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Calculate the Thermal Properties of (S_2F_2) Using Semi-empirical Quantum Mechanics (MNDO / PM_3)

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Abstract

In this paper, thermal properties were performed by using semi-empirical theoretical calculations to study the molecular structure of a nonlinear molecular system, the (S_2F_2) molecule in the infrared region, by using semi-empirical quantum programs in the (MNDO / PM_3) method. This study is under the condition of obtaining the stable structure of the molecule in which the molecule obtains the minimum value of the total energy. The thermodynamic properties were also calculated, including the heat of formation, whose value was (-61.002kcal / mol), the entropy and its value (78.2916 cal / mol.k), as well as the heat capacity (15.9454 cal / mol.k) and the enthalpy (3763.434 cal /mol), Gibbs Free Energy, it was valued at (-19567.5 cal / mol), these values were taken at the standard temperature 298 k, withdrawing these relationships in graphs and showing the changes in the state That the molecule passes through, and comparing these values with the experimental results.

Key words: S_2F_2, PM_3, thermal properties, molecular structure, semi-empirical.

1. Introduction

The sulfur halide molecules are of great scientific and industrial importance. made scientists interested in studying their properties theoretically and practically. All molecules have three main spectral transitions: (electronic transitions, their frequencies are located in the visible and ultraviolet regions, vibrational transitions and their frequencies are located in the near and middle infrared region, and rotational transitions and their frequencies are located in the far-infrared region and microwave).

The molecule of sulfur fluoride (S_2F_2) is one of the semiconducting substances treated with halogen (F), as its molecular weight is (Molecular Weight = 102.117 amu), and its melting point reaches the limits of (-120.5 ^oC), the boiling point reaches the limits of (-38.4^oC) [1]. It was prepared from the reaction of silver fluoride with sulfur at a temperature of 200 ^oC. S2F2 is rapidly dissociating, and therefore it is difficult to obtain it in the pure state [2]. Haider M.J. Haider studied spectral and thermal characteristics utilizing theoretical semi-empirical calculations to examine the molecular structure for non-linear systems, that moleculer (S2F2) in infrared, using semi-empirical programs and methods (MNDO/PM3). The aim of this paper thermal properties is achieved by using semi-empirical theoretical calculations to study the molecular structure of a nonlinear molecular system, which is the (S_2F_2) molecule in the infrared region, by using semi-empirical quantum programs in the (MNDO / PM_3) method.

2. Theoretical Background

To study the molecular spectra for any molecule, however complex, there are two main methods: Raman spectra, which depend on the principle of electromagnetic rays scattering, and the second is infrared frequencies, which depend on the interaction of electromagnetic radiation with the molecules of the material, where the molecule absorbs infrared radiation and converts its energy into vibrational energy for the atoms that form the molecule. According to quantum laws, this energy is quantized (meaning it takes specific values according to energy levels), and then the molecule moves from one level to another higher [3]. The approximation methods used in solving the Schrödinger equation for systems that are important for the chemical and physical point of view usually lead to complex calculations that could not be achieved, as the theoretical quantum calculations were complicated due to the complexities associated with mathematical solutions in terms of the high cost of huge calculations and the slow calculation speed that lasts for months to solve the particles Simple and years of solving medium particles. Because of the rapid development in the past few years in the field of high-speed electronic computers, approximation methods have been developed to provide solutions that sometimes come close in terms of accuracy to the approximate solutions of the Schrödinger equation.

