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ORIGINAL RESEARCH ARTICLE

Exploring the Thermodynamic Characteristics of Isoelectronic Diatomic Interstellar Molecular Species: Oxygen and Sulfur Containing Specie

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ABSTRACT

Interstellar molecular species, particularly isoelectronic diatomic molecules, exhibit distinct thermodynamic traits, setting them apart from other molecular species. This study investigates the thermodynamic properties of isoelectronic diatomic interstellar molecular species containing oxygen and sulfur atoms, employing computational methods to analyze entropy, free energy, heat capacity, and internal energy across a spectrum of interstellar temperatures. Graphical representations highlight intriguing trends, revealing Oxygen and sulfur-containing molecules' earlier responsiveness to temperature changes compared to oxygen counterparts. Notably, molecule size emerges as a key determinant, with larger mass molecules exhibiting higher entropy, free energy, and heat capacity. We showed the isoelectronic effect of these Sulfur and Oxygen containing molecular species (OH, SN, CO, CS, SiO, SiS, FeO, FeS, PO, PS O_2, OS, ZnO, ZnS, TiO, TiS) on several interstellar molecules at temperatures ranging from $0K$ to $2 \times 10^6 K$ (i.e., from the coldest place in the universe to the mean temperature of the interstellar medium). These findings offer valuable insights into the thermodynamic behavior of interstellar molecular species, paving the way for future research on the role of oxygen and sulfur atoms in complex molecular systems.

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Interstellar medium (ISM); Atoms-ISM; Isoelectronic molecules; Laws of thermodynamics, Astrochemistry

INTRODUCTION

A fascinating area of astrophysics that provides insight into the intricate chemistry in the wide reaches of space is the study of interstellar molecular species. These extrasolar chemicals are essential for the development of stars, planets, and even the beginnings of life. These interstellar molecular species have several unique thermodynamic characteristics, especially in the case of isoelectronic diatomic molecules. Scientists may investigate the complex interplay between energy, temperature, and molecular behavior inside the interstellar medium by learning about the thermodynamic characteristics of these isoelectronic diatomic interstellar molecules. These characteristics include entropy, enthalpy, Free energy, heat capacity, internal energy, etc.… (Cernicharo, Agúndez *et al.,* 2021; Etim & Arunan, 2016, 2017; Shinggu *et al*., 2023.; Sil *et al.,* 2018).

Isoelectronic diatomic interstellar molecular species, regardless of the atomic elements of the molecules involved, are molecules made up of two atoms with the same amount of electrons. Diatomic interstellar molecules are crucial in determining how the interstellar medium is chemically structured because they have unique electrical structures and may combine to generate a variety of stable and reactive compounds of Oxygen (O) and sulfur (S), bringing intriguing dynamics into play. These molecules play pivotal roles in shaping the chemical landscape of the cosmos, influencing the formation of stars planets, and potentially the emergence of life itself. Investigating the unique thermodynamic characteristics of these molecules offers insights into their stability, reactivity, and spectroscopic properties in the diverse environments of interstellar space. Through the application of thermodynamic principles, scientists aim to unravel the complex interplay of energy, temperature, and

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molecular behavior in isoelectronic diatomic interstellar species, shedding light on their evolution and survival (Agúndez *et al.*, 2021; Cernicharo, Cabezas, Agúndez, *et al.*, 2021; Cernicharo, Cabezas, Endo, *et al.*, 2021; Etim, 2023; Etim, 2017; Etim *et al.*, 2021; Etim & Arunan, 2016).

Oxygen and sulfur-based diatomic interstellar species frequently develop through intricate chemical processes, including ion-molecule interactions, photodissociation, and radiative association mechanisms (Heays *et al.*, 2017). Theoretical simulations, laboratory studies, and astronomical observations all help to reveal the fundamental processes that led to their genesis and the circumstances that made them possible. Scientists investigate these diatomic species to understand the complicated interstellar chemistry and learn more about the development of molecular complexity (Samuel *et al.*, 2023). Diatomic interstellar species that include Oxygen and sulfur also have significant astrophysical consequences. For instance, sulfur monoxide (SO) and sulfur dioxide (SO_2) play important roles in the chemistry of sulfur in interstellar clouds, influencing the creation of other compounds containing sulfur. Diatomic species that include Oxygen, such as the oxygen molecule *(O_2)* and carbon monoxide *(CO)*, serve as important tracers of the physical environments (Booth *et al.,* 2023; Cabezas *et al.,* 2022; Samuel *et al.,* 2023; Etim, Gorai, Das, & Arunan, 2018; Etim, Gorai, Das, Chakrabarti, *et al.,* 2018; Mondal *et al.,* 2021; Etim and Arunan, 2017; Etim *et al.*, 2017a; Etim *et al.*, 2017b).

Thermodynamics provides a framework for analysing and understanding the changes in energy and matter, which also offers insights into molecules' physical characteristics and behavior. Scientists study these molecules' stability, reactivity, and spectroscopic properties in the particular conditions of interstellar space by applying thermodynamic concepts to isoelectronic diatomic interstellar species. Diatomic interstellar molecules containing Oxygen and sulfur are fascinating research targets because of their distinctive thermodynamic features, such as entropy, enthalpy, free energy, internal energy, and heat capacity. These qualities control the stability and reactivity of these molecules in the interstellar medium through factors including bond energies, enthalpy changes, and equilibrium constants. Investigating these thermodynamic properties contributes to our knowledge of how these species develop, evolve, and survive in various interstellar environments, from dense molecular clouds to diffuse interstellar medium (Samuel *et al.*, 2023).

This work aims to derive the partition functions q and establish suitable thermodynamic properties for isoelectronic diatomic interstellar molecular species containing Oxygen and Sulfur. The parameters obtained in this study will find applications in modeling a wide range of astrophysical environments, such as the interstellar medium, protoplanetary disks, star-forming regions, etc. The outline of our paper is as follows: In Section 2, we present the methodology of our work, while in Section 3, we discuss the derived results, and we retire with concluding remarks in Section 4.

