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Thermodynamic functions of 1, 2, 3- tri-meth-oxy-benzene and m-methyl-meth-oxy benzene

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ABSTRACT

The statistical computation of an ideal gas state thermodynamic functions namely enthalpy, entropy, free energy, heat capacity of 1,2,3 – Trimethoxy benzene, m-methyl methoxybenzene have been performed. These calculations have been made at a pressure of 1 atmosphere in the temperature range 100°K to 1500°K under rigid rotor harmonic oscillator approximation for 1 mole of perfect gas & on the basis of vibrational frequencies obtained from FTIR & Raman spectra & also with the help of moment of inertia.

Keywords: Enthalpy; Entropy; Free energy; Heat capacity; FTIR; Raman spectra.

1.0 Introduction

Infrared and Raman spectra of polyatomic molecules to the determination of the structures of these molecules, there are a number of other important applications. Of these the calculation of thermodynamic quantities appears to be most important application. On the basis of the molecular data obtained from the spectra as was first suggested by Urey and Tolman & Badger, it is possible to predict with great precision the values of thermodynamic quantities, such as the heat capacity of the particular gases. This possibility is of great practical importance, particularly since the direct experimental measurement of these quantities is usually difficult and tedious and sometimes impossible. Frequently the values calculated from the spectroscopic data are more accurate than those determined by direct thermal measurements. These calculations are carried out at different temperatures from 100K to 1500K in the rigid rotor harmonic oscillator approximation for 1 mole of the perfect gas at 1 atmosphere. These thermodynamical parameters can be calculated by using the standard expression given by Clothup, Herzberg and other project reports given by Pitzer, Viney, Pitzer & Gwinn, Pitzer & Scott and other refined on time to time. We can also determine the rotational contribution by knowing the structural parameters of the molecule. The principal

moment of inertia along the three axes (x, y, z) of the molecule can also be calculated by knowing the Cartesian coordinates of each atoms attached to the molecule. Therefore this chapter has been devoted to calculate the principal moment of inertia, rotational constants and thermodynamic functions of all title molecules such as 1, 2, 3–Trimethoxy Benzene, m-methylmethoxy Benzene, p-Anisic acid, 3, 4, 5–Trifluoro and 2, 4, 6–Trifluoro Benzonitrile, 5–Chloro-o–Anisidine.

2.0 Method

The principal moment of inertia and the thermodynamic functions viz. entropy, enthalpy, heat capacity and free energy can be calculated by adopting the following procedure of formulae by using spectroscopic data & structural parameters.(4-6)

$$Q = Q_{tr} \cdot Q_{rot} \cdot Q_{vib} \quad (1)$$

$$\text{Energy} : E^0 = E_0^0 - RT^2 \frac{d(I_n Q)}{dT} \quad (2)$$

$$\text{Enthalpy Function: } \frac{H^0 - E_0^0}{T} + RT^2 \frac{d(I_n Q)}{dT} = R \quad (3)$$

$$\text{Heat Capacity} : C_p + R = \frac{d}{dT} RT^2 \left(\frac{d I_n q}{dT} \right) \quad (4)$$

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$$\text{Entropy} : S^0 + RT \frac{d \ln q}{dT} - \frac{RT}{N} \ln N = R \quad (5)$$

$$\text{Free Energy Function: } \frac{G^0 - E_0^0}{T} - \frac{R}{N} \ln Q \quad (6)$$

Where the Q , Q_{tr} , Q_{rot} , Q_{vib} , R , and other factor are given.

However, in case of those molecules which possess more internal rotational oscillations, it is necessary to apply certain modifications in their partition functions as discussed by various workers (11-17). To a good approximation, free internal rotation partition function of a molecule with a single rotor is given as

$$Q_r = \frac{8\pi^2 I_m K T^{1/2}}{h \sigma_i}$$

Where, σ_i is then of potential minima per revolution, also the symmetry number of the internal and I_m is the reduced moment of inertia of the rotating top (3) expressed as

$$I_m = A_m - A_{mn} = A_m - \sum_i \frac{(\alpha_m U_m)^2}{m} + \frac{(\beta_m)^2}{I_i}$$

Here $A_m = \sum M_k (X_k + Y_k)^2$ the top moment of inertia about the rotating bond where m_k is the mass of K^{th} atom.

3.0 Results

For determination of the rotational contribution of bond length, bond angle are described as -

$C - C = 1.04 \text{ \AA}$,

$C - H (\text{ring}) = 1.08 \text{ \AA}$, $C_{\text{ring}} - O = 1.37 \text{ \AA}$

$O - C_{\text{group}} = 1.47 \text{ \AA}$

$C - H (\text{in OCH}_3) = 1.09 \text{ \AA}$

$\angle C - O - C = 120^\circ$

$\angle O - C - H = 109.5^\circ$, $C - Cl = 1.67 \text{ \AA}$

All other angles are taken as 120°

— CH_3 group: $C - C = 1.53 \text{ \AA}$, $C - H = 1.091 \text{ \AA}$,

$\angle \text{HCH} = 109.5^\circ$, $\angle \text{CCH} = 109.5^\circ$

Symmetry number is taken as 1 for C_{2v} symmetry and internal rotation is taken as 2 for all the compounds. (3n-6) is noted as the vibrational frequencies of the compounds taken from the previous chapter i.e. second, third and fifth. The molecules and z-axis to pass through the para - positions of the ring. The principle moment of inertia about x, y and z-axis are calculated by the procedure given in the literature.

