thermodynamic remediations in binary and multicomponent systems.

### Experimental Work

The solvent was de-ionised water and the solute, tetraoxosulphate (vi) acid  $\text{H}_2\text{SO}_4$  both purchased from BDH Limited. The  $\text{H}_2\text{SO}_4$  was used without further purification. The reaction was carried out in a well-insulated vessel, known as the calorimeter as described elsewhere [17, 20]. 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  $1^\circ\text{C}$ . 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.

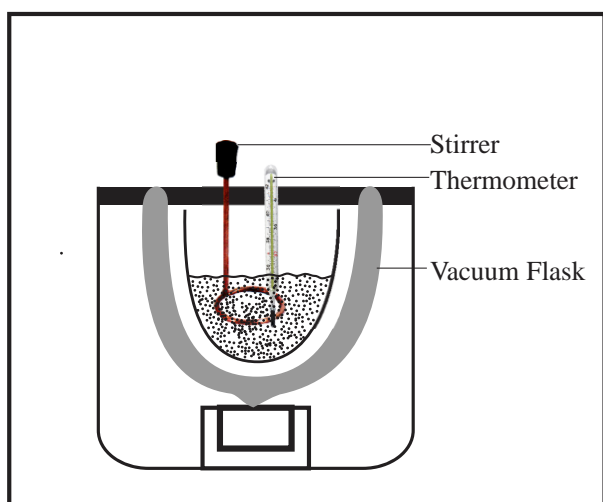


Figure 1: Dewar Flask for Thermochemical Measurements

### Results and Discussion

The results are presented in Tables 1 – 4. Relevant plots are presented in Figures 1 – 7.



**Table 1:** Thermo chemical Data from the Calorimetric Determinations

Percentage Solution (v/v%)	Moles of Solute n <sub>2</sub> (mol)	T <sub>1</sub> (K)	T <sub>2</sub> (K)	ΔT (K)	k (Kmolg <sup>-1</sup> )	kb <sup>2</sup> (mol)	18kb <sup>2</sup> (g)	ΔT - 18kb <sup>3</sup> (g)
16	0.30	302	348	46	0.086	0.340	6.19	33.6
20	0.38	302	359	57	0.106	0.430	7.63	41.7
22	0.41	302	364	62	0.116	0.460	8.35	45.3
24	0.45	302	366	64	0.119	0.480	8.57	46.6
25	0.47	302	367	65	0.121	0.490	8.71	47.6

$$\left. \begin{aligned} k &= \frac{\Delta T}{536} = \text{thermal constant} & [15] \\ kb^2 &= \text{basic constant where } b = \text{basicity} \\ 18kb^2 &= \text{Hydrobasic constant} \\ \Delta T - 18kb^3 &= \text{Thermohydrobasic constant} \end{aligned} \right\}$$

**Table 2:** Integral and Partial (Differential) Heats of Solution for one mole of H<sub>2</sub>SO<sub>4</sub> in Water at 25°C

Mole of water n <sub>1</sub>	ΔH Joule	ΔH J/mole	ΔH <sub>2</sub> J/mole
4.70	-64501	-5113	-40468
4.40	-60384	-4787	-39323
4.30	-59011	-4678	-38896
4.20	-57639	-4568	-38437
4.17	-57229	-4536	-38316

**Table 3:** Theoretical Partial Molar quantities for 4.70mole of water at various acid concentration at room temperature for ideal system.