THEORY AND CALCULATION

For all the presented quantum chemical computations, the GAUSSIAN 09 software suite has been a very useful tool (Frisch *et al.,* 1999). This program's computation of the partition function is succinctly described as explored by (McQuarrie & Simon, 1999) and in the white paper titled *"Thermochemistry in GAUSSIAN"* where they provided a detailed description of the equations utilized in the program's calculation of the various partition functions (Ochterski, 2000) Following this trend, we also applied the GAUSSIAN 09 software suite to derive the partition functions (i.e., total q, translational q_t, electronic q_e, rotational q_r and vibrational q_v) of isoelectric interstellar molecules made of Sulfur and Oxygen atoms as shown in Table 1 *(OH, SN, CO, CS, SiO, SiS, FeO, FeS, PO, PS O_2, OS, ZnO, ZnS, TiO, TiS).* The partition functions were computed through the optimization and frequency calculations of the Oxygen and sulfur-containing interstellar molecules using the popular compound model G4, the fourth-order Gaussian theory. Since the particles are assumed to not interact, the equations in this study apply to ideal gases for all the systems in consideration. The degree of the system's non-ideality under examination determines the error induced by this assumption. However, it is necessary to state that since the systems under discussion are all isomers with several similar features, this inaccuracy can be negligible (Etim & Arunan, 2017). For this work, we shall remind our readers of the textbook definition of partition functions used in deriving our data. We begin with the translational partition function, which is defined as:

$$q_t = \left(\frac{2\pi n k_B T}{\hbar^2}\right)^{\frac{3}{2}} \frac{k_B T}{P} \tag{1}$$

Where q_t= translational partition function; m= mass of the molecule; k_B= Boltzmann constant; T=Temperature; $\hbar$=Plank's constant; P=pressure. The equation for determining the electronic partition function q_e is given as:

$$q_e = \omega_0 e^{-\frac{\varepsilon_0}{k_B T}} + \omega_1 e^{-\frac{\varepsilon_1}{k_B T}} + \omega_1 e^{-\frac{\varepsilon_2}{k_B T}} + \omega_3 e^{-\frac{\varepsilon_3}{k_B T}} + \cdots + \omega_n e^{-\frac{\varepsilon_n}{k_B T}} \tag{2}$$

As outlined in the paper, ε_n is the energy of the n_{th} level, and ω is the degeneracy of the energy level. The first (which is greater than $k_B T$) and higher excited states are assumed to be inaccessible at any temperature, thereby reducing q_e to:

$$q_e = \omega_0 \tag{3}$$

This equation is simply the electronic spin multiplicity of the molecule under consideration. Equations (4) and (5) are used in computing the rotational partition function for

linear molecules and nonlinear polyatomic molecules respectively.

$$q_r = \frac{1}{\sigma_r}\left(\frac{T}{\theta_r}\right) \quad (4)$$

$$q_r = \frac{\pi^{\frac{1}{2}}}{\sigma_r}\left(\frac{T^{\frac{2}{3}}}{(\theta_{r,x}\theta_{r,y}\theta_{r,z})^{\frac{1}{2}}}\right) \quad (5)$$

The parameter σ_r in Eqs. (4) and (5) is called the symmetry number, which is the number of indistinguishable orientations of the molecule. The quantity θ_r, $\theta_r(x, y, z)$ is the characteristic temperature for rotation (in the x, y or z plane).

For all the calculations reported here, only equilibrium structures were considered with no imaginary frequency. Hence, the vibrational partition function is computed considering real modes only. The zero-point energy is included in computing the vibrational partition function; therefore, the first vibrational level is chosen to be the zero of the energy $(V = 0)$ and the partition function for each vibrational level is given as

$$q_{v,K} = \frac{1}{1 - e^{-\frac{\theta_{v,K}}{T}}} \quad (6)$$

while the overall vibrational partition function is given as

$$q_v = \prod_K^n \frac{1}{1 - e^{-\frac{\theta_{v,K}}{T}}} \quad (7)$$

where K is the index of vibrational modes and $\theta_{v,K}$ is the characteristic temperature for vibration K. (McQuarrie & Simon, 1999)

Table 1: Molecular partition function(q) of vibrational temperature (k) of isoelectronic interstellar molecular species containing Oxygen and Sulfur.

Molecules	Partition Function (KCal/Mol)					
	q_e	q_t	q_r	q_v	q	Vibrational Temprature (K)
HO	0	0.889	0.592	5.49	6.971	5524.89
HS	0	0.889	0.592	4.002	5.483	4027.81
CO	0	0.889	0.592	3.041	4.522	4153.35
CS	0	0.889	0.592	1.901	3.382	1906.76
SiO	0	0.889	0.592	1.703	3.185	1703.03
SiS	0	0.889	0.592	1.135	2.617	1083.89
FeO	0	0.889	0.592	1.38	2.861	1359.77
FeS	0	0.889	0.592	0.995	2.477	911.99
PO	0	0.889	0.592	3.622	5.103	3644.91
PS	0	0.889	0.592	1.919	3.401	1925.78
O2	0	0.889	0.592	1.814	3.295	1817.44
OS	0	0.889	0.592	1.409	2.89	1391.76
TiO	0	0.889	0.592	1.698	3.179	1697.31
TiS	0	0.889	0.592	1.150	2.631	1100.71
OH+	0	0.889	0.592	4.644	6.125	4674.16
SH+	0	0.889	0.592	3.857	5.338	3881.60
NO+	0	0.889	0.592	3.098	4.576	3117.43
NS+	0	0.889	0.592	1.803	3.285	1806.61

Following the description of the Partition functions q, (i.e., translational, electronic, rotational, and vibrational motion) of these isoelectronic interstellar molecules, the application of statistical mechanics to derive the thermodynamic properties of these interstellar species is apparent since all these properties may be defined in terms of the partition function (Franz, 2014; Garanin, 2017; Gosachinskij & Morozova, 1996; Ochterski & Ph, 2000; Pathria & Paul, 2011; Rudoy & Oladimeji, 2017) The equations used in the calculation of these thermodynamic properties such as entropy S, internal energy U, free energy F, and heat capacity H resulting from (total q, translational q_t, electronic q_e, rotational q_r and vibrational q_v) partition functions as stated below are described in detail in 'Thermochemistry in Gaussian" (Ochterski, 2000) which are equivalent to standard texts on thermodynamics (Adkins, 1979; Bipin K. Agarwal & Eisner, 1989; Franz, 2014; Gallavotti, 1999; Garanin, 2017; Matus *et al.*, 2019; Pathria & Beale, 2011; Pathria & Paul, 2011; Penrose, 1979; Sears & Salinger, 1982; Seddon & Gale, 2002; Shell, 2015; Smirnov, 2006; Stowe, 2007) These terms are grouped according to the translational$t$,

electronic e, rotational r and vibrational v motion is derived by simply using the relations:

$$S = Nk_B + Nk_B \ln\left(\frac{q(V,T)}{N}\right) + Nk_BT\left(\frac{\partial \ln q}{\partial T}\right)_V \quad (8)$$

$$U = Nk_BT^2\left(\frac{\partial \ln q}{\partial T}\right)_V \quad (9)$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} \quad (10)$$

respectively (University, 2008; Vaz, 2004) Where N=number of moles, k_B=Boltzmann constant, R=gas constant, V=volume and T=Temperature.

