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Thermodynamic Functions of Benzene, 1-Methoxy-2-Methyl, Benzene, 1-Methoxy-4-Methyl

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ABSTRACT
The statistical computation of an ideal gas state thermodynamic functions namely enthalpy, entropy, free energy, heat capacity of Benzene,1-methoxy-2-methyl,Benzene,1-methoxy-4-methyl 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.

INTRODUCTION:-

In addition to the application of the study of infrared and Raman spectra of polyatomic molecules to the determination of the structure 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 Tolman& Badger [1], 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 100°K to 1500°K 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 Colthup [2], Herzberg [3] and other project reports given by Pitzer [4 to 6], and others [7 to 10] 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 work has been devoted to calculate the principal moment of inertia, rotational constants and thermodynamic functions of all title molecules such as Benzene,1-methoxy-2-methyl,Benzene,1-methoxy-4-methyl respectively.

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)

$$Q = Q_{tr}.\ Q_{rot}.\ Q_{vib} \qquad \text{.....[1]}$$

Energy: $$E^0 - E_0^{\ 0} = RT^2 \frac{d\ I_n\ Q}{dT} \qquad \text{..... [2]}$$

Enthalpy Function: $$\frac{H^0 - E_0^0}{T} = RT^2 \frac{d\ I_n\ Q}{dT} + R \qquad \text{..... [3]}$$

Heat Capacity: $C_P = R + \frac{d}{dT}[RT^2\left(\frac{d\, I_n\, Q}{dT}\right)]$ ..... [4]

Entropy: $S^0 = RT\frac{d\, I_n\, Q}{dT} + RI_{nQ} - RI_nN + R$ ..... [5]

Free Energy Function: $\frac{G^0 - E_0^0}{T} = -RI_n\frac{Q}{N}$ ..... [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 approximations, free internal rotation partition function of a molecule with a single rotor is given as

$$Q_f = \frac{(8\pi^2 I_m KT)^{1/2}}{h\sigma_i}$$

Where σ_i is theno 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

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

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.

RESULTS

For determining the rotational contribution the structural parameters viz. bond length, bond angle etc are taken from the literature [10-13] and described here for all the above said molecules.

C – C = 1.04 A°,
C– H (ring) = 1.08 A°
C_{ring}– O = 1.37 A°
O – C_{group} = 1.47 A°
C – H($_{in}OCH_3$) = 1.09 A°
< C-O-C = 120°
< O- C-H= 109.5°
C-Cl=1.67 A°
All other angles are taken as 120°
—CH_3group : C-C = 1.53 A°, C-H = 1.091A°,
<HCH = 109.5°, <CCH = 109.5°

The symmetry number for overall rotation is taken as 1 for C_{2v} symmetry and internal rotation is taken as 2 for all compounds. The vibrational frequencies (3n-6) of these compounds are taken from the table of previous chapter viz. second, third, fifth. The molecules which are studied contain single top group –CH_3 respectively.
The x,y plane are taken for molecules and z axis to pass through the para position of the ring. The principle moment of inertia about x,y& z axis are calculated by the procedure given in the literature [2,3,8] and the calculated moment of inertia for all molecules are given in Table-[1].

The calculations of total contribution of thermodynamic functions using (3n-6) fundamental frequencies at various temperatures viz-100° K to 1500° K 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 gaseousstate, 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 entropy is regarded as the measure of randomness in a system. As the temperature increases, entropy also increases as shown in the Table. Similar trend will be followed for the values of free energy & heat capacity for title molecules under investigations. It was also found that the thermodynamic functions rise more rapidly in the low temp range and less rapidly in the high temp range. The variation of these thermodynamic functions with temp are in good agreement with the trend reported in the literature. [12-18].

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
Benzene,1-methoxy-2-methyl,	156.258	101.288	55.111
Benzene,1-methoxy-4-methyl	156.795	102.325	54.986

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 ofBenzene,1-methoxy-2-methyl (in cal/mole^{0}K)

Temp.^{0}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 OFBenzene,1-methoxy-4-methyl (in cal/mole^{0}K)

Temp.^{0}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

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