Mole of acid n <sub>2</sub>	ΔT (K)	ΔG <sub>mix</sub> (J)	ΔG <sub>mix</sub> (Jmol <sup>-1</sup> )	ΔH <sub>mix</sub> (Jmol <sup>-1</sup> )	ΔS <sub>mix</sub> (Jmol <sup>-1</sup> K <sup>-1</sup> )	ΔS <sub>mix</sub> (Jmol <sup>-1</sup> K <sup>-1</sup> )
0.30	0	- 2858.72	- 571.85	0	9.435	1.8873
0.38	0	- 3402.61	- 669.79	0	11.230	2.2105
0.41	0	- 3596.08	- 702.34	0	11.868	2.3180
0.45	0	- 3845.72	- 744.41	0	12.692	2.4568
0.47	0	- 3967.40	- 767.83	0	13.094	2.5341

**Table 4:** Partial Molar Free Energy and Enthalpy of the Real Solution at various Acid Concentrations Evaluated from Table 3.
$$(\Delta G_{mix} = \Delta H_{mix} = T\Delta S_{mix})$$

Mole of acid n <sub>2</sub>	ΔT (K)	ΔG <sub>mix</sub> (J)	ΔG <sub>mix</sub> (Jmol <sup>-1</sup> )	ΔH <sub>mix</sub> (Jmol <sup>-1</sup> )	ΔH <sub>mix</sub> (Jmol <sup>-1</sup> )
0.30	46	- 3292.72	- 658.66	- 2858.72	- 571.85
0.38	57	- 4042.70	- 795.79	- 3402.61	- 669.79
0.41	62	- 3034.61	- 846.05	- 3596.08	- 702.34
0.45	64	- 4658.02	- 901.64	- 3845.72	- 744.41
0.47	65	- 4818.49	- 932.55	- 3967.40	- 767.83

### The Effect of Solution ΔT (Kelvin) on Partial Molar Enthalpy of Solute at Specified Volume of Solvent (H<sub>2</sub>O = 4.7 Moles)

Table 4 and Fig 2 reveal direct proportion relationship between ΔT and ΔH<sub>mix</sub>. Analogous to spectroscopic calibration curve, the ΔT versus ΔH<sub>mix</sub> plot is a thermodynamic calibration curve for reference, extrapolations and evaluations of ΔH<sub>mix</sub> of other solutes in non-ideal or real systems. This is obvious because neither ΔS<sub>mix</sub> nor ΔG<sub>mix</sub> contains any factor specific of the nature of the substance involved.



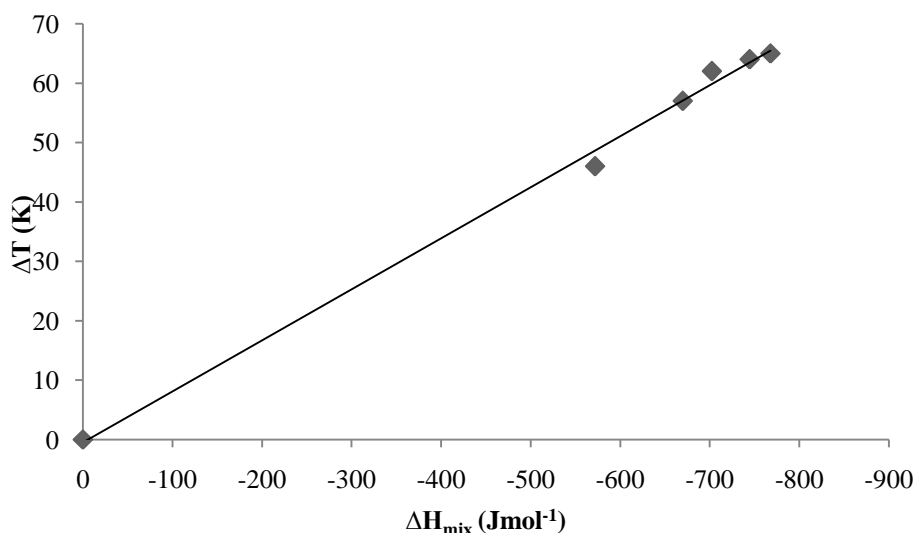


Figure 2: Variation of  $(\Delta T)$  (K) with Partial Molar Enthalpy at fix Volume of  $H_2O$  (4.7 moles) with Different Acid Concentrations at  $30^\circ C$

### Variation of Partial Molar Free Energy of Mixing with Acid Concentration

Figure 3 depicts a summary of the relationship between  $\overline{\Delta G}_{mix}$  and  $n_2$ , the number of moles of the  $H_2SO_4$  recorded in Table 4.  $\overline{\Delta G}_{mix}$  values tend to be more negative with increasing acid concentration indicating increased spontaneity with increase in acid concentration. This observation is further supported by the rise in solution  $\Delta T$  value with the observed evolution of heat which heats up the solution thus leading to a lowering of the Free energy.