The calculations of the semi-empirical methods are characterized by the speed of implementation, as quantum scientists have resorted to methods of approximation, and among these advanced semi-empirical methods that were used in the research is the MNDO-PM3 method, as this method rises to somewhat advanced levels, especially when dealing with molecules that contain electron-electron effects. Electrons or electron pairs, which are the property of all high-energy molecules (HEM). Therefore, the MNDO-PM3 method calculated within the WinMopac7.21 program made there is a great convergence between the results of this method and the experimental values measured experimentally, this convergence is the motivation for using the PM3 method. In this research, three basic mathematical programs were used [2]:

2.1. Pcmodel Program

A program in the form of Molecular Mechanics (MM)) that uses analytical functions (r, θ, Φ) represent the interior coordinates such as the length of the bond, the curvature of the angle, and the angle of the surfaces. (Angle dihedral). Compared with the appropriate method for reducing energy to an optimum (geometry improvement), by correcting the geometry of the molecule. In this program, a file is obtained that contains the internal coordinates of the position that have been distributed in the form of a geometrically or spatially formed particle. This file is in an image and is wrapped and through it the lengths of the bonds, the values of the interaction angles, the values of the angles of the surfaces, etc. This file is a gateway to the following program, WinMopac7.21.

2.2. WinMopac 7.21

Such other Molecular Modeling software, the applications of this software have grown in recent years, it has become a large presence in many research and studies and in various scientific fields. Substances due to their sensitivity, danger, and speed of reaction. These programs have also provided many efforts in the field of scientific research, including determining the curves of the band surfaces [5], determining the geometry of polymers, and the relative energies of other complex molecules [6], and others. We have also calculated, through this program, some properties and thermal functions of the molecules, such as heat of formation, heat capacity, enthalpy, and entropy, in addition to Gibb's free energy, with a graphical relationship for each state. Of thermal states. WinMopac7.21 reads the values generated from the PCMODEL program and thus calculates many quantities and molecular properties such as vibrational spectra, thermodynamic quantities, force constants .... and others.

2.3. Hyper Chem Program

This program is considered a supplementary program to calculate the remaining features. After drawing the molecule and identifying the atoms with specific dimensions, the preference for molecular engineering is performed to obtain the stable shape with the lowest voltage energy by choosing one of the quasi-experimental methods, as this program was based on the MNDO-PM3 method then, the properties are calculated [5].

3. Results and Discussion

To clarify the molecular structure, the calculation of the internal coordinates (r,θ,φ) is adopted through a PC-Model program, the angle between the joints and its amount (113°) was drawn, and Figure (1) shows the schematic figure For (S_2F_2) molecule and the angle between the bonds, indicating the internal axes of the molecule.

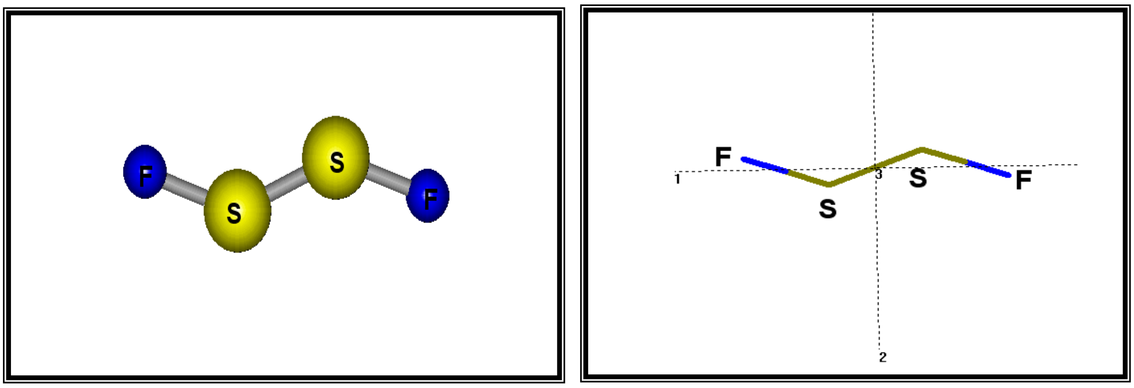

Figure 1. Represents the molecular structure of (S_2F_2) molecule with an indication of the internal axes and the angle between the bonds

As the number of atoms that constitute the molecule is (N = 4), so the number of degrees of freedom is (3N = 12) degrees, the number of vibrational patterns according to the rule (3N-6) for being a non-linear molecule is (6) degrees; There are (3) degrees for rotational motion and (3) degrees for translational motion. The structural shape of the molecule has been drawn through the

