

## Estimation of thermodynamical quantities of tin chalcogenides from spectroscopic data

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Statistical thermodynamics and spectroscopy have been combined to evaluate thermodynamical quantities of tin chalcogenides (SnO, SnS, SnSe and SnTe). Their temperature dependence has been studied in the temperature range 100-2200K. The authenticity of data is established by the comparison of reported values. Discrepancies between calculated values and observed values can mainly be attributed to contributions from excited electronic states.

**Keywords:** Partition function, Rotational constant, Vibrational constant, Thermodynamical quantities

### 1 Introduction

Thermodynamical study of a molecular system basically concerns with estimation of free energy ( $F$ ), enthalpy ( $H$ ), entropy ( $S$ ) and heat capacity ( $C$ ). The knowledge of these quantities is essential for chemical transport reactions such as Van Arkel-de Boer process in the purification of titanium or the Mond process in the purification of nickel<sup>1</sup>. Recently these quantities have also been used in sensor technology<sup>2</sup> and medical field<sup>3</sup>. These quantities can be applicable for calculating equilibrium constant of chemical reaction and liberated energy in various chemical processes. There is considerable technological and scientific interest in thermodynamical properties of tin chalcogenides. Tin has valuable contributions for fabricating junction diodes and transistors. Therefore it is an important component for electronic industry.

In 1923, Tolman founded the basis for calculation of thermodynamical quantities from spectroscopic data. He calculated rotational specific heat from a priori probability. Later on Cardelino and co-workers<sup>4</sup> reported structural, electronic and thermodynamical properties for indium compounds that are of interest in halide transport and organometallic chemical vapour deposition. Kratzer and Sax<sup>5</sup> incorporated impact of anharmonic molecular vibrations in the estimation of thermodynamical quantities. Using estimated thermodynamical quantities from quantum chemical calculation Hindenbrand and Lau<sup>6</sup>, determined dissociation energies of the copper and silver monohalides and of nickel monofluorides. Recently thermodynamical properties of AgCl and AgBr were measured by differential scanning

calorimetry and thermodynamic functions for these were ascertained by Rycerz *et al.*<sup>7</sup>. Zielkiewicz<sup>8</sup> calculated entropy of water using harmonic approximation and discussed the accuracy of the method. More recently, thermodynamical quantities of potassium monohalides<sup>9</sup>, alkali metal monohydrides<sup>10</sup> and platinum diatomics<sup>11</sup> have been calculated.

There is renewed interest in the study of thermodynamical quantities of diatomic molecules. In the present paper, thermodynamical quantities of tin chalcogenides are calculated by using partition function theory. The choice of the temperature range 100-2200K is due to the fact that it covers its applications in high temperature chemistry, electronic industry and biological sciences.

### 2 Theory

Partition function of a molecular system contains all the relevant information of that system. It is approximately equal to the number of quantum states having energies below the thermal energy available to the molecule in the given volume. The expression of partition function can be written as<sup>12-13</sup>:

$$Z = \sum_i g_i e^{-\frac{E_i}{kT}} \quad \dots (1)$$

where,  $g_i$  is the degeneracy of  $i^{\text{th}}$  energy level,  $E_i$  is the total energy of  $i^{\text{th}}$  level,  $K$  is Boltzmann constant,  $T$  is absolute temperature and  $i$  ranges over all quantum states. The total energy of a diatomic molecule is the sum of rotational, vibrational electronic and translational contributions.

$$E_t = E_{\text{rot}} + E_{\text{vib}} + E_{\text{ele}} + E_{\text{tran}} \quad \dots (2)$$

The expression in Eq. (2) implies that the coupling between rotation and vibration is very negligible and that the geometry of a molecule does not change considerably during rotation, vibration and in excited electronic states. According to these four types of energies there are four types of partition functions viz. translational partition function ( $Z_{\text{tran}}$ ), rotational partition function ( $Z_{\text{rot}}$ ), vibrational partition function ( $Z_{\text{vib}}$ ) and electronic partition function ( $Z_{\text{ele}}$ ). The total partition function of a molecular system can be expressed as:

$$Z_t = Z_{\text{tran}} Z_{\text{rot}} Z_{\text{vib}} Z_{\text{ele}} \quad \dots (3)$$

