

# Isobaric Molar Heat Capacity Model for the Improved Tietz Potential

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**Abstract:** In this study, the improved Tietz potential was used to describe the internal vibration of a diatomic molecule. With the help of the expression for bound state energy levels, a more generalized equation for the upper bound vibrational quantum number and canonical partition function were obtained for the diatomic system. The obtained partition function was used to derive analytical equation for the prediction of constant pressure (isobaric) molar heat capacity of diatomic molecules. The analytical model was used to predict the constant pressure molar heat capacity data of the ground state CO, BBr, HBr, HI, P<sub>2</sub>, KBr, Br<sub>2</sub>, PBr, SiO and Cl<sub>2</sub> molecules. The upper bound vibrational quantum number obtained for the molecules are 85, 100, 21, 21, 115, 301, 89, 157, 110 and 67. The computed average absolute deviation are 2.3462%, 1.1342%, 2.3350%, 1.9078%, 0.7268%, 2.4041%, 1.7849%, 1.8989%, 2.5209% and 2.1523%. The present results are in good agreement with available literature data on gaseous molecules.

**Keywords:** Partition function, diatomic molecules, heat capacity, thermal properties, improved Tietz potential

## 1. Introduction

The investigation of thermal properties of substances has been a subject of intrinsic importance to the chemist and physicist, this may not be unconnected with their numerous applications in the physical and biological sciences. Measurements of heat capacity has been successfully used to determine transition and melting temperatures of niobium nanoclusters and to study thermoelastic property of crystallographic perovskite [1, 2]. The knowledge of isobaric heat capacity has also led to the construction of efficient dual fuel diesel engine and the thermal strengthening of low expansion glass products [3, 4].

So much interest has been devoted to the theoretical investigation of thermodynamic properties of substances using analytical equations. The analytical models are constructed from diatomic molecule potential energy functions (or oscillators), some examples of oscillators are

given in ref. [5-8]. Analytical (statistical-mechanical) equations for the prediction of thermal properties of gaseous substances are modeled not only in terms of the internal vibration of a molecule, the rotational and translational effects of the molecule are also taken into cognizance. Amongst the thermodynamic properties analyzed include Helmholtz free energy, mean thermal energy, entropy, enthalpy, Gibbs free energy, and heat capacities [9-24].

Quantum statistical ensemble theory (QSET) has recently being used to compute isobaric molar heat capacity data on HCl and HBr molecules [25]. Various formulations of the hyperbolical-type oscillators have also been used to construct statistical-mechanical models, the analytical equations obtained have been successfully used to predict thermal properties of substances [26-32]. The improved Tietz potential (ITP) and some oscillator models derivable from it, such as the shifted Tietz-Wei potential, improved Rosen-Morse oscillator and modified Rosen-Morse oscillator have also been used to derive analytical equations for the prediction of molar entropy, enthalpy and Gibbs free energy of diatomic and triatomic systems [33-47].

It is important to mention that in previous studies, analytical equation for the prediction of isobaric molar heat capacity have not been reported for the ITP. To this end, this paper is aimed at obtaining isobaric molar heat capacity model for the ITP. The paper is organized as follows, in section 2, the expression for isobaric molar heat capacity is derived for the ITP. Results of numerical computations carried out on some selected diatomic molecules are discussed in section 3. A brief conclusion of the work is given in section 4.

## **2. The governing equations**

In this section, analytical equation for the prediction of molar heat capacity at constant pressure is derived for a diatomic system represented by the ITP. The equation is obtained from a simplified version of canonical partition of the system.

### **2.1. The ITP and vibrational energy levels of diatomic molecules**

The potential energy function describing the motion of a diatomic molecule represented by the ITP reads [5]

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

where  $D_e$  and  $r_e$  are the equilibrium dissociation energy and bond length, respectively. The potential parameters  $\alpha$  and  $q$  are given as [48, 49]

$$\alpha = \pi c \omega_e \left( \frac{8\mu}{D_e} \right)^{\frac{1}{2}} - \frac{8\pi^2 c^2 \mu^2 r_e^3 \alpha_e \omega_e}{3\hbar^2} - \frac{1}{r_e}, \quad (2)$$

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

$\alpha_e$  denotes the rotational-vibrational coupling constant,  $\hbar = h/2\pi$ ,  $h$  being the Planck constant.  $\omega_e$  is the equilibrium harmonic vibrational frequency,  $c$  is the speed of light and  $\mu$  denotes the reduced mass of the molecule. For such a system, bound state pure vibrational energy levels are obtained from the following formula [49]

$$E_v = D_e - \frac{\alpha^2 \hbar^2}{2\mu} \left( \frac{\eta}{\nu + \sigma} - \frac{\nu + \sigma}{2} \right)^2, \quad (4)$$

where  $\nu$  is the vibrational quantum number,  $\eta = \frac{\mu D_e}{\alpha^2 \hbar^2} \left( \frac{e^{2\alpha r_e}}{q^2} - 1 \right)$ ,  $\sigma = \frac{1}{2} \pm \sqrt{\frac{1}{4} + \frac{2\mu D_e}{\alpha^2 \hbar^2} \left( \frac{e^{\alpha r_e}}{q} + 1 \right)^2}$ ,  $\pm$  is the usual plus or minus sign. The positive square root is chosen for those molecules with  $q < 0$  and vice-versa.

## 2.2. The upper bound vibrational quantum number

The pure vibrational state energy  $E_v$  is known to increase with increasing  $\nu$  and ceases to increase at the upper bound vibrational quantum number,  $\nu_{\max}$  [11, 49].  $\nu_{\max}$  is a positive quantity, it is obtained by requiring that  $E'_\nu(\nu_{\max}) = 0$ , where prime denotes derivative with respect to  $\nu$ . Solving this equation gives

$$\nu_{\max} = \pm (2\eta)^{\frac{1}{2}} - \sigma. \quad (5)$$

Expression (5) is general and applicable to any diatomic system as opposed to equation (3) of ref. [49] which applies only to diatomic systems with  $q > 0$ .

### 2.3. The canonical partition function

The canonical partition function,  $Q$  of a system of gas molecules is expressed by the product  $Q(T) = Q_v Q_r Q_t$  where  $T$  is the temperature,  $Q_v$ ,  $Q_r$ , and  $Q_t$  are the vibrational, rotational and translational partitions, respectively [48]. The vibrational partition function of the ITP can be expressed as [49]

$$Q_v = \frac{1}{2} e^{-\omega} \left\{ e^{\theta_1^2} - e^{\theta_2^2} + \frac{\sqrt{\pi}}{\varepsilon} \left[ \operatorname{erfi} \theta_1 - \operatorname{erfi} \theta_2 - e^{-2\eta\varepsilon^2} (\operatorname{erfi} \theta_3 - \operatorname{erfi} \theta_4) \right] \right\}, \quad (6)$$

where  $\omega = \beta D_e$ ,  $\varepsilon = \alpha \hbar (\beta / 2\mu)^{1/2}$ ,  $\beta = (k_B T)^{-1}$ ,  $k_B$  is the Boltzmann's constant,  $\theta_1 = \varepsilon \left( \frac{\eta}{\sigma} - \frac{\sigma}{2} \right)$ ,  $\theta_2 = \varepsilon \left( \frac{\eta}{\nu_{\max} + 1 + \sigma} - \frac{\nu_{\max} + 1 + \sigma}{2} \right)$ ,  $\theta_3 = \varepsilon \left( \frac{\eta}{\sigma} + \frac{\sigma}{2} \right)$ ,  $\theta_4 = \varepsilon \left( \frac{\eta}{\nu_{\max} + 1 + \sigma} + \frac{\nu_{\max} + 1 + \sigma}{2} \right)$ ,  $\operatorname{erfi}(x)$  is the well-known imaginary error function of parameter  $x$ . To ensure continuity of the concept, a detailed derivation of expression (6) is given in Appendix A. Based on spectroscopic parameters of several diatomic molecules, the factor  $e^{-2\eta\varepsilon^2} \rightarrow 0$ , therefore, equation (6) is reduced to

$$Q_v = \frac{1}{2} e^{-\omega} \left\{ e^{\theta_1^2} - e^{\theta_2^2} + \frac{\sqrt{\pi}}{\varepsilon} (\operatorname{erfi} \theta_1 - \operatorname{erfi} \theta_2) \right\}. \quad (7)$$

By regarding the atoms of a diatomic molecule as rigid rotors and neglecting the interactions between the molecules,  $Q_r$  and  $Q_t$  can be written as [41, 45]

$$Q_r = \frac{1}{\pi \Theta_r} \left( \frac{1}{k_B \beta} + \frac{\Theta_r}{3} + \frac{\Theta_r k_B}{15} \beta + \frac{4 \Theta_r^2 k_B^2}{315} \beta^2 \right), \quad (8)$$

$$Q_t = \frac{1}{p} \left( \frac{m}{2\pi \hbar^2} \right)^{\frac{3}{2}} \beta^{-\frac{5}{2}}. \quad (9)$$

where  $\Theta_r = \hbar^2 / 2\mu r_e^2 k_B$  is the characteristic temperature,  $p$  is the gas pressure and  $m$  is the mass of the enclosed gas,  $\tau = 1, 2$  for heteronuclear and homonuclear, respectively [25].

### 2.4. The isobaric molar heat capacity model of the ITP

The isobaric molar heat capacity  $C_p$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) of the ITP can be deduced from the expression [25]

$$C_p = -k_B \beta^2 \frac{\partial H}{\partial \beta}, \quad (10)$$

where  $H$  ( $\text{J mol}^{-1}$ ) is the molar enthalpy of the gas molecules expressed through the following equation

$$H = -N_A \left( \frac{\partial \ln Q}{\partial \beta} \right)_V + RTV \left( \frac{\partial \ln Q}{\partial V} \right)_\beta, \quad (11)$$