$\overline{\Delta G}_{mix}$  value decreases from  $-658.66 \text{ Jmol}^{-1}$  at 0.300 mole of solute to  $-932.55 \text{ Jmol}^{-1}$  at 0.47 mole of the solute.

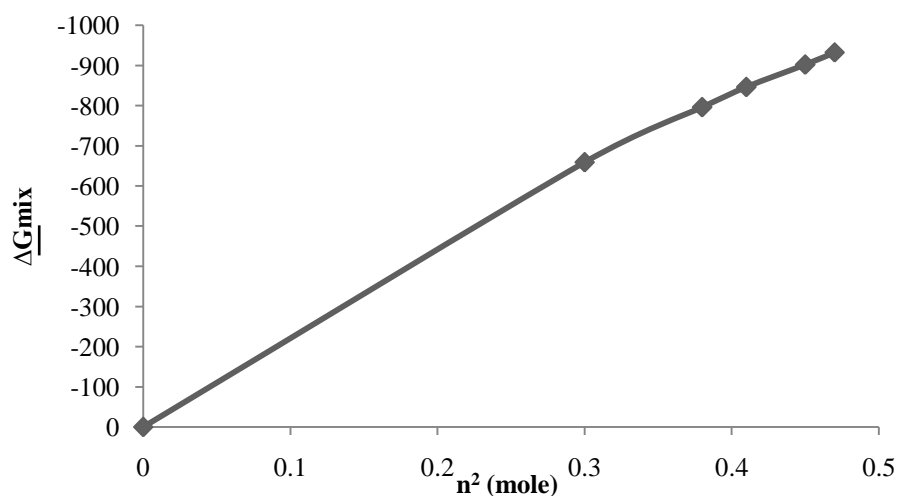


Figure 3: Variation of Partial Molar Free Energy with Acid Concentration in the Binary System

### Variation of Partial Molar Entropy of Mixing with Acid Concentration

The data obtained for  $\overline{\Delta S}_{mix}$  and  $n_2$  at the specified solvent volume are recorded in Table 3 and summarised graphically in Figure 4.



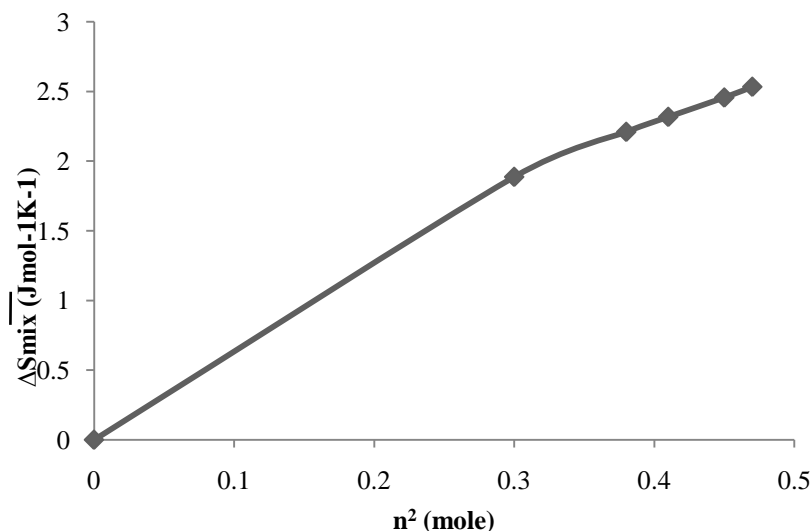


Figure 4: Variation of Partial Molar Entropy with Acid Concentration in the Binary System

