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Short Communication

Gibbs free energy of gaseous phosphorus dimer

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HIGHLIGHTS

- We present an explicit representation of molar Gibbs free energy for gaseous substances.
- The molar Gibbs free energy calculation model is only related to three molecular constants.
- Gibbs free energies of gaseous phosphorus dimer are excellently predicted.

GRAPHICAL ABSTRACT
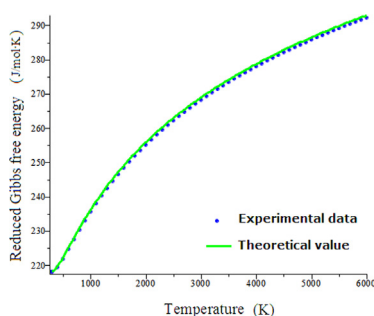
ARTICLE INFO

ABSTRACT

We establish an analytical representation for the prediction of the molar Gibbs free energies of gaseous diatomic molecule substances. By comparing the predicted values to the experimental data for the gaseous phosphorus dimer, the availability of the Gibbs free energy calculation model is verified. The present model is related to three molecular constants and away from the need of lots of experimental spectroscopy data.

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1. Introduction

The Gibbs free energy is an important basic datum involved in dealing with a wide range of fundamental chemical quantities, including the chemical reaction equilibrium constant (Solsvik et al., 2016; Amin and Yaw, 2007); vapor–liquid phase equilibrium (Dragoescu et al., 2013; Chávez et al., 2015; Roh, 2015), and adsorption coefficient (Singh and Kumar, 2016; Ammendola et al., 2017; Chowdhury et al., 2011). In a spontaneous process the entropy increases, it corresponds to a decrease in the Gibbs free energy. Otherwise, if the Gibbs free energy increases, the corresponding process will be non-feasible and non-spontaneous. Calculations of equilibrium chemical compositions can be carried out by the minimization of the total Gibbs free energy of a chemical reaction system. Direct minimization of the total Gibbs free energy subject to the vapor–liquid system is also very effective for the complicated phase equilibrium. Obtaining analytical representation of the Gibbs free energy is one of the challenges in chemical engineering. The description of the internal vibration of a molecule with the improved Rosen-Morse oscillator has led to an analytical representation of molar enthalpy for gaseous diatomic molecule substances (Jia et al., 2018a). This molar enthalpy calculation model is only related to three molecular constants without the need for a large amount of experimental spectroscopy data, and it can offer good predictions of molar enthalpy of gaseous phosphorus dimer from a comparison of theoretically calculated results and experimental data. This situation leads us to develop a model that can be used to predict the Gibbs free energies of gaseous substances.

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By introducing the dissociation energy and equilibrium bond length as explicit parameters, one of present authors and co-workers (Wang et al., 2012; Jia et al., 2012, 2017a) established the improved models of the well-known Rosen-Morse, Tietz, Manning-Rosen, and Pöschl-Teller oscillators. On the basis of the improved oscillator models for representing the internal vibration of a molecule, some thermodynamic quantities have been investigated for some diatomic molecule substances, including the phosphorus dimer, lithium dimmer, boron monobromide, sodium dimer, carbon monoxide, hydrogen chloride, hydrogen fluoride, and nitrogen monoxide (Jia et al., 2017b, 2017c, 2018a, 2018b; Wang et al., 2017; Buchowiecki, 2018; Song et al., 2017). It is not surprising then that there have been many studies of phosphorus dimer (P_2) due to the contribution to the etching and epitaxial growth of phosphorus-containing semiconductors (Kobayashi and Kobayashi, 1996). Many efforts have been made to investigate the structure and properties of P_2 molecule (Kobayashi and Kobayashi, 1996; Jones and Hohl, 1990; Mielke et al., 1990; Maroulis, 2003; Bu, 1995; Wilson et al., 2006; Katsidis and Siapkas, 2009). In this short communication, we construct a new analytical representation of molar Gibbs free energy for gaseous diatomic molecule substances. This approach is used to investigate the variation of molar Gibbs free energy of the gaseous P_2 dimer with respect to temperature. Experimental data and prediction results are then used to validate the calculation model.

2. Analytical representation of Gibbs free energy

By the aid of the Poisson summation formula Song et al. (2017) derived the expression for the vibrational partition function of the improved Rosen-Morse oscillator,

$$Q^v_{\mathrm{IRMO}} = \frac{1}{2} e^{-\frac{D_e}{kT}} \left[e^{\frac{\lambda \eta_1^2}{kT}} - e^{\frac{\lambda \eta_2^2}{kT}} + \sqrt{\frac{\pi kT}{\lambda}} \left(\mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} \eta_1 \right) \right. \right.$$
$$\left. - \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} \eta_2 \right) - e^{-\frac{2\lambda a}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}}(2a + \eta_1) \right)$$
$$\left. \left. + e^{-\frac{2\lambda a}{kT}} \mathrm{erfi}(\sqrt{\frac{\lambda}{kT}}(2a + \eta_2)) \right) \right] \quad (1)$$

