ABSTRACT: We first report three reliable analytical expressions of the entropy, enthalpy and Gibbs free energy of carbon dioxide (CO₂) and perform predictions of these three thermodynamic quantities on the basis of the proposed analytical expressions and in terms of experimental values of five molecular constants for CO₂. The average relative deviations of the calculated values from the National Institute of Standards and Technology database over the temperature range from 300 to 6000 K are merely 0.053, 0.95, and 0.070%, respectively, for the entropy, enthalpy, and Gibbs free energy. The present predictive expressions are away from the utilization of plenty of experimental spectroscopy data and are applicable to treat CO₂ capture and storage processes.

1. INTRODUCTION

Carbon dioxide (CO₂) as a greenhouse gas has been regarded a main contributor of global warming. Davis et al.¹ suggested that the people would continue to confront increasing global mean temperatures and sea level rise if current greenhouse gas concentrations remain constant in the atmosphere. As CO₂ has a key influence to global climate change, CO₂ capture and storage (CCS) technologies are becoming more and more important topics for reducing CO₂ emission. CO₂ capture technologies can be classified as three types: post-combustion, pre-combustion, and oxy-fuel combustion. Adsorbing CO₂ is one of post-combustion capture technologies.² Many efforts have been made to develop efficient approaches of adsorbing CO₂.³⁻⁻³⁵ To optimally design such processes, we require accurate and reliable thermodynamic property data on CO₂. For some diatomic substances, the improved versions of some well-known oscillators such as the improved Tietz oscillator have been applied to represent the internal vibration of a diatomic molecule for constructions of universal analytical expressions of thermodynamic properties.³⁶⁻⁻⁵⁰ A CCS process simulation needs a combination of an equation of state (EoS) with the Helmholtz free energy or Gibbs free energy.⁵¹⁻⁻⁵⁵ The accurate three-parameter EoS proposed by Jaubert et al.⁵⁶ and the EoS developed by Span and Wagner⁵⁷ on the basis of the Helmholtz free energy are available in CCS process simulators. An analytical expression of the thermodynamic property can combine the simplicity of the analytical expression with the solid theoretical background of the statistical thermodynamic theory. However, it is difficult for chemists and engineers to obtain reliable analytical expressions of the thermodynamic quantities for gaseous substances. Although Span and Wagner⁵⁷ proposed an empirical polynomial analytical representation for the ideal-gas part of the Helmholtz free energy of CO₂, it includes 13 adjustable parameters, which were determined by fitting plenty of experimental data points. To date, one has not reported any analytical expressions governing the entropy, enthalpy, and Gibbs free energy for CO₂ from the view of the first principle. Therefore, it is of considerable interest to explore suitable analytical expressions of the thermodynamic properties for CO₂.

The aim of this work is to establish suitable analytical expressions of the thermodynamic properties for the triatomic substance CO₂. Compared with a diatomic substance, the generation of analytical expressions of the thermodynamic properties shows considerably greater challenges. To verify the effectiveness of the present predictive models, we apply three analytical expressions to predict the variations of the entropy, enthalpy, and Gibbs free energy with respect to temperature for CO₂ and compare the predictive results with the available data from the National Institute of Standards and Technology.
The NIST data are compiled by the utilization of NIST-JANAF Thermochemical Tables, which is constructed by Chase in terms of plenty of theoretical or experimental spectroscopic constants.

