1. INTRODUCTION

Reduced sulfur species, including carbon disulfide (CS$_2$), sulfur dioxide (SO$_2$), and carbonyl sulfide (OCS) as trace sulfur gases exist in most atmospheric and surface natural water samples, and play a role in the global climate change.$^{1-2}$ CS$_2$ originates widely from the combustion process of coal and natural gas, and also originates from industrial processes, such as production of insecticides and manmade cellulose.$^{3-5}$ The CS$_2$ radical has long been used as a starting material for production of a variety of useful chemicals for agricultural, medicinal, and pharmaceutical applications. The chemical properties and real applications of the CS$_2$ radical have drawn much recent interest.$^{6-18}$ However, as far as we know, the questions of what are efficient analytical representations of thermodynamic quantities for CS$_2$, including entropy, enthalpy, and Gibbs free energy, remain to be solved from the view of the first principles. Knowledge of the thermodynamic properties of substances is essential for understanding natural phenomena such as phase transition, chemical reaction, and adsorption,$^{19-25}$ and for the engineering design of industrial processes. Providing efficient analytical representations of thermodynamic quantities for triatomics still remains elusive in the communality of science and engineering.

Our overall strategy for constructing effective analytical representations of thermodynamic quantities relies on exploiting the available oscillators to describe internal vibrations of the CS$_2$ molecule. Recent work from our group on establishing efficient closed-form representations of entropy, enthalpy, and Gibbs free energy for diatomic substances has been performed by taking advantage of the improved Rosen–Morse, Manning–Rosen, and Tietz oscillators to represent the internal vibration of a diatomic molecule.$^{26-35}$ Inspired by this work, as well as the importance of the applications for CS$_2$, we further design efficient analytical representations of the thermodynamic quantities for triatomic substances such as carbon disulfide.

The purpose of the present study is to establish two analytical representations for the molar entropy and Gibbs free energy of CS$_2$. To evaluate the ability of the proposed prediction models, we utilize five molecular constants of CS$_2$ as an input to determine the molar entropy and Gibbs free energy values in the temperature range from 298 to 6000 K, and compare the predicted values with the experimental data available in the literature.

2. RESULTS AND DISCUSSION

In order to ascertain the validity of the proposed models, the molar entropy and reduced Gibbs free energy are plotted against temperature as shown in Figure 1, where five molecular constant values for the CS$_2$ molecule are taken from the work reported by Wentink$^7$ and Yang et al.$^8$ In Figure 1A, the green solid line stands for the theoretical value of the molar entropy and reduced Gibbs free energy predicted by using the improved Tietz oscillator to describe the symmetric stretching vibration of the CS$_2$ molecule, the red solid line represents the entropy values obtained by using the traditional harmonic oscillator to describe the symmetric stretching vibration, and blue solid circles indicate the experimental data from the National Institute of Standards and Technology (NIST) database.$^{36}$ We can observe from Figure 1A that the molar entropy values based on the pure harmonic oscillator possess large deviations from the experimental data. All the data predicted from expressions 13 and 14, in the temperature range of 300–6000 K, are in good agreement with the experimental data from the NIST database.
the NIST database. The average relative deviations from the NIST data for the entropy and reduced Gibbs free energy values of CS2 are 0.250 and 0.108%, respectively. These deviation values strongly suggest that the proposed analytical representations of the entropy and Gibbs free energy for gaseous carbon disulfide are efficient in the temperature range from 300 to 6000 K.

Conventional calculation models for the thermodynamic quantities of substances are required to apply a great number of experimental spectroscopy data. The present analytical representations of entropy and Gibbs free energy for CS2 merely require experimental values of five molecular constants of the CS2 molecule. This merit may stimulate one to develop analytical representations of thermodynamic quantities for other triatomics with the help of the present methodology.

3. CONCLUSIONS

In this work, we first construct reliable analytical representations of entropy and Gibbs free energy for gaseous carbon disulfide from the first principles. The average relative deviations of entropy and reduced Gibbs free energy values for CS2 from the NIST database, in the temperature range of 300−6000 K, are 0.250 and 0.108%, respectively. The proposed analytical representations merely rely on experimental values of five molecular constants of the CS2 molecule. The compromise of the simplicity and accuracy of the proposed analytical representations provide a new path toward construction of analytical expressions of thermodynamic quantities for other triatomics.