Hyper Chem program, which is the geometric shape at the equilibrium state of the molecule; that is, the lowest level of energy is standard in stable shape. After drawing the molecule using the internal coordinators of the molecule (r,θ,Φ), (where (r) represents the length of the bond, and (θ) is the angle between three atoms, which is measured (in degrees), while ()Φ is the angle of surfaces (Dihedral angle), which is also measured by degree, and obtaining the preference for the best geometrical position of the molecule (Optimization) by using a program of (PC-Model). We get the elementary matrix of the molecule, as in **Table (1)**, which contains the atoms that constitute the molecule, the distance between these atoms, the best position of these atoms (Opt.), and the values of the angles between the bonds and the angles of the surfaces [6].

Table 1. Initial Matrix of (S_2F_2) molecule

Atom	Distance (r) (Å)	Opt.	Angle (θº)	Opt.	Dihedral (φº)	Opt.	A	B	C
F	0.00000	0	0.000000	0	0.000000	0	0	0	0
S	1.462062	1	0.000000	0	0.000000	0	1	0	0
S	1.625056	1	113.058400	1	0.000000	0	2	1	0
F	1.502882	1	114.009300	1	180.000000	1	3	2	1

After obtaining the initial matrix and inserting it into the WinMopac7.21 program, the final matrix shown in Table 2 is obtained, then the main window is reopened again and the final matrix is copied instead of the primary matrix and then an execution instruction is given to the program to start the calculation.

Table 2. Final Matrix of (S_2F_2) molecule

Atom	Distance r(Å)	Opt.	Angle (θº)	Opt.	Dihedral (φº)	Opt.	A	B	C	Charge
F	0.000000	0	0.000000	0	0.000000	0	0	0	0	-0.225
S	1.5770059	1	0.000000	0	0.000000	0	1	0	0	0.2295
S	1.7497311	1	137.255868	1	0.000000	0	2	1	0	0.2294
F	1.5769474	1	137.348768	1	180.000000	1	3	2	1	-0.2295

3.1. Calculation of Heat of Formation (S_2F_2)

The temperature of the formation of the particle was calculated using the (Win Mopac7.21) program and by the method (MNDO / pm3), and for different values of temperature ranging from (100K) to (1000K) as in Table (3), a relationship was drawn between the two variables as in the figure (2) The relationship was linear, indicating the dependence of the Formation energy of the molecule on the temperature. As the temperature increases, the formation energy increases during the three phases. Also, the temperature of the formation of the molecule was calculated at the standard temperature (298K), which is then equal to (-61.002 Kcal / mol)[6].

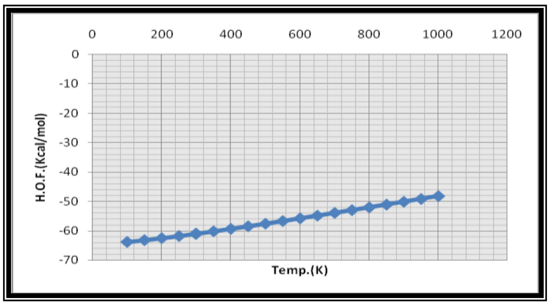

Figure 2. The relationship between the temperature of S2F2 formation and the temperature.

3.2. Calculation of Entropy for (S_2F_2) Molecule

The distribution and regularity of the atoms that constitute the molecule are closely related to this thermal property, so the entropy of the molecule, symbolized by the symbol (So), was calculated through the WinMopac 7.21 program for a some of temperatures shown in Table 3, and the entropy of the molecule was calculated at the standard temperature was 78.291 Cal / K / mol, which is close from the experimentally measured value (76.25 cal / K / mol)[6].