2. RESULTS AND DISCUSSION

To show the accuracy and reliability of the proposed predictive models, we calculate the entropy, enthalpy, and Gibbs free energy values at the pressure of 1 bar and different temperatures. This performance needs experimental data on the O−CO bond energy, O−C equilibrium bond length, and stretching and bending vibrational frequencies in the CO2 molecule. We consult the experimental data given by Itikawa, and list the required molecular constant values for the ground electronic state of CO2: $D_\Sigma = 5.451 \text{ eV}$, $r_{\text{CO}} = 1.160 \text{ Å}$, $\omega_{aa} = 1388 \text{ cm}^{-1}$, $\omega_{ab} = 2349 \text{ cm}^{-1}$, and $\omega_{bb} = 667.4 \text{ cm}^{-1}$. Taking $q = -10$ and employing the experimental data of the five molecular constants $D_\Sigma$, $r_{\text{CO}}$, $\omega_{aa}$, $\omega_{ab}$, and $\omega_{bb}$, the predictive values of molar entropy, enthalpy, and reduced Gibbs free energy for CO2 are produced in terms of eqs 13−15 from 298 up to 6000 K. The predictive results are depicted in Figure 1, in which the green solid lines represent the theoretically predictive results and the blue solid circles refer to the NIST data. From Figure 1, we observe that the predictive values show excellent agreement with the NIST data in the entire temperature range. The average relative deviations of the predictive data from the NIST data in a wide range of temperatures from 300 up to 6000 K for the entropy, enthalpy, and reduced Gibbs free energy are 0.053, 0.95, and 0.070%, respectively. These results indicate that our three predictive models are of very high accuracy to predict the entropy, enthalpy, and Gibbs free energy for CO2. In our calculations, the reduced molar Gibbs free energy, $G_r = -\left(\frac{G - H_{298.15}}{T}\right)$, of CO2 from the NIST database is 213.8 J mol$^{-1}$ K$^{-1}$ at 298 K. The molar Gibbs free energy calculated by the aid of eq 20 is $-22.901.65$ J mol$^{-1}$ at 298 K. On the basis of these two values, we obtain the value of 40,810.75 J mol$^{-1}$ at 298.15 K for the molar enthalpy. When $T = 6000$ K and $\omega_e = \omega_{ab}$, the value of $e^{-\Theta_e/T}$ reaches at the maximum, $e^{-\Theta_e/T} = 0.852 < 1$; thus, eq 2 is always valid in our calculations.

3. CONCLUSIONS

In summary, we first present suitable analytical expressions of the molar entropy, enthalpy, and Gibbs free energy for CO2. The average relative deviations between the theoretical predictive values and the NIST data ranging from the temperatures of 300 to 6000 K are 0.053, 0.95, and 0.070%, respectively, for the entropy, enthalpy, and reduced Gibbs free energy of CO2. The present predictive expressions exhibit satisfactorily accuracies and simple and straightforward characteristics and are away from the requirements of plenty of experimental spectroscopy data. The methodology developed in our work opens up a new pathway serving as constructions of accurate and efficient analytical expressions of thermodynamic properties for other triatomic substances such as water and hydrogen sulfide. It is expected that the present predictive models could aid the design and optimization of CCS processes.

4. COMPUTATIONAL METHODS

Figure 2 shows that CO2 is a centrosymmetric linear molecule and possesses symmetric stretching, antisymmetric stretching, and bending vibration modes. However, as a diatomic molecule is consisted of two atoms, it merely possesses a kind of stretching vibration. Hence, addressing vibrations of the CO2 molecule is much more difficult than treating the vibration of the diatomic molecule such as the nitrogen molecule. Here, we treat the internal symmetric stretching vibration of the CO2 molecule in terms of the improved Tietz oscillator and deal with the antisymmetric stretching and bending vibrations with the help of the harmonic oscillator. According to the vibrational partition function given in eq 14 of ref 50 for the improved Tietz oscillator, the partition function corresponding to the symmetric stretching vibration of CO2 is expressed as

$$Q_s = \frac{1}{2} e^{-D_s/kT} \left[ e^{\lambda_s/kT} - e^{-\lambda_s/kT} + \frac{\pi kT}{\lambda_s} \left( \text{erf} \left( \frac{\lambda_s}{kT} \right) - \text{erf} \left( \frac{\lambda_s}{kT} \right) \right) \right] \times e^{1/9}$$

in which $D_s$ denotes the energy serving as dissociating CO2 into O−CO, $k$ refers to the Boltzmann constant, $T$ is the temperature, symbol erf represents the imaginary error function, $\lambda = \lambda_s/kT$, $a = \frac{\lambda_s}{kT} - \frac{\lambda_s}{kT} + \frac{\lambda_s}{kT} + 1$, $b = \frac{1}{2} \left( \lambda_s + \lambda_s \right)$.