In this expression  $Z_{\text{ele}}$  plays no important role as electronic energy 1-10 eV is very high as compare to vibrational energy  $10^{-2}$  eV and rotational energy  $10^{-3}$  eV. Theory shows that molecules lie in their ground state at about 2200 K and hence electronic partition function can be neglected up to this temperature. Rotational and vibrational motions of a diatomic molecule are not independent of each other but they are coupled. Hence instead of taking individual rotational partition function ( $Z_{\text{rot}}$ ) and vibrational partition function ( $Z_{\text{vib}}$ ), vibrational-rotational partition function ( $Z_{\text{vr}}$ ) is considered in this paper. The total partition function can be expressed as:

$$Z_t = Z_{\text{tran}} Z_{\text{vr}} \quad \dots (4)$$

According to quantum mechanics the translational energy for a particle of mass  $m$  in a cubical box of sides  $a$ ,  $b$  and  $c$  can be written as:

$$E_{\text{tran}} = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad \dots (5)$$

where,  $n_x$ ,  $n_y$  and  $n_z$  are the various quantum states.

Translational partition function corresponding to this energy can be written as

$$Z_{\text{tran}} = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-\frac{h^2}{8mKT} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)} \quad \dots (6)$$

Here approximation is made and summation is changed into integration.

$$Z_{\text{tran}} = \int e^{-\frac{h^2}{8mKT} \left( \frac{n_x^2}{a^2} \right)} dn_x \int e^{-\frac{h^2}{8mKT} \left( \frac{n_y^2}{b^2} \right)} dn_y \int e^{-\frac{h^2}{8mKT} \left( \frac{n_z^2}{c^2} \right)} dn_z \quad \dots (7)$$

Using standard result of integration, we get

$$Z_{\text{tran}} = \left[ \frac{a}{2} \left( \frac{8\pi mKT}{h^2} \right)^{1/2} \cdot \frac{b}{2} \left( \frac{8\pi mKT}{h^2} \right)^{1/2} \cdot \frac{c}{2} \left( \frac{8\pi mKT}{h^2} \right)^{1/2} \right] \quad \dots (8)$$

$$Z_{\text{tran}} = V \left( \frac{2\pi mKT}{h^2} \right)^{3/2} \quad \dots (9)$$

where  $V=abc$  (volume of enclosure)

$$\frac{Z_{\text{tran}}}{N} = \left( \frac{2\pi mKT}{h^2} \right)^{3/2} \frac{V}{N} \quad \dots (10)$$

where,  $m$ ,  $N$ ,  $K$ ,  $h$  and  $T$  represent the mass of molecule, total number of particles, Boltzmann's constant, Planck's constant and absolute temperature in Kelvin respectively.

In this study,  $Z_{\text{tran}}/N$  is considered instead of  $Z_{\text{tran}}$  as the quantity  $Z_{\text{tran}}/N$  is an intensive quantity and depends on the concentration  $N/V$  whereas  $Z_{\text{tran}}$  itself is proportional to  $V$  and independent of the number of particles. Using ideal gas equation, Eq. (10) can be written as:

$$\frac{Z_{\text{tran}}}{N} = \left( \frac{2\pi mKT}{h^2} \right)^{3/2} \frac{KT}{P_0} \quad \dots (11)$$

where  $P_0$  ( $1.01325 \times 10^5 \text{ Nm}^{-2} \text{ atm}^{-1}$ ) denotes standard state of one atmospheric pressure.