$V$  represents the volume of the enclosed gas,  $R = N_A k_B$  is the universal (molar) gas constant and  $N_A$  is the Avogadro's number. Inserting (11) into (10) gives

$$C_p = R \left\{ \beta^2 \frac{Q''(\beta)}{Q(\beta)} - \left[ \beta \frac{Q'(\beta)}{Q(\beta)} \right]^2 \right\}, \quad (12)$$

where prime denotes derivative with respect to  $\beta$ . Substituting  $Q = Q_v Q_r Q_t$  into (12) leads to

$$C_p = C_p^v + C_p^r + C_p^t, \quad (13)$$

which is the isobaric molar heat capacity model of the ITP.  $C_p^v$ ,  $C_p^r$ ,  $C_p^t$  are the vibrational, rotational and translation components of the total heat capacity of the system, they are written in compact form as

$$C_p^\delta = R \left\{ \beta^2 \frac{Q_\delta''(\beta)}{Q_\delta(\beta)} - \left[ \beta \frac{Q_\delta'(\beta)}{Q_\delta(\beta)} \right]^2 \right\}, \quad (14)$$

where  $\delta \equiv (v, r, t)$ . The first and second derivatives of  $Q_v(\beta)$  required to obtain  $C_p^v$  are deduced in Appendix B. Using expressions (7)- (9) to eliminate  $Q_\delta$  ( $\delta \equiv (v, r, t)$ ) in (14) gives

$$C_p^t = \frac{5}{2} R, \quad (15)$$

$$C_p^r = R + \frac{2Rk_B\beta}{15\tau\Theta_r} \left( 1 + \frac{4}{7} \Theta_r k_B \beta \right) + \frac{R}{9\tau^2\Theta_r^2} \left( 1 + \frac{2}{5} k_B \beta + \frac{4}{35} \Theta_r k_B^2 \beta^2 \right)^2, \quad (16)$$

$$C_p^v = \frac{R e^{-\omega}}{2Q_v} \left\{ \left( \theta_1^4 + \frac{\theta_1^3}{\varepsilon} - \frac{3}{2\varepsilon} \right) e^{\theta_1^2} - \left( \theta_2^4 + \frac{\theta_2^3}{\varepsilon} - \frac{3}{2\varepsilon} \right) e^{\theta_2^2} + \frac{3\sqrt{\pi}}{4\varepsilon} (\operatorname{erfi} \theta_1 - \operatorname{erfi} \theta_2) \right\} - \frac{R\gamma^2}{4Q_v^2}, \quad (17)$$

where the parameter  $\gamma$  is given by expression (18)

$$\gamma = \left( \theta_1^2 + \frac{\theta_1}{\varepsilon} \right) e^{\theta_1^2 - \omega} - \left( \theta_2^2 + \frac{\theta_2}{\varepsilon} \right) e^{\theta_2^2 - \omega} - \frac{\sqrt{\pi}}{2\varepsilon} e^{-\omega} (\operatorname{erfi} \theta_1 - \operatorname{erfi} \theta_2). \quad (18)$$

### 3. Results and discussion

In this section, the isobaric molar heat capacity model ( $C_p$ ) and the expression for the upper bound vibrational quantum number ( $v_{\max}$ ) are analyzed on some selected diatomic molecules. Experimental values of the relevant molecular constants;  $D_e$ ,  $r_e$ ,  $\omega_e$  and  $\alpha_e$  of the ground state CO [51], BBr [52], HBr [53], HI [54], P<sub>2</sub> [55], KBr [56], Br<sub>2</sub> [57], PBr [58], SiO [59] and Cl<sub>2</sub> [51-60] molecules are listed in Table 1. Potential parameters and upper bound vibrational quantum numbers of the molecules are obtained as listed in Table 1. The last column of the table was computed from equation (3) of ref. [49].

The data in the last-two columns of Table 1 shows that the for molecules with  $q > 0$  (Br<sub>2</sub>, HBr, HI, Cl<sub>2</sub> and P<sub>2</sub>), agreement exists between the results obtained with formula 3 of ref. [49], and equation (5) when the negative square root is used. On the other hand, expression (3) of ref. [49] gives unexpected results ( $v_{\max} < 0$ ) when  $q < 0$  (CO, SiO, BBr, KBr and PBr). Nevertheless, by choosing the positive square root, equation (5) yields  $v_{\max} > 0$  as required. With other potential models,  $v_{\max}$  reported for the Cl<sub>2</sub> and CO molecules are 62 and 83, [61, 62]. Evidently, the results are in good agreement with the data given by equation (5). Therefore, it can be concluded that  $v_{\max} = \pm (2\eta)^{1/2} - \sigma$  is the more general expression for the upper bound vibrational quantum number of the ITP.

The effect of the factor  $e^{-2\eta\varepsilon^2}$  which appears in the partition function (6) is confirmed by evaluating the product  $2\eta\varepsilon^2$  for each of the selected diatomic molecules, the results are summarized in Tables 2-6. From the computed data, it is clear that in the temperature range

300-6000 K, the factor  $e^{-2\eta\epsilon^2} \approx 0$  for each of the molecules. This means that the last-two terms of the partition function (6) can be ignored.

Tables 2-6 also includes theoretical and experimental results on isobaric molar heat capacity of the diatomic molecules. The experimental data were extracted from the National Institute of Standards and Technology (NIST) database [63]. Equation (13) was used to generate the theoretical data at  $p = 0.1$  MPa, and  $T$  ranging from 300- 6000 K. As can be seen from the tables,  $C_p < C_{p\text{NIST}}$  for most of the diatomic molecules, the discrepancy in the results could be linked to lowest-order approximation of expression (7) which by extension, applies to equation (13). The lowest order approximation excludes contributions from quantum correction terms.

To assess the efficiency of the proposed heat capacity model, the average absolute deviation from experimental results ( $\sigma_{\text{ave}}$ ) is adopted as the accuracy indicator, it is written as [25]

$$\sigma_{\text{ave}} = \frac{\Delta C_p}{N_p}, \quad (19)$$

where  $N_p$  is the number of experimental data points

$$\Delta C_p = 100 \left| 1 - \frac{C_p}{C_{p\text{NIST}}} \right|, \quad (20)$$

$C_{p\text{NIST}}$  denotes the experimental data on isobaric molar heat capacity,  $\Delta C_p$  is the relative absolute deviation. The smaller the  $\sigma_{\text{ave}}$ , the more efficient is the model and the more accurate the predicted data.

Using expression (19) and the data in Tables 2-6, average absolute deviations are computed by taking all the data points in the range  $300 \leq T \leq 6000$  K. The computed results, and available literature data are shown in Table 7. The literature results were those reported with  $C_p$  models of QSET, improved generalized Pöschl-Teller potential (IGPTP) and modified hyperbolical-type potential (MHTP). The results show that the present data agrees with existing literature

results on CO and P<sub>2</sub> molecules. From the results in Table 7, it is also evident that equation (13) yields the better results for Br<sub>2</sub> molecules compared to the C<sub>p</sub> model of the IGPTP [30]. The last column of Table 7 evidently depicts the near equivalence of the C<sub>p</sub> models of the ITP and MHTP on gaseous chlorine molecules.

The applicability of the C<sub>p</sub> model to different regions of the temperature domain, viz low (Low), moderate (Moderate) and high (High) temperature range is examined on the selected diatomic molecules. Table 7 gives the average absolute deviation obtained for the different regions. Figure 1-10 shows the variation of relative absolute deviation ( $\Delta C_p$ ) versus temperature of the molecules. The blue line segment in the figures represent the average absolute deviation ( $\sigma_{ave}$ ) for the temperature range 300- 6000 K.

In the low temperature region of figures 1-6,  $\Delta C_p > \sigma_{ave}$  for the CO, BBr, HBr, HI and P<sub>2</sub> molecules, in addition,  $C_p > C_{pNIST}$ . The results show that contributions from quantum correction terms are not required to improve the performance of the model. The presence of these terms will only increase  $\Delta C_p$  and decrease the efficiency of the model. The discrepancy in the C<sub>p</sub> and C<sub>pNIST</sub> data can be attributed to the rigid-rotor approximation of expression (13). In the moderate to high temperature range,  $\Delta C_p < \sigma_{ave}$ , the average absolute deviations obtained for the molecules are 1.4721%, 0.9898%, 1.2341%, 0.8451% and 0.4604%, respectively. The results show that, the C<sub>p</sub> model suggested for the ITP is a near perfect analytical equation for predicting molar heat capacity data on these diatomic molecules.

In the low to moderate temperature region shown in figure 6 representing the KBr molecule,  $\Delta C_p \leq \sigma_{ave}$ , the average absolute deviation is deduced as 1.3524%. Thus, it can be inferred that within an error limit of about 1% of NIST data, the proposed C<sub>p</sub> model can effectively be used to obtain isobaric molar heat capacity data for the ground state KBr molecule. However, the model gives less accurate results when used to predict data in the high temperature domain, in this region,  $\Delta C_p > \sigma_{ave}$ .

The variation of  $\Delta C_p$  with temperature is given in figure 7 for the gaseous  $\text{Br}_2$  molecule. The figure reveals that in the moderate temperature region,  $\Delta C_p > \sigma_{\text{ave}}$ . This means that results predicted by expression (13) are accurate to within an error limit of 2% of experimental data. The average absolute deviation computed for the molecule in the low and high temperature regions are 1.1069% and 0.6762%, respectively. It is also noted that in each of the regions,  $\Delta C_p < \sigma_{\text{ave}}$ . The results reveal that the analytical model yields more accurate results for predictions in the low and high temperature regions.

With the aid of the plot shown in figure 8 representing data points obtained with the PBr molecule,  $\Delta C_p < \sigma_{\text{ave}}$  in the low to moderate temperature region. For this region, the average absolute deviation calculated is 1.5335%. The result does not differ appreciably from  $\sigma_{\text{ave}} = 1.8989\%$ . Also, in the high temperature region,  $\Delta C_p > \sigma_{\text{ave}}$ , therefore, regional variations are not necessary with the PBr molecule

The data in Table 6 shows that in the low temperature range (300- 1000 K), the observed heat capacity data on SiO molecules are slightly lower than the predicted results. In figure 9,  $\Delta C_p > \sigma_{\text{ave}}$  in the low, and high temperature regimes, in virtue of this, the isobaric heat capacity results predicted by the current model are only accurate to within 2.5% of the NIST data. Considering the moderate temperature range, it is obvious that  $\Delta C_p < \sigma_{\text{ave}}$ , average absolute deviation computed for the molecule in this temperature range is 1.2859%. Thus, it can be concluded that results predicted by the model are more accurate for predictions in the moderate temperature region and less accurate for predictions in the low and high temperature range.

The data points in figure 10 depicts the variation of  $\Delta C_p$  with temperature for the chlorine molecule. It can be seen that in the low and high temperature range,  $\Delta C_p < \sigma_{\text{ave}}$ , the average absolute deviations obtained are 1.3182 and 1.1202%, respectively. The obtained result clearly demonstrates the applicability of the  $C_p$  model to predict heat capacity data for the  $\text{Cl}_2$

molecule. However, in the high temperature regime, the analytical model is less efficient since in this temperature range,  $\Delta C_p > \sigma_{\text{ave}}$ .