Figure 1. Temperature variation of the thermodynamic properties of CO2 for (A) molar entropy, (B) molar enthalpy, and (C) reduced molar Gibbs free energy.

Figure 2. Schematic diagram of the vibration modes of the carbon dioxide molecule.
\[ \delta_1 = \frac{\mu_w D}{k_B q}(e^{\frac{2\pi q}{\delta_1}} - q^2), \quad \delta_2 = \frac{1}{2}\left( 1 \pm \sqrt{1 + \frac{8\mu_w D(e^{\frac{2\pi q}{\delta_1}} - q^2)^2}{k_B q}} \right), \]

and \( h = \frac{\hbar}{2\pi} \). Here, \( h \) is the Planck constant, \( \mu_w \) refers to the reduced mass of two oxygen atoms, \( r_{\text{CO}} = 2r_{\text{CO}} \) (\( r_{\text{CO}} \) represents the C–O equilibrium length), \( q \) denotes a dimensionless variable, and the symbol \( \pm \) stands for the plus and minus in the cases of a positive value and negative value of \( q \), respectively. The parameter \( \alpha \) reads as

\[ \alpha = \pi c\omega_r e\Omega_{\text{CO}} \sqrt{\frac{2\pi q}{\hbar}} \left( 1 - \frac{\ln(1 + \ln(1 + \alpha))}{2 + \ln(1 + \alpha)} \right) \ln(1 + \alpha), \]

where \( A = \pi c\omega_r e\Omega_{\text{CO}} \sqrt{\frac{2\pi q}{\hbar}} \), \( c \) is the speed of light, and \( \omega_r \) represents the symmetric stretching vibration frequency. The contributions of the excited states to the partition function are represented by the factor \( e^{\frac{\alpha}{9}} \).

The highest vibrational quantum number, \( \nu_{\text{max}} \), reads as

\[ \nu_{\text{max}} = \left\lfloor \frac{1}{\hbar a_q}\sqrt{2\mu_w D(e^{\frac{2\pi q}{\delta_1}} - q^2)} - \frac{1}{2}\left( 1 \pm \sqrt{1 + \frac{8\mu_w D(e^{\frac{2\pi q}{\delta_1}} - q^2)^2}{k_B q}} \right) \right\rfloor \]

where \( \lfloor x \rfloor \) refers to the greatest integer, which is less than \( x \).

The vibrational partition function for a harmonic oscillator is given by

\[ Q_{\text{HO}} = \frac{\Theta_v}{e^{\Theta_v/kT} - 1} \]

where \( \Theta_v \) refers to the vibrational characteristic temperature and is expressed as \( \Theta_v = h\omega_r / k \). Here, \( \omega_r \) denotes the vibrational frequency.

We consider the canonical ensemble. From the following basic thermodynamic relationships

\[ S = k\ln Q + kT \frac{\partial \ln Q}{\partial T} \]

\[ H = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T \]

\[ G = H - TS = kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T - kT\ln Q \]

we obtain the molar vibrational entropy, enthalpy, and Gibbs free energy referring to the symmetric stretching vibration for \( \text{CO}_2 \), respectively

\[ S_n = R \ln \left( \frac{1}{2} \right) \frac{e^{\alpha q/kT} - e^{-\alpha q/kT} + \frac{\pi kT}{\alpha} \left\{ \text{erf} \left( \frac{\alpha}{kT} \right) - \text{erf} \left( \frac{\alpha}{kT} - 2 \text{erf} \left( \frac{\alpha}{kT} \right) \right) \right\}}{\alpha} \]

\[ + \frac{e^{-2\alpha q/kT}}{\alpha} \left\{ \text{erf} \left( \frac{\alpha}{kT} \right) + e^{-2\alpha q/kT} \text{erf} \left( \frac{\alpha}{kT} - 2 \text{erf} \left( \frac{\alpha}{kT} \right) \right) \right\} \]
respectively by37

