Research paper

Predictions of entropy for diatomic molecules and gaseous substances

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ABSTRACT

We present an explicit representation of molar entropy for gaseous substances. Fortunately, through comparison of theoretical and experimental results, we discover that the molar entropies can be successfully predicted by applying experimental values of only four molecular constants for the carbon monoxide, hydrogen chloride, hydrogen fluoride, deuterium fluoride, gaseous boron monobromide, and nitrogen monoxide. The present entropy calculation scheme provides opportunities for predicting successfully entropy values of other gaseous substances with no use of a large number of experimental spectroscopy data.

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1. Introduction

Entropy is an important physical quantity, which has applications in dealing with many issues, including phase transition [1,2], dissolution [3–5], adsorption [6–10], synthesis of materials [11], fluorescence microscopy [12], and protein activity [13–15]. Analytical representation of entropy for molecule systems is one of the most important contemporary chemistry, physics and engineering challenges. Up to date, as far as we know, one has not reported an excellent agreement between the experimental data and theoretical values predicted by using a few molecular constants for entropy values of gaseous diatomic molecule substances in a wide range of temperature. In many statistical mechanics and physical chemistry textbooks, an analytical representation of entropy for diatomic molecule gases is based on a conventional scheme as follows: the internal vibration of a molecule is represented by a harmonic oscillator, and the molecule is treated as a rigid rotor, and the interaction between two molecules is neglected. Unfortunately, when one use the harmonic oscillator to describe the internal vibration of a molecule, the corresponding analytical representation of entropy cannot well predict the entropy values for real gases at high temperatures through comparison of theoretical values and experimental data. This situation leads us to explore a new approach to calculate entropies for actual gases.

With the application of the partition function, one can deduce an analytical representation of entropy. Recently, available analytical expressions of vibrational partition functions have been obtained for the improved versions of the well-known Manning-Rosen, Rosen-Morse, and Tietz molecular potential energy models [16–18]. Based on the necessary conditions satisfied by the molecular potential energy functions, the authors in literature [19] proposed an improved version to the original Tietz potential energy model [20] serving as a more convenient form for the practical applications in dealing with diatomic molecule systems. At high temperatures, the vibrations are apart from harmonicity of vibrations, and the harmonic oscillator approximation works badly. To obtain more accurate vibrational partition functions, one should take into account the effects subject to anharmonicity [21–25]. Here, we employ the improved Tietz oscillator to describe the internal vibration of a molecule, and present a new analytical representation of entropy for gaseous diatomic molecule substances. To verify our model, we simulate the variation of the molar entropy with respect to temperature for some gaseous substances by the aid of four molecular constants given in literature [26–28]. Fortunately, comparison of theoretically calculated results and experimental data reported in literature [29] shows that the molar entropy values can be successfully predicted by using

experimental values of only four molecular constants for the carbon monoxide (CO), hydrogen chloride (HCl), hydrogen fluoride (HF), deuterium fluoride (DF), gaseous boron monobromide (BBr), and nitrogen monoxide (NO). Carbon monoxide is of quite general interest in the fields of medicine, energy technologies and environmental protection [30–32]. Among all the products obtained by the catalytic reductive transformation of CO to fuels and commodity chemicals, CO stores the largest amount of energy per molecule and serves as an important bulk chemical in manufacturing. Carbon monoxide is a highly toxic gas. A great amount of CO are released from tail gases, including coke oven gas, carbon black manufacturing tail gas, blast furnace gas, etc. Air pollution is a heterogeneous mixture of gases and particulate matter. Carbon monoxide is one of the main gaseous components of air pollution, which include ozone, carbon dioxide, nitrogen dioxide, and sulfur dioxide, etc. Hydrochloric acid (HCl) and the mixture of HCl and hydrofluoric acid (HF) have been extensively used as the main stimulation treatments to increase hydrocarbon production in carbonate reservoirs and sandstone reservoirs [33–35]. An acidic solution is injected into the rock where it dissolves the rock and increases the permeability. Halogenated boron species have been widely studied for a long time because of their utility in many semiconductor and metal material etching processes [36]. Nitrogen monoxide is formed in nitrogen-oxygen mixtures under high temperature circumstances, such as those found in internal combustion piston engines, gas turbines, and boilers. Nitrogen monoxide plays a significant role in many issues, including the chemical syntheses, combustion processes, and atmospheric pollutants [37–39].

2. Analytical representation of entropy

The improved Tietz potential energy model provides a quantitative description of the energy-distance relationship between two atoms in a molecule, and is given by [19],

$$U(r) = D_e \left(1 - \frac{e^{\alpha r_e} + q}{e^{\alpha r} + q} \right)^2 \tag{1}$$

where D_e denotes the dissociation energy, and r_e denotes the equilibrium bond length for a diatomic molecule. Parameters α and q are determined by the aid of two expressions [19]:

$$\alpha = 2\pi c \omega_e \sqrt{\frac{2\mu}{D_e} - \frac{32\pi^4 c^2 \mu^2 r_e^3 \alpha_e \omega_e}{3h^2}} - \frac{1}{r_e} \tag{2}$$

$$q = \left(\frac{\alpha}{\pi c \omega_e} \sqrt{\frac{D_e}{2\mu}} - 1 \right) e^{\alpha r_e} \tag{3}$$

where c is the speed of light, h is the Planck constant, μ represents the reduced mass of a diatomic molecule, ω_e represents the equilibrium harmonic vibrational frequency, and α_e represents the vibrational rotational coupling constant.

