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Research Article

Thermodynamical Quantities of Chalcogenide Dimers (O₂, S₂, Se₂, and Te₂) from Spectroscopic Data

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Attempts have been made to calculate the thermodynamical quantities of diatomic molecules such as O_2 , S_2 , Se_2 , and Te_2 from spectroscopic data with the help of partition function theory. The results have been calculated in the temperature range $100-3000^{\circ}$ C. In order to increase accuracy of the calculated quantities, we have incorporated nonrigidity, anharmonicity, and stretching effects of molecules. The variation of these quantities with temperature have been studied and explained in terms of various modes of molecular motions.

1. Introduction

The diatomic molecules have gained increased interest over the past several years in both experiment and theoretical studies because of their importance in astrophysical processes and many chemical reactions. Thermodynamical quantities such as enthalpy, entropy, heat capacity, and free energy have their potential application in various fields of science. For instance, enthalpy is one of the most important thermophysical properties required for calculating heat loads in process design. Entropy data are used for heart disease diagnosis [1]. These quantities are required for a large number of experimental methods and processes such as chemical transport reaction like Van Arkel-deBoer process and Mond process in the purification of nickel [2]. Recently, these quantities are also used in fabrication of thermal sensors and applied in medical field [3]. With the use of heat capacities and entropy values of the gaseous substances involved, heat of reaction can be determined and converted to different temperatures, which is necessary for process optimization of such reactions. Enthalpy and entropy have provided valuable insights into microscopic factors that complement those provided by conventional structural techniques.

Investigations in high temperature chemistry, astrophysics, and other disciplines require the knowledge of the thermodynamic properties of diatomic molecules. The plausibility of predictive models obtained in such investigations relies on the accuracy of these data. The scrutiny of the literature reveals that thermodynamic data are often absent or have scattered values in different research articles and handbooks. The main requirements to thermodynamic values are their reliability, mutual consistency, and so forth. In our theoretical study, thermodynamic values are estimated by using spectroscopic data which are microscopic in nature, whereas thermodynamical quantities are macroscopic in nature.

The elements of VI group of periodic table (O, S, Se, and Te) have potential applications. Oxygen is essential for respiration of all plants and animals and for practically all combustion. Sulphur is used extensively in making phosphatic fertilizers, vulcanization of natural rubber, sulfite paper, and so forth. Selenium is very important for human health, photovoltaic action, xerography, photographic toner, and so forth. Tellurium is used in corrosive action, ceramics, p-type semiconductor, and for making thermoelectric devices.

Over the decade there had been increasing interest in the estimation of thermodynamical quantities. Tolman [4] was the first to estimate thermodynamical quantities from

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Table 1: Calculated thermodynamical properties of oxygen molecule (O_2) at 1 Atm.

O2 molecule T(K)F (kJ/mole) H (kJ/mole) S (J/mole/K) C_n (J/mole/K) 100 13.52 2.07 173.35 29.07 31.03 200 5.44 193.37 29.08 300 50.08 8.58 205.15 29.33 400 70.11 30.04 11.48 213.66 500 90.91 14.45 220.45 31.00 600 112.33 17.38 31.98 226.19 700 134.29 20.31 231.19 32.84 800 156.71 23.23 235.63 33.56 900 179.56 239.63 26.16 34.15 1000 202.78 29.08 243.26 34.63 1100 226.35 32.01 246.59 35.01 250.25 34.95 1200 249.66 35.33 274.43 37.89 252.51 35.59 1300 1400 298.89 40.83 255.17 35.81 1500 323.61 43.78 257.66 35.99 348.56 260.00 1600 46.73 36.14 1700 373.74 49.69 262.20 36.27 399.14 52.65 264.29 1800 36.38 1900 424.74 55.62 266.28 36.47 2000 450.53 58.59 268.16 36.55 269.96 2100 476.50 61.57 36.62 2200 502.65 64.55 271.68 36.69 2300 528.96 67.54 273.32 36.74 555.44 70.53 274.90 36.79 2400 2500 582.06 73.53 276.42 36.83 2600 608.84 76.53 277.88 36.87 2700 635.76 79.54 279.28 36.90 2800 662.81 82.55 280.64 36.93 2900 689.99 85.57 281.95 36.96 3000 717.31 88.59 283.21 36.99