The molar translational and rotational entropies are given as

\[ S_{vt} = R \left[ \frac{\Theta_v^t}{T} - \ln \left( 1 - e^{-\Theta_v^t/T} \right) \right] + 2R \left[ \frac{\Theta_r^t}{T} - \ln \left( 1 - e^{-\Theta_r^t/T} \right) \right] \]

and

\[ S_{rt} = \frac{1}{2} R \Theta_v^t + \frac{1}{2} R \Theta_r^t + \frac{1}{2} R \Theta_v^r + \frac{1}{2} R \Theta_r^r \]

in which \( \Theta_v^t \) and \( \Theta_r^t \) are the respective vibrational characteristic temperatures for the antisymmetric stretching mode and bending mode. They are defined as \( \Theta_v^t = h\omega_v^t/k \) and \( \Theta_r^t = h\omega_r^t/k \), where \( \omega_v^t \) and \( \omega_r^t \) are the vibrational frequencies corresponding to the antisymmetric stretching vibration and bending vibration, respectively.

To simplify the mathematical calculation, it is reasonable to assume that the interaction between two molecules is not considered and the CO\(_2\) molecule is regarded as a rigid rotor. The molar translational and rotational enthalpies can be written as

\[ H = H^t + H^r + H_{vs} + H_{rt} \]

and

\[ G = G^t + G^r + G_{vs} + G_{rt} \]

By inputting the experimental values of \( D_{rt} \), \( r_{CO2}^t \), \( \omega_v^t \), \( \omega_r^t \), and \( \omega_v^r \), we can predict the molar entropy, enthalpy, and Gibbs free energy for carbon dioxide. Our prediction approaches rely on requirements of experimental data of five molecular constants for CO\(_2\). It is superior to the conventional computation models, which need a large amount of experimental spectroscopy data.

### ACKNOWLEDGMENTS

This work was supported by the Key Program of National Natural Science Foundation of China under grant no. 51534006 and the Sichuan Province Foundation of China for Fundamental Research Projects under grant no. 2018JY0468.

### REFERENCES

1. Davis, S. J.; Caldeira, K.; Matthews, H. D. Future CO\(_2\) emissions and climate change from existing energy infrastructure. *Science* 2010, 329, 1330–1333.

2. Lee, S. Y.; Park, S. J. A review on solid adsorbents for carbon dioxide capture. *Ind. Eng. Chem.* 2015, 23, 1–11.

3. Datta, S. J.; Khumnoon, C.; Lee, Z. H.; Moon, W. K.; Doco, S.; Nguyen, T. H.; Hung, I. C.; Moon, D.; Olenyikov, P.; Terasaki, O.; Yoon, K. B. CO\(_2\) capture from humid flue gases and humid atmosphere using a microporous copolymer. *Science* 2015, 350, 302–306.

4. Wang, B.; Côté, A. P.; Furukawa, H.; O’Keeffe, M.; Yaghi, O. M. Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs. *Nature* 2008, 453, 207–211.

5. Nugent, P.; Belmekbouth, Y.; Burd, S. D.; Cairns, A. J.; Luebek, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. Porous materials with optimal adsorption thermodynamics and kinetic for CO\(_2\) separation. *Nature* 2013, 495, 80–84.

6. McDonald, T. M.; Mason, J. A.; Kong, X.; Bloch, E. D.; Gygi, D.; Dani, A.; Crocella, V.; Giordanino, F.; Odo, S. O.; Drisdell, W. S.; Vlasakivich, B.; Drubak, A. L.; Poloni, R.; Schnell, S. K.; Planas, N.; Lee, K.; Pascal, T.; Wan, L. F.; Prendegast, D.; Neaton, J. B.; Smit, B.; Kortright, J. B.; Gagliardi, L.; Bordiga, S.; Reimer, J. A.; Long, J. R. Cooperative insertion of CO\(_2\) in diamine-appended metal-organic frameworks. *Nature* 2015, 519, 303–308.

7. Trickett, C. A.; Helal, A.; Al-Myahthaly, B. A.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M. The chemistry of metal–organic frameworks for CO\(_2\) capture, regeneration and conversion. *Nat. Rev. Mater.* 2017, 2, 17045.