In performing the computation of these properties, we observe the interstellar isomers at different temperatures T from $0K$ (the temperature of a Black hole) up to $2 \times 10^6 K$ (the mean temperature of interstellar gas) (Chiang *et al.,* 2020; Goldsmith *et al.,* 1969) at constant pressure since the temperature plays a huge factor in observing thermodynamic properties and the thermal pressure of this region is at equilibrium. In *section 3*, we evaluate the numerical values of the thermodynamic properties of OH, SN, CO, CS, SiO, SiS, FeO, FeS, PO, PS O_2, OS, TiO, TiS, ZnO, ZnS, NS, and NO and present the results with relevant discussion.

RESULTS AND DISCUSSION

Following the method of statistical thermodynamics introduced in Section 2 to calculate the thermodynamics properties of isoelectric molecules made of Sulfur and Oxygen atoms located in the interstellar medium, we further analyzed and discussed our results by computing these properties, i.e., the entropy S, Free Energy E, Heat capacity C, and Internal energy U of interstellar molecules of interest against several values of interstellar temperature T.

We begin our analysis with entropy's S relation to temperature T, as illustrated in Figure 1. It is observed that all the molecules initially remain relatively unresponsive to the increase in temperature till $T \sim < 80K$ where FeS's entropy level began to rise as other molecules followed at a later temperature increase. This pattern was observed among all the interstellar molecules but at different temperatures and entropic values. The FeS molecule appears to have the best response to temperature increase while OH is the least. For every observed molecule, the molecules that contain the Sulfur atom react earlier to temperature increase than their counterparts made up of Oxygen atoms (Heay *et al.*, 2017). OH, which has the smallest mass, has the least entropy, while FeS has the most mass conversely has the highest entropy. This shows that the higher the mass, the higher the molecule's entropy. The continuous increase in entropy as the temperature increases indicates its agreement with the second law of thermodynamics, often referred to as the generalized second law of thermodynamics (GSLT), as this increase is from the enhanced thermal energy of the molecules, which leads to increased disorderliness in the form of random motion (Nammas, 2018; Tu *et al.*, 2019).

As shown in Figure 2, the free energy of all the molecules reduces linearly with increased temperature. This is most evident in oxygen molecules O_2 and least in HS, which at 100^0C, has reduced to $\sim -3 \times 10^{-21} J$ and $\sim -1 \times 10^{-21} J$ respectively. At $\sim 6000^0 C$ (the approximate temperature of our sun's surface), the free energy has reduced to $\sim -3 \times 10^{-21} J$ and $\sim -1 \times 10^{-21} J$ respectively. The plot also depicts that OH, which has the smallest mass, has the least free energy, while FeS has the most mass and, hence, the highest free energy (Shinggu *et al.*, 2023b; Alahira *et al.*, 2024). This divergence of the Free energy E continues with an increase in temperature, especially at the (the mean temperature of interstellar gas). To observe the Free Energy E of molecules in this region, the region is assumed to be isolated and at constant pressure p, volume v. In general, it appears that molecules made up of Oxygen tend to lose their initial Free Energy E faster than their Sulfur-contained counterparts as the temperature increases. This means the lower the mass, the faster the free energy is lost.

The reaction of the molecule's Internal energy U in relation to Temperature T, as illustrated in Figure 3, appears to be the most interesting result in this work. The FeS molecule appears to react early with an increase in temperature, such that at $T \approx 40K$, its internal energy U is 6.47×10^{11} while other molecules remain unreactive till $\approx 100K$. However, the rate of the FeS Internal energy remained steady from $\approx 150K$. This pattern appears to reverse with other molecules, especially OH, which is the least reactive molecule at lower temperatures, even till $\approx 200K$. However, from $\approx 300K$, we observe a spontaneous increase in the value of Internal energy U from the least reactive molecules, while the most reactive molecules at lower temperatures maintained a steady increase. This led to total reversal at higher temperatures.

Following the premise that the interstellar region is observed as a closed system through which energy can be transferred, the volume of matter that passes through it is very insignificant in relation to the vast size of the interstellar region. As shown in Figure 4, at absolute zero, the heat capacity of all the observed molecules remains non-zero, as expected for a non-adiabatic system. However, the rate of increase in the molecule's heat capacity C in relation to temperature differs. The FeS and SiS remain the most reactive molecules, while the least reactive are the OH and SiO, this differences between the most reactive and least reactive molecules continues to widen as their value diverges. This high reactivity of FeS is due to its large mass compared to the other molecules, meaning the increase in mass leads to an increase in the heat capacity of a molecule. Figure 4 is a graphical representation that indicates that among the substances plotted, OH, characterized by the smallest mass, exhibits

the lowest heat capacity. Conversely, FeS, with the greatest mass among the molecules considered, demonstrates the highest capacity. It is necessary to note that the heat capacity for all the *sulfide*-containing molecules responds better to an increase in temperature than their *-oxide* counterpart.

