International Journal of Education and Science Research Review

Volume-1, Issue-1 February2014 ISSN 2348-6457

Thermodynamics Functions of 5-Bromo-2,4 (1H, 3H) Pyrimidinedione

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ABSTRACT

The Statistical computation of an ideal gas state thermodynamic functions namely enthalpy, entropy, free energy, heat capacity of 5-Bromo-2,4(1H,3H) pyrimidinedione , 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 vibration frequencies obtained from FTIR & Raman spectra & also with the help of moment of inertia.

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 Urey [1] and Tolman & Badger [2], 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 thermodynamic parameters can be calculated by using the standard expression given by Colthup [3], Herzberg [4] and other project reports given by Pitzer [5 ,6], viney [7],Pitzer & Scott [8] and others [9,10] 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.

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.

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

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

Enthalphy Function**:** $$\mathbf{\frac{H^0 - E_0^0}{T} = RT^2 \frac{d\, I_n\, Q}{dT} + R} \quad \text{.......... [3]}$$

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

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

Free Energy Function: $$\mathbf{\frac{G^0 - E_0^0}{T} = - RI_n \frac{Q}{N}} \quad \text{.......... [6]}$$

Where the Q is the Partition function, $\mathbf{E_0^0}$ is the energy at absolute zero, $\mathbf{E^0}$is the total internal Energy, T is absolute temperature, $\mathbf{I_n}$ is the principal moment of Inertia.

RESULT

For determining the rotational contribution the structural parameters viz. bond length, bond angle etc are taken from the literature [11 to 13] and described here for the above said molecule.

$N_1 – C_2$ = 1.34 A°, $C_2 – N_2$ = 1.40 A°

$N_2 – C_4$ = 1.42 A°, $C_4 – C_5$ = 1.42 A°

$C_5 – C_6$ = 1.45 A°, $C_6 – N_1$ = 1.33 A°

$C_2 – H_2$ = 1.084, $C_4 – H_4$ = 1.085

$C_5 – H_5$ = 1.084, $C_6 – H_6$ = 1.084

< $C_2\, N_2\, C_4$ = 121°, <$N_2\, C_4\, C_5$ = 120.5°

< $C_4\, C_5\, C_6$ = 1170°, <$C_5\, C_6\, N_1$ = 122.5°

< $C_6\, N_1\, C_2$ = 122°, <$N_1\, C_2\, N_2$ = 120°

All other angles are taken as 120°

—NH group : C-N = 1.65 A°, < NCN = 122°

—Ch_3 group : C-C = 1.53 A°, C — H = 1.091 A°,

<HCH = 109.5°, <CCH = 109.5°

OH group : O – H = .97 A°, C – O = 1.35 A°,

< COH = 107°, <CCO – 120°

C-Br = 1.9025, <CC Br = 120.530°

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 literature. The molecule which is studied contain single top group N-O.

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The x,y plane are taken for molecule 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 [3,4,10] and the calculated moment of inertia for the molecule is given in Table-[1].

The rotational constants for the molecule is calculated by the method of Herzberg [4] and 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 above said molecule is presented in Table-[2]

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 [14 to 17].

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 molecule 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 – 2 . Similar trend will be followed for the values of free energy & heat capacity for title molecule 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. [12-20].

The rotational constants of the molecules presently investigated are given in Table: 1 respectively. Whereas the molecular polarizability of the said molecules are calculated with the help of literature present [12] and depicted in Table : 3, which shown closed result to the work of previous workers [12 to 15].

TABLE-1

PRINCIPAL MOMENT OF INERTIA OF PRESENT MOLECULE WITH X,Y,Z & ROTATIONAL CONSTANTS

Molecules	Principal Moment of inertia X 10-40 gm. cm			Rotational Constants		
	IA	IB	IC			
5,2,4-BHP	70.01	99.39	83.59			

TABLE-2

THERMODYNAMIC FUNCTIONS OF 5,2,4-BP (in Cal Mol –K^{-1}) ^{2}

Temp.^{0}K.	Enthalpy	Free Energy(-)	Entropy	Heat Capacity
100	11.85	56.08	68.25	17.78
200	13.42	58.11	70.22	19.33
273	14.89	62.28	78.26	21.87
298	15.98	64.21	80.95	23.01
300	16.11	70.18	81.89	23.87
400	18.33	75.01	86.75	26.79
500	19.88	78.35	95.65	30.95
600	21.85	82.12	103.23	33.70
700	23.79	84.44	107.03	35.12
800	26.11	87.54	112.29	37.29
900	27.21	91.56	116.93	38.44
1000	28.33	93.23	120.36	40.22
1100	29.57	95.61	125.16	42.13
1200	30.28	97.61	128.87	43.06
1300	31.46	100.46	132.55	43.97
1400	32.22	103.90	137.26	44.28
1500	33.10	107.10	140.15	44.92

TABLE – 3

Computed values of Molecular polarizability of molecule subjected.

SL NO.	MOLECULES	MOLECULAR POLARIJABILITY Cm^3
1	5,2,4-BP	8.359

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