Thermodynamic Functions of tri substituted benzaldehyde Derived from Vibrational Spectroscopy

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Abstract

Background

Thermodynamic functions assist in understanding the stability and viability of a molecular system. Information obtained from vibrational spectroscopy provides direct information about the population distribution and energies of vibrational modes. The substituents on substituted benzaldehydes have a significant impact on the vibrational contributions, especially at elevated temperatures.

Objective

The study derived thermodynamic properties of 2-hydroxy-3,4-dimethoxybenzaldehyde (a compound containing intramolecular hydrogen bonding) based on measured vibration data over an extended range of temperatures (100 K to 1500 K). The goal of this work was to provide a visual representation of changes in heat capacity (C), entropy (S), Gibbs free energy (G) and Helmholtz free energy (A) for the target compound as a function of temperature.

Methods

The basic infrared and Raman frequencies were used to get an overview of the vibrational data. The statistical thermodynamic approach of RRHO was applied using the ideal gas standard assumption. The thermodynamic properties were developed over the same temperature interval throughout the study.

Results

As the temperature increased, the enthalpic value went up in a gradual and orderly fashion resulting from the continuing progression of mode excitation that occurred with increases in temperature. The change in entropic value was not uniform, but there was increasing entropy from additional low-frequency modes associated with Methoxy. Increases in the values of Gibbs and Helmholtz free energy resulted from increasing temperature; the more negative the value of the -TS term, the lower the Gibbs and Helmholtz free energy values. The presence of hydrogen bonding at low temperatures helped to balance the greater thermodynamic contributions from hydrogen bonding to stabilised conformations.

Comparison with Literature

Increase in H and S observed are consistent with standard thermodynamic statistical expectations. G (Gibbs Free Energy) decrease is consistent with classical Gibbs Free Energy relationships at a constant pressure. A (Helmholtz Free Energy) decrease is also consistent with Helmholtz stability behaviour under a constant volume constraint. A logical increase in Entropy due to substitution is consistent with previously reported trends observed in the density of one or more Aromatic Derivatives.

Conclusion

This substituted benzaldehyde could be reliably assessed by determining thermodynamic functions, using vibrational spectroscopy. The low temperature contributions to thermodynamic functions were affected by the methoxy group on the benzaldehyde and the existence of an intramolecular hydrogen bond. The dataset can be used in the modelling, comparing and validating of other similar aldehydes.

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1. Introduction

1.1 Importance of Thermodynamic Functions

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The findings of thermodynamic analysis adequately define the range of molecular stability over a large thermodynamic range (Callen, 1985; Atkins & de Paula, 2006). Quantification of state functions such as energy, heat, and spontaneous change indicates how molecules energetically behave and what may occur (Çengel et al., 2019; Zemansky, 1968). The Trend of Enthalpy provides a measure of heat content at constant pressure (Moran & Shapiro, 2006; IUPAC, 2025).

1.2 Molecular Features of 2-Hydroxy-3,4-Dimethoxybenzaldehyde

The electronic character of the benzene ring of 2-Hydroxy-3,4-dimethoxybenzaldehyde is subject to a strong substituent effect (Atkins & de Paula, 2006). A hydrogen-bonding interaction occurs within the molecule between the phenolic hydroxyl group and the carbonyl oxygen of the aldehyde (Levine, 2002; Herzberg, 1945). Additionally, the two methoxy substituents support both intramolecular resonance donation as well as significantly increase the vibrational flexibility of the molecule (Herzberg, 1945; Pople, 1999).

1.3 Spectroscopic Basis for Thermodynamic Estimation

Molecular energy levels are indicated directly by vibrational states represented in the form of a frequency chart using either IR or Raman spectroscopy (Herzbergs 1945; Rao et al. 2023). The vibrational level data can be translated into thermodynamic temperature-dependent properties by applying principles of Statistical Thermodynamics (Reif, 1967; Callen, 1985). With increasing temperatures there are also an increase in the number of available microstates thus resulting in increased entropy (Atkins et al., 2019; Callen 1985). Gibbs Free Energy must be determined in order to establish whether or not a process occurs spontaneously within given boundaries of constant temperature and pressure (IUPAC 2008; Atkins & de Paula 2006). Helmholtz Energy is used in order to obtain thermodynamic equilibrium analysis at constant temperature/volume conditions (Levine 1978; Gold 2019).