Table 3. the Entropy values of the molecule and the corresponding temperatures

Temp (K)	**Entropy(S°) (cal/K*mol) Cal.**	**Entropy(S°) (cal/K*mol) Exp.**
100	63.3731	-
150	68.4005	-
200	72.3005	-
250	75.5630	-
298	78.2916	76.25
300	78.3984	76.36
350	80.9142	-
400	83.1757	81.14
450	85.2281	-
500	87.1047	85.1
550	88.8317	-
600	90.4299	88.44
650	91.9163	-
700	93.3046	91.33
750	94.6065	-
800	95.8318	93.86
850	96.9885	-
900	98.0838	96.11
950	99.1237	-
1000	100.1133	98.13

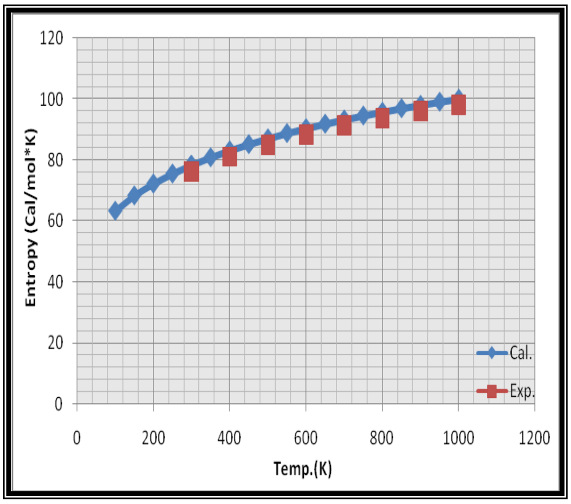

Figure 3. the relationship between entropy and temperatures of S_2F_2 for the two experimental and practical values.

It noticed through **Figure 3** the positive relationship between entropy and temperature and the observed increase in entropy. Since the entropy is a measure of the randomness of the atoms that constitute the molecule, so the entropy value increases with the increase in temperature, and the entropy of the gas state is greater than the liquid, and the liquid is greater than the solid with a variation in values, but in the S2F2 molecule, the entropy effect was large in the liquid phase approximately, i.e., at a temperature between (300K-100K) and gradually reduced until it reached a gaseous state. Also, we notice an approximation between the practically measured value (Cal.) And calculated by (MNDO / PM3) and the experimentally measured values (Exp.) Taken from the literature. And since the entropy signal is a positive signal indicating that the process is automatic for the transformation of (S2F2) because it changed from the state of the system to the form of irregularity when it transformed from solid to liquid, and also when it changed from the state of the system (liquid) to disorder (gas).

3.3. Calculation of Heat Capacity of (S_2F_2) Molecule

The heat capacity of the molecule, symbolized by C_p, was calculated utilizing (Win Mopac 7.21), from (100K-1000K) temperature. As well as the expense of its thermal capacity at room temperature was equal to (15.9454 Cal / K / mol) is close to the experimental value where (15.67 Cal / K / mol) [6].

Figure 4 shows the graphical relationship between heat capacity and the corresponding temperature, as we notice the rise in temperature, and it is proportional to it as the temperature increases. Every pattern has a vibration. The temperature ranges from (100K-350K), an increase in heat capacity in the phase and the liquid, and afterward by stability.

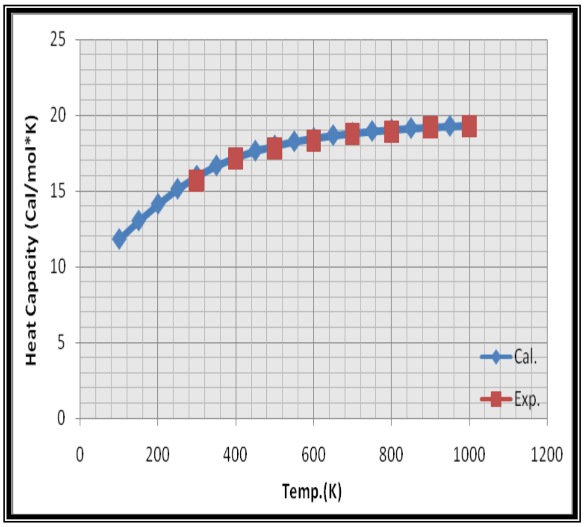

Figure 4. the graphical relationship between the heat capacity of S_2F_2 and the temperatures of the two experimental and practical values