#### **4. Concluding remarks**

In this work, the improved Tietz potential was used to model the internal vibration of a diatomic molecule. By employing an existing equation for bound state energy eigenvalues of the improved Tietz potential, equation to determine the upper bound vibrational quantum number and canonical partition function were derived. Explicit equation for predicting the isobaric molar heat capacity of diatomic molecules was deduced from the partition function. The equations obtained were applied to some selected diatomic molecules in their ground states viz CO, BBr, HBr, HI, P<sub>2</sub>, KBr, Br<sub>2</sub>, PBr, SiO and Cl<sub>2</sub>. Upper bound vibrational quantum number calculated for the molecules are 85, 100, 21, 21, 115, 301, 89, 157, 110 and 67. The average absolute deviation obtained for the diatomic molecules are 2.3462%, 1.1342%, 2.3350%, 1.9078%, 0.7268%, 2.4041%, 1.7849%, 1.8989%, 2.5209% and 2.1523%. The results obtained are in good agreement with existing literature data on gaseous molecules. The proposed molar heat capacity model could have useful applications in statistical mechanics, engineering and in thermochemical processes related to diatomic molecules

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## Appendix A

### Explicit expression of vibrational partition function for the ITP

The vibrational partition function is given by [49, 50]

$$Q_\nu(\beta) = \sum_{\nu=0}^{\nu_{\max}} e^{-\beta E_\nu}. \quad (\text{A1})$$

Replacing equation (2) into (A1) gives

$$Q_\nu(\beta) = e^{-\omega} \sum_{\nu=0}^{\nu_{\max}} G(\nu), \quad (\text{A2})$$

where

$$G(\nu) = e^{\varepsilon^2 \left( \frac{\eta}{\nu+\sigma} - \frac{\nu+\sigma}{2} \right)^2}, \quad (\text{A3})$$

$\omega = \beta D_e$ ,  $\varepsilon = \alpha \hbar (\beta / 2\mu)^{1/2}$ ,  $\beta = (k_B T)^{-1}$ ,  $k_B$  is the Boltzmann's constant. The summation which appears in (A2) can be evaluated with the aid of Poisson summation formula [50], it is written as

$$\sum_{\nu=0}^{\nu_{\max}} G(\nu) = \frac{1}{2} \{G(0) - G(\nu_{\max} + 1)\} + \sum_{j=-\infty}^{j=+\infty} \int_0^{\nu_{\max}+1} G(x) e^{-i2\pi jx} dx. \quad (\text{A4})$$

Expression (A4) contains infinitely many terms, the terms with  $j \neq 0$  are the quantum correction terms. An approximate summation can be obtained by neglecting the terms with  $j \neq 0$ , that is

$$\sum_{\nu=0}^{\nu_{\max}} G(\nu) = \frac{1}{2} \{G(0) - G(\nu_{\max} + 1)\} + \int_0^{\nu_{\max}+1} G(x) e^{-i2\pi jx} dx. \quad (\text{A5})$$

Putting (A3) into the right hand side of (A5) yields

$$\sum_{\nu=0}^{\nu_{\max}} G(\nu) = \frac{1}{2} (e^{\theta_1^2} - e^{\theta_2^2}) + I_1, \quad (\text{A6})$$

where  $\theta_1 = \varepsilon \left( \frac{\eta}{\sigma} - \frac{\sigma}{2} \right)$ ,  $\theta_2 = \varepsilon \left( \frac{\eta}{\nu_{\max}+1+\sigma} - \frac{\nu_{\max}+1+\sigma}{2} \right)$ , and

$$I_1 = \int_0^{\nu_{\max}+1} e^{\varepsilon^2 \left( \frac{\eta}{x+\sigma} - \frac{x+\sigma}{2} \right)^2} dx. \quad (\text{A7})$$

Letting

$$y = \varepsilon \left( \frac{\eta}{x + \sigma} - \frac{x + \sigma}{2} \right), \quad (\text{A8})$$

we note that the new integration limits in (A5) are  $y(0) \equiv \theta_1$  and  $y(v_{\max}+1) \equiv \theta_2$ . Also, expression (A8) gives

$$x = \frac{-y + \sqrt{y^2 + 2\eta\varepsilon^2}}{\varepsilon} - \sigma. \quad (\text{A9})$$

From (A9), we obtained

$$dx = \frac{1}{\varepsilon} \left( -1 + \frac{y}{\sqrt{y^2 + 2\eta\varepsilon^2}} \right) dy. \quad (\text{A10})$$

Using (A8), (A10),  $y(0) \equiv \theta_1$  and  $y(v_{\max}+1) \equiv \theta_2$  in (A7) yields

$$I_1 = \frac{1}{\varepsilon} \int_{\theta_1}^{\theta_2} e^{y^2} \left( -1 + \frac{y}{\sqrt{y^2 + 2\eta\varepsilon^2}} \right) dy \equiv -\frac{\sqrt{\pi}}{2\varepsilon} (\operatorname{erfi} \theta_2 - \operatorname{erfi} \theta_1) + I_2, \quad (\text{A11})$$

where  $\operatorname{erfi} x$  is the imaginary error function of  $x$ ,

$$I_2 = \frac{1}{\varepsilon} \int_{\theta_1}^{\theta_2} \frac{e^{y^2} y dy}{\sqrt{y^2 + 2\eta\varepsilon^2}}. \quad (\text{A12})$$

To obtain  $I_2$ , consider the following transformation

$$z = \sqrt{y^2 + 2\eta\varepsilon^2}, \quad (\text{A13})$$

The integration limits in (A12) transform to

$$\theta_3 = z(\theta_1) = \sqrt{\varepsilon^2 \left( \frac{\eta}{\sigma} - \frac{\sigma}{2} \right)^2 + 2\eta\varepsilon^2} \equiv \varepsilon \left( \frac{\eta}{\sigma} + \frac{\sigma}{2} \right), \quad (\text{A14})$$

$$\theta_4 = z(\theta_2) = \sqrt{\varepsilon^2 \left( \frac{\eta}{v_{\max} + 1 + \sigma} - \frac{v_{\max} + 1 + \sigma}{2} \right)^2 + 2\eta\varepsilon^2} \equiv \varepsilon \left( \frac{\eta}{v_{\max} + 1 + \sigma} + \frac{v_{\max} + 1 + \sigma}{2} \right). \quad (\text{A15})$$

Putting (A13)- (A15) into (A12)

$$I_2 = \frac{1}{\varepsilon} \int_{\theta_3}^{\theta_4} \frac{e^{z^2 - 2\eta\varepsilon^2} z dz}{z} \equiv \frac{e^{-2\eta\varepsilon^2}}{\varepsilon} \int_{\theta_3}^{\theta_4} e^{z^2} dz. \quad (\text{A16})$$

The definite integral in (A16) yields

$$I_2 = \frac{e^{-2\eta\epsilon^2}}{\epsilon} \frac{\sqrt{\pi}}{2} (\operatorname{erfi} \theta_4 - \operatorname{erfi} \theta_3). \quad (\text{A17})$$

Inserting expressions (A17), (A11) and (A6) into (A2), the approximate expression of the vibrational partition function is obtained as

$$Q_v = \frac{1}{2} e^{-\omega} \left\{ e^{\theta_1^2} - e^{\theta_2^2} + \frac{\sqrt{\pi}}{\epsilon} \left[ \operatorname{erfi} \theta_1 - \operatorname{erfi} \theta_2 - e^{-2\eta\epsilon^2} (\operatorname{erfi} \theta_3 - \operatorname{erfi} \theta_4) \right] \right\}. \quad (\text{A18})$$

Given the parameters of physical system such as the diatomic molecules in this study, the factor  $e^{-2\eta\epsilon^2}$  which appears in (A18) is infinitesimally small, letting  $e^{-2\eta\epsilon^2} \rightarrow 0$  gives

$$Q_v = \frac{1}{2} e^{-\omega} \left\{ e^{\theta_1^2} - e^{\theta_2^2} + \frac{\sqrt{\pi}}{\epsilon} (\operatorname{erfi} \theta_1 - \operatorname{erfi} \theta_2) \right\}. \quad (\text{A19})$$

## Appendix B

### First and second derivatives of vibrational partition function

In this section, the first and second derivatives of the vibrational partition function are obtained. These derivatives are required to obtaining the explicit expression of the vibrational component of the isobaric molar heat capacity. For simplicity, expression (A19) is re-written as

$$Q_v = A - B + C - D, \quad (\text{B1})$$

where

$$A = \frac{1}{2} e^{\theta_1^2 - \omega}, \quad (\text{B2})$$

$$B = \frac{1}{2} e^{\theta_2^2 - \omega}, \quad (\text{B3})$$

$$C = \frac{\sqrt{\pi}}{2\varepsilon} e^{-\omega} \operatorname{erfi} \theta_1, \quad (\text{B4})$$

$$D = \frac{\sqrt{\pi}}{2\varepsilon} e^{-\omega} \operatorname{erfi} \theta_2. \quad (\text{B5})$$

We first note that  $\omega' = \omega/\beta$ ,  $\varepsilon' = 1/2\beta$ ,  $\theta_1' = \theta_1/2\beta$  and  $\theta_2' = \theta_2/2\beta$ , where prime denotes derivative with respect to  $\beta$ . Equation (B2) gives

$$A' = (2\theta_1\theta_1' - \omega') \frac{1}{2} e^{\theta_1^2 - \omega} \equiv \frac{1}{\beta} (\theta_1^2 - \omega) A, \quad (\text{B6})$$

the derivative of (B6) yields

$$A'' = \left\{ \frac{1}{\beta^2} (\theta_1^2 - \omega)^2 + \frac{\beta(2\theta_1\theta_1' - \omega') - (\theta_1^2 - \omega)}{\beta^2} \right\} A \equiv \frac{1}{\beta^2} (\theta_1^2 - \omega)^2 A. \quad (\text{B7})$$

The mapping  $\theta_1 \rightarrow \theta_2$ ,  $A \rightarrow B$  transform expressions (B6) and (B7) to

$$B' = \frac{1}{\beta} (\theta_2^2 - \omega) B, \quad (\text{B8})$$

$$B'' = \frac{1}{\beta^2} (\theta_2^2 - \omega)^2 B. \quad (\text{B9})$$

Next is to consider the derivative of equation (B4), the work is simpler if logarithm is introduced, thus

$$\ln C = \ln(\operatorname{erfi} \theta_1) - \ln \varepsilon + \ln \left( \frac{\sqrt{\pi}}{2} \right) - \omega, \quad (\text{B10})$$

Differentiating (B10) with respect to  $\beta$  yields

$$\frac{C'}{C} = \frac{1}{\operatorname{erfi} \theta_1} \frac{2e^{\theta_1^2}}{\sqrt{\pi}} \theta_1' - \frac{\varepsilon'}{\varepsilon} - \omega' \equiv \frac{1}{\operatorname{erfi} \theta_1} \frac{2e^{\theta_1^2}}{\sqrt{\pi}} \frac{\theta_1}{2\beta} - \frac{1}{2\beta} - \frac{\omega}{\beta}, \quad (\text{B11})$$

Expression (B11) gives

$$C' = \frac{\theta_1 A}{\beta \varepsilon} - \frac{1}{\beta} \left( \omega + \frac{1}{2} \right) C. \quad (\text{B12})$$

To obtain  $C''$  (B12) is re-written as

$$\frac{C'}{C} = X - \frac{1}{\beta} \left( \omega + \frac{1}{2} \right), \quad X = \frac{\theta_1 A}{\beta \varepsilon C} \quad (\text{B13})$$

The logarithm of (B13) is  $\ln X = \ln \theta_1 - \ln \varepsilon - \ln \beta + \ln A - \ln C$ , differentiating this expression gives

$$\frac{X'}{X} = \frac{\theta_1'}{\theta_1} - \frac{\varepsilon'}{\varepsilon} - \frac{1}{\beta} + \frac{A'}{A} - \frac{C'}{C} \equiv -\frac{1}{\beta} + \frac{A'}{A} - \frac{C'}{C}. \quad (\text{B14})$$

Inserting equations (B13) and (B6) into (B14) and simplifying, we have

$$X^2 + X' = \frac{X}{\beta} \left( \theta_1^2 - \frac{1}{2} \right). \quad (\text{B15})$$

Differentiate (B13) to get

$$\begin{aligned} \frac{C''}{C} &= X^2 - \frac{X}{\beta} (2\omega + 1) + \frac{1}{\beta^2} \left( \omega + \frac{1}{2} \right)^2 + X' - \frac{\beta \omega' - \omega}{\beta} + \frac{1}{2\beta^2} \\ &\equiv X^2 + X' - \frac{X}{\beta} (2\omega + 1) + \frac{1}{\beta^2} \left( \omega^2 + \omega + \frac{3}{4} \right). \end{aligned} \quad (\text{B16})$$