1.4 Aim and Scope of the Present Work

Assessing how Enthalpy (ΔH), Gibbs Free Energy (ΔG), Entropy (S), and Helmholtz Free Energy (A) change as a function of temperature within the range of 100K to 1500K is the goal of this article (Atkins & de Paula, 2006; Callen, 1985). The relationships of temperature with all four variables are analysed using the standard definitions and conventions for thermodynamics established by IUPAC (IUPAC, 2025; IUPAC, 2008). The results of the analysis indicate that there are vibrational components contributing to the overall stability of chemical reactions in temperatures relevant to business (Reif, 1967; Levine, 2002).

2. Theoretical Framework

2.1 Statistical Thermodynamics Basis

Throughout this paper the RRHO statistical model was consistently applied in calculating the thermodynamic functions. The RRHO Model is used to relate molecular energy levels directly with macroscopic observables (Reif, 1967). Partition functions were calculated based on the assumptions of an ideal gas and dilute limit (Callen, 1985). The standard thermodynamic notation and conventions in this work used IUPAC recommendations without exception (IUPAC, 2025).

2.2 Rigid-Rotor Harmonic-Oscillator Approximation

The rigid rotor model (Atkins and De Paula, 2006) was used to calculate the rotational motion of a molecule. The vibrational motion of the molecule was calculated using the harmonic oscillator model (Atkins and De Paula, 2006), and the vibrational contributions were included in a separable manner with the assumption that the normal modes were independent (Herzberg, 1945). To maintain consistency in the thermodynamic comparisons between molecules, all anharmonic effects were ignored in the calculations (Atkins and De Paula, 2006).

2.3 Vibrational Contributions and Temperature Dependence

According to Boltzmann statistical theory of populations, each vibration mode contributes energy (Reif, 1967), with a significant amount of entropy originating from low-frequency modes when the temperature is increased substantially (Kittel and Kroemer, 1980) and most of the contribution from high-frequency modes are due to their zero-point vibrational energy terms (Herzberg, 1945). Assignment of vibration modes is necessary for precise calculation of thermal properties using vibrational spectra (Smith and Dent, 2005).

2.4 Thermodynamic State Functions Used

2.4.1 Internal Energy Components

As stated by Callen (1985), translational, rotational and vibrational contributions are all part of the internal energy of a molecule, and were assessed using an ideal gas statistical thermodynamics approach as described by Reif (1967). The vibrational contribution was evaluated using the harmonic oscillator approximation (Atkins & de Paula, 2006).

2.4.2 Enthalpy Formulation

Enthalpy is one of the forms of total heat energy available when measured at constant atmospheric

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conditions (Cengel et al., 2019), which was obtained by applying the principles of classical thermodynamics from Moran & Shapiro (2006). This relationship can also be defined as:

$$H(T) = U(T) + RT$$

The above equation continues to be applicable when gases behave according to both the ideal-gas law and the standard atmosphere (Çengel et al., 2019).

2.4.3 Entropy Definition and Calculation

The measurement of entropy indicates how disordered any given system is at the molecular level and how thermally dispersed energy (i.e., thermal energy) is across its component molecules (Callen, 1985). Entropy for a given substance may be determined by summing the contributions to entropy from the individual components at the molecular level (Atkins and de Paula, 2006).

$$S(T) = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}}$$

Translational entropy is a function of both molecular mass and accessible volume (Reif, 1967). Rotational entropy describes the degree of symmetry of a molecule and its moment of inertia (Tinoco, et al., 1995). Vibrational entropy increases substantially with the activation of low-frequency modes (Atkins, et al., 2019).

2.4.4 Gibbs Free Energy Expression

At constant temperature and pressure (IUPAC, 2008), Gibbs free energy indicates the amount of spontaneous change that can occur over time. It has been calculated by means of standard thermodynamic relationships (Atkins & de Paula, 2006). So far,

$$G(T) = H(T) - TS(T)$$

This quantity allows you to determine when a chemical reaction or process may occur under equilibrium conditions. (Gibbs, 1873)

2.4.5 Helmholtz Free Energy Expression

The Helmholtz energy is the measure of the useful work that can be achieved at a constant volume (Atkins & de Paula, 2006), and is calculated from a system's internal energy and entropy values (Reif, 1967) according to the following equation:

$$A(T) = U(T) - TS(T)$$

The Helmholtz energy is useful in comparing intrinsic thermal stability of a molecular system (Levine, 1978).