Table 4. represents the heat capacity of S_2F_2 and the corresponding temperatures

Temp (K)	**Heat capacity (cal/K*mol) Cal.**	**Heat capacity (cal/K*mol) Exp.**
100	11.8223	-
150	13.0288	-
200	14.1304	-
250	15.1299	-
298	15.9454	15.67
300	15.9761	15.72
350	16.6619	-
400	17.2071	17.14
450	17.6389	-
500	17.9821	17.82
550	18.2570	-
600	18.4791	18.29
650	18.6603	-
700	18.8097	18.74
750	18.9340	-
800	19.0383	18.93
850	19.1266	-
900	19.2019	19.17
950	19.2665	-
1000	19.3224	19.28

3.4. Enthalpy Calculation of (S_2F_2) Molecule

From (WinMopac7.21) program, the Enthalpy of the molecule was calculated for different values of temperature ranging from (100K-1000K) as in Figure 6. The enthalpy value of the molecule was calculated at the standard temperature and was (3.7634 kcal / mol) as in **Table 5**. The amount of change in enthalpy $H^{\circ}_{298}$for each degree of temperature was calculated by subtracting the enthalpy value at room temperature from its value at the degree to which the change is to be found. We notice through Figure 5 that the relationship between enthalpy and temperature is a direct one, as the amount of change in the enthalpy increases with the increase in temperature. We cannot find the absolute values of the enthalpies of materials experimentally, but we can measure changes in the amounts of enthalpy following the laws of thermodynamics [8].

Table 5. The enthalpy values of S_2F_2 and the corresponding temperatures and the amount of change in enthalpy (Ho)

Temp (K)	**Enthalpy (kcal/mol) Cal.**	**(ΔH°) Cal.**	**(ΔH°) Exp.**
100	0.9835	-2.779	-
150	1.6056	-2.157	-
200	2.2844	-1.478	-
250	3.0170	-0.746	-
298	3.7634	0	0
300	3.7953	0.032	0.034
350	4.6119	0.848	-
400	5.4561	1.693	1.698
450	6.3307	2.567	-
500	7.2216	3.458	3.47
550	8.1278	4.364	-
600	9.0464	5.283	5.31
650	9.9750	6.211	-
700	10.911	7.148	7.18
750	11.855	8.091	-
800	12.805	9.042	9.07
850	13.759	9.995	-
900	14.717	10.95	10.98
950	15.679	11.91	-
1000	16.643	12.88	12.91

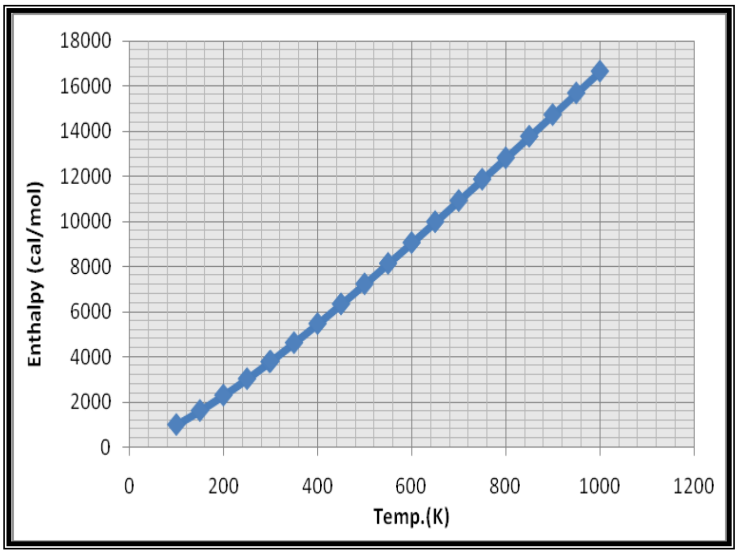

Figure 5. the graphical relationship between the enthalpy of S_2F_2 and the temperature