4. COMPUTATIONAL METHODS

The CS2 molecule is a linear triatomic molecule. As shown in Figure 2, the CS2 molecule has four vibration modes, including internal symmetric stretching vibration, antisymmetric stretching vibration, and a degenerate pair of bending vibrations. Herein, the improved Tietz oscillator is used to illustrate the symmetric stretching vibration of the CS2 molecule. The vibrational partition function to represent the symmetric stretching mode of CS2 is given from eq 14 of ref 28 as follows

\[
Q^*_{\text{v}} = \frac{1}{2} e^{-\beta D_{\text{v}}} \left[ e^{\beta q_{\text{SS}}} - e^{-\beta q_{\text{SS}}} \right] + \frac{\beta kT}{\alpha} \left( \text{erfi} \left( \frac{\Delta q_{\text{SS}}}{\sqrt{2kT}} \right) - \text{erfi} \left( \frac{-\Delta q_{\text{SS}}}{\sqrt{2kT}} \right) \right)
\]

where \( D_{\text{v}} \) represents the energy to dissociate CS2 into CS and S, \( k \) denotes the Boltzmann constant, \( T \) denotes the absolute temperature, \( \lambda = \frac{\hbar \omega_{\text{SS}}}{kT} \), \( a = \frac{\delta_1}{\delta_2 - \frac{\delta_1}{2}} \), \( b = \frac{1}{\Delta q_{\text{SS}}} + \frac{1 + \delta_1}{2} \), \( \delta_1 = \frac{\mu_{\text{SS}} D_{\text{v}}}{h^2 q^2} \left( e^{2\omega_{\text{SS}}} - q^2 \right) \), and \( h = \frac{\hbar}{2\pi} \). Here \( \hbar \) denotes the Planck constant, \( \mu_{\text{SS}} \) is the reduced mass of two sulfur atoms, \( r_{\text{CSS}} = 2r_{\text{CS}} \) stands for the C−S equilibrium distance, \( q \) is a dimensionless adjustable parameter. The symbol \( \mu \) corresponds to two cases that the plus is chosen when \( q < 0 \) and the minus is taken if \( q > 0 \). The parameter \( \alpha \) is determined by

\[
\alpha = \pi c a \sqrt{\frac{2\mu_{\text{SS}}}{D_{\text{v}}} + 1 + \frac{1}{2} \ln \left( 1 + \frac{1 + \Delta q_{\text{SS}}}{2 + \Delta q_{\text{SS}}} \right)} \ln (1 + A), \text{ here}
\]

\[
A = \pi c a \sqrt{\frac{2\mu_{\text{SS}}}{D_{\text{v}}} e^{-\omega_{\text{SS}}^2 q^2} \frac{r_{\text{CSS}}^2}{\Delta q_{\text{SS}}} e^{-2\omega_{\text{SS}} q^2}}}
\]

\( c \) represents the speed of light and \( \omega_{\text{SS}} \) stands for the symmetric stretching frequency. The symbol \( \text{erfi} \) denotes the imaginary error function. The factor \( e^{\alpha/3} \) illustrates the contributions of the excited states of the CS2 molecule to the vibrational partition function. The symbol \( v_{\text{max}} \) represents the highest vibrational quantum number which is given by

\[
v_{\text{max}} = \left[ -\frac{1}{\hbar a q} \sqrt{\frac{2\mu_{\text{SS}}}{D_{\text{v}}} \left( e^{2\omega_{\text{SS}}} - q^2 \right)} - 1 \pm \sqrt{1 + \frac{8\mu_{\text{SS}} D_{\text{v}} \left( e^{2\omega_{\text{SS}}} + q^2 \right)}{\hbar^2 a^2 q^2}} \right]
\]

where \( [x] \) denotes the greatest integer, which is less than or equal to \( x \) for the noninteger \( x \).