Note that in arriving at (B16), the identity  $C''/C = (C'/C)^2 + (C'/C)'$  has been used. Substituting (B15) in (B16), we obtained

$$\frac{C''}{C} = \frac{X}{\beta} \left( \theta_1^2 - 2\omega - \frac{3}{2} \right) + \frac{1}{\beta^2} \left( \omega^2 + \omega + \frac{3}{4} \right). \quad (\text{B17})$$

Therefore, by substituting  $X = \frac{\theta_1 A}{\beta \epsilon C}$  into (B17), we obtained

$$C'' = \frac{\theta_1}{\beta^2 \epsilon} \left( \theta_1^2 - 2\omega - \frac{3}{2} \right) A + \frac{1}{\beta^2} \left( \omega^2 + \omega + \frac{3}{4} \right) C. \quad (\text{B18})$$

The transformations  $\theta_1 \rightarrow \theta_2$ ,  $A \rightarrow B$ ,  $C \rightarrow D$  applied to (B12) and (B18) yields

$$D' = \frac{\theta_2 B}{\beta \epsilon} - \frac{1}{\beta} \left( \omega + \frac{1}{2} \right) D, \quad (\text{B19})$$

$$D'' = \frac{\theta_2}{\beta^2 \epsilon} \left( \theta_1^2 - 2\omega - \frac{3}{2} \right) B + \frac{1}{\beta^2} \left( \omega^2 + \omega + \frac{3}{4} \right) D. \quad (\text{B20})$$

These relations make it possible to obtain the first and second derivatives of the vibrational partition function from equation (B1) as

$$Q_v' = A' - B' + C' - D', \quad (\text{B21})$$

$$Q_v'' = A'' - B'' + C'' - D''. \quad (\text{B22})$$

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## List of Tables

Table 1: Spectroscopic and molecular parameters of the diatomic molecules investigated in the present work along with upper bound vibrational quantum numbers.

Molecule	Molecular state	Molecular parameter				Ref.	Potential parameter		$v_{\max}$	
		$D_e$ (cm <sup>-1</sup> )	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$\alpha_e$ (cm <sup>-1</sup> )		$\alpha$ (Å <sup>-1</sup> )	$q$	Eqn. (5)	[49]
CO	X <sup>1</sup> Σ <sup>+</sup>	90670	1.12832320	2169.8129	0.01750406	[51]	2.2047	-0.4913	85	-4179
BBr	X <sup>1</sup> Σ <sup>+</sup>	32711	1.887	685.1892	0.0042392	[52]	1.2795	-1.1327	100	-1987
HBr	X <sup>1</sup> Σ <sup>+</sup>	30165.13 <sup>b</sup>	1.417	2668	0.225	[53]	2.0346	1.6107	21	21
HI	X <sup>1</sup> Σ <sup>+</sup>	25776.67 <sup>c</sup>	1.609	2309.01	0.16886	[54]	1.9288	2.2580	21	21
P <sub>2</sub>	X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	40247.06 <sup>d</sup>	1.8934	672.20	0.0015	[55]	1.7207	1.8602	115	115
KBr	X <sup>1</sup> Σ <sup>+</sup>	2273.91	2.937	196.6	0.000393	[56]	0.4986	-1.6689	301	-1500
Br <sub>2</sub>	X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	15894	2.2810213	325.314194	0.00032057	[57]	2.3753	44.1762	89	89
PBr	X <sup>3</sup> Σ <sup>-</sup>	36000	2.1714	458.35	0.00069	[58]	1.3748	-0.1805	157	-34616
SiO	X <sup>1</sup> Σ <sup>+</sup>	66494.76 <sup>a</sup>	1.5169	1232.51	0.0049	[59]	1.7739	-0.6594	110	-4936
Cl <sub>2</sub>	X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	20276.44	1.98720	559.7507	0.0015163	[60]	2.3060	14.8611	67	67

66494.76<sup>a</sup> cm<sup>-1</sup> = 8.2443 eV; 30165.13<sup>b</sup> cm<sup>-1</sup> = 3.74 eV; 25776.67<sup>c</sup> cm<sup>-1</sup> = 3.1959 eV; 40247.06<sup>d</sup> cm<sup>-1</sup> = 4.99 eV

Table 2: Isobaric molar heat capacity (experimental and theoretical) data as a function of temperature for the selected diatomic molecules along with the product  $2\eta\epsilon^2$

CO ( $X^1\Sigma^+$ )				BBr ( $X^1\Sigma^+$ )											
$T$ (K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )		$2\eta\epsilon^2$	$T$ [63]	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )		$2\eta\epsilon^2$	$T$ (K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )		$2\eta\epsilon^2$	$T$ (K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )		$2\eta\epsilon^2$
	[63]	(13)			[63]	(13)			[63]	(13)			[63]	(13)	
300	29.142	31.665	260363.586	3300	37.392	36.839	23669.417	300	32.824	34.515	15132.774	3100	38.573	38.050	1464.462
400	29.342	32.263	195272.690	3400	37.443	36.880	22973.258	350	33.684	34.885	12970.949	3200	38.617	38.095	1418.698
500	29.794	32.776	156218.152	3500	37.493	36.918	22316.879	400	34.373	35.193	11349.581	3300	38.660	38.140	1375.707
600	30.443	33.217	130181.793	3600	37.543	36.955	21696.966	450	34.921	35.453	10088.516	3400	38.703	38.187	1335.245
700	31.171	33.601	111584.394	3700	37.589	36.991	21110.561	500	35.359	35.673	9079.664	3500	38.746	38.234	1297.095
800	31.899	33.936	97636.345	3800	37.631	37.025	20555.020	600	35.999	36.028	7566.387	3600	38.789	38.283	1261.065
900	32.577	34.231	86787.862	3900	37.673	37.057	20027.968	700	36.435	36.298	6485.475	3700	38.831	38.333	1226.982
1000	33.183	34.493	78109.076	4000	37.715	37.089	19527.269	800	36.747	36.511	5674.790	3800	38.873	38.385	1194.693
1100	33.710	34.725	71008.251	4100	37.756	37.119	19050.994	900	36.981	36.683	5044.258	3900	38.915	38.437	1164.060
1200	34.175	34.933	65090.897	4200	37.794	37.148	18597.399	1000	37.164	36.825	4539.832	4000	38.957	38.491	1134.958
1300	34.572	35.120	60083.905	4300	37.832	37.176	18164.901	1100	37.311	36.944	4127.120	4100	38.999	38.546	1107.276
1400	34.920	35.288	55792.197	4400	37.869	37.203	17752.063	1200	37.434	37.047	3783.194	4200	39.040	38.603	1080.912
1500	35.217	35.441	52072.717	4500	37.903	37.229	17357.572	1300	37.539	37.136	3492.179	4300	39.082	38.660	1055.775
1600	35.480	35.580	48818.172	4600	37.941	37.255	16980.234	1400	37.631	37.215	3242.737	4400	39.123	38.719	1031.780
1700	35.710	35.706	45946.515	4700	37.974	37.280	16618.952	1500	37.714	37.287	3026.555	4500	39.164	38.778	1008.852
1800	35.911	35.822	43393.931	4800	38.007	37.304	16272.724	1600	37.788	37.351	2837.395	4600	39.205	38.838	986.920
1900	36.091	35.929	41110.040	4900	38.041	37.327	15940.628	1700	37.857	37.411	2670.490	4700	39.246	38.899	965.922
2000	36.250	36.027	39054.538	5000	38.074	37.350	15621.815	1800	37.921	37.467	2522.129	4800	39.287	38.960	945.798
2100	36.392	36.118	37194.798	5100	38.104	37.372	15315.505	1900	37.982	37.519	2389.385	4900	39.328	39.021	926.496
2200	36.518	36.202	35504.125	5200	38.137	37.394	15020.976	2000	38.039	37.568	2269.916	5000	39.369	39.082	907.966
2300	36.635	36.280	33960.468	5300	38.171	37.415	14737.561	2100	38.094	37.616	2161.825	5100	39.409	39.143	890.163
2400	36.740	36.353	32545.448	5400	38.200	37.436	14464.644	2200	38.147	37.662	2063.560	5200	39.450	39.204	873.045
2500	36.836	36.421	31243.630	5500	38.233	37.457	14201.650	2300	38.199	37.706	1973.840	5300	39.491	39.264	856.572
2600	36.924	36.485	30041.952	5600	38.263	37.477	13948.049	2400	38.249	37.750	1891.597	5400	39.531	39.323	840.710
2700	37.003	36.545	28929.287	5700	38.296	37.496	13703.347	2500	38.297	37.793	1815.933	5500	39.571	39.381	825.424
2800	37.083	36.601	27896.099	5800	38.325	37.516	13467.082	2600	38.345	37.835	1746.089	5600	39.612	39.438	810.684
2900	37.150	36.654	26934.164	5900	38.355	37.535	13238.826	2700	38.392	37.878	1681.419	5700	39.652	39.494	796.462
3000	37.217	36.704	26036.359	6000	38.388	37.554	13018.179	2800	38.438	37.920	1621.369	5800	39.693	39.548	782.730
3100	37.279	36.751	25196.476	...	...	...	...	2900	38.483	37.963	1565.459	5900	39.733	39.600	769.463
3200	37.338	36.796	24409.086	...	...	...	...	3000	38.528	38.006	1513.277	6000	39.773	39.650	756.639

Table 3: Isobaric molar heat capacity (experimental and theoretical) data as a function of temperature for the selected diatomic molecules along with the product  $2\eta\epsilon^2$