All the  $\overline{\Delta S}_{mix}$  values are positive and tends to increase with increasing acid concentration. Entropy values greater than zero indicate a spontaneous system. Furthermore, the observed increase of  $\overline{\Delta S}_{mix}$  with increase in acid concentration lends credence to the decreasing or more negative trend observed in  $\Delta G_{mix}$  values which is the thermodynamic counterpart of entropy. Several thermodynamic theories can be used to explain this observation. Normally, all exothermic systems are accompanied with increase in molecular motions as well as increase in entropy. Increasing entropy favours bond breaking and a lowering of activation energy as well as Free energy.

$\Delta S_{mix}$  value was observed to increase from  $9.435 \text{ Jmol}^{-1}\text{K}^{-1}$  at 0.30 mole of solute to  $13.094 \text{ Jmol}^{-1}\text{K}^{-1}$  at 0.47 mole of the solute.

#### Variation of Differential or Partial Molar Heat of Solution with Acid Concentration

The relevant data for  $\overline{\Delta H}_{mix}$  and  $n_2$  are recorded in Table 4 and summarised graphically in Fig. 5.

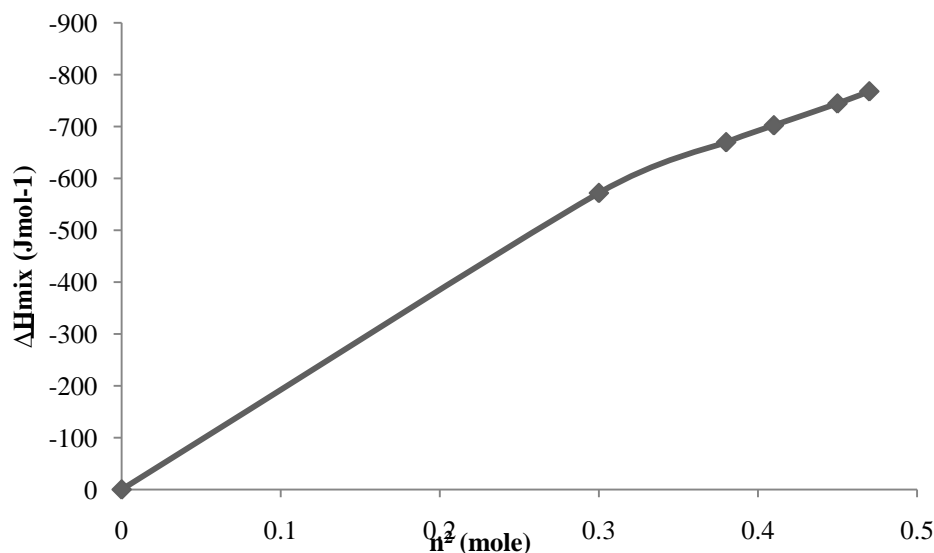


Figure 5: Variation of Differential or Partial Molar Heat of Solution with Acid Concentration in the Binary System

It is observed that all the  $\overline{\Delta H}_{mix}$  values are large and negative indicating that the system under study is highly exothermic.  $\overline{\Delta H}_{mix}$  values are observed to decrease with increase in the acid concentration. Progressive decrease in  $\overline{\Delta H}_{mix}$  values indicates the extent of deviation of the system from ideality to real solution.

$\overline{\Delta H}_{mix}$  value of  $-571.85 \text{ Jmol}^{-1}$  was obtained at the addition of 0.30 mole of the solute. The value decreased to  $-767.83 \text{ Jmol}^{-1}$  at 0.47 mole of solute.



### Variation of Partial Molar Free Energy with Partial Molar Entropy

The computed data for  $\overline{\Delta G}_{mix}$  and  $\overline{\Delta S}_{mix}$  for ideal system is recorded in Table 3 and illustrated graphically in Fig. 6.