where $\lambda = \frac{h^2 \alpha^2}{2\mu}$, $a = \frac{\mu}{h^2 \alpha^2} D_e (e^{2\alpha r_e} - 1)$, $b = \frac{1}{2}\left(1 - \sqrt{1 + \frac{8\mu D_e (e^{\alpha r_e}+1)^2}{h^2 \alpha^2}}\right)$, $\eta_1 = \frac{a}{b} - \frac{b}{2}$, $\eta_2 = \frac{a}{v_{\max}+1+b} - \frac{v_{\max}+1+b}{2}$, $\alpha = \pi c \omega_e \sqrt{\frac{2\mu}{D_e}} + \frac{1}{r_e} W(\pi c \omega_e r_e \sqrt{\frac{2\mu}{D_e}} e^{-\pi c \omega_e r_e \sqrt{\frac{2\mu}{D_e}}})$, and $\hbar = h/2\pi$. In these expressions, k is the Boltzmann's constant, T is the temperature, h is the Planck constant, c is the speed of light, μ is the reduced mass of a diatomic molecule, D_e is the dissociation energy, r_e is the equilibrium bond length, ω_e is the harmonic vibration frequency, and $v_{\max}$ is the maximum vibration quantum number which is equal to $v_{\max} = \left[\sqrt{\frac{1}{4} + \frac{2\mu D_e (e^{\alpha r_e}+1)^2}{h^2 \alpha^2}} - \frac{1}{2}\left(1 + \sqrt{\frac{8\mu D_e (e^{2\alpha r_e}-1)}{h^2 \alpha^2}}\right)\right]$, where $[n]$ represents the maximum integer referring to n. The symbols W and erfi denotes the Lambert function and imaginary error function, respectively. Their definitions are given by $z = W(z)e^{W(z)}$ (Corless et al., 1996), and $\mathrm{erfi}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{t^2} dt$, respectively.

Based on two assumptions of neglecting the interaction between two molecules and treating diatomic molecules as rigid rotors, one can obtain the translational partition function and rotational partition function for a molecule with occupying the spatial volume V, respectively (Schwabl, 2006);

$$Q^t = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V, \quad (2)$$

$$Q^r = \frac{T}{\sigma \Theta_r}\left(1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\Theta_r}{T}\right)^3\right), \quad (3)$$

where m denotes the molecule mass, Θ_r is the rotational characteristic temperature, $\Theta_r = \frac{h^2}{8\pi^2 \mu r_e^2 k}$, and σ equals one and two for heteronuclear and homonuclear diatomic molecules, respectively.

The first step in preparing the total molar Gibbs free energy calculation model is to derive the translational, rotational, and vibrational Gibbs free energy with the help of the following thermodynamic formula (Schwabl, 2006);

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

where H and S represent the enthalpy and entropy, respectively. We describe the internal vibration of the molecule with the aid of the improved Rosen-Morse oscillator. The translational, rotational, and vibrational contributions to the Gibbs free energy of one molar gas are given by, respectively,

$$G^t = -RT \ln \left(\frac{(2\pi m)^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{h^3 P}\right) \quad (5)$$

$$G^r = -RT \ln \left(\frac{T}{\sigma \Theta_r}\left(1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\Theta_r}{T}\right)^3\right)\right), \quad (6)$$

$$G^v = -RT \ln \left(\frac{1}{2} e^{-\frac{D_e}{kT}}\left(e^{\frac{\lambda \eta_1^2}{kT}} - e^{\frac{\lambda \eta_2^2}{kT}} + \sqrt{\frac{\pi kT}{\lambda}}\left(\mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}}\eta_1\right)\right.\right.\right.$$
$$\left. - \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}}\eta_2\right) - e^{-\frac{2\lambda a}{kT}}\mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}}(2a + \eta_1)\right)$$
$$\left.\left.\left. + e^{-\frac{2\lambda a}{kT}}\mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}}(2a + \eta_2)\right)\right)\right)\right), \quad (7)$$

where R is the universal gas constant, and P is gas pressure. The total molar Gibbs free energy is given by

$$G = G^t + G^r + G^v. \quad (8)$$

If we know the experimental values of three molecular constants D_e, r_e, and ω_e, we can easily predict the variations of the total molar Gibbs free energy of the gaseous diatomic molecule system with respect to the temperature.

3. Application to gaseous phosphorus dimer

In order to show the availability of our proposed Gibbs free energy calculation scheme, the above model is applied to the gaseous phosphorus dimer and the results are compared with the experimental data. The experimental values of molecular constants D_e, r_e, and ω_e are obtained by referring to literature (Bu, 1995): $D_e = 4.99$ eV, $r_e = 1.8934$ Å and $\omega_e = 672.20$ cm^{-1}. At one atmosphere pressure and in the temperature range of 298–6000 K, the values of the reduced molar Gibbs free energy, $-(G - H_{298.15})/T$, are presented in Fig. 1, and the experimental data from literature (NIST, 2017) are compared to the predicted values. As indicated in Fig. 1, agreement is excellent in a wide range of temperature. Expression (11) in literature (Jia et al., 2018a) summarizes a calculation scheme for the molar enthalpy of gaseous substance. Applying the molar enthalpy calculation model given in literature (Jia et al., 2018a), we obtain the molar enthalpy value of the gaseous phosphorus dimer at the temperature of 298.15 K, $H_{298.15} = 13.6153 \times 10^3$ J·mol^{-1}. The proposed molar Gibbs free energy calculation model are only related to three molecular constants without the need for a large amount of experimental spec-