HBr ( $X^1\Sigma^+$ )							HI ( $X^1\Sigma^+$ )								
$T$ (K)	$C_p$ (J mol $^{-1}$ K $^{-1}$ )		$2\eta\epsilon^2$	$T$ [63]	$C_p$ (J mol $^{-1}$ K $^{-1}$ )		$2\eta\epsilon^2$	$T$ (K)	$C_p$ (J mol $^{-1}$ K $^{-1}$ )		$2\eta\epsilon^2$	$T$ (K)	$C_p$ (J mol $^{-1}$ K $^{-1}$ )		$2\eta\epsilon^2$
	[63]	(13)			[63]	(13)			[63]	(13)			[63]	(13)	
300	29.141	31.112	17658.567	3100	37.673	36.928	1708.894	300	29.158	31.345	11905.582	3100	38.009	37.392	1152.153
350	29.167	31.380	15135.915	3200	37.767	37.023	1655.491	350	29.216	31.635	10204.784	3200	38.095	37.502	1116.148
400	29.220	31.632	13243.925	3300	37.857	37.118	1605.324	400	29.328	31.906	8929.186	3300	38.178	37.613	1082.326
450	29.313	31.870	11772.378	3400	37.943	37.213	1558.109	450	29.502	32.161	7937.055	3400	38.258	37.722	1050.493
500	29.453	32.096	10595.140	3500	38.025	37.307	1513.591	500	29.736	32.401	7143.349	3500	38.335	37.832	1020.478
600	29.870	32.511	8829.284	3600	38.104	37.400	1471.547	600	30.348	32.839	5952.791	3600	38.409	37.941	992.132
700	30.427	32.886	7567.957	3700	38.181	37.494	1431.776	700	31.064	33.231	5102.392	3700	38.481	38.050	965.317
800	31.055	33.225	6621.963	3800	38.254	37.587	1394.097	800	31.798	33.581	4464.593	3800	38.550	38.158	939.914
900	31.698	33.534	5886.189	3900	38.325	37.680	1358.351	900	32.496	33.898	3968.527	3900	38.618	38.265	915.814
1000	32.319	33.815	5297.570	4000	38.394	37.773	1324.393	1000	33.135	34.185	3571.675	4000	38.684	38.371	892.919
1100	32.897	34.073	4815.973	4100	38.461	37.866	1292.090	1100	33.706	34.447	3246.977	4100	38.749	38.475	871.140
1200	33.425	34.311	4414.642	4200	38.526	37.959	1261.326	1200	34.211	34.686	2976.395	4200	38.812	38.577	850.399
1300	33.902	34.530	4075.054	4300	38.589	38.051	1231.993	1300	34.655	34.907	2747.442	4300	38.874	38.676	830.622
1400	34.329	34.734	3783.979	4400	38.651	38.143	1203.993	1400	35.046	35.111	2551.196	4400	38.934	38.773	811.744
1500	34.711	34.923	3531.713	4500	38.711	38.235	1177.238	1500	35.391	35.301	2381.116	4500	38.994	38.867	793.705
1600	35.053	35.100	3310.981	4600	38.770	38.325	1151.646	1600	35.696	35.478	2232.297	4600	39.052	38.958	776.451
1700	35.360	35.266	3116.218	4700	38.828	38.414	1127.143	1700	35.967	35.644	2100.985	4700	39.110	39.045	759.931
1800	35.635	35.422	2943.095	4800	38.885	38.502	1103.660	1800	36.209	35.801	1984.264	4800	39.166	39.127	744.099
1900	35.884	35.569	2788.195	4900	38.941	38.589	1081.137	1900	36.427	35.949	1879.829	4900	39.222	39.206	728.913
2000	36.109	35.709	2648.785	5000	38.996	38.674	1059.514	2000	36.623	36.090	1785.837	5000	39.277	39.280	714.335
2100	36.313	35.841	2522.652	5100	39.050	38.757	1038.739	2100	36.802	36.224	1700.797	5100	39.332	39.349	700.328
2200	36.500	35.967	2407.986	5200	39.103	38.838	1018.763	2200	36.966	36.354	1623.488	5200	39.385	39.413	686.860
2300	36.672	36.088	2303.291	5300	39.155	38.917	999.542	2300	37.116	36.479	1552.902	5300	39.439	39.473	673.901
2400	36.830	36.204	2207.321	5400	39.207	38.993	981.032	2400	37.255	36.600	1488.198	5400	39.491	39.526	661.421
2500	36.976	36.316	2119.028	5500	39.258	39.067	963.195	2500	37.384	36.718	1428.670	5500	39.544	39.575	649.395
2600	37.111	36.424	2037.527	5600	39.309	39.137	945.995	2600	37.504	36.833	1373.721	5600	39.595	39.618	637.799
2700	37.238	36.530	1962.063	5700	39.359	39.204	929.398	2700	37.617	36.947	1322.842	5700	39.647	39.656	626.610
2800	37.357	36.632	1891.989	5800	39.408	39.269	913.374	2800	37.723	37.060	1275.598	5800	39.698	39.688	615.806
2900	37.468	36.732	1826.748	5900	39.457	39.329	897.893	2900	37.823	37.171	1231.612	5900	39.748	39.714	605.369
3000	37.573	36.831	1765.857	6000	39.506	39.386	882.928	3000	37.918	37.282	1190.558	6000	39.798	39.735	595.279

Table 4: Isobaric molar heat capacity (experimental and theoretical) data as a function of temperature for the selected diatomic molecules along with the product  $2\eta\epsilon^2$

P <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )								KBr (X <sup>1</sup> Σ <sup>+</sup> )							
T (K)	C <sub>p</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )		2ηε <sup>2</sup>	T [63]	C <sub>p</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )		2ηε <sup>2</sup>	T (K)	C <sub>p</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )		2ηε <sup>2</sup>	T (K)	C <sub>p</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )		2ηε <sup>2</sup>
	[63]	(13)			[63]	(13)			[63]	(13)			[63]	(13)	
300	32.069	34.123	37504.817	3100	38.017	37.815	3629.498	300	36.932	37.076	623.090	3200	39.932	38.898	58.415
350	32.945	34.504	32146.986	3200	38.045	37.849	3516.077	350	37.155	37.180	534.077	3300	40.012	38.982	56.645
400	33.679	34.825	28128.613	3300	38.072	37.883	3409.529	400	37.316	37.258	467.317	3400	40.091	39.067	54.978
450	34.280	35.099	25003.211	3400	38.099	37.916	3309.249	450	37.440	37.319	415.393	3500	40.170	39.152	53.408
500	34.770	35.335	22502.890	3500	38.126	37.950	3214.699	500	37.541	37.368	373.854	3600	40.249	39.237	51.924
600	35.499	35.719	18752.408	3600	38.152	37.985	3125.401	600	37.701	37.447	311.545	3700	40.328	39.320	50.521
700	36.000	36.015	16073.493	3700	38.178	38.019	3040.931	700	37.829	37.508	267.038	3800	40.408	39.402	49.191
800	36.356	36.251	14064.306	3800	38.204	38.054	2960.907	800	37.940	37.561	233.659	3900	40.487	39.482	47.930
900	36.618	36.442	12501.606	3900	38.229	38.090	2884.986	900	38.041	37.607	207.697	4000	40.566	39.558	46.732
1000	36.819	36.600	11251.445	4000	38.254	38.126	2812.861	1000	38.136	37.651	186.927	4100	40.645	39.632	45.592
1100	36.976	36.732	10228.586	4100	38.279	38.162	2744.255	1100	38.226	37.694	169.934	4200	40.724	39.701	44.506
1180	37.079	36.824	9535.058	4200	38.304	38.200	2678.915	1200	38.314	37.735	155.772	4300	40.803	39.766	43.471
1200	37.103	36.846	9376.204	4300	38.328	38.238	2616.615	1300	38.400	37.776	143.790	4400	40.882	39.826	42.483
1300	37.208	36.944	8654.958	4400	38.353	38.277	2557.147	1400	38.484	37.817	133.519	4500	40.961	39.881	41.539
1400	37.296	37.030	8036.746	4500	38.377	38.317	2500.321	1500	38.568	37.859	124.618	4600	41.040	39.930	40.636
1500	37.373	37.106	7500.963	4600	38.401	38.358	2445.966	1600	38.650	37.902	116.829	4700	41.119	39.973	39.772
1600	37.440	37.175	7032.153	4700	38.425	38.399	2393.924	1700	38.732	37.946	109.957	4800	41.198	40.010	38.943
1700	37.499	37.237	6618.497	4800	38.449	38.442	2344.051	1800	38.814	37.991	103.848	4900	41.277	40.041	38.148
1800	37.553	37.294	6250.803	4900	38.473	38.485	2296.213	1900	38.895	38.038	98.383	5000	41.356	40.065	37.385
1900	37.602	37.346	5921.813	5000	38.497	38.529	2250.289	2000	38.975	38.087	93.463	5100	41.435	40.084	36.652
2000	37.647	37.395	5625.723	5100	38.521	38.574	2206.166	2100	39.056	38.139	89.013	5200	41.514	40.095	35.947
2100	37.689	37.441	5357.831	5200	38.544	38.620	2163.739	2200	39.136	38.193	84.967	5300	41.593	40.100	35.269
2200	37.728	37.485	5114.293	5300	38.568	38.667	2122.914	2300	39.216	38.250	81.273	5400	41.672	40.099	34.616
2300	37.766	37.526	4891.933	5400	38.591	38.714	2083.601	2400	39.296	38.310	77.886	5500	41.751	40.091	33.987
2400	37.801	37.566	4688.102	5500	38.615	38.762	2045.717	2500	39.376	38.373	74.771	5600	41.830	40.078	33.380
2500	37.835	37.604	4500.578	5600	38.638	38.810	2009.187	2600	39.456	38.439	71.895	5700	41.909	40.058	32.794
2600	37.868	37.641	4327.479	5700	38.661	38.859	1973.938	2700	39.535	38.508	69.232	5800	41.988	40.032	32.229
2700	37.899	37.677	4167.202	5800	38.685	38.908	1939.904	2800	39.615	38.581	66.760	5900	42.067	40.000	31.683
2800	37.930	37.712	4018.373	5900	38.708	38.957	1907.025	2900	39.694	38.657	64.458	6000	42.146	39.963	31.154
2900	37.960	37.747	3879.809	6000	38.731	39.006	1875.241	3000	39.774	38.735	62.309	...	...	...	...
3000	37.989	37.781	3750.482	...	...	...	...	3100	39.853	38.816	60.299	...	...	...	...

Table 5: Isobaric molar heat capacity (experimental and theoretical) data as a function of temperature for the selected diatomic molecules along with the product  $2\eta\epsilon^2$