Translational contribution to the thermodynamical quantities can be calculated using following relations:

$$\text{Free energy } F_{\text{tran}} = -\frac{3}{2} RT \ln m - \frac{5}{2} RT \ln T + 7.2836T$$

$$\text{Enthalpy } H_{\text{tran}} = \frac{5}{2} RT$$

$$\text{Entropy } S_{\text{tran}} = \frac{5}{2} R + \frac{F_{\text{tran}}}{T}$$

$$\text{Heat capacity at constant pressure } Cp_{\text{tran}} = \frac{5}{2} R$$

If it is assumed that rotational and vibrational motions do not interact with each other, total partition function will be the multiplication of rotational, vibrational and translational partition functions. But in actual case both types of motion affect each other. There are coupled rotational and vibrational motions and due to involvement of non-rigidity, anharmonicity and stretching effect, the  $D_e$ ,  $\omega_e x_e$  and  $\alpha_e$  have to be considered. Then total internal energy can be taken as:

$$E = \omega_0 v - \omega_e x_e \left( v + \frac{1}{2} \right) + B_e J(J+1) - D_e J^2 (J+1)^2 - \alpha_e \left( v + \frac{1}{2} \right) J(J+1) \quad \dots (12)$$

Putting  $B_0 = B_e - \frac{\alpha_e}{2}$ ,  $\omega_0 = \omega_e - 2\omega_e x_e$  and  $\omega_0 x = \omega_e x_e$  energy expression can be written as:

$$E = \omega_0 v - \omega_0 x v(v-1) + J(J+1)[B_0 - D_e J(J+1) - \alpha_e v] \quad \dots (13)$$

For simplification, further substitution of  $u = \frac{hc\omega_0}{KT}$ ,

$$y = \frac{hcB_0}{KT}, \quad \beta = \frac{D_e}{B_0}, \quad \delta = \frac{\alpha_e}{B_0} \text{ gives:}$$

$$E = uv[1 - (v-1)x] + J(J+1)y[1 - \beta J(J+1) - v\delta] \quad \dots (14)$$

Corresponding to this energy vibrational-rotational partition function  $Z_{vr}$  can be simplified as:

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

$$Z_{vr} = Z_1 Z_C \quad \dots (16)$$

where,  $Z_1$  represents the ideal partition function which is valid for perfectly rigid-rotator harmonic oscillator model and  $Z_C$  represents corrected partition function and gives contribution due to centrifugal stretching, non-rigidity and anharmonicity of diatomic molecule. The  $\sigma$  is called symmetry number and is defined as the number of regions of phase space included in the partition function calculation, which differ only by the exchange of indistinguishable particles. In quantum theory the symmetry number arises from the fact that only a fraction of the rotational states are allowed for a symmetrical molecule and this fraction is  $1/\sigma$ . For homonuclear molecule its value is one and for heteronuclear molecule its value is two. Expressions for  $Z_1$  and  $Z_C$  can be written as:

$$Z_1 = \frac{1}{\sigma y(1 - e^{-u})} \quad \dots (17)$$

$$Z_C = \left[ 1 + \frac{2\beta}{y} + \frac{\delta}{e^u - 1} + \frac{2xu}{(e^u - 1)^2} + \frac{y}{3} + \frac{y^2}{15} \right] \quad \dots (18)$$

With the help of vibrational-rotational partition function its contribution to free energy, enthalpy, entropy and heat capacity can be estimated by the following formulae:

$$\text{Free energy } F_{vr} = -RT \ln Z_{vr}$$

$$\text{Enthalpy } H_{vr} = RT^2 \frac{\partial}{\partial T} (\ln Z_{vr})$$

$$\text{Entropy } S_{vr} = R[(1 + \ln Z_{vr})] + RT \left[ \frac{\partial}{\partial T} (\ln Z_{vr}) \right]$$

Heat capacity at constant pressure

$$Cp_{vr} = RT \frac{\partial}{\partial T} (\ln Z)$$

Finally, thermodynamical quantities like free energy, enthalpy, entropy and heat capacity of tin chalcogenides are calculated by adding translational contribution and vibrational-rotational contribution.