Where F is free energy (kJ/mole), H is enthalpy (kJ/mole), S is entropy (J/mole/K), C_p is specific heat (J/mole/K), and T is temperature (K).

spectroscopic data using statistical mechanics. Hicks and Mitchell [5] applied the suggested method for the estimation of thermodynamical quantities of HCl molecule. Using stretching and interaction terms for the diatomic molecules Giauque and Overstreet [6] modified the methods and calculated various thermodynamical quantities of HCl, Br₂, and NO, and so forth. Later on, several workers [7-12] had contributed for the development of subject by estimating thermodynamical quantities of different molecular species. In continuation, authors applied partition function theory and spectroscopic data for the estimation of thermodynamical quantities of dimer of chalcogenide. In the present account, thermodynamical quantities of O₂, S₂, Se₂, and Te₂ have been calculated in the temperature range 100-3000 K. The choice of temperature range 100–3000 K is due to the fact that it covers its applications in biological sciences, industry, and high temperature chemistry.

TABLE 2: Calculated thermodynamical properties of sulphur molecule (S₂) at 1 Atm.

T (K)	S ₂ molecule						
	F (kJ/mole)	H (kJ/mole)	S (J/mole/K)	C_p (J/mole/K)			
100	15.67	2.07	194.91	29.10			
200	35.37	5.64	215.32	30.34			
300	56.66	8.65	228.02	32.41			
400	79.04	11.57	237.58	33.95			
500	102.28	14.51	245.28	34.95			
600	126.23	17.43	251.73	35.59			
700	150.76	20.36	257.26	36.01			
800	175.82	23.29	262.10	36.30			
900	201.33	26.22	266.41	36.51			
1000	227.24	29.16	270.28	36.67			
1100	253.52	32.11	273.79	36.79			
1200	280.14	35.06	277.01	36.88			
1300	307.06	38.02	279.98	36.95			
1400	334.27	40.98	282.73	37.00			
1500	361.75	43.94	285.30	37.05			
1600	389.47	46.92	287.71	37.09			
1700	417.42	49.89	289.97	37.12			
1800	445.59	52.88	292.11	37.14			
1900	473.97	55.86	294.13	37.17			
2000	502.55	58.86	296.05	37.18			
2100	531.31	61.85	297.88	37.20			
2200	560.24	64.86	299.62	37.21			
2300	589.35	67.86	301.29	37.23			
2400	618.62	70.88	302.89	37.24			
2500	648.04	73.90	304.42	37.25			
2600	677.62	76.92	305.89	37.25			
2700	707.33	79.95	307.31	37.26			
2800	737.19	82.98	308.68	37.27			
2900	767.17	86.02	310.00	37.27			
3000	797.29	89.07	311.28	37.28			

Where F is free energy (kJ/mole), H is enthalpy (kJ/mole), S is entropy (J/mole/K), C_D is specific heat (J/mole/K), and T is temperature (K).

2. Method of Calculation

The energy of a molecular system can be divided into four categories: translational energy, due to the motion of the molecule's centre of mass through space, rotational energy, due to the rotation of the molecule about its centre of mass, vibrational energy due to the vibration of the molecule's constituent atoms, and electronic energy, due to the interactions between the molecule's electrons and nuclei. Since in the real case of motion of the diatomic molecule, during vibration, rotation also occurs, therefore, instead of taking individual rotational and vibrational energy, rovibrational energy has to be used. Then, the total energy of a diatomic molecule will be the sum of translational, rovibrational, and electronic energy

$$E_t = E_{\text{tran}} + E_{\text{rot-vib}} + E_{\text{ele}}.$$
 (1)

Table 3: Calculated thermodynamical properties of selenium molecule (Se_2) at 1 Atm.