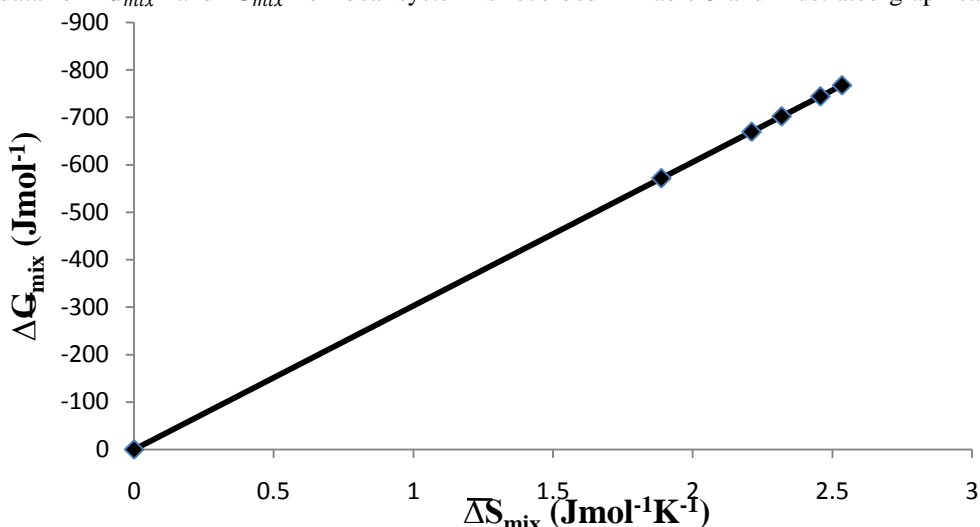


Figure 6: Variation of Partial Molar Free Energy with Partial Molar Entropy in the Binary System

It is observed that all values of  $\overline{\Delta G}_{mix}$  are large but negative compared to  $\overline{\Delta S}_{mix}$  values which are considerably small but positive. As  $\overline{\Delta G}_{mix}$  values become more negative,  $\overline{\Delta S}_{mix}$  values become more positive. The observed trend in both potentials show that the solution under study is spontaneous and tend to be more spontaneous with increase in solute concentration.

The  $\overline{\Delta S}_{mix}$  values recorded for the ideal solution is independent of temperature. It is a function of only the concentration and quantity of constituents present. The calculated values of  $\overline{\Delta S}_{mix}$  at various solute concentration in the ideal solution is the same for the real solution at corresponding solute concentrations. Further, since the mole fractions of solvent and solute ( $X_1$  and  $X_2$  respectively) are less than unity, then for the conditions specified,  $\overline{\Delta S}_{mix}$  is positive and hence the mixing process is accompanied by an increase in entropy.

### Variation of Partial Molar Heat of Solution with Partial Molar Entropy of Mixing

Relevant data for partial molar heat of solution and partial molar entropy are recorded in Table 4 and 3 respectively and shown graphically in Figure 7. The value obtained for the  $\overline{\Delta H}_{mix}$  are highly negative.  $\overline{\Delta S}_{mix}$  values are all positive.  $\overline{\Delta H}_{mix}$  shows increasing negativity while  $\overline{\Delta S}_{mix}$  shows increasing positivity with increase in solute concentration. Both trends signify that the solution is highly exothermic progressing with increase in entropy at increasing solute concentration.

For 0.30 mole of solute, the calculated values of  $\overline{\Delta H}_{mix}$  and  $\overline{\Delta S}_{mix}$  are  $-571.85 \text{ Jmol}^{-1}$  and  $1.8873 \text{ Jmol}^{-1}\text{K}^{-1}$  respectively. These values increased to  $-767.83 \text{ Jmol}^{-1}$  and  $2.5341 \text{ Jmol}^{-1}\text{K}^{-1}$  respectively at 0.47 mole solute concentration.