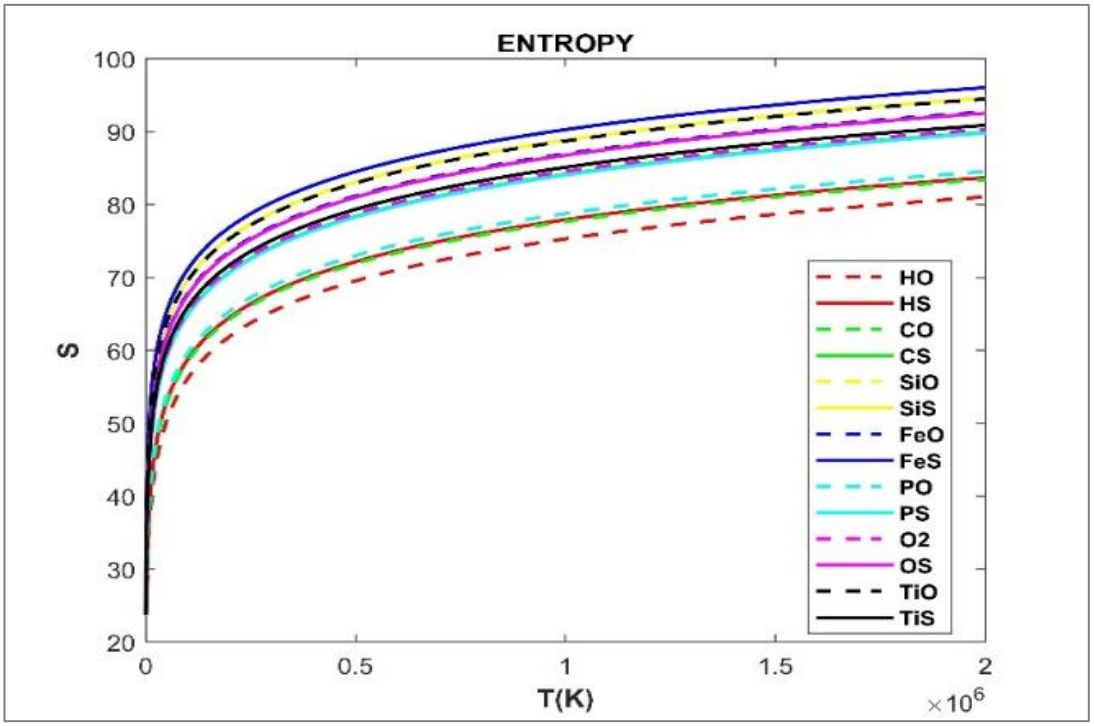

Figure 1: Plot of Entropy (S) against Temperature (T).

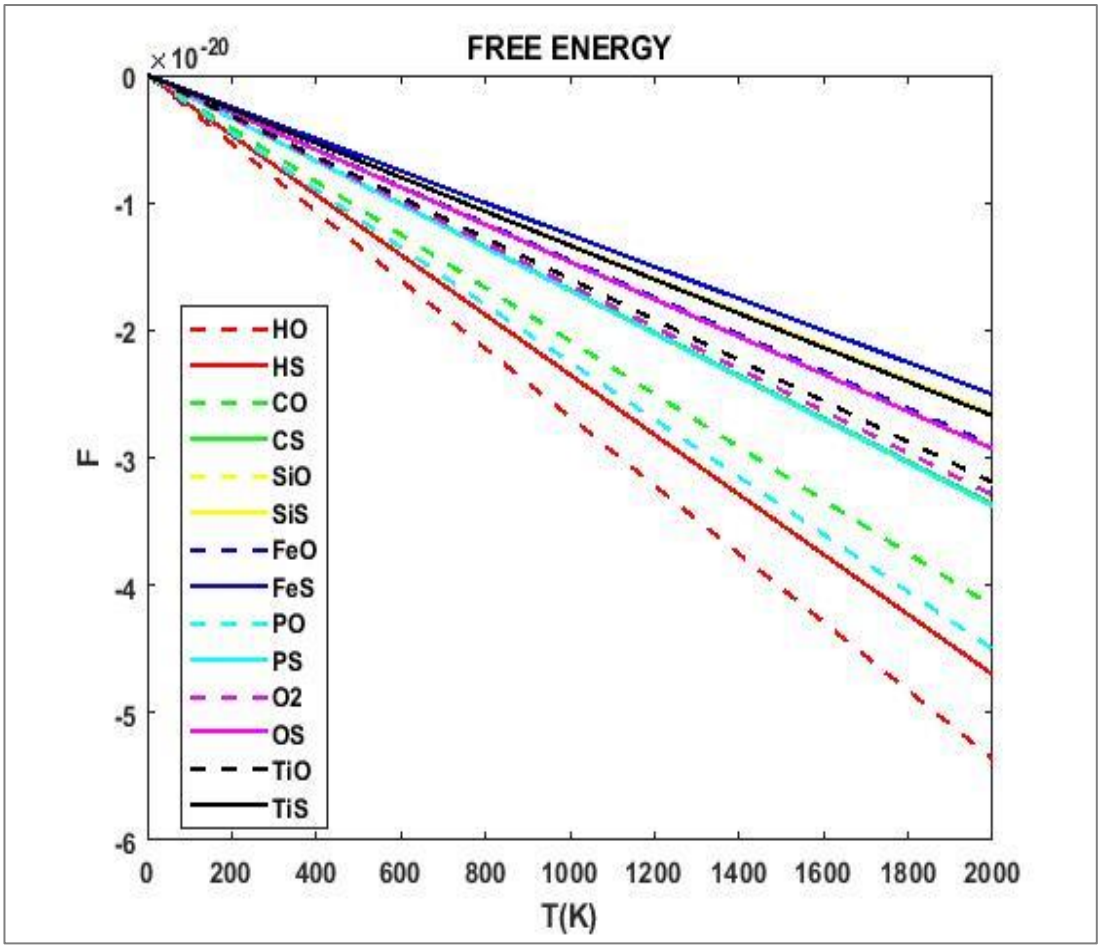

Figure 2: Free Energy (F) plot against Temperature (T).