Se₂ molecule T(K)F (kJ/mole) H (kJ/mole) S (J/mole/K) C_p (J/mole/K) 100 17.79 2.07 216.34 30.09 200 39.72 5.72 238.37 33.64 300 63.39 8.68 252.40 35.38 400 88.25 11.60 262.72 36.17 500 114.02 14.53 270.86 36.58 600 140.54 17.46 277.57 36.81 700 167.67 20.40 283.27 36.96 800 195.32 23.34 288.23 37.05 900 223.45 26.29 292.61 37.12 1000 251.98 29.24 296.54 37.16 1100 280.89 32.20 300.10 37.20 1200 310.14 35.17 303.36 37.23 1300 339.70 38.14 306.35 37.25 369.54 41.12 309.13 1400 37.26 1500 399.65 44.10 311.71 37.28 430.01 1600 47.09 314.14 37.29 1700 460.61 50.09 316.41 37.29 1800 491.42 53.09 318.56 37.30 522.44 1900 56.10 320.59 37.31 2000 553.65 59.11 322.52 37.31 2100 585.06 62.13 324.36 37.32 2200 616.64 65.16 326.11 37.32 648.39 2300 68.19 327.78 37.32 2400 680.30 71.23 329.38 37.32 712.37 2500 74.27 330.92 37.33 2600 744.59 77.32 332.40 37.33 2700 776.95 80.38 333.83 37.33 809.45 83.44 37.33 2800 335.20 2900 842.09 86.51 336.52 37.33 3000 874.85 89.59 337.80 37.33

Where F is free energy (kJ/mole), H is enthalpy (kJ/mole), S is entropy (J/mole/K), C_p is specific heat (J/mole/K), and T is temperature (K).

Statistical Mechanics show that partition function is a measure of extent to which energy is partitioned among the different states. Partition function is concerned with degeneracy as well as the energy of that level mainly vibrational and rotational and these energies are determined very accurately by spectroscopic methods. The molecular partition function gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system. The larger the value of the partition function, the larger the number of thermally accessible states is. The partition function for a set of energy levels in a molecule is given by

$$Z = \sum_{i} g_i e^{-E_i/kT}, \qquad (2)$$

Table 4: Calculated thermodynamical properties of tellurium molecule (Te_2) at 1 Atm.

T (K)	Te ₂ molecule						
1 (11)	F (kJ/mole)	H (kJ/mole)	S (J/mole/K)	C_p (J/mole/K)			
100	19.11	2.07	230.20	32.27			
200	42.51	5.75	253.87	35.51			
300	67.75	8.69	268.57	36.47			
400	94.23	11.64	279.20	36.84			
500	121.64	14.63	287.51	37.02			
600	149.79	17.64	294.35	37.12			
700	178.57	20.65	300.15	37.17			
800	207.88	23.68	305.18	37.21			
900	237.65	26.73	309.64	37.22			
1000	267.85	29.80	313.63	37.23			
1100	298.41	32.89	317.25	37.24			
1200	329.32	35.99	320.55	37.24			
1300	360.53	39.12	323.60	37.23			
1400	392.04	42.26	326.43	37.22			
1500	423.81	45.42	329.06	37.21			
1600	455.83	48.59	331.53	37.20			
1700	488.08	51.79	333.85	37.19			
1800	520.55	55.01	336.04	37.18			
1900	553.23	58.24	338.12	37.18			
2000	586.11	61.49	340.09	37.17			
2100	619.17	64.76	341.96	37.15			
2200	652.42	68.05	343.75	37.14			
2300	685.83	71.36	345.46	37.12			
2400	719.40	74.68	347.10	37.10			
2500	753.13	78.02	348.68	37.09			
2600	787.01	81.39	350.19	37.07			
2700	821.04	84.77	351.65	37.05			
2800	855.20	88.17	353.06	37.04			
2900	889.49	91.58	354.42	37.02			
3000	923.92	95.02	355.73	37.00			

Where F is free energy (kJ/mole), H is enthalpy (kJ/mole), S is entropy (J/mole/K), C_p is specific heat (J/mole/K), and T is temperature (K).

where g_i is the degeneracy of the *i*th energy level, E_i is the total energy of *i*th level, *k* is Boltzmann constant, *T* is absolute temperature, and *i* ranges over all quantum states.