Figure 2. Schematic diagram of the vibration modes of the CS2 molecule.
To tackle the problems of the antisymmetric stretching vibration and bending vibrations of the CS$_2$ molecule, we choose the harmonic oscillator and write the corresponding vibrational partition function as follows:\(^2\)

$$Q_{\text{v HO}} = \frac{e^{\Theta v/T}}{e^{\Theta v/T} - 1}$$  \hspace{1cm} (2)

where \(\Theta v = \hbar \omega v / k\), \(\omega v\) represents the equilibrium frequency.

The vibrational entropy and Gibbs free energy corresponding to four vibration modes can be deduced from the following thermodynamic relationships and expressions\(^1,2\)

$$S = k \ln Q + kT \frac{\partial \ln Q}{\partial T}$$  \hspace{1cm} (3)

$$G = H - TS = kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T - kT \ln Q$$  \hspace{1cm} (4)

The molar vibrational entropy and Gibbs free energy accompanied by contributions of the symmetric stretching vibration of CS$_2$ are determined as follows, respectively

$$S^v_s = R \ln \left( \frac{1}{2} e^{\Theta s/T} e^{\Theta v/2T} - e^{\Theta v/2T} + \frac{akT}{\Theta s} \left( \text{erf} \left( \frac{\lambda}{\sqrt{2kT}} \right) \right) \right) - e^{\Theta v/2T} \left( \text{erf} \left( \frac{\lambda}{\sqrt{2kT}} \right) \right) \frac{1}{2} e^{\Theta s/T} e^{\Theta v/2T}$$

$$G^v_s = -RT \ln \left( \frac{1}{2} e^{\Theta s/T} e^{\Theta v/2T} - e^{\Theta v/2T} + \frac{akT}{\Theta s} \left( \text{erf} \left( \frac{\lambda}{\sqrt{2kT}} \right) \right) \right) - e^{\Theta v/2T} \left( \text{erf} \left( \frac{\lambda}{\sqrt{2kT}} \right) \right) \frac{1}{2} e^{\Theta s/T} e^{\Theta v/2T}$$

where \(R\) represents the universal gas constant. The molar vibrational entropy and Gibbs free energy accompanied by contributions of the antisymmetric stretching vibration and two bending vibrations of CS$_2$ can be yielded as follows, respectively

$$S^v_{as+bv} = R \left[ \frac{\Theta_{as}^v/T}{e^{\Theta_{as}^v/T} - 1} - \ln(1 - e^{-\Theta_{as}^v/T}) \right] + 2R \left[ \frac{\Theta_{bv}^v/T}{e^{\Theta_{bv}^v/T} - 1} - \ln(1 - e^{-\Theta_{bv}^v/T}) \right]$$  \hspace{1cm} (7)

$$G^v_{as+bv} = -RT \ln \left( \frac{e^{\Theta_{as}^v/T}}{e^{\Theta_{as}^v/T} - 1} \right) - 2RT \ln \left( \frac{e^{\Theta_{bv}^v/T}}{e^{\Theta_{bv}^v/T} - 1} \right)$$  \hspace{1cm} (8)

where \(\Theta_{as}^v = \hbar \omega_{as} / k\), \(\Theta_{bv}^v = \hbar \omega_{bv} / k\), \(\omega_{as}\) and \(\omega_{bv}\) represent the antisymmetric stretching vibration and bending vibration frequencies of CS$_2$, respectively.

The molar entropies accompanied by contributions of translation and rotation of CS$_2$ are given by eqs \(^9\) and \(^10\), respectively

$$S' = R \left[ \frac{S}{2} + \ln \left( \frac{2\pi m_{CS_2} kT}{h^2} \right)^{3/2} \right]$$  \hspace{1cm} (9)

$$S'' = R \left[ 1 + \ln \left( \frac{T}{\Theta} \right) \right]$$  \hspace{1cm} (10)

where \(\Theta = \frac{\hbar^2}{2m_{CS_2}v^2}\), \(m_{CS_2}\) denotes the mass of the CS$_2$ molecule, \(\mu_{CS}\) denotes the reduced mass of carbon and sulfur atoms, and \(P\) denotes the gas pressure. The molar Gibbs free energies corresponding to translation and rotation of CS$_2$ are expressed as follows, respectively

$$G' = -RT \ln \left( \frac{2\pi m_{CS_2} kT}{h^2} \right)^{3/2}$$  \hspace{1cm} (11)

$$G'' = -RT \ln \left( \frac{T}{\Theta} \left( 1 + \frac{1}{3} \frac{\Theta}{T} + \frac{1}{15} \frac{(\Theta/T)^2}{\Theta} + \frac{4}{315} \frac{(\Theta/T)^3}{\Theta} \right) \right)$$  \hspace{1cm} (12)