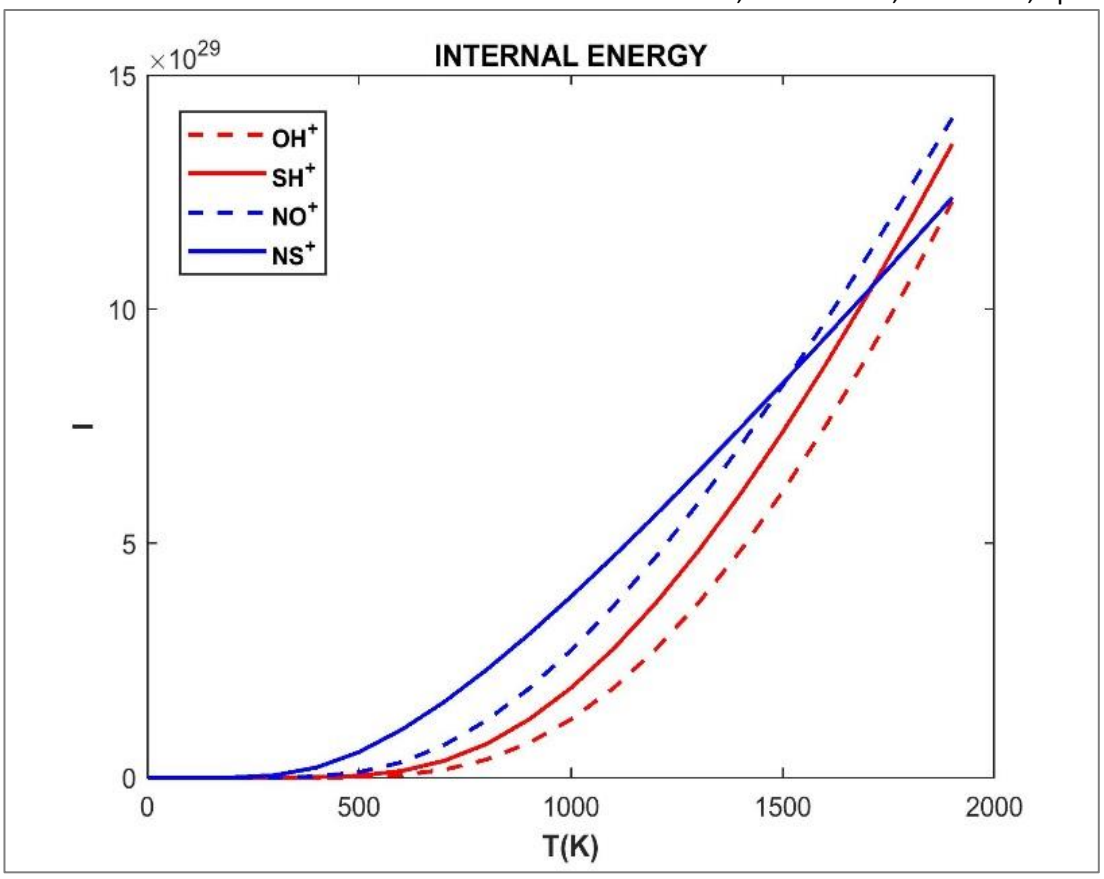

Figure 3: Internal Energy (I) plot against Temperature (T).

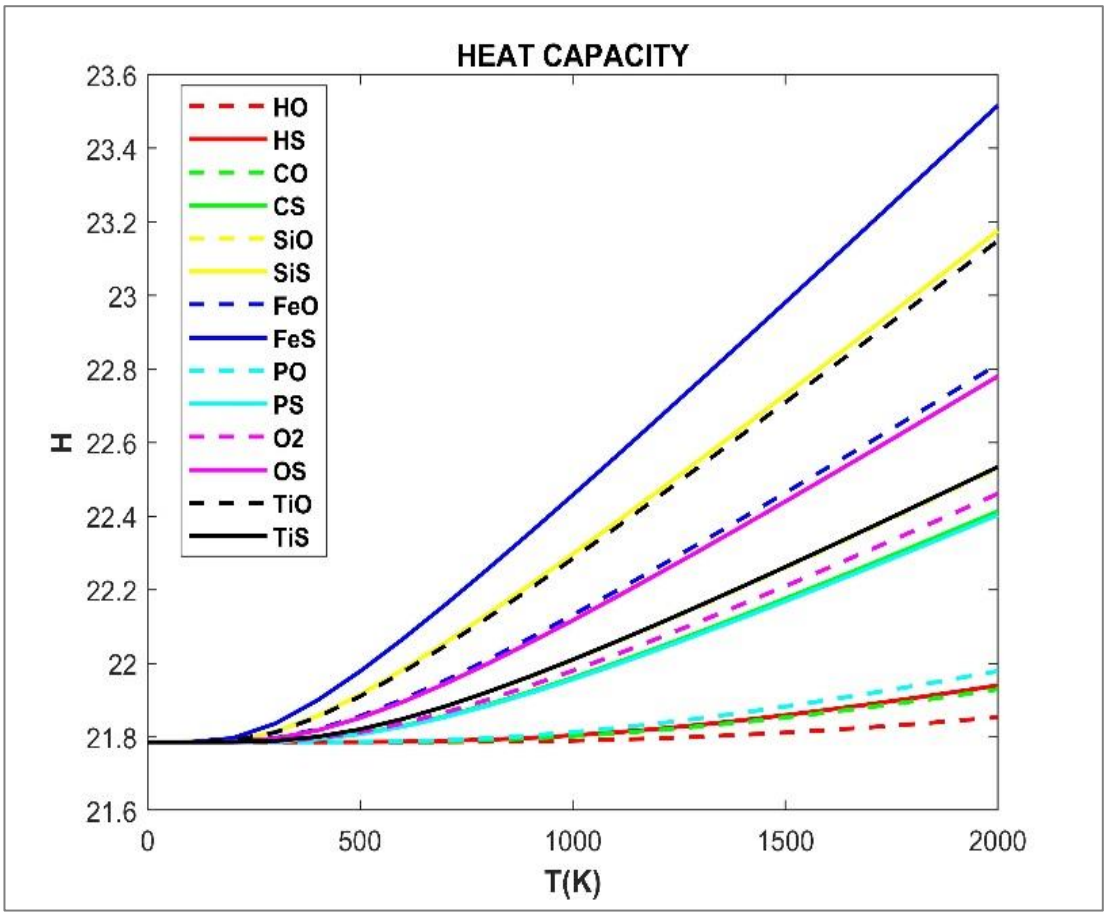

Figure 4: Heat Capacity (H) vs Temperature (T).