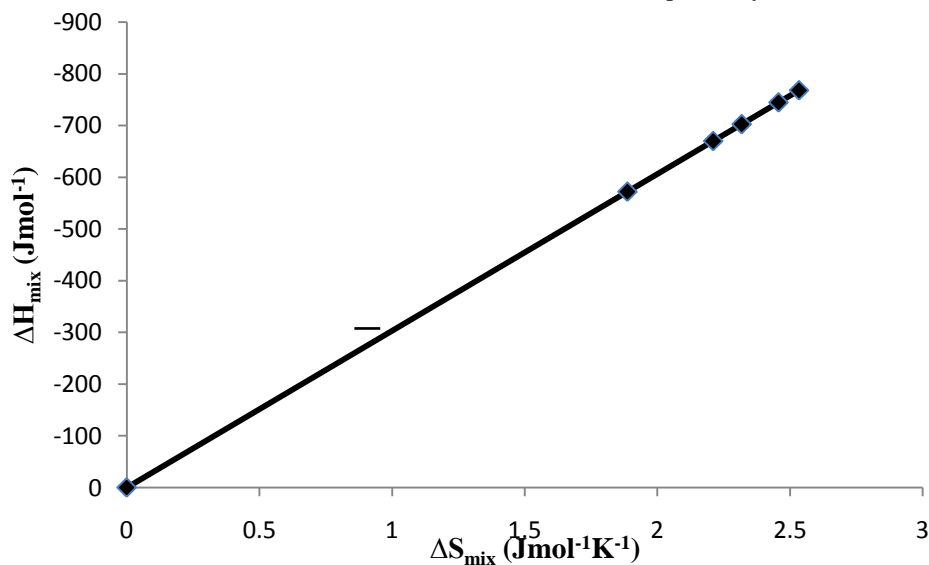


Figure 7: Variation of Differential or Partial Molar Enthalpy with Partial Molar Entropy in the Binary System



### Deductions from the Measured Thermochemical Potentials $kb^2$ and $\Delta T - 18kb^3$

The quantity  $kb^2$  defined as basic constant gives an estimate of the number of moles  $n_2$  of the completely ionized acid expended in the solution while the quantity  $\Delta T - 18kb^3$  described as thermohydrobasic constants gives an estimate of the diluted acid in grammes.

It is expected that the graph of  $kb^2$  (moles) versus  $\Delta T - 18kb^3$  (grammes) should yield a straight line with slope equal to the reciprocal of the molecular mass of the acid from which the actual molecular mass of the acid (solute) is estimated. Values of  $kb^2$  and  $\Delta T - 18kb^3$  are recorded in Table 1 and plotted in Fig. 8. A linear relationship is obtained from origin and the slope equals to the reciprocal of the molar mass of the solute ( $H_2SO_4$ ). From evaluation, the molar mass of  $H_2SO_4$  ( $98\text{gmol}^{-1}$ ) is obtained.

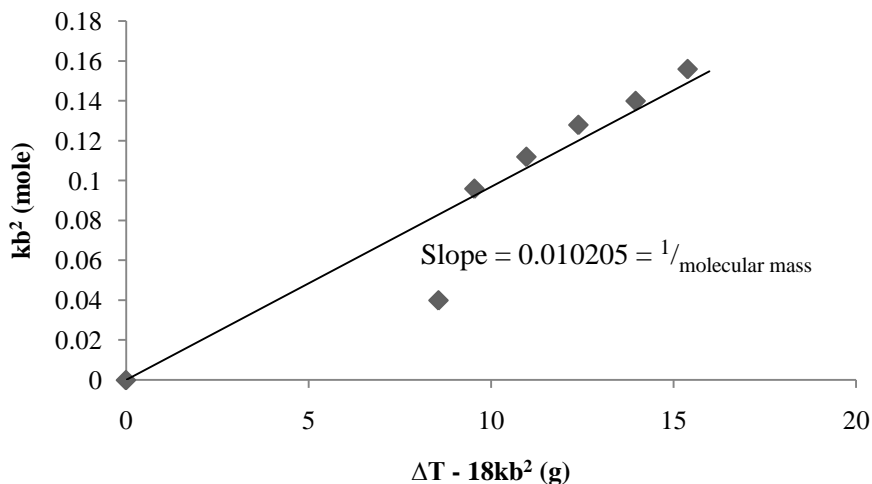


Figure 8: Plot of basic constant (mole) versus thermohydrobasic constant (g) for the determination of molecular mass of  $H_2SO_4$