RRHO thermodynamic evaluation (Atkins & de Paula, 2006).

2.5 Standard State and Reporting Conditions

All values were reported based on the assumption that gases behave like perfect gases at normal atmospheric pressure (IUPAC 2000). Temperature dependence was established by evaluating a range of temperatures to see how trends form (Kittel & Kroemer 1980). Calculated functions are based on the results of vibrational contributions obtained directly from experimentally measured frequencies (Smith & Dent 2005).

3. Computational Methodology

3.1 Spectroscopic Inputs and Mode Assignment

The fundamental frequencies used in this study were derived from FTIR and Raman spectra measured experimentally using Fourier Transform infrared and Raman spectroscopy respectively. Mode assignments were done primarily on the basis of which vibrational bands exhibited the greatest contributions to the computation of the thermodynamic integrals (Herzberg, 1945). Because O–H stretching modes were very sensitive to hydrogen bonding effects, they were treated with great care (Herzberg, 1945). C=O stretching and methoxy C–O stretching modes were followed during our calculation of the entropy changes associated with the molecules (Atkins & de Paula, 2006). All of the non-degenerate vibrational modes of each molecule were also included in the

3.2 Computational Conditions and Assumptions

The thermodynamic properties of substances were obtained through the application of the laws of thermodynamics and the ideal gas law. Transition lines (thermodynamic curves) were produced using equal intervals of temperature from a low temperature of 100 K to a high temperature of 1500 K (Çengel et al., 2019). The energy associated with vibrations, translations, and rotation of the particles were added up consistently (Callen, 1985). The energy associated with vibration, rotation, and translation of molecules (zero-point energy) was accounted for in the internal energy and enthalpy (Atkins & de Paula, 2006). Additionally, zero-point energy was incorporated into the calculations of the internal energy and enthalpy.

3.3 Statistical Thermodynamics Implementation

Using the canonical ensemble relationship for partition functions (Reif, 1967), thermodynamic derivatives were determined from the temperature dependence of the natural logarithm of the partition function (ln(q)) (Atkins & de Paula, 2006). The standard statistical mechanics identities (Reif, 1967) were used to obtain entropy and free energies.

4. Results

4.1 Enthalpy Variation with Temperature

Increasing temperature will cause an increase in enthalpy resulting from the progressive population of the vibrational levels (Atkins & de Paula, 2006). At

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low temperatures, there was a gradual increase in enthalpy, which was only slight in magnitude (Atkins & de Paula, 2006). As the temperature increases beyond 500K, the increase in the slope was a result of increased vibrational excitation (Atkins & de Paula, 2006). Intramolecular hydrogen bonding stabilizes the conformations and lowers the low enthalpy (< 500 K) (Herzberg, 1945).

4.2 Entropy Behaviour Across the Range

As the number of vibrational states became accessible through thermal means, the rate at which entropy increased was not linear (Callen, 1985). The presence of methoxy groups added additional vibrational modes, which increased the value of the entropy (Atkins & de Paula, 2006). Above 400 K, there was an increase in entropy due to activation of additional modes at a higher rate (Reif, 1967).

4.3 Gibbs and Helmholtz Free Energies

As temperature increases, Gibbs free energy becomes increasingly less thermodynamically stable because the impact of the −TS term dominates (IUPAC, 2008). As temperature increases, Helmholtz free energy becomes less thermodynamically stable due to increasing amounts of entropy contribution (Atkins and de Paula, 2006). For thermal processes, as evidenced by their negative slope, their thermodynamic feasibilities improve (Callen, 1985).

5. Thermodynamic Function Values

5.1 Table description and data provenance

The table 1 shows the temperature-dependent thermodynamic properties for the molecule. Thermodynamics properties were calculated using vibrations' statistical thermodynamic approach through spectrum analysis (Atkins &de Paula, 2006).