CONCLUSION

In this work, we observed the thermodynamic properties of isoelectronic diatomic interstellar molecular species, Oxygen, and Sulfur containing species by using GUASSIAN 09 to derive the partition functions (total q, translational q_t, electronic q_e, rotational q_r and vibrational q_v), the thermodynamic properties, e.g., entropy S, internal energy U, free energy F, and heat capacity H in relation to the temperature T from $0K$ (the temperature of a Black hole) up to $2 \times 10^6 K$ (the mean temperature of interstellar gas) was further computed and discussed. The thermodynamic analysis revealed intriguing trends among isoelectric molecules in the interstellar medium. Entropy (S) increased with temperature, indicating compliance with the second law of thermodynamics. Molecules with Sulfur atoms exhibited earlier reactivity to temperature changes, potentially linked to higher mass and entropy. Free Energy (E) decreased linearly with temperature, with Oxygen-containing molecules showing a faster decline, highlighting the impact of mass on energy reduction rates. Internal energy (U) displayed dynamic behavior, with FeS reacting early and steadily increasing, while other molecules showed delayed reactions and reversal at higher temperatures, suggesting complex molecular interactions. Heat capacity (C) varied significantly among molecules, with heavier molecules like FeS and SiS exhibiting higher reactivity, emphasizing mass's influence on capacity, particularly evident with increasing temperature. The increase in mass of the molecules leads to a slower loss in free energy The data computed will be useful in future thermodynamic studies on the effect of Oxygen and Sulfur atoms in interstellar molecular species made up of more than 2 atoms.

CONFLICT OF INTEREST STATEMENT

The authors declare that there is no conflict of interest.

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The authors have no relevant financial or non-financial interests to disclose.

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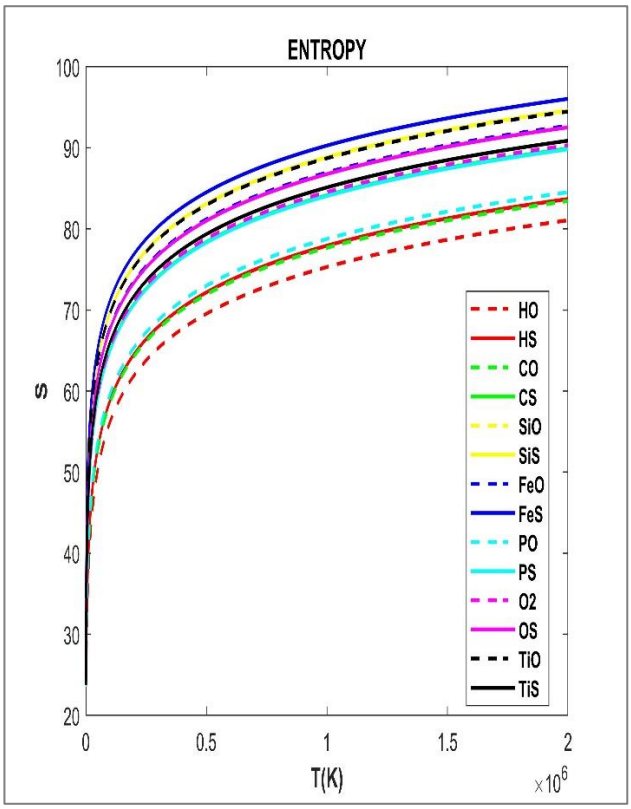
APPENDIX 1

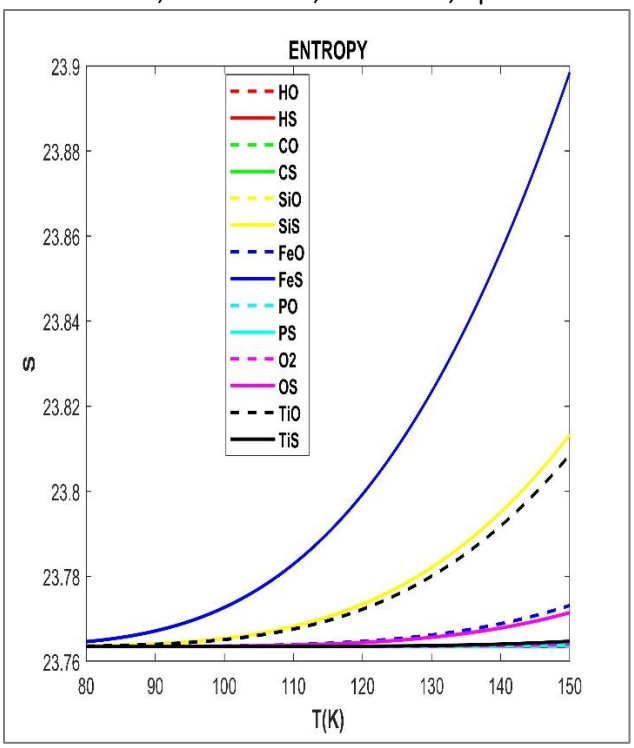
Table 2: *Mean thermodynamic properties of interstellar molecules with temperature* T