### Thermodynamic Implication and Chemical Hypothesis Arising from the Present Study

The present study has given birth to a new chemical hypothesis stated below:

“ In a binary solution at equal solute concentrations,  
 $\Delta G_{mix}$  (Ideal Solution) =  $\Delta H_{mix}$  (Real Solution) and  
 $\overline{\Delta G}_{mix}$  (Ideal Solution) =  $\overline{\Delta H}_{mix}$  (Real Solution)”.

The thermodynamic equilibrium plot between  $\Delta G_{mix}$  (Ideal Solution) and  $\Delta H_{mix}$  (Real Solution) is presented below in Fig. 9.

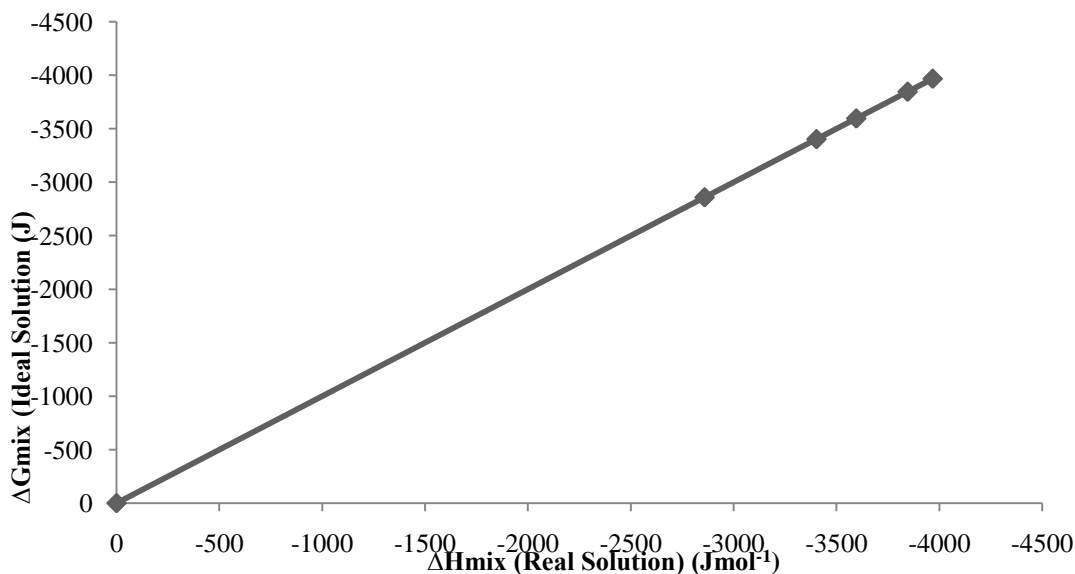


Figure 9: Thermodynamic Equilibrium Plot between  $\Delta G_{mix}$  (Ideal Solution) and  $\Delta H_{mix}$  (Real Solution)





## Conclusion

The study reveals that in ideal solutions, although there is no evolution or absorption of heat, there is residual entropy of mixing in line with the third law of thermodynamics.  $\Delta H_{\text{mix}}$  values in non ideal systems for other solutes can conveniently be extrapolated from the thermodynamic calibration curve of  $\Delta H_{\text{mix}}$  of  $\text{H}_2\text{SO}_4$ , the later being highly exothermic and the differential heat of solution being independent of molecular structure.

## Acknowledgements

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## Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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