Br <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )						PBr (X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )									
T (K)	C <sub>p</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )		2ηϵ <sup>2</sup>	T [63]	C <sub>p</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )		2ηϵ <sup>2</sup>	T (K)	C <sub>p</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )		2ηϵ <sup>2</sup>	T (K)	C <sub>p</sub> (J mol <sup>-1</sup> K <sup>-1</sup> )		2ηϵ <sup>2</sup>
	[63]	(13)			[63]	(13)			[63]	(13)			[63]	(13)	
300	36.066	35.591	1909.531	3100	41.190	39.794	184.793	300	35.417	35.205	2076704.205	3100	38.817	38.004	200971.375
350	36.451	35.907	1636.740	3200	41.318	39.874	179.018	350	35.935	35.535	1780032.175	3200	38.865	38.039	194691.019
400	36.723	36.160	1432.148	3300	41.420	39.941	173.594	400	36.304	35.801	1557528.153	3300	38.912	38.075	188791.291
450	36.923	36.368	1273.020	3400	41.496	39.996	168.488	450	36.578	36.019	1384469.470	3400	38.959	38.111	183238.606
500	37.077	36.541	1145.718	3500	41.545	40.038	163.674	500	36.786	36.200	1246022.523	3500	39.007	38.148	178003.218
600	37.301	36.815	954.765	3600	41.567	40.066	159.128	600	37.083	36.482	1038352.102	3600	39.054	38.186	173058.684
700	37.460	37.024	818.370	3700	41.563	40.081	154.827	700	37.285	36.692	890016.088	3700	39.100	38.225	168381.422
800	37.586	37.193	716.074	3800	41.533	40.083	150.752	800	37.434	36.852	778764.077	3800	39.147	38.265	163950.332
900	37.692	37.334	636.510	3900	41.480	40.072	146.887	900	37.552	36.980	692234.735	3900	39.194	38.307	159746.477
1000	37.787	37.457	572.859	4000	41.404	40.048	143.215	1000	37.649	37.084	623011.261	4000	39.241	38.349	155752.815
1100	37.876	37.568	520.781	4100	41.306	40.012	139.722	1100	37.734	37.171	566373.874	4100	39.288	38.393	151953.966
1200	37.962	37.672	477.383	4200	41.190	39.964	136.395	1200	37.810	37.246	519176.051	4200	39.334	38.437	148336.015
1300	38.049	37.771	440.661	4300	41.056	39.906	133.223	1300	37.879	37.311	479239.432	4300	39.381	38.483	144886.340
1400	38.140	37.869	409.185	4400	40.907	39.837	130.195	1400	37.943	37.369	445008.044	4400	39.427	38.530	141593.468
1500	38.239	37.966	381.906	4500	40.744	39.759	127.302	1500	38.004	37.421	415340.841	4500	39.474	38.579	138446.947
1600	38.348	38.065	358.037	4600	40.569	39.671	124.535	1600	38.062	37.468	389382.038	4600	39.520	38.628	135437.231
1700	38.471	38.168	336.976	4700	40.383	39.576	121.885	1700	38.118	37.512	366477.213	4700	39.567	38.678	132555.588
1800	38.611	38.274	318.255	4800	40.189	39.474	119.346	1800	38.173	37.554	346117.367	4800	39.613	38.730	129794.013
1900	38.769	38.386	301.505	4900	39.987	39.364	116.910	1900	38.226	37.593	327900.664	4900	39.660	38.782	127145.155
2000	38.945	38.502	286.430	5000	39.780	39.249	114.572	2000	38.278	37.630	311505.631	5000	39.706	38.835	124602.252
2100	39.137	38.623	272.790	5100	39.568	39.128	112.325	2100	38.329	37.667	296672.029	5100	39.753	38.888	122159.071
2200	39.345	38.747	260.391	5200	39.353	39.003	110.165	2200	38.380	37.702	283186.937	5200	39.799	38.942	119809.858
2300	39.563	38.874	249.069	5300	39.136	38.874	108.087	2300	38.430	37.736	270874.461	5300	39.845	38.996	117549.295
2400	39.789	39.003	238.691	5400	38.917	38.741	106.085	2400	38.479	37.770	259588.026	5400	39.892	39.051	115372.456
2500	40.018	39.130	229.144	5500	38.698	38.606	104.156	2500	38.529	37.803	249204.505	5500	39.938	39.105	113274.775
2600	40.244	39.256	220.330	5600	38.480	38.468	102.296	2600	38.577	37.836	239619.716	5600	39.984	39.159	111252.011
2700	40.463	39.378	212.170	5700	38.263	38.328	100.502	2700	38.626	37.870	230744.912	5700	40.030	39.214	109300.221
2800	40.672	39.495	204.593	5800	38.047	38.187	98.769	2800	38.674	37.903	222504.022	5800	40.077	39.267	107415.735
2900	40.864	39.604	197.538	5900	37.834	38.044	97.095	2900	38.722	37.936	214831.469	5900	40.123	39.320	105595.129
3000	41.038	39.704	190.953	6000	37.624	37.901	95.477	3000	38.770	37.970	207670.420	6000	40.169	39.373	103835.210

Table 6: Isobaric molar heat capacity (experimental and theoretical) data as a function of temperature for the selected diatomic molecules along with the product  $2\eta\epsilon^2$

SiO (X $^1\Sigma^+$ )				Cl <sub>2</sub> (X $^1\Sigma_g^+$ )											
T (K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )		$2\eta\epsilon^2$	T [63]	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )		$2\eta\epsilon^2$	T (K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )		$2\eta\epsilon^2$	T (K)	$C_p$ (J mol <sup>-1</sup> K <sup>-1</sup> )		$2\eta\epsilon^2$
	[63]	(13)			[63]	(13)			[63]	(13)			[63]	(13)	
300	29.918	32.908	159127.737	3100	37.816	37.341	15399.458	300	33.981	34.435	4110.416	3100	40.267	38.991	397.782
350	30.500	33.283	136395.203	3200	37.853	37.371	14918.225	350	34.731	34.816	3523.214	3200	40.451	39.094	385.352
400	31.135	33.615	119345.803	3300	37.891	37.400	14466.158	400	35.296	35.135	3082.812	3300	40.624	39.195	373.674
450	31.768	33.910	106085.158	3400	37.929	37.428	14040.683	450	35.728	35.407	2740.277	3400	40.783	39.294	362.684
500	32.365	34.172	95476.642	3500	37.968	37.455	13639.520	500	36.064	35.640	2466.250	3500	40.925	39.390	352.321
600	33.399	34.620	79563.868	3600	38.009	37.482	13260.645	600	36.546	36.018	2055.208	3600	41.048	39.482	342.535
700	34.213	34.986	68197.602	3700	38.052	37.507	12902.249	700	36.872	36.312	1761.607	3700	41.149	39.569	333.277
800	34.845	35.288	59672.901	3800	38.097	37.532	12562.716	800	37.109	36.548	1541.406	3800	41.226	39.650	324.507
900	35.336	35.542	53042.579	3900	38.145	37.556	12240.595	900	37.291	36.743	1370.139	3900	41.278	39.726	316.186
1000	35.722	35.758	47738.321	4000	38.196	37.579	11934.580	1000	37.438	36.908	1233.125	4000	41.305	39.795	308.281
1100	36.030	35.942	43398.474	4100	38.251	37.602	11643.493	1100	37.562	37.050	1121.023	4100	41.306	39.856	300.762
1200	36.279	36.102	39781.934	4200	38.311	37.624	11366.267	1200	37.672	37.176	1027.604	4200	41.280	39.911	293.601
1300	36.484	36.241	36721.785	4300	38.375	37.647	11101.935	1300	37.771	37.290	948.558	4300	41.229	39.957	286.773
1400	36.655	36.363	34098.801	4400	38.445	37.668	10849.618	1400	37.864	37.394	880.803	4400	41.152	39.995	280.256
1500	36.800	36.471	31825.547	4500	38.521	37.690	10608.516	1500	37.954	37.491	822.083	4500	41.051	40.026	274.028
1600	36.923	36.568	29836.451	4600	38.602	37.711	10377.896	1600	38.042	37.583	770.703	4600	40.927	40.048	268.071
1700	37.031	36.655	28081.365	4700	38.690	37.732	10157.090	1700	38.131	37.671	725.368	4700	40.781	40.061	262.367
1800	37.125	36.733	26521.289	4800	38.785	37.753	9945.484	1800	38.223	37.758	685.069	4800	40.615	40.067	256.901
1900	37.209	36.804	25125.432	4900	38.887	37.774	9742.515	1900	38.322	37.843	649.013	4900	40.429	40.064	251.658
2000	37.283	36.869	23869.161	5000	38.997	37.794	9547.664	2000	38.428	37.929	616.562	5000	40.226	40.053	246.625
2100	37.351	36.928	22732.534	5100	39.114	37.815	9360.455	2100	38.544	38.016	587.202	5100	40.007	40.035	241.789
2200	37.412	36.983	21699.237	5200	39.239	37.835	9180.446	2200	38.672	38.104	560.511	5200	39.774	40.009	237.139
2300	37.469	37.034	20755.792	5300	39.372	37.855	9007.230	2300	38.813	38.194	536.141	5300	39.528	39.976	232.665
2400	37.521	37.081	19890.967	5400	39.513	37.876	8840.430	2400	38.966	38.286	513.802	5400	39.271	39.936	228.356
2500	37.569	37.125	19095.328	5500	39.662	37.896	8679.695	2500	39.132	38.381	493.250	5500	39.004	39.889	224.205
2600	37.615	37.166	18360.893	5600	39.820	37.917	8524.700	2600	39.308	38.479	474.279	5600	38.729	39.836	220.201
2700	37.658	37.205	17680.860	5700	39.986	37.937	8375.144	2700	39.493	38.578	456.713	5700	38.447	39.777	216.338
2800	37.700	37.242	17049.400	5800	40.161	37.958	8230.745	2800	39.685	38.680	440.402	5800	38.159	39.712	212.608
2900	37.739	37.276	16461.490	5900	40.343	37.978	8091.241	2900	39.880	38.783	425.215	5900	37.867	39.642	209.004
3000	37.778	37.310	15912.774	6000	40.534	37.999	7956.387	3000	40.075	38.887	411.042	6000	37.571	39.567	205.521

Table 7: Average absolute deviations (%) obtained for the diatomic molecules along with available literature data

Molecule	Temperature range				300-6000 K		
	Low(19)	Moderate(19)	High(19)	300-6000 K(19)	[25]	[30]	[31]
CO	large	1.4721	1.4721	2.3462	...	2.3665	...
BBr	large	0.9898	0.9898	1.1342	...	...	...
HBr	large	1.2341	1.2341	2.3350	2.61	...	...
HI	large	0.8451	0.8451	1.9078	...	...	...
P <sub>2</sub>	large	0.4604	0.4604	0.7268	...	...	0.6078
KBr	1.3524	1.3524	large	2.4041	...	...	...
Br <sub>2</sub>	1.1069	large	0.6762	1.7849	...	4.5055	...
PBr	1.5335	1.5335	large	1.8989	...	...	...
SiO	large	1.2859	large	2.5209	...	...	...
Cl <sub>2</sub>	1.3182	Large	1.1202	2.1523	...	2.5308	...

## List of Figures

Figure 1: Variation of relative absolute deviation versus temperature for CO ( $X^1\Sigma^+$ ) molecule

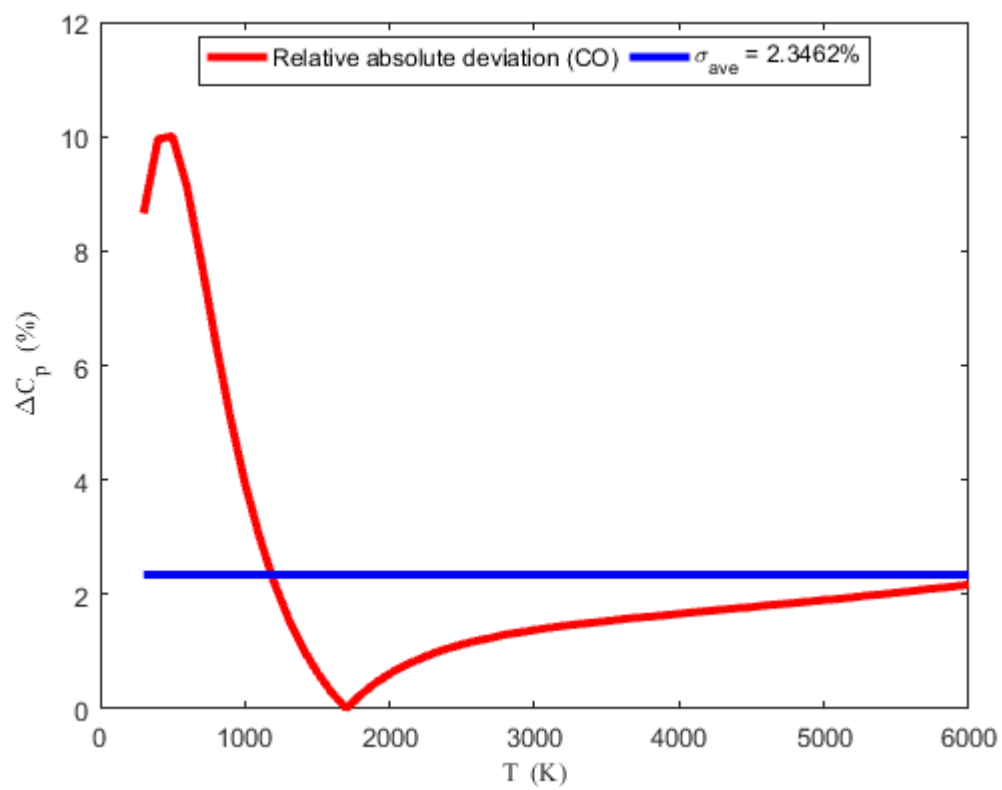


Figure 2: Variation of relative absolute deviation versus temperature for BBr ( $X^1\Sigma^+$ ) molecule