### 3 Results and Discussion

The calculated thermodynamical data are listed in Tables 1 and 2. The spectroscopic constants from which the thermodynamical quantities are derived are presented in Table 3 (Ref.14). Table 4 (Ref.14) shows the comparison of calculated and reported values of thermodynamical quantities of SnO molecule. There is an excellent agreement between calculated and reported values of entropy and heat capacity of SnO

molecule. For the calculation of  $Z_{vr}$ ,  $B_0 = B_e - \frac{\alpha_e}{2}$  has

been used which is due to the fact that during vibration, rotation also occurs. Therefore instead of taking  $B_e$ ,  $B_0$  has to be considered for getting better results. Similarly deviation from harmonic behaviour has been introduced by including  $\omega_0 x = \omega_e x_e$ . These substitutions give accurate as well as simplified expressions. Results of the study reveal that free energy, enthalpy and entropy increase continuously with temperature while heat capacity initially increases with temperature and remain almost constant beyond a particular temperature. At low temperatures only translational part of motion gives its contribution but as temperature increases rotational and vibrational motions are excited. Beyond a certain value of temperature there is no further increase in molecular motion and therefore heat capacity becomes almost constant. Enthalpy of any system represents the quantity of heat contained in that system and it depends on internal energy, pressure and volume. In the case of ideal gas, internal energy is the only function of temperature and therefore value of enthalpy increases with temperature. Entropy is a

Table 1 — Calculated thermodynamical quantities for SnO and SnS molecules

<i>T</i>	SnO molecule				SnS molecule			
	<i>F</i>	<i>H</i>	<i>S</i>	<i>C<sub>p</sub></i>	<i>F</i>	<i>H</i>	<i>S</i>	<i>C<sub>p</sub></i>
100	17.03	2.08	199.34	29.08	17.96	2.08	208.70	29.45
200	38.09	5.81	219.65	29.90	40.10	5.80	229.96	32.36
300	60.71	8.68	232.11	31.73	63.70	8.45	243.54	34.47
400	83.40	11.35	241.47	33.32	88.58	10.79	253.63	35.56
500	108.94	13.85	249.04	34.43	114.35	13.00	261.65	36.15
600	134.16	16.21	255.40	35.17	140.86	15.17	268.29	36.50
700	159.98	18.21	260.88	35.68	167.97	17.32	273.95	36.72
800	186.30	20.73	265.68	36.04	195.60	19.45	278.88	36.87
900	213.08	22.94	269.96	36.30	223.70	21.59	283.24	36.97
1000	240.26	25.13	273.81	36.49	252.22	23.72	287.16	37.05
1100	267.81	27.31	277.31	36.63	281.10	25.85	290.71	37.10
1200	295.69	29.48	280.51	36.74	310.32	27.99	293.95	37.15
1300	323.88	31.64	283.47	36.84	339.85	30.13	296.94	37.18
1400	352.35	33.81	286.22	36.91	369.67	32.27	299.71	37.21
1500	381.08	35.97	288.78	36.97	399.75	34.42	302.29	37.23
1600	410.06	38.14	291.18	37.01	430.08	36.57	304.71	37.24
1700	439.27	40.31	293.44	37.05	460.64	38.73	306.98	37.26
1800	468.70	42.48	295.57	37.09	491.43	40.89	309.12	37.27
1900	498.34	44.65	297.59	37.11	522.42	43.06	311.15	37.28
2000	528.17	46.83	299.51	37.14	553.61	45.23	313.08	37.29
2100	558.19	49.00	301.34	37.16	584.98	47.41	314.91	37.29
2200	588.39	51.19	303.08	37.18	616.53	49.60	316.66	37.30

*F* is free energy (kJ/mole), *H* is enthalpy (kJ/mole), *S* is entropy (J/mole/K), *C<sub>p</sub>* is specific heat (J/mole/K) and *T* is temperature (K)