Corresponding to three types of energies, there are three partition functions, namely, translational partition function ($Z_{\rm tran}$), rotational-vibrational partition function ($Z_{\rm rot-vib}$), and electronic partition function ($Z_{\rm ele}$). The total partition function of a molecular system can be expressed as

$$Z_t = Z_{\text{tran}} Z_{\text{rot-vib}} Z_{\text{ele}}.$$
 (3)

The electronic energy levels contribute to the thermodynamic properties only at high temperature or if unpaired electrons are present. Therefore, total partition function will be the multiplication of translational partition function

TABLE 5: Spectroscopic constants of chalcogenide dimers.	TABLE 5: S	spectroscopic	constants of	chalcogenid	le dimers.
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Molecules	MW (amu)	$\omega_e (\mathrm{cm}^{-1})$	$\omega_e x_e \text{ (cm}^{-1})$	$B_e \text{ (cm}^{-1})$	$\alpha_e \text{ (cm}^{-1})$	Ground state
O_2	32	1580.3	12.071	1.43668	0.0159	³ ∑ ⁻
S_2	64	725.65	2.84	0.29443	0.001570	$^{3}\Sigma^{-}$
Se_2	156	390.36	1.0109	0.092377	0.000339	$^{3}\Sigma^{-}$
Te_2	260	247.07	0.52192	0.03967	0.000993	$^{3}\Sigma^{-}$

Where ω_e , $\omega_e x_e$, α_e , B_e , and MW represent vibrational constant (cm⁻¹), anharmonic constant (cm⁻¹), stretching constant (cm⁻¹), rotational constant (cm⁻¹), and molecular weight (amu), respectively.

Table 6: Comparison of calculated and observed thermodynamical quantities at 300 K.

Molecule	S _{cal} (J/mole/K)	S _{obs} (J/mole/K)	C _{pcal} (J/mole/K)	C _{pobs} (J/mole/K)
S_2	228.02	228.2	32.41	32.5
Se_2	252.40	252.0	35.38	35.4
Te_2	268.57	268.1	36.47	36.7

Where S is the entropy (J/mole/K) and C_p is specific heat (J/mole/K).

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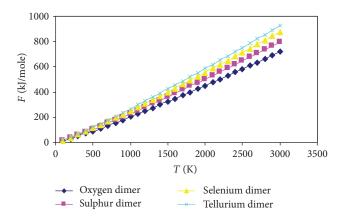


FIGURE 1: Variation of free energy (F) with temperature (T).

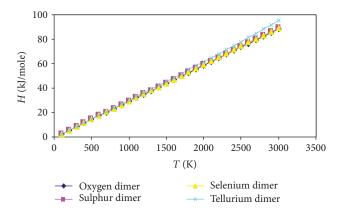


Figure 2: Variation of enthalpy (H) with temperature (T).

 $(Z_{\rm tran})$ and rovibrational partition function $(Z_{\rm rot\text{-}vib})$. The total partition function can be expressed as

$$Z_t = Z_{\text{tran}} Z_{\text{rot-vib}}.$$
 (4)

Translational contribution to the thermodynamical quantities can be calculated by the following relations [13].

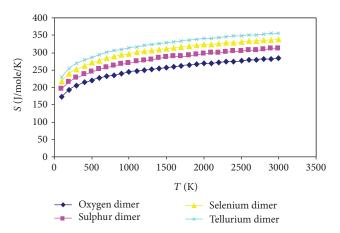


FIGURE 3: Variation of entropy (S) with temperature (T).

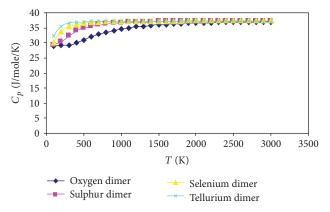


Figure 4: Variation of specific heat (C_p) with temperature (T).