The vibrational partition function for the improved Tietz oscillator is given by [18],

$$Q = \frac{1}{2} e^{-\frac{D_e}{kT}} \left[e^{\frac{\lambda b_1^2}{kT}} - e^{\frac{\lambda b_2^2}{kT}} + \sqrt{\frac{\pi kT}{\lambda}} \left(\mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} b_1 \right) - \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} b_2 \right) \right. \right.$$
$$\left. \left. - e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_1) \right) + e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_2) \right) \right) \right] \tag{4}$$

where k is the Boltzmann's constant, T is the temperature, $\lambda = \frac{\hbar^2 \alpha^2}{2\mu}$, $\hbar = h/2\pi$, and the parameters b_1, b_2 and δ_1 are defined as

$$b_1 = \frac{\delta_1}{\delta_2} - \frac{\delta_2}{2} \tag{5}$$

$$b_2 = \frac{\delta_1}{v_{\max} + 1 + \delta_2} - \frac{v_{\max} + 1 + \delta_2}{2} \tag{6}$$

$$\delta_1 = \frac{\mu D_e}{\hbar^2 \alpha^2 q^2} (e^{2\alpha r_e} - q^2) \tag{7}$$

here δ_2 is given by

$$\delta_2 = \frac{1}{2} \left(1 \pm \sqrt{1 + \frac{8\mu D_e (e^{\alpha r_e} + q)^2}{\hbar^2 \alpha^2 q^2}} \right),$$

where the plus and minus in $\pm$ correspond to the cases of $q < 0$ and $q > 0$, respectively. The symbol erfi represents the imaginary error function, which is defined as $\mathrm{erfi}(z) = -i\,\mathrm{erf}(iz) = \frac{2}{\sqrt{\pi}} \int_0^z e^{t^2} dt$, and implemented in mathematical software Maple as erfi(z), where erf represents the usual error function. The symbol $v_{\max}$ represents the most vibration quantum number, and is defined as

$$v_{\max} = \left[-\frac{1}{\hbar \alpha q} \sqrt{2\mu D_e (e^{2\alpha r_e} - q^2)} - \frac{1}{2} \left(1 \pm \sqrt{1 + \frac{8\mu D_e (e^{\alpha r_e} + q)^2}{\hbar^2 \alpha^2 q^2}} \right) \right] \tag{8}$$

where [x] represents the greatest integer less than x for non-integer x.

By the aid of the vibrational partition function, we can deduce the expression of the vibrational entropy for the improved Tietz oscillators as follows:

$$S^v = k \ln Q + kT \frac{\partial \ln Q}{\partial T} = k \ln Q - k\beta \frac{\partial \ln Q}{\partial \beta}$$

$$= k \ln \left(\frac{1}{2} e^{-\frac{D_e}{kT}} \left(e^{\frac{\lambda b_1^2}{kT}} - e^{\frac{\lambda b_2^2}{kT}} + \sqrt{\frac{\pi kT}{\lambda}} \left(\mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} b_1 \right) - \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} b_2 \right) \right. \right. \right.$$
$$\left. \left. \left. - e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_1) \right) + e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_2) \right) \right) \right) \right)$$

$$- \frac{k}{kT} \left[e^{\frac{\lambda b_1^2}{kT}} - e^{\frac{\lambda b_2^2}{kT}} + \sqrt{\frac{\pi kT}{\lambda}} \left(\mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} b_1 \right) - \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} b_2 \right) \right. \right.$$
$$\left. \left. - e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_1) \right) + e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_2) \right) \right) \right]^{-1}$$

$$\times \left[-\left(D_e - \lambda b_1^2 \right) e^{\frac{\lambda b_1^2}{kT}} + \left(D_e - \lambda b_2^2 \right) e^{\frac{\lambda b_2^2}{kT}} - \sqrt{\frac{\pi kT}{\lambda}} \left(D_e + \frac{kT}{2} \right) \right.$$

$$\times \left(\mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} b_1 \right) - \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} b_2 \right) - e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_1) \right) \right.$$

$$\left. + e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_2) \right) \right) + b_1 kT e^{\frac{\lambda b_1^2}{kT}} - b_2 kT e^{\frac{\lambda b_2^2}{kT}}$$

$$+ 2\sqrt{\pi \lambda kT} \delta_1 e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_1) \right) - kT\sqrt{2\delta_1 + b_1} e^{\frac{\lambda b_1}{kT}}$$

$$\left. - 2\sqrt{\pi \lambda kT} \delta_1 e^{-\frac{2\lambda \delta_1}{kT}} \mathrm{erfi}\left(\sqrt{\frac{\lambda}{kT}} (2\delta_1 + b_2) \right) + kT\sqrt{2\delta_1 + b_2} e^{\frac{\lambda b_2}{kT}} \right] \tag{9}$$

Entropy values derived from experimental measurements are a combination of the translational, rotational and vibrational entropies. We treat the diatomic molecules as rigid rotors and do not consider the interaction between two molecules. For a system of N identical diatomic molecules, the translational entropy and rotational entropy are given by [40], respectively,