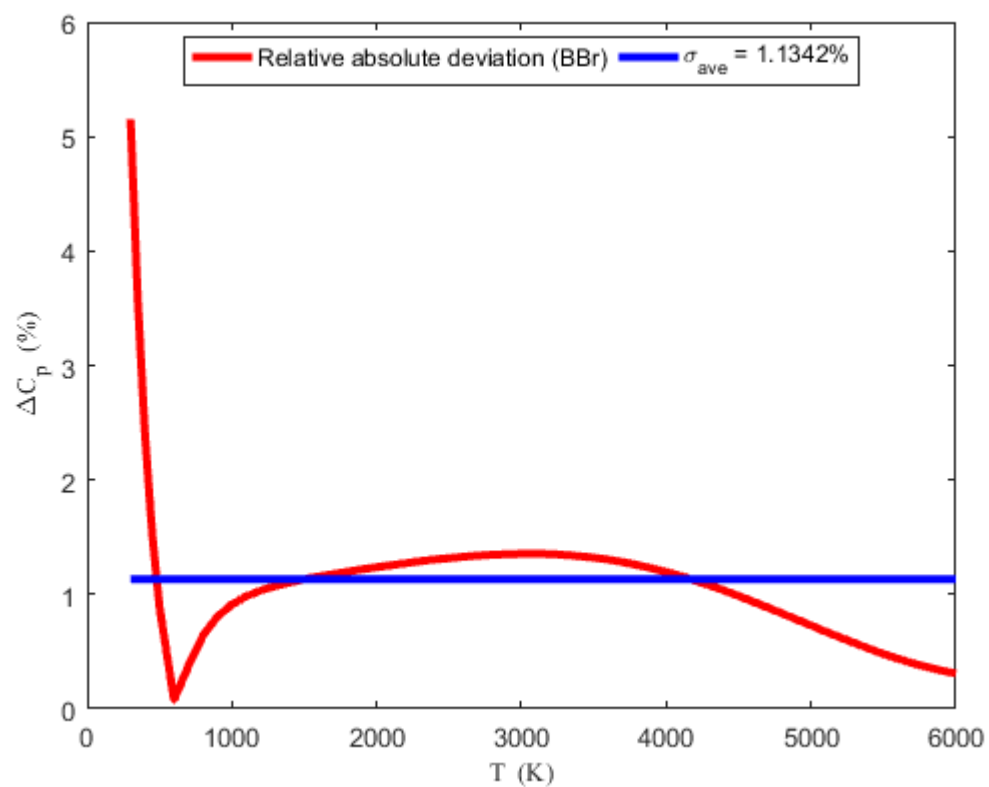


Figure 3: Variation of relative absolute deviation versus temperature for HBr ( $X^1\Sigma^+$ ) molecule

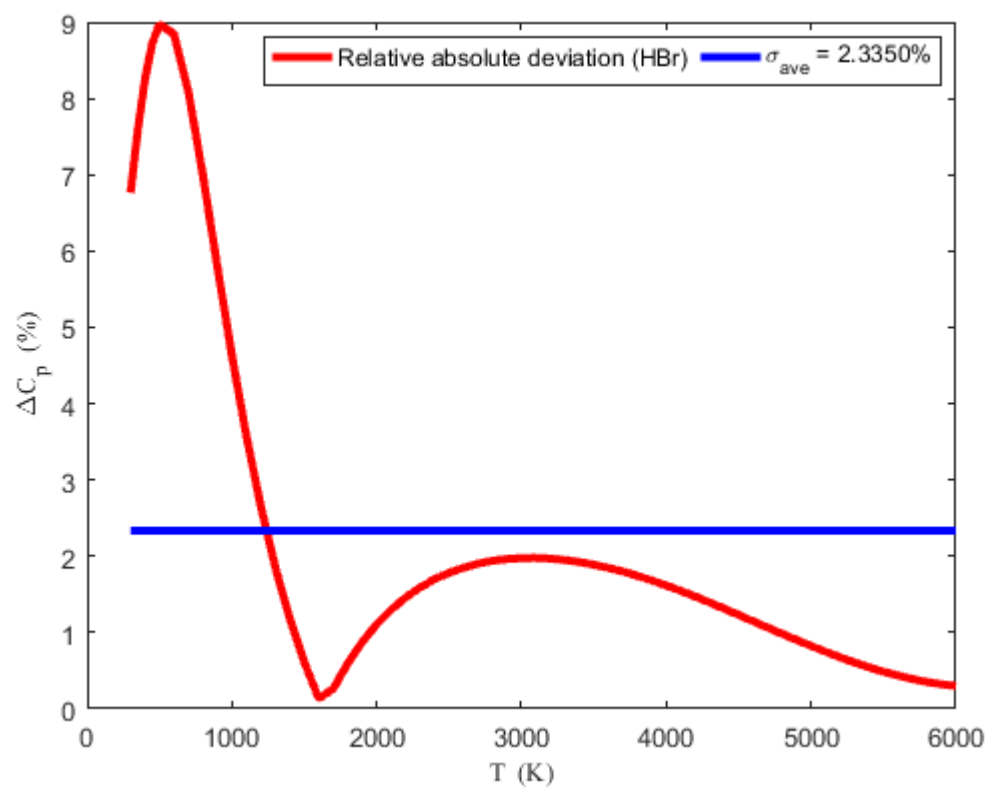


Figure 4: Variation of relative absolute deviation versus temperature for HI ( $X^1\Sigma^+$ ) molecule

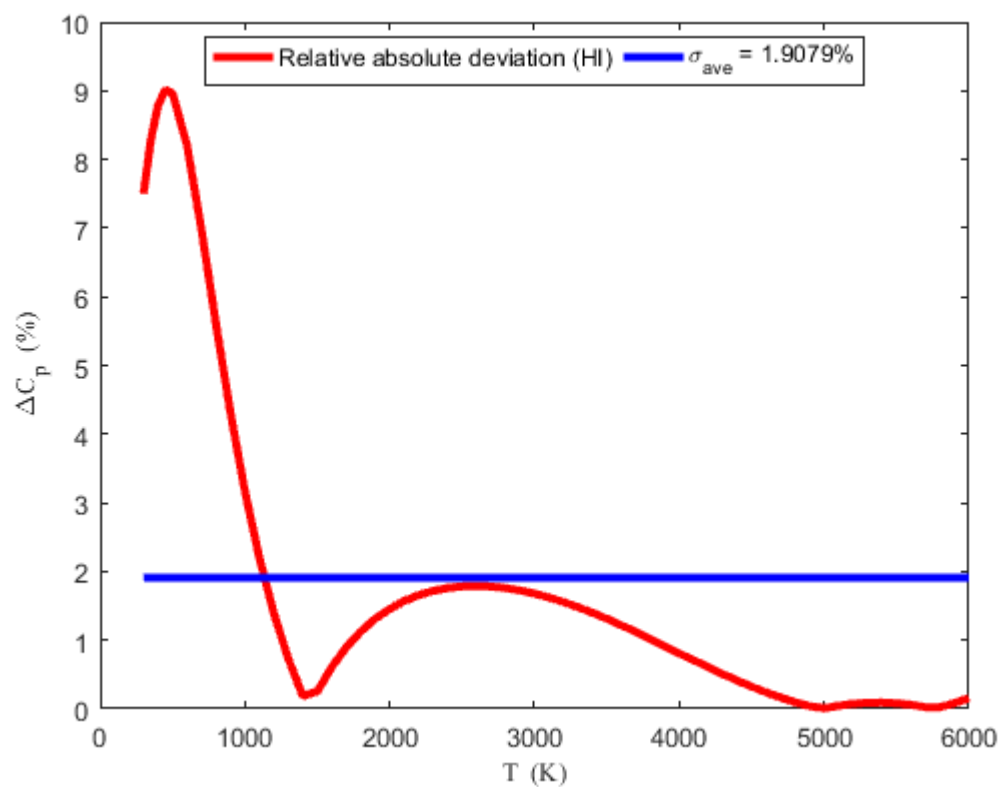


Figure 5: Variation of relative absolute deviation versus temperature for  $P_2$  ( $X^1\Sigma_g^+$ ) molecule

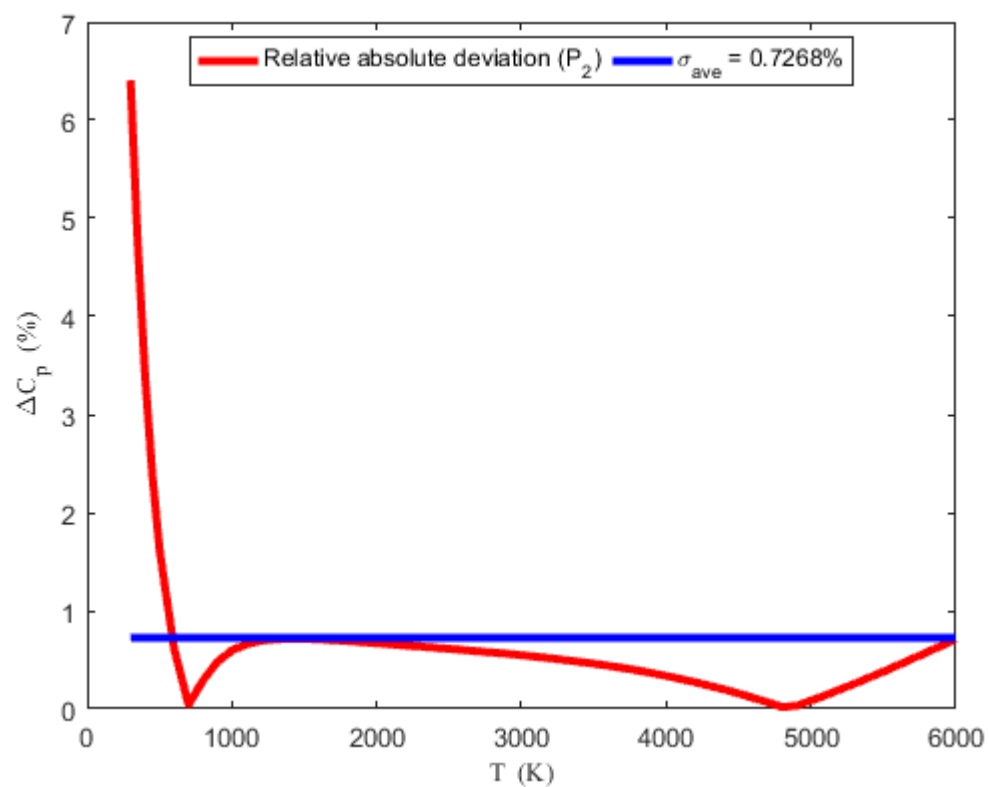


Figure 6: Variation of relative absolute deviation versus temperature for KBr ( $X^1\Sigma^+$ ) molecule