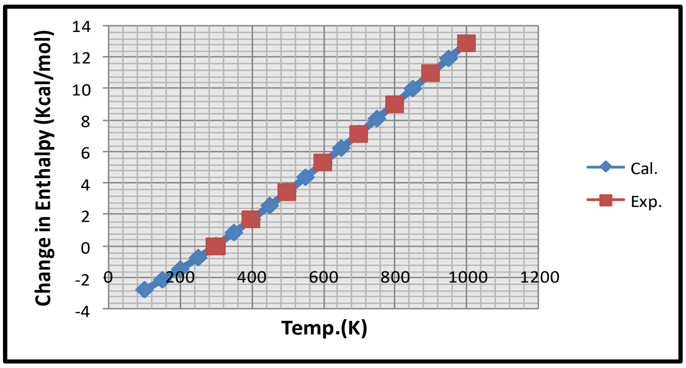

Figure 6. the graphical relationship between the change in enthalpy and temperature for the two experimental and practical values

3.5. Calculation of the Gibbs Free Energy (S_2F_2) Molecule

After calculating the enthalpy and entropy of the S_2F_2 molecule, and for different degrees of temperature, they were linked to compute an important function through which we know whether the reaction takes place automatically or not, which is the Gibbs free energy symbolized by the symbol G and is equal to: ($G = H-TS$) and therefore the amount of change in Gibbs free energy equal to: ($\Delta G = \Delta H-T\Delta S$). The Gibbs free energy of the molecule was calculated for different temperature values starting from 100 K up to 1000K, and the change was calculated for it. The practical value was compared with the experimental value, and these values were close to each other, as in **Table (6)**. As for the energy value of Gibbs at the standard temperature (-19567.5 Kcal / mol). It noticed through Figure 7 that the relationship between free Gibbs energy and temperature is a stable linear inverse relationship, as Gibbs energy decreases with increasing temperature. We also note from Figure 8 that the relationship between the change in the free energy of gypsum (ΔG) and the temperature is also a linear inverse relationship, and we also notice a great convergence between the practical and experimental values of the amount of change in the energy of Gibbs [9,10].

Table 6. free Gibbs energy values and thecorresponding temperature and the amount of change in free energy

Temp (K)	G.F.E. (kcal/mol)	(ΔG^o) Cal.	(ΔG^o) Exp.
100	-5353.74	1489	-
150	-8654.40	1481	-
200	-12175.6	1196	-
250	-15873.7	681	-
298	-19567.5	0	0
300	-19724.2	-32.0	-32.9
350	-23708.0	-874	-
400	-27814.1	-1951	-1954
450	-32021.9	-3115	-
500	-36330.7	-4403	-4421
550	-40729.6	-5792	-
600	-45211.5	-7277	-7308
650	-49770.5	-8846	-
700	-54401.2	-10501	10548
750	-59099.2	-12224	-
800	-63860.4	-14027	-14078
850	-68681.0	-15876	-
900	--73558.0	-17802	-17867