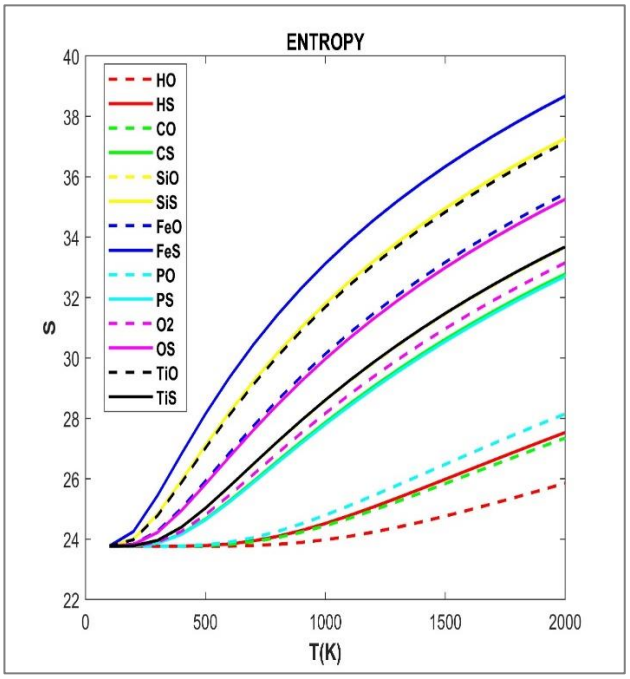
Temp T	Internal Energy U	Free Energy F	Entropy S	Heat Capacity C_V
0	0	0		21.7861495
10	207.861495	-1.33559E-22	23.76350195	21.7861495
20	415.7229902	-2.67118E-22	23.76350195	21.7861495
30	466418.0708	-4.00677E-22	23.76350195	21.7861495
40	6.47089E+11	-5.34236E-22	23.76350195	21.7861495
50	3.1378E+15	-6.67795E-22	23.76350195	21.7861495
60	8.98946E+17	-8.01354E-22	23.76350195	21.7861495
70	5.11459E+19	-9.34913E-22	23.76350196	21.7861495
80	1.05954E+21	-1.06847E-21	23.76350206	21.7861495
90	1.11922E+22	-1.20203E-21	23.76350302	21.78614951
100	7.37819E+22	-1.33559E-21	23.76350831	21.78614954
200	3.5785E+26	-2.67118E-21	23.77977112	21.78635577
300	6.07693E+27	-4.00677E-21	23.9573471	21.78965226
400	2.52769E+28	-5.34236E-21	24.39779454	21.80071921
500	6.02325E+28	-6.67795E-21	25.02716906	21.82086771
600	1.08935E+29	-8.01354E-21	25.74668996	21.84893997
700	1.6845E+29	-9.34913E-21	26.49144065	21.88324478
800	2.36208E+29	-1.06847E-20	27.22654967	21.92230041
900	3.1023E+29	-1.20203E-20	27.93523665	21.96496729
1000	3.89056E+29	-1.33559E-20	28.61048774	22.01040285
2000	1.29809E+30	-2.67118E-20	33.68748559	22.53437127
3000	2.28035E+30	-4.00677E-20	36.92362169	23.10055007
4000	3.28229E+30	-5.34236E-20	39.2676277	23.67807472
5000	4.29226E+30	-6.67795E-20	41.10065483	24.26022164
6000	5.30626E+30	-8.01354E-20	42.6044212	24.84469726
7000	6.32258E+30	-9.34913E-20	43.87877117	25.43050876
8000	7.34035E+30	-1.06847E-19	44.98425117	26.01715708
9000	8.3591E+30	-1.20203E-19	45.96028719	26.60436411
10000	9.37852E+30	-1.33559E-19	46.83396566	27.19196261
20000	1.95877E+31	-2.67118E-19	52.58963151	33.07657208
30000	2.98051E+31	-4.00677E-19	55.95946906	38.96589095
40000	4.00244E+31	-5.34236E-19	58.35090499	44.85638806
50000	5.02447E+31	-6.67795E-19	60.20599854	50.74735655
60000	6.04653E+31	-8.01354E-19	61.72178181	56.63856075
70000	7.06861E+31	-9.34913E-19	63.0033879	62.52989965
80000	8.09071E+31	-1.06847E-18	64.11358156	68.42132273
90000	9.11282E+31	-1.20203E-18	65.09285114	74.31280194
100000	1.01349E+32	-1.33559E-18	65.9688435	80.20432043
200000	2.03563E+32	-2.67118E-18	71.73191302	139.1203697
300000	3.05777E+32	-4.00677E-18	75.1031225	198.0368905
400000	4.07991E+32	-5.34236E-18	77.49503868	256.9535292
500000	5.10205E+32	-6.67795E-18	79.35035452	315.870215
600000	6.12419E+32	-8.01354E-18	80.86625855	374.7869243
700000	7.14634E+32	-9.34913E-18	82.14793745	433.7036472
800000	8.16848E+32	-1.06847E-17	83.25817837	492.6203784
900000	9.19062E+32	-1.20203E-17	84.23748035	551.5371153
1000000	1.02128E+33	-1.33559E-17	85.11349589	610.4538561
2000000	2.04342E+33	-2.67118E-17	90.87663951	1199.621351

APPENDIX 2

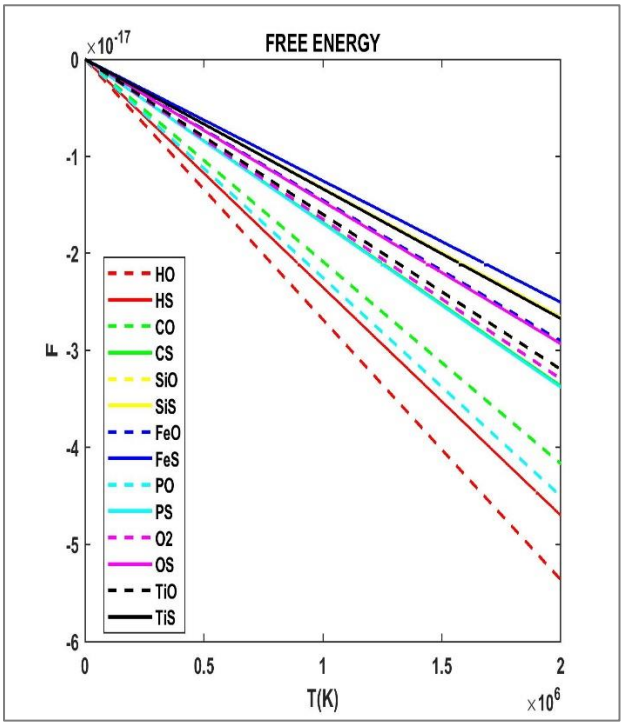
a. Entropy (S)