Table 2 — Calculated thermodynamical quantities for SnSe and SnTe molecules

<i>T</i>	SnSe molecule				SnTe molecule			
	<i>F</i>	<i>H</i>	<i>S</i>	<i>C<sub>p</sub></i>	<i>F</i>	<i>H</i>	<i>S</i>	<i>C<sub>p</sub></i>
100	18.92	2.08	218.65	30.73	19.57	2.08	225.51	32.00
200	42.02	5.75	241.23	34.38	43.40	5.66	248.96	35.35
300	66.90	8.11	255.58	35.85	69.07	7.87	263.55	36.39
400	92.99	10.27	265.93	36.47	95.97	9.96	274.10	36.81
500	120.00	12.39	274.12	36.78	123.80	12.04	282.35	37.00
600	147.76	14.49	280.86	36.96	152.38	14.14	289.13	37.12
700	176.13	16.60	286.59	37.07	181.58	16.24	294.87	37.19
800	205.03	18.72	291.56	37.14	211.31	18.35	299.90	37.23
900	234.40	20.83	295.95	37.19	241.50	20.47	304.26	37.26
1000	264.18	22.96	299.88	37.22	272.11	22.59	308.20	37.28
1100	294.33	25.09	303.45	37.25	303.10	24.73	311.77	37.39
1200	324.83	27.22	306.71	37.27	334.42	26.87	315.04	37.30
1300	355.63	29.37	309.71	37.28	366.06	29.02	318.04	37.31
1400	386.72	31.51	312.48	37.30	397.98	31.17	320.82	37.32
1500	418.08	33.67	315.07	37.30	430.17	33.34	323.41	37.33
1600	449.69	35.83	317.50	37.31	462.61	35.51	325.84	37.33
1700	481.53	38.10	319.77	37.32	495.29	37.68	328.12	37.34
1800	513.59	40.17	321.92	37.32	528.18	39.87	330.27	37.34
1900	545.86	42.35	323.95	37.33	561.28	42.06	332.30	37.34
2000	578.32	44.54	325.88	37.33	594.58	44.25	334.24	37.34
2100	610.97	46.73	327.72	37.33	628.06	46.46	336.07	37.34
2200	643.80	48.93	329.47	37.34	661.72	48.67	337.83	37.35

*F* is free energy (kJ/mole), *H* is enthalpy (kJ/mole), *S* is entropy (J/mole/K), *C<sub>p</sub>* is specific heat (J/mole/K) and *T* is temperature (K)

Table 3 — Spectroscopic constants of tin chalcogenides

Molecule	$\omega_e$	$\omega_e x_e$	$B_e$	$\alpha_e$	$MW$
SnO	822.13	3.72	0.35572	0.0214430	136
SnS	487.26	1.36	0.1368614	0.0050563	152
SnSe	331.20	0.74	0.0649978	0.0001705	200
SnTe	259.50	0.50	0.04247917	0.00009543	250

where  $\omega_e$ ,  $\omega_e x_e$ ,  $\alpha_e$ ,  $B_e$  and  $MW$  represent vibrational constant ( $\text{cm}^{-1}$ ), anharmonic constant ( $\text{cm}^{-1}$ ), stretching constant ( $\text{cm}^{-1}$ ), rotational constant ( $\text{cm}^{-1}$ ) and molecular weight (amu) respectively

Table 4 — Comparison of calculated and reported thermodynamical quantities of SnO molecule

$T$	$S_{\text{cal}}$	$S_{\text{obs}}$	$C_{\text{Pcal}}$	$C_{\text{Pobs}}$
300	232.11	232.10	31.73	31.6

where  $S$ ,  $C_p$  and  $T$  represent entropy (J/mol/K), specific heat (J/mol/K) and temperature (K) respectively

measure of molecular disorder of a system and molecules in a system at high temperature are highly disorganized either in terms of their locations or in terms of occupation of their available translational, rotational and vibrational energy states. In contrast, the molecules at low temperature have less disorderliness and thus have lower value of entropy. Behaviour of free energy is similar to that of entropy. Free energy is function of temperature as internal energy and entropy are also functions of temperature and hence its value increases with temperature. These results are in accordance with theoretical results of thermal physics.

#### 4 Conclusions

The paper deals with calculation of thermodynamical quantities of tin chalcogenides (SnO, SnS, SnSe and SnTe) from spectroscopic data. Prediction of thermodynamical quantities of chemically unstable species is quite important for

application. Due to involvement of spectroscopic data, results are highly accurate. These data may be useful to mechanical, chemical and electronic industry where the performance of the device is affected by its thermodynamic properties.

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