950	-78488.3	-19776	-
1000	-83469.3	-21808	-21867

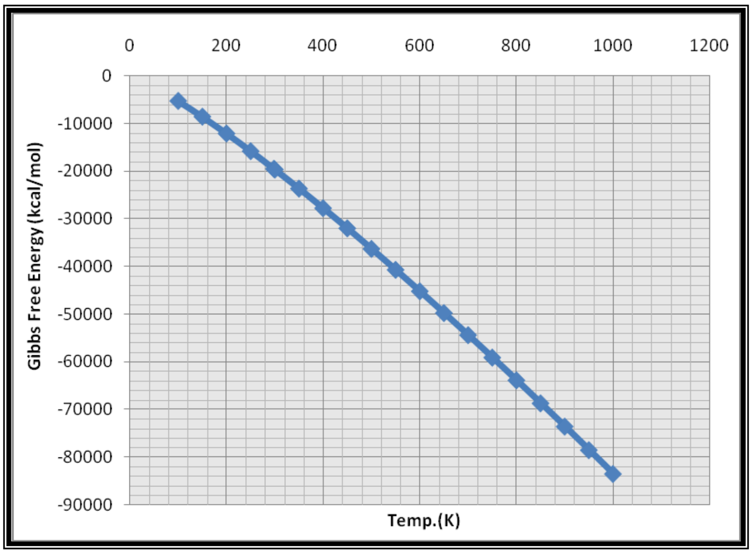

Figure 7. the graphical relationship between Gibbs energy and temperature of S_2F_2 molecule

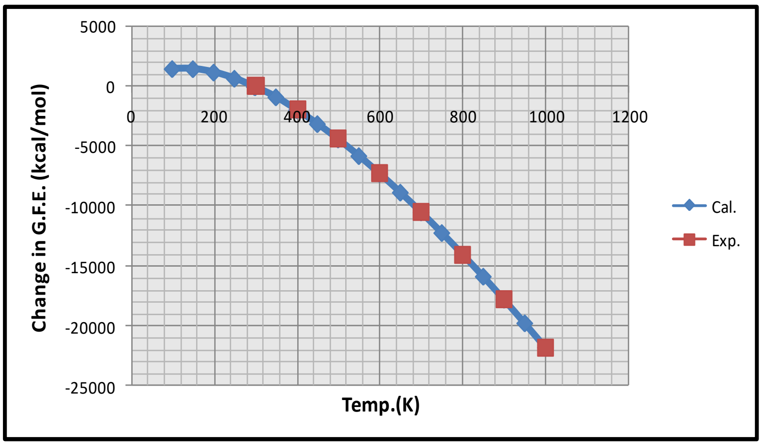

Figure 8. The graphical relationship between the change in Gibbs energy and the experimental and practical temperature

3.6. Comparison of Semi-Empirical Methods in Calculating Some of the Physical Properties of S_2F_2

Some optical spectral and thermal properties of S2F2 have been calculated by various methods WinMopac7.21 took these calculations when the equilibrium condition $r = r_{eq}$ (in the stable shape of the molecule) is achieved, as shown in **Table 8.**

Table 7. represents the calculation of some thermal properties of S_2F_2 by different semi-empirical methods when the equilibrium condition $r = r_{eq}$ is achieved.

PHYSICALPROPERTIES	MNDO-PM3	MNDO-AM1	MINDO/3	MNDO
FINAL HEAT OF FORMATION (kcal/mol)	-61.00164	-46.80588	-49.88321	-41.26043
NO.OF FIELD LEVELS	13	13	13	13
MOLECULAR WEIGHT (amu)	102.117	102.117	102.117	102.117
HEAT CAPACITY (cal/mol.k) at 298 K°	15.9454	16.2458	16.01254	17.12569
ENTHALPY(cal/mol) at 298 K°	3763.433	3658.356	3486.245	3325.236
ENTROPY(cal/mol.k) at 298 K°	78.2916	79.02453	78.98542	77.6632

4. Conclusion

By studying the thermal properties of (S_2F_2) molecule, the following could be concluded:

1. The temperature of the formation of the molecule was at (-61.00164cal / mol), and the negative sign for the amount of the Formation energy indicates that the molecule is exothermic.
2. The thermal properties increase with the increasing complexity of the molecule, so the entropy, heat capacity, and difficulty of the molecule were, respectively, (78.2916Cal / mol * k), (15.9454Cal / mol * k), (3.7634Cal / mol), respectively.
3. To find out the extent of this molecule being more stable, one can observe the value of Gibbs energy (-19567.5Cal / mol), through which it can be known that the less negative particle is more stable.
4. The stable position of (S_2F_2) molecule makes it take the shape of a boat (boat) or the shape of a chair (chair), as the balanced geometry and spectral and thermal properties of (S_2F_2) molecule have been calculated as it is more stable than other molecules.

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