8. Sherman, B. J.; Ciftja, A. F.; Rochelle, G. T. Thermodynamic and mass transfer modeling of carbon dioxide absorption into aqueous 2-piperidinethanol. *Chem. Eng. Sci.* 2016, 153, 293–307.

9. Ammendola, P.; Raganati, F.; Chirone, R. CO\(_2\) adsorption on a fine activated carbon in a sound assisted fluidized bed: Thermodynamics and kinetics. *Chem. Eng. J.* 2017, 322, 302–313.

10. Singh, V. K.; Kumar, E. A.; Saha, B. B. Adsorption isotherms, kinetics and thermodynamic simulation of CO\(_2\)-CSA pair for cooling application. *Energy* 2018, 160, 1158–1173.
(11) Sherman, B. J.; Rochelle, G. T. Thermodynamic and mass-transfer modeling of carbon dioxide absorption into aqueous 2-amino-2-methyl-1-propanol. Ind. Eng. Chem. Res. 2017, 56, 319–330.

(12) Gargiulo, V.; Alfé, M.; Ammendola, P.; Raganati, F.; Chirone, R. CO₂ sorption on surface-modified carbazole support: Probing the influence of the carbon black microporosity and surface polarity. Appl. Surf. Sci. 2016, 360, 329–337.

(13) Gargiulo, V.; Alfé, M.; Raganati, F.; Lisi, L.; Chirone, R.; Ammendola, P. RBC-based metal-organic frameworks: Correlation between relevant structural features and CO₂ adsorption performances. Fuel 2018, 222, 319–326.

(14) Raganati, F.; Alfé, M.; Gargiulo, V.; Chirone, R.; Ammendola, P. Isotherms and thermodynamics of CO₂ adsorption on a novel carbon-magnetite composite sorbent. Chem. Eng. Res. Des. 2018, 134, 540–552.

(15) Raganati, F.; Alfé, M.; Gargiulo, V.; Chirone, R.; Ammendola, P. Kinetic study and breakthrough analysis of the hybrid physical/chemical CO₂ adsorption/desorption behavior of a magnetite-based sorbent. Chem. Eng. J. 2019, 372, 526–535.

(16) Ben-Mansour, R.; Habib, M. A.; Bamidele, O. E.; Basha, M.; Qasem, N. A. A.; Peedikakkal, A.; Laoui, T.; Ali, M. Carbon capture by efficient vacuum pressure swing adsorption process to separate CO₂ from CO₂/N₂ mixture using Mg-MOF-74: A CFD simulation. Chem. Eng. J. 2018, 325, 221–235.

(17) Qasem, N. A. A.; Ben-Mansour, R. Energy and productivity efficient vacuum pressure swing adsorption process to separate CO₂ from CO₂/N₂ mixture using Mg-MOF-74: A CFD simulation. Appl. Energy 2018, 209, 190–202.

(18) Qasem, N. A. A.; Ben-Mansour, R. Adsorption breakthrough and cycling stability of carbon dioxide separation from dry and humid CO₂/N₂ mixture. Comput. Chem. Eng. 2018, 117, 221–235.

(19) Qasem, N. A. A.; Ben-Mansour, R. Adsorption breakthrough and cycling stability of carbon dioxide separation from dry and humid CO₂/N₂ mixture under ambient conditions using 13X and Mg-MOF-74. Appl. Energy 2018, 230, 1093–1107.

(20) Qasem, N. A. A.; Ben-Mansour, R. Adsorption breakthrough and cycling stability of carbon dioxide separation from dry and humid CO₂/N₂ mixture under ambient conditions using 13X and Mg-MOF-74. Appl. Energy 2018, 230, 1093–1107.

(21) Ferreira, D.; Magalhães, R.; Taveira, P.; Mendes, A. Effective adsorption equilibrium isotherms and breakthroughs of water vapor and carbon dioxide on different adsorbents. Ind. Eng. Chem. Res. 2011, 50, 10201–10210.

(22) Lei, M.; Vallieres, C.; Grevillot, G.; Latifi, M. A. Thermal swing adsorption process for carbon dioxide capture and recovery: Modeling, simulation, parameters estimability, and identification. Ind. Eng. Chem. Res. 2013, 52, 7526–7533.