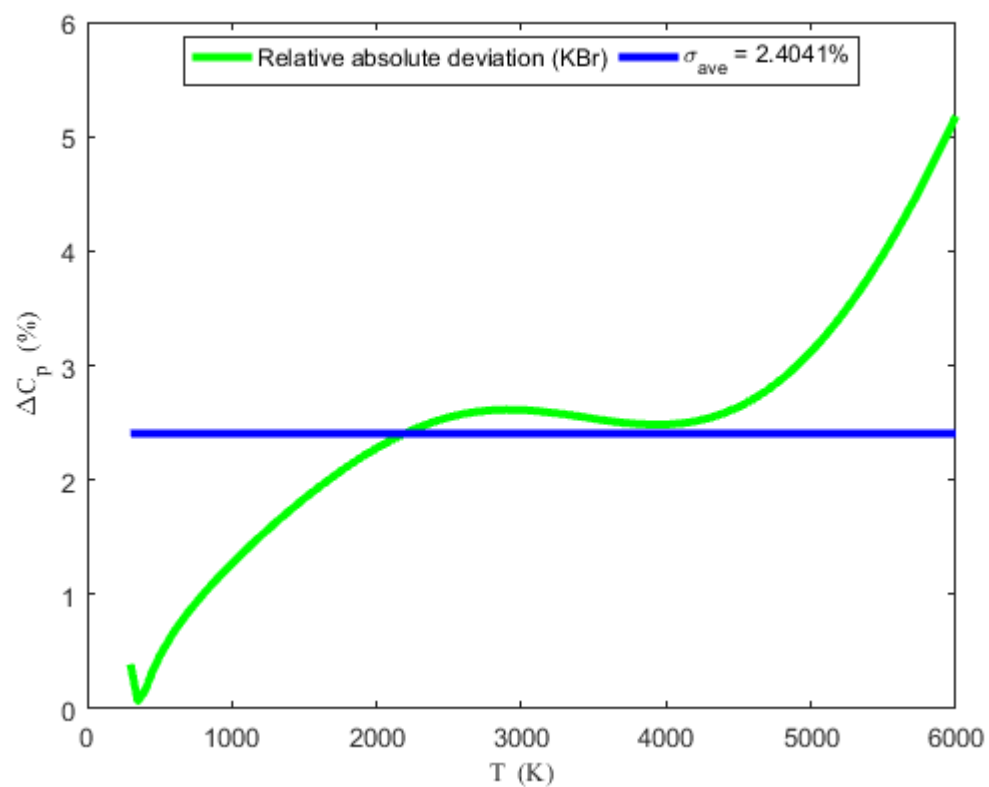


Figure 7: Variation of relative absolute deviation versus temperature for  $\text{Br}_2$  ( $X^1\Sigma_g^+$ ) molecule

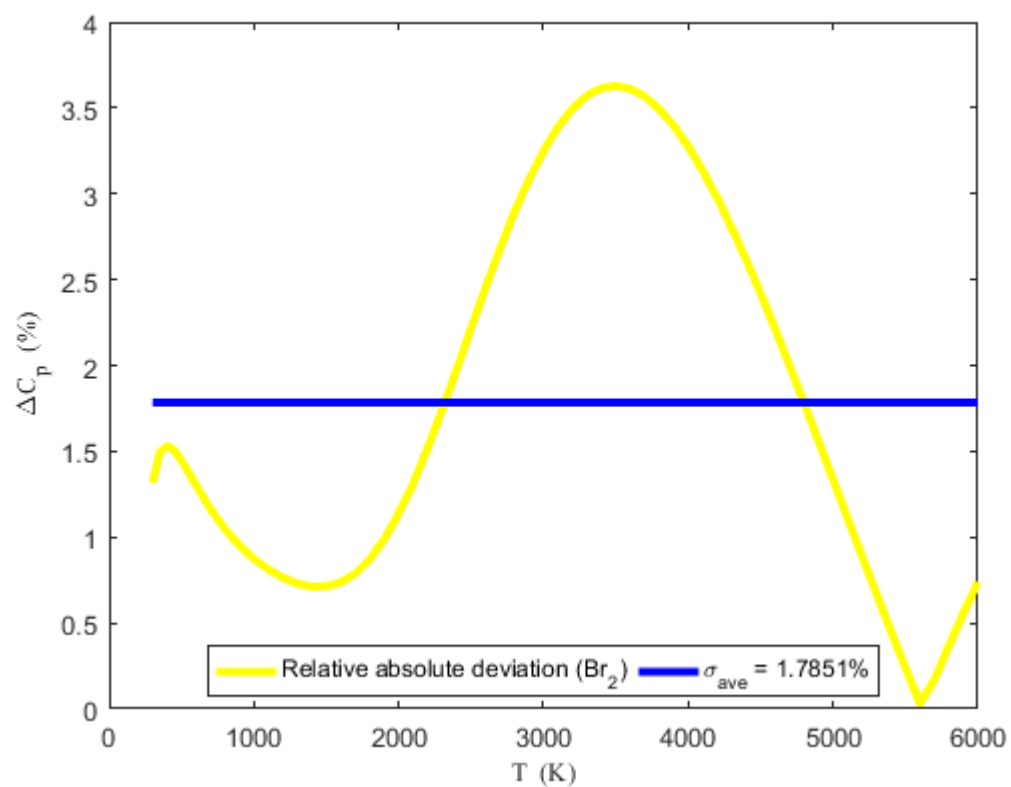


Figure 8: Variation of relative absolute deviation versus temperature for PBr ( $X^3\Sigma_g^-$ ) molecule

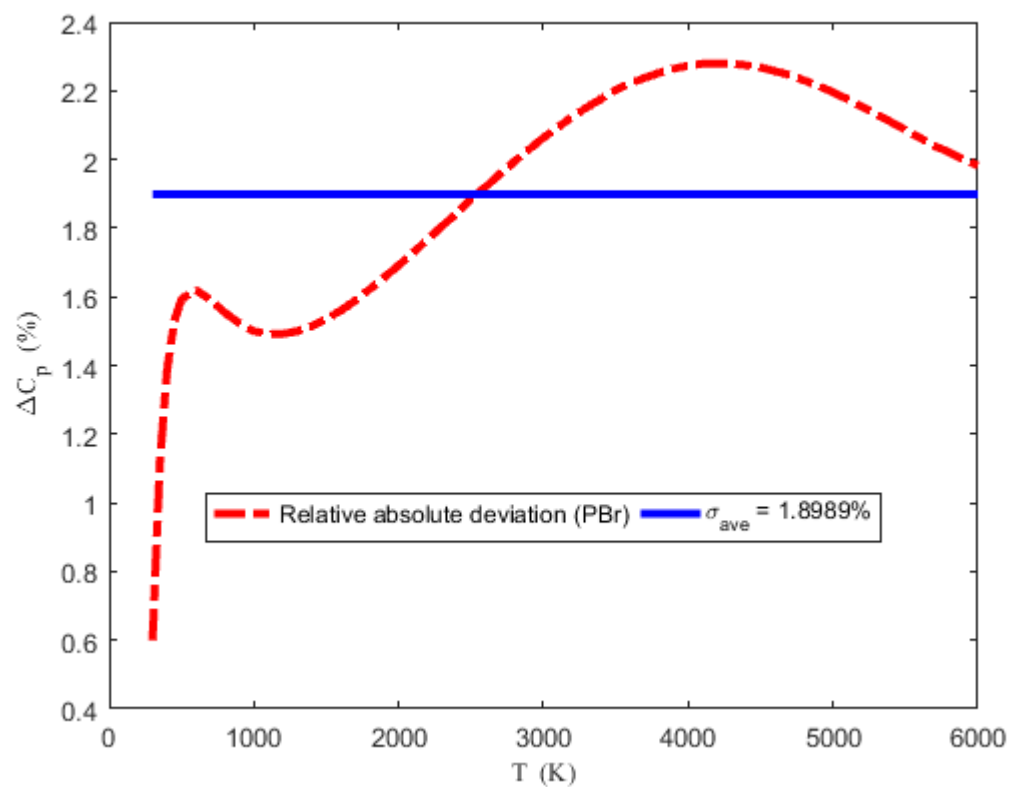


Figure 9: Variation of relative absolute deviation versus temperature for SiO ( $X^1\Sigma^+$ ) molecule

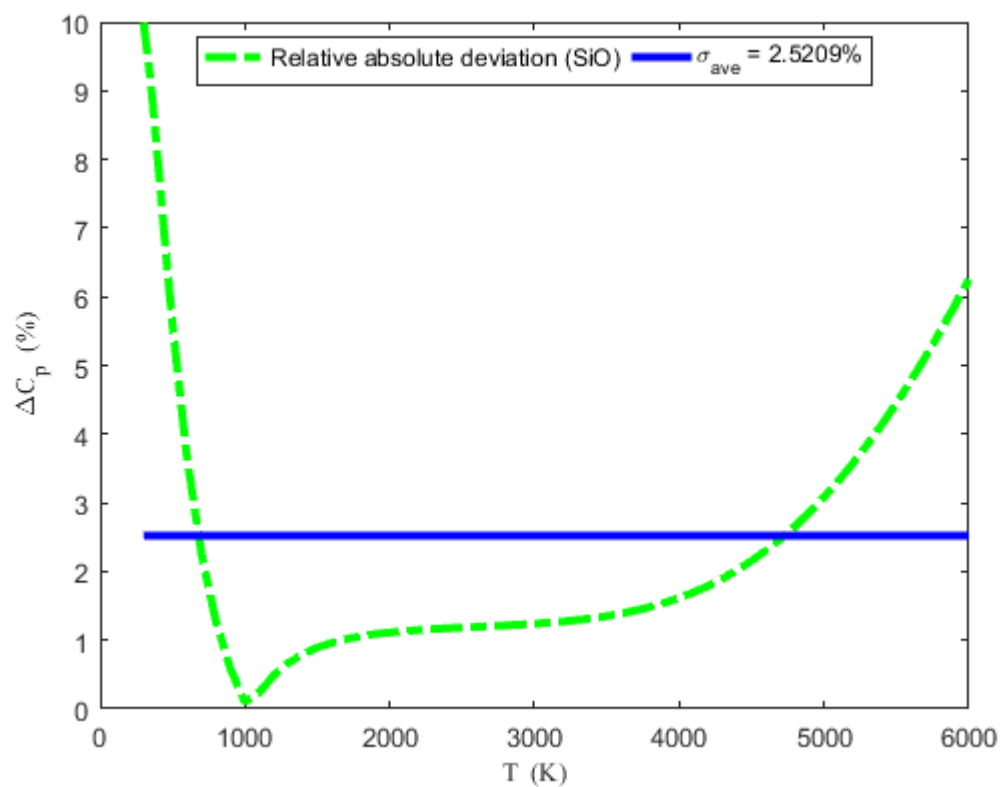


Figure 10: Variation of relative absolute deviation versus temperature for  $\text{Cl}_2$  ( $X^1\Sigma_g^+$ ) molecule