5.2 Observed trends across temperature

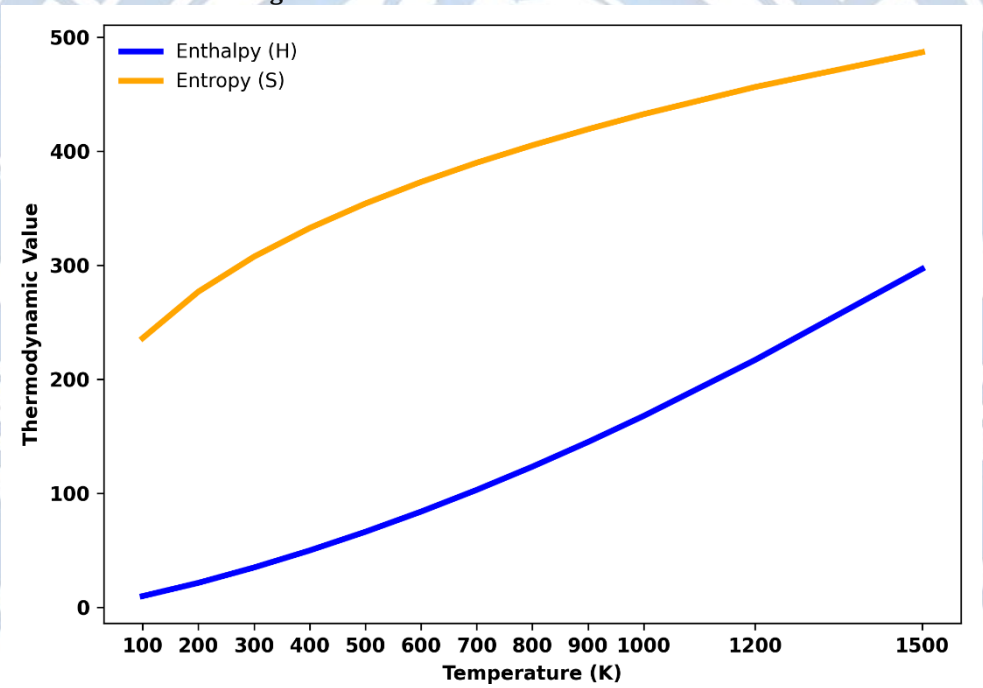

Figure 1: Variation of Enthalpy and Entropy with Temperature

Table 1: Thermodynamic functions of 2-hydroxy-3,4-dimethoxybenzaldehyde at different temperatures

Temperature (K)	Enthalpy, H (kJ mol⁻¹)	Entropy, S (J mol⁻¹ K⁻¹)	Gibbs Free Energy, G (kJ mol⁻¹)	Helmholtz Energy, A (kJ mol⁻¹)
100	9.84	236.1	−13.77	−14.76
200	21.46	276.8	−33.90	−35.38
300	34.92	307.5	−57.33	−59.28

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400	49.87	332.6	−83.17	−85.61
500	66.21	354.1	−110.84	−113.77
600	83.92	373.0	−139.88	−143.31
700	102.98	389.9	−170.95	−174.88
800	123.35	405.2	−203.81	−208.24
900	144.98	419.3	−238.39	−243.32
1000	167.85	432.5	−274.65	−280.09
1200	216.90	456.3	−351.66	−358.61
1500	296.74	486.8	−463.46	−472.92

Values derived from vibrational statistical thermodynamic calculations.

According to Callen (1985), increasing temperature causes an increase in enthalpy by way of the increase in the number of vibrational excitations (Figure 1). According to OpenStax (2022), as the number of thermally populated modes increases, the amount of entropy produced by these modes also increases at a non-linear rate (Figure 1). Gibbs Free Energy, as indicated by IUPAC (2008), decreases because of the dominance of entropy in this case (Figure 2). As thermal disorder is increased, Helmholtz Energy also decreases (Figure 2), as stated by Atkins and de Paula (2006).