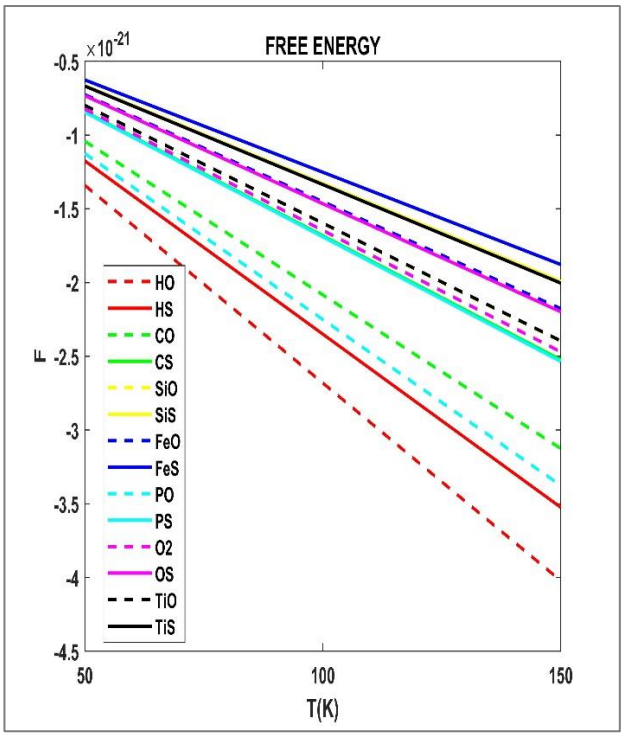




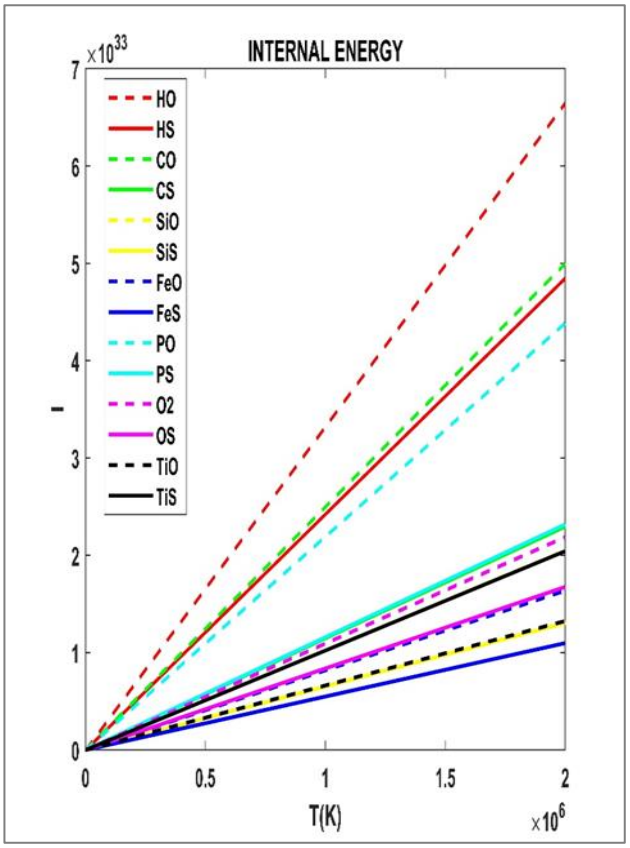


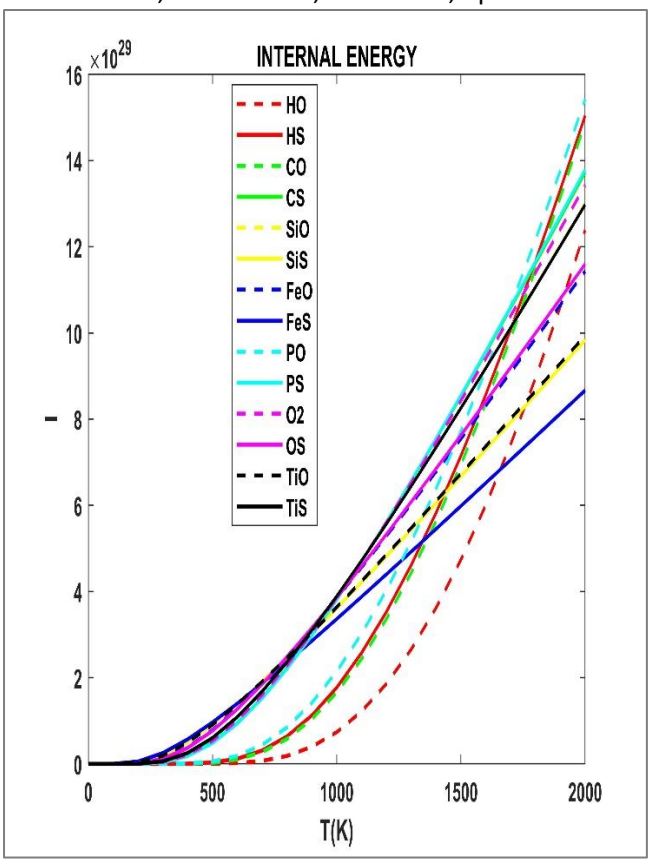
b. *Free Energy (F)*

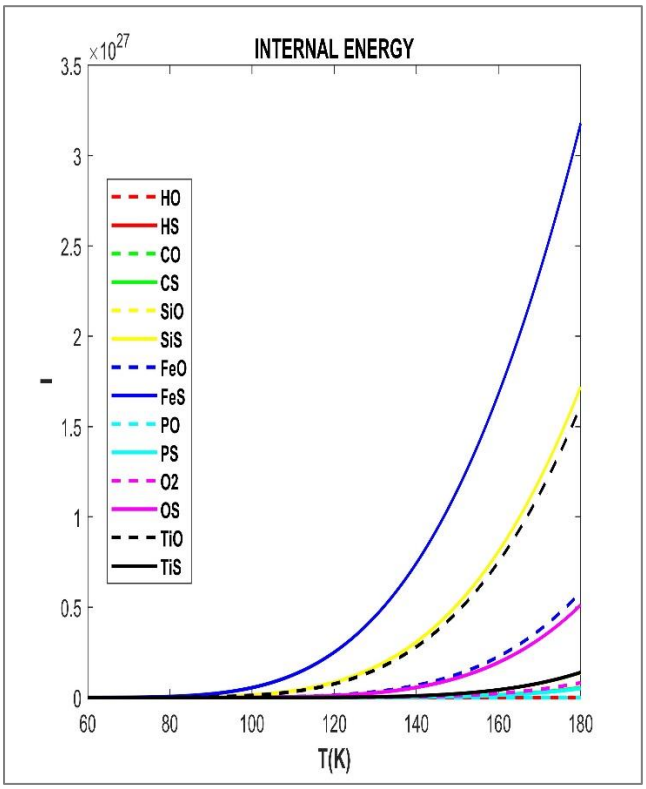




c. ***Internal Energy (U)***







d. ***Heat Capacity (C)***