The total molar entropy and Gibbs free energy of CS$_2$ are obtained from eqs \(^5\)–\(^12\) as follows, respectively

$$S = S' + S'' + S^v_s + S^v_{as+bv}$$  \hspace{1cm} (13)

$$G = G' + G'' + G^v_s + G^v_{as+bv}$$  \hspace{1cm} (14)

When we know the experimental values of \(D_{sv}\), \(r_{CS}\), \(\Theta_{as}\), \(\omega_{as}\), \(\omega_{bv}\) and \(\Theta_{as}\) for CS$_2$, the molar entropy and Gibbs free energy values can be easily predicted from eqs \(^13\) and \(^14\). Here, we establish the quantitative relationships between the entropy and Gibbs free energy of CS$_2$ and the basic molecular constants. Keeping the pressure invariant, the temperature dependence of the entropy and Gibbs free energy of CS$_2$ can be simply depicted in terms of eqs \(^13\) and \(^14\).

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### Notes

The authors declare no competing financial interest.
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REFERENCES

(1) Kim, K.-H.; Andreat, M. O. Carbon disulfide in seawater and the marine atmosphere over the North Atlantic. J. Geophys. Res. 1987, 92, 14733–14738.
(2) Watts, S. F. The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide. Atmos. Environ. 2000, 34, 761–779.
(3) Li, L.; Shudong, W.; Quan, Y. Removal of carbon disulfide: Experimental and modeling results. Fuel 2010, 89, 1716–1720.
(4) Zeng, Z.; Dlugogorski, B. Z.; Oluwoye, I.; Altarawneh, M. Co-oxidation of methane (CH₄) and carbon disulfide (CS₂). Proc. Combust. Inst. 2019, 37, 677–688.
(5) Zeng, Z.; Altarawneh, M.; Dlugogorski, B. Z. Atmospheric oxidation of carbon disulfide (CS₂). Chem. Phys. Lett. 2017, 669, 43–48.
(6) Bisgaard, C. Z.; Clarkin, O. J.; Wu, G.; Lee, A. M. D.; Gessner, O.; Hayden, C. C.; Stolow, A. Time-resolved molecular frame dynamics of fixed-in-space CS₂ molecules. Science 2009, 323, 1464–1468.
(7) Wentink, T. Triatomic linear molecules containing carbon and oxygen, sulfur, selenium, or tellurium. I. Vibrational spectra of CS₂, CSe₂, SCSe, and SCTe. J. Chem. Phys. 1958, 29, 188–200.
(8) Yang, S. C.; Freedman, A.; Kawasaki, M.; Bersohn, R. Energy distribution of the fragments produced by photodissociation of CS₂ at 193 nm. J. Chem. Phys. 1980, 72, 4058–4062.
(9) Ochiai, B.; Endo, T. Carbon dioxide and carbon disulfide as reagents for functional polymers. Prog. Polym. Sci. 2005, 30, 183–215.
(10) Xuan, Y.; Hu, J.; Xu, K.; Hou, X.; Lv, Y. Development of sensitive carbon disulfide sensor by using its cataluminescence on nanosized-CeO₂. Sens. Actuators B 2009, 136, 218–223.
(11) Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C. Functionalization of carbon dioxide and carbon disulfide using a stable uranium(III) alkyl complex. J. Am. Chem. Soc. 2011, 133, 4948–4954.