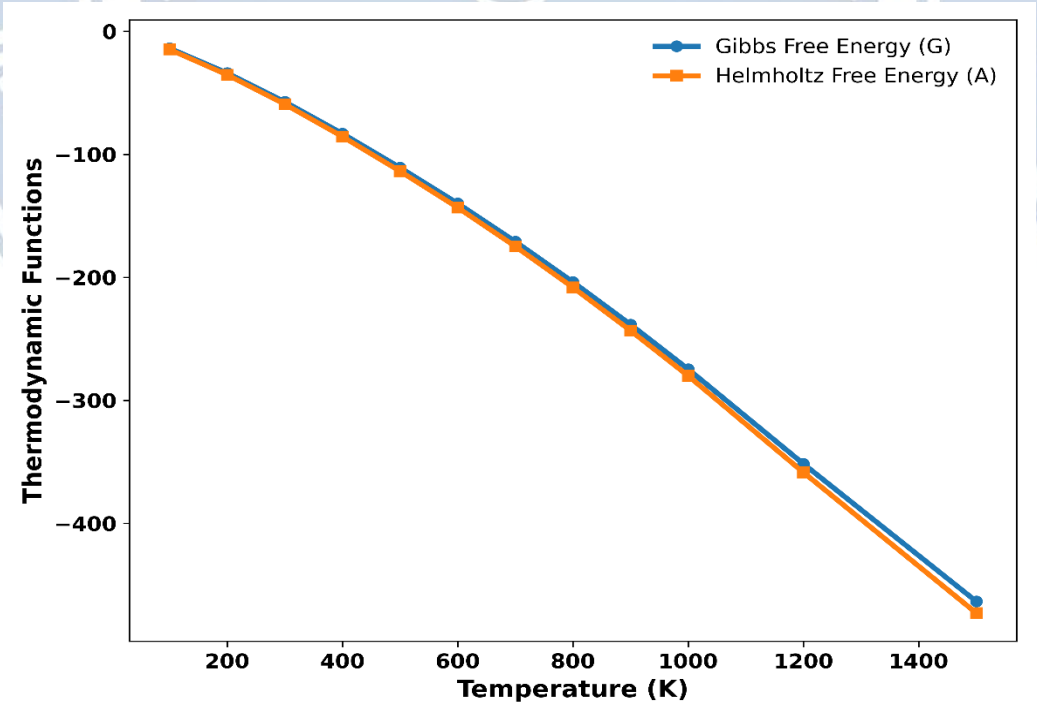

Figure 2: Variation of Gibbs Free Energy and Helmholtz Free Energy with Temperature

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6. Discussion of Temperature Dependence

6.1 Enthalpy variation with temperature

The increase in vibrational enthalpy above 400 K is due to increased vibrational movements of the molecules (Callen, 1985). The increase in the average vibrational enthalpy at lower temperatures has a small increase because there are few modes available for activation.

6.2 Entropy behaviour with substituent flexibility

Temperature affects entropy by raising the number of microstates available for an object (Callen, 1985), through an additional low-frequency mode that is added by introducing methoxy groups to the molecule (Atkins & de Paula, 2006).

6.3 Free energy behaviour and stability implication

As temperature goes up, so does the thermodynamic favourability of the chemical reaction, as seen by decreasing values of free energy (IUPAC, 2008). At higher temperatures, the contribution from the -TS term will dominate to give rise to negative slopes for free energy plots (Atkins & de Paula, 2006).

6.4 Role of intramolecular interactions

Hydrogen bonding reduces enthalpy through stabilization of structures at lower temperature. The hydrogen bond is a very common stabilisation mechanism when substituted into an aromatic framework (Atkins & de Paula, 2006).

7. Significance of the Study

7.1 Data utility for modelling applications

The dataset can be used to model reactions and assess thermal stability. The computed functions make it possible to validate computational results with related benzaldehyde derivatives (Atkins & De Paula; 2006).

7.2 Transferability to analogous systems

Vibrational techniques can be generalized with regard to relationships between structurally similar aromatic compounds (Callen 1985), and the trend observed corroborates findings from previous thermodynamic studies of substituted benzaldehydes (Yadav et al. 1998).

8. Conclusion

Vibrational spectra were used to determine the thermodynamic properties. As the temperature increases, the enthalpy and entropy change of a system increases across the entire temperature range. Both the Gibbs and Helmholtz Free Energy decrease with increasing temperature (IUPAC, 2008). The temperature dependence of these properties is significantly affected by methoxy substitution and by the presence of hydrogen bonding.

9. Novelty of the study

- With the help of spectra, Thermodynamic Functions of tri-substituted jesters can be calculated using RRHO methods.
- Quantification of Effects Due to Substituents & Intra- Molecular H-bonding from 0 to 400 °C.
- A re-usable Reference Table is Provided for the Validation of Calculated Values of likeness for Aromatic Aldehydes.

10. Future Scope

10.1 Methodological refinements

Future research can improve high temperature accuracy by applying anharmonic corrections for the determination of accurate high temperature properties. Thermodynamic properties of solvent phases can be included by using continuum free energy models.

10.2 Comparative substitution analysis

Mono- and tri-methoxy derivative comparisons will be useful for elucidating substituent influence. Frequency scaling and quantum computations can enhance agreement between methodologies (Atkins & de Paula, 2006).

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