- (i) Free energy $(F H_0)_{\text{tran}} = -(3/2)RT \ln m (5/2)RT \ln T + 0.87601RT$.
- (ii) Enthalpy $(H H_0)_{tran} = (5/2)RT$.
- (iii) Entropy $S_{\text{tran}} = (5/2)R + F_{\text{tran}}/T$.
- (iv) Heat capacity at constant pressure $C_{ptran} = (5/2)R$.

Where H_0 represents enthalpy at a temperature of 298.15 K and R is the gas constant.

With the help of vibrational-rotational partition function, its contribution in free energy, enthalpy, entropy, and heat capacity can be estimated by the following formulae [13].

- (i) Free energy $(F H_0)_{vr} = -RT \ln Z_{vr} RT \ln x$.
- (ii) Enthalpy $(H H_0)_{vr} = RT^2 (\partial/\partial T)(\ln Z_{vr}) + RT \ln x$.
- (iii) Entropy $S_{vr} = R[(1 + \ln Z_{vr})] + RT[(\partial/\partial T)(\ln Z_{vr})].$
- (iv) Heat capacity at constant pressure $Cp_{vr} = RT(\partial/\partial T)(\ln Z_{vr})$.

Where x represents the multiplicity of the ground state and

$$Z_{vr} = \frac{1}{\sigma y (1 - e^{-u})} \left[1 + \frac{2\beta}{y} + \frac{\delta}{e^{u} - 1} + \frac{2xu}{(e^{u} - 1)^{2}} + \frac{y}{3} + \frac{y^{2}}{15} \right],$$
(5)

in which

$$u = \frac{hc\omega_0}{KT}, \qquad y = \frac{hcB_0}{KT}, \qquad \beta = \frac{D_e}{B_0}, \qquad \delta = \frac{\alpha_e}{B_0}$$

$$B_0 = B_e - \frac{\alpha_e}{2}, \qquad \omega_0 = \omega_e - 2\omega_e x_e, \qquad \omega_0 x = \omega_e x_e.$$
 (6)

Finally, the thermodynamic quantities like free energy, enthalpy, entropy, and heat capacity of chalcogenide dimers are calculated by adding the translational contribution and the vibrational-rotational contribution.

3. Results and Discussion

The thermodynamical quantities (free energy, enthalpy, entropy, and heat capacity at constant pressure) of dimer of chalcogenide have been calculated in the temperature range 100–3000 K. The calculated values are listed in Tables 1, 2, 3, and 4. The spectroscopic data used for the present calculation are collected in Table 5 [14-18], whereas Table 6 shows the comparison of thermodynamical quantities with reported values in the literature [18]. From Table 6, it is clear that heat capacity shows the deviation from 0.056% to 0.626% from reported values while entropy shows the deviation from 0.078% to 0.175%. Variation of these quantities with temperature reveals that free energy, enthalpy, and entropy (Figures 1, 2, and 3) increase with temperature while heat capacity (Figure 4) becomes constant. At low temperature only translational motion of molecules contributes while as temperature increases rotational motion also occurs. On further increasing the temperature vibrational motion of the molecules gives its significant contribution. This explains the increase in the thermodynamical quantities like entropy, free energy, and enthalpy with temperature. After a certain value of temperature, there is no additional motion in the molecules which account for constancy of specific heat at a very high temperature. In this calculation, B_0 has been used instead of B_e which involves the impact of stretching of bonds between the both atoms of diatomic molecules. Incorporation of Z_{vr} instead of taking individual contribution

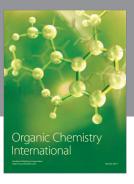
of Z_v and Z_r increases the accuracy of the computed data. Dimers of chalcogenides have $^3\Sigma$ ground state; therefore, ground state multiplicity has been included in the calculation of thermodynamical quantities which gives authentic values of thermodynamical quantities.

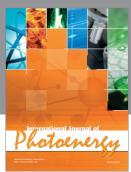
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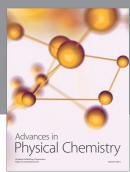
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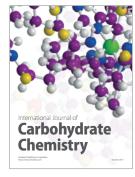
















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