(12) Asadian, N.; Kaghazchi, T. Comparison of dimethyl disulfide and carbon disulfide in sulfurization of activated carbons for producing uranium(III) alkyl complex: Dependence on the symmetric and antisymmetric stretching vibrations of CS₂. Chem. Phys. Lett. 2016, 648, 147–151.
(13) Qin, Z.-H.; Chen, H.; Yan, Y.-J.; Li, C.-S.; Song, R.-M.; Yang, L.-X.; Liu, J.-Y.; Xiong, Y.; Zeng, R. Predictions of entropy and Gibbs free energy for the lithium dimer. Chem. Phys. Lett. 2017, 667, 211.
(14) Qin, Z.-H.; Chen, H.; Yan, Y.-J.; You, X.-T.; Liu, J.-Y.; Xiong, Y.; Zeng, R. Predictions of entropy and Gibbs free energy for the sodium dimer. Chem. Phys. Lett. 2017, 673, 50–55.
(15) Qin, Z.-H.; Chen, H.; Yan, Y.-J.; You, X.-T. Partition function of improved Tietz oscillators. Chem. Phys. Lett. 2017, 676, 150.
(16) Tang, J.-F.; Peng, X.-L.; Zhang, L.-H.; Wang, C.-W.; Jia, C.-S. Equivalence of the Wei potential model and Tietz potential model for the lithium dimer. Chem. Phys. Lett. 2017, 685, 131–133.
(17) Tang, J.-F.; Peng, X.-L.; Zhang, L.-H.; Wang, C.-W.; Jia, C.-S. Entropy of gaseous boron monobromide. Chem. Phys. Lett. 2017, 668, 131–133.
(18) Jia, C.-S.; Wang, C.-W.; Zhang, L.-H.; Peng, X.-L.; Tang, H.-M.; Liu, J.-Y.; Xiong, Y.; Zeng, R. Predictions of entropy for diatomic molecules and gaseous substances. Chem. Phys. Lett. 2018, 692, 57–60.
(19) Jia, C.-S.; Wang, C.-W.; Zhang, L.-H.; Peng, X.-L.; Zeng, R.; You, X.-T. Prediction of entropy of improved Tietz oscillators. Chem. Phys. Lett. 2018, 125, 26–29.
(20) Jiang, R.; Jia, C.-S.; Wang, Y.-Q.; Peng, X.-L.; Zhang, L.-H. Prediction of enthalpy for the gases CO, HCl, and BF. Chem. Phys. Lett. 2019, 715, 186–189.
(21) Jia, C.-S.; You, X.-T.; Liu, J.-Y.; Zhang, L.-H.; Peng, X.-L.; Wang, Y.-T.; Wei, L.-S. Prediction of enthalpy for the gases Cl₂, Br₂, and gaseous Br₂. Chem. Phys. Lett. 2019, 717, 16–20.
(22) Jia, C.-S.; Wang, Y.-Q.; Peng, X.-L.; Zhang, L.-H.; Wei, L.-S. Prediction of entropy for the gases Cl₂, Br₂, and gaseous Br₂. Chem. Phys. Lett. 2019, 726, 83–86.
(23) Jia, C.-S.; Zhang, L.-H.; Peng, X.-L.; Luo, J.-X.; Zhao, Y.-L.; Liu, J.-Y.; Guo, J.; Tang, L.-D. Prediction of entropy and Gibbs free energy for nitrogen. Chem. Eng. Sci. 2019, 202, 70–74.
(24) National Institute of Standards and Technology (NIST). NIST Chemistry WebBook, NIST Standard Reference Database Number 69, 2017 (http://webbook.nist.gov/chemistry/).
(25) Jia, C.-S.; Xiao, Y.; Liu, J.-Y.; Zhang, L.-H.; Zheng, G.-D. Equivalence of the Wei potential model and Tietz potential model for diatomic molecules. J. Chem. Phys. 2012, 137, 014101.
(26) Jia, C.-S.; Zeng, R.; Peng, X.-L.; Zhang, L.-H.; Zhao, Y.-L. Entropy of gaseous phosphorus dimer. Chem. Eng. Sci. 2018, 190, 1–4.
(27) Peng, X.-L.; Jia, C.-S.; Zhang, L.-H.; Zhao, Y.-L. Gibbs free energy of gaseous phosphorus dimer. Chem. Eng. Sci. 2018, 190, 122–125.