(23) Ntianomah, A.; Ling, J.; Xiao, P.; Webley, P. A.; Zhai, Y. CO₂ Capture by Temperature Swing Adsorption: Use of Hot CO₂-Rich Gas for Regeneration. Ind. Eng. Chem. Res. 2015, 55, 703–713.

(24) Richou, M.; Martin, C.; Denoyel, R.; Llewellyn, P.; Roubin, P. Microporosity of carbon deposits collected in the Tore Supra tokamak probed by nitrogen and carbon dioxide adsorption. Carbon 2009, 47, 109–116.

(25) Mason, J. A.; Sumida, K.; Heme, Z. R.; Krishna, R.; Long, J. R. Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption. Energy Environ. Sci. 2011, 4, 3030–3040.

(26) Wang, L.; Liu, Z.; Li, P.; Yu, J.; Rodrigues, A. E. Experimental and modeling investigation on post-combustion carbon dioxide capture using zeolite 13X-APG by hybrid VTSA process. Chem. Eng. J. 2012, 197, 151–161.

(27) Hedlin, N.; Andersson, L.; Bergström, L.; Yan, J. Adsorbents for the post-combustion capture of CO₂ using rapid temperature swing or vacuum swing adsorption. Appl. Energy 2013, 104, 418–433.

(28) Zhang, Z.; Yao, Z.; Xiang, S.; Chen, B. Perspective of microporous metal-organic frameworks for CO₂ capture and separation. Energy Environ. Sci. 2014, 7, 2868–2899.

(29) Ribolli, L.; Bolland, O. Evaluating pressure swing adsorption as a CO₂ separation technique in coal-fired power plants. Int. J. Greenhouse Gas Control 2015, 39, 1–16.
“Peng-Robinson + residual Helmholtz energy-based” model. Fluid Phase Equilib. 2017, 437, 166–180.

(53) Xu, X.; Lasala, S.; Privat, R.; Jaubert, J.-N. E-PPR78: A proper cubic EoS for modelling fluids involved in the design and operation of carbon dioxide capture and storage (CCS) processes. Int. J. Greenhouse Gas Control 2017, 56, 126–154.

(54) Lasala, S.; Chiesa, P.; Privat, R.; Jaubert, J.-N. Sizing and operating units for the purification and compression of CO2-based streams: The impact of thermodynamic model accuracy. J. Supercrit. Fluids 2018, 140, 336–347.

(55) Najafi-Marghamaleki, A.; Barati-Harooni, A.; Mohammadi, A. H. Impact of gas impurities on CO2 mole fraction: Application in carbon capture and storage (CCS) processes. Int. J. Greenhouse Gas Control 2017, 57, 173–184.

(56) Le Guennec, Y.; Privat, R.; Jaubert, J.-N. Development of the translated-consistent tc-PR and tc-RK cubic equations of state for a safe and accurate prediction of volumetric, energetic and saturation properties of pure compounds in the sub- and super-critical domains. Fluid Phase Equilib. 2016, 429, 301–312.

(57) Span, R.; Wagner, W. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. J. Phys. Chem. Ref. Data 1996, 25, 1509–1596.

(58) National Institute of Standards and Technology (NIST) NIST Chemistry WebBook; National Institute of Standards and Technology, NIST Standard Reference Database Number 69, 2017, http://webbook.nist.gov/chemistry/.

(59) Chase, M. W. NIST-JANAF Thermochemical Tables; Journal of Physical and Chemical Reference Data Monographs No. 9; American Institute of Physics: 1998.

(60) Itikawa, Y. Cross sections for electron collisions with carbon dioxide. J. Phys. Chem. Ref. Data 2002, 31, 749–767.

(61) Jia, C.-S.; Diao, Y.-F.; Liu, X.-J.; Wang, P.-Q.; Liu, J.-Y.; Zhang, G.-D. Equivalence of the Wei potential model and Tietz potential model for diatomic molecules. J. Chem. Phys. 2012, 137, No. 014101.