The calculations of total contribution of thermodynamic functions using the calculations of total contribution of thermodynamic functions using

(3n-6) fundamental frequencies at various temperatures i.e., 100K to 1500K are carried out on the rigid rotor harmonic oscillator approximation & these related to one mole of perfect gas at one atmospheric pressure. The thermodynamic functions calculated for all above said molecules are presented in Table-[2] & [3]. The values of thermodynamic quantities viz. entropy, enthalpy, free energy, & heat capacity at constant pressure calculated for title molecules show good relationship to the values calculated by various investigators [12 to 14].

The enthalpy function represents the total energy stored in a system. When a system changes from solid to liquid, to gaseous state, the enthalpy of the system increases. Similar trend is reflected from the enthalpy values for present molecules as we increase the temperature in the range 100 - 1500 K.

The degree of randomness in a system is marked as entropy. On increasing the temperature, entropy of the system also increases. Similar trend is followed for the values of free energy and heat capacities. It can be observed that thermodynamic functions rise more rapidly in the low temperature range and less rapidly in the high temperature range. The variations in these thermodynamic functions with the temperature are in good agreement with the trend report in the literature.

Table 1: Computed Values of Principal Moment of Inertia of Present Molecules

Molecules	Principal Moment of inertia X 10-39 gmcm ²		
	I _x	I _y	I _z
1,2,3 - Trimethoxy benzene	150.258	106.255	58.111
m-methyl methoxybenzene	152.098	105.897	54.986
5-Chloro-o-Anisidine	148.201	98.367	51.642

I_x = Moment of inertia along x-axis. I_y = Moment of inertia along y-axis. I_z = Moment of inertia along z-axis.

Table 2: Thermodynamic Functions of 1,2,3 – trimethoxy benzene (in cal/mole K)

Temp.(K)	Enthalpy	Free Energy (-)	Entropy	Heat Capacity
100	9.01	54.94	64.74	14.32
200	13.18	58.07	70.63	17.63
273.15	16.29	67.56	77.75	20.76
298.15	17.26	68.99	82.81	21.21
300	17.91	72.15	83.97	28.53
400	22.65	76.73	90.63	32.81
500	27.79	79.48	97.40	38.73
600	31.81	83.70	105.27	43.25
700	35.52	87.76	117.40	47.61
800	37.78	89.68	125.50	50.75
900	40.91	92.42	133.67	56.82
1000	43.62	97.87	142.81	61.91
1100	45.31	105.74	151.71	64.11
1200	49.52	109.23	161.23	68.26
1300	52.73	116.33	170.18	71.65
1400	53.84	122.34	177.27	77.22
1500	55.68	127.72	183.88	82.07

Table 3: Thermodynamic Functions of m-methoxymethyl benzene (in cal/mole K)

Temp. (K)	Enthalpy	Free Energy (-)	Entropy	Heat Capacity
100	14.35	58.39	68.31	16.61
200	17.28	60.12	70.05	19.75
273.15	19.16	65.31	75.58	22.19
298.15	20.03	68.33	79.29	22.88
300	20.99	68.95	82.68	28.25
400	23.91	75.61	95.98	32.15
500	25.81	79.12	110.66	38.62
600	28.85	83.39	121.75	41.31
700	32.62	88.56	129.39	46.56
800	34.75	95.87	137.61	58.57
900	37.32	98.28	145.16	55.21
1000	40.21	105.63	152.35	59.53
1100	45.67	112.57	167.12	63.93
1200	49.85	117.44	170.58	69.79
1300	52.99	121.72	175.69	74.26
1400	55.51	125.35	179.26	78.51
1500	57.12	127.15	181.35	81.67

Table 4: Thermodynamic Function of 5–Chloro–o–Anisidine (in cal/ mole K)

Temp (K)	Enthalpy	Free energy (-)	Entropy	Heat capacity
100	8.61	55.99	65.44	13.22
200	13.13	58.32	70.53	17.63
273.15	16.29	67.64	77.25	20.73
298.15	17.61	68.45	82.71	21.28
300	17.91	72.15	83.87	28.6
400	22.66	76.66	90.43	32.11
500	28.79	79.11	97.10	38.73
600	31.81	83.54	105.37	43.25
700	35.52	86.76	117.10	47.61
800	37.78	88.68	125.60	50.75
900	40.91	92.42	133.47	56.82
1000	43.62	97.87	142.71	61.91
1100	45.31	105.74	151.61	64.11
1200	49.52	109.23	161.93	68.46
1300	53.73	116.33	170.68	71.45
1400	54.84	123.44	177.37	77.12
1500	56.38	128.88	185.44	84.86

4.0 Conclusions

Statistical computation of an ideal gas state thermodynamic functions namely enthalpy, entropy, free energy, heat capacity of 1, 2, 3 – Trimethoxy benzene, m-methyl methoxybenzene and 5–Chloro–o–Anisidine have been performed. These calculations have been made at a pressure of 1 atmosphere in the temperature range 100°K to 1500°K under rigid rotor harmonic oscillator approximation for 1 mole of perfect gas & on the basis of vibrational frequencies obtained from FTIR & Raman spectra & also with the help of moment of inertia.

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