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Thermodynamic Properties of Oxygen Molecules at High Temperatures[1]

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Calculations of the second virial coefficients and their derivatives, obtained by fitting the Hulburt–Hirschfelder potential to accurate ab initio quantum mechanical calculations for the seven bound states of molecular oxygen that dissociate to ground state atoms, are used to determine thermodynamic properties of oxygen molecules at high temperatures. Unlike the usual statistical thermodynamic method for obtaining partition functions by summing over vibrational–rotational energy levels, the virial coefficient method depends on integrating over the potential energy. This may provide an accurate description of energies near the top of the potential energy well, where vibrational–rotational energy levels are usually not accurately determined. This makes the virial coefficient method particularly useful for predicting high-temperature thermodynamic properties outside the range of laboratory investigation and beyond the limits of the partition function approach. In the work presented here, the virial coefficient method is used to calculate the heat capacity and enthalpy of oxygen molecules up to 25,000 K.

KEY WORDS: enthalpy; heat capacity; high temperature; oxygen; virial coefficients.

1. INTRODUCTION

This paper presents theoretical calculations of the thermodynamic properties of molecular oxygen at high temperatures, where experimental thermodynamic data are sparse. Knowledge of the high-temperature properties of oxygen is important for understanding upper atmosphere chemistry [1], atmospheric reentry [2], and combustion.

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The usual method for calculating thermodynamic properties is given in terms of the partition function, Q [3]. For 1 mol of an ideal diatomic gas, Q is written as

$$Q=\frac{1}{N_0!}(q_{\text{nu}}q_{\text{tr}}q_{\text{in}})^{N_0} \tag{1}$$

where N_0 is Avogradros's number and q is the partition function for a single particle, with the subscripts denoting nuclear, translational, and internal contributions to Q.

The term q_{in} involves sums over electronic, vibrational, and rotational energy levels. For diatomic molecules, standard methods of calculating the vibrational–rotational energy levels, $\varepsilon_{v,J}$, where v is the vibrational quantum number and J is the rotational quantum number, become significantly less accurate at high temperatures, where v and J are large [4–8]. Under these conditions, the population of high v and J states is less than the population of states with lower values of v and J, but the density of the higher v, J states is greater [9]. This affects the accuracy of the partition function and poor results may be obtained if this approach is used to calculate the thermodynamic properties of molecules at high temperatures.

2. CLUSTER APPROACH TO STATISTICAL THERMODYNAMICS

Alternatively, thermodynamic properties of diatomic molecules can be calculated by a cluster approach to statistical thermodynamics [3–11] based on the second virial coefficient. Considering the reaction

$$2\text{O}(g) \rightleftarrows \text{O}_2(g) \tag{2}$$

the equilibrium constant in concentration units can be written as [10]

$$K_C=N_0\frac{q(\text{O}_2)/V}{[q(\text{O})/V]^2}=-B(T) \tag{3}$$

where $q(\text{O})$ is the partition function for an oxygen atom, $q(\text{O}_2)$ is the partition function for O_2, and $B(T)$ is the second virial coefficient for the molecule.

At high temperatures, several molecular electronic states may be occupied and the second virial coefficient is given by [6, 10]

$$B(T)=\frac{\sum_i B_i(T)\,g_i(\text{O}_2)\,e^{-\varepsilon_i/kT}}{q_{\text{el}}(\text{O})^2} \tag{4}$$

where i denotes the sum over the occupied electronic states of O_2, $q_{el}(O)$ denotes the electronic partition function for the oxygen atom, $g_i(O_2)$ denotes the eletronic degeneracies of O_2, ε_i denotes the electronic energy levels of O_2, and $B_i(T)$ represents the second virial coefficient of O_2 in the electronic state i; i.e.,

$$B_i(T) = 2\pi N_0 \int_0^\infty [1 - e^{-V_i(r)/kT}]\, r^2\, dr \tag{5}$$

where $V_i(r)$ is the electronic potential energy curve for the O_2 molecule in electronic state i and the symbol r represents the separation of the two oxygen atoms in the molecule.

This cluster approach allows the thermodynamic properties to be written in terms of $B_i(T)$ and its derivatives. It is often useful to use reduced variables for this purpose. Here one can define

$$B_i(T) = b_{i,\mathrm{o}} B_i^*(T_i^*) \tag{6}$$

where $b_{i,\mathrm{o}}$ is the hard-sphere second virial coefficient for a molecule in electronic state i,

$$b_{i,\mathrm{o}} = \frac{2\pi}{3}\sigma_i^3 \tag{7}$$

and σ_i is the effective hard-sphere diameter for the molecule in electronic state i. Also,

$$B_i^{\mathrm{cl},*}(T_i^*) = 3\int_0^\infty [1 - e^{-V_i^*(r_i^*)/T_i^*}](r_i^*)^2\, dr_i^* \tag{8}$$

where

$$r_i^* = \frac{r_i}{\sigma_i}, \qquad V_i^* = \frac{V_i}{\varepsilon_i}, \qquad T_i^* = \frac{kT}{\varepsilon_i}$$

and ε_i is the depth of the potential for a molecule in electronic state i at the equilibrium separation, $r_{e,i}$, with the superscript "cl" denoting the classical approximation to the second virial coefficient.

The thermodynamic properties can be written in terms of these reduced quantities with [8]

$$H_T^\circ - H_0^\circ = RT(4 + B_1^*/B^* + D_\mathrm{o}/kT) \tag{9}$$

and

$$C_{\mathrm{P}}^{\circ} = R\{4 + 2B_1^*/B^* + B_2^*/B^* - (B_1^*/B^*)^2\} \tag{10}$$

where

$$B_n^* = (T^*)^n \left(\frac{d^n B^*}{dT^{*n}}\right) \tag{11}$$

Clearly, the accuracy with which the thermodynamic properties are determined will depend on the accuracy of the electronic potentials, $V_i(r)$. If these are accurately known, the second virial coefficient approach may be more accurate than the approach based on summing over vibrational–rotational energy levels, especially at high temperatures.

3. INTERACTION POTENTIALS FOR O_2

Of the 18 electronic states of O_2 that dissociate to ground-state (^{3}P) oxygen atoms, 7 are bound [12]. With the notation of Ref. 13, these are the $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^-$, $C^3\Delta_u$, $A^3\Sigma_u^+$, and $^5\Pi_g$ states. Some, or all, of these states will be populated and contribute to the thermodynamic properties of O_2 as the temperature increases. The lowest-lying bound electronic state that dissociates to excited-state atoms is the $B^3\Sigma_u^-$ state [13] which dissociates to ^{3}P and ^{1}D atoms. However, even at 25,000 K, only about 2% of the molecules are in this state. Thus it can be assumed that only the seven lowest bound electronic states, which all dissociate to ground-state atoms, contribute to the thermodynamic properties for temperatures up to 25,000 K.

The best general-purpose potential [14, 15] for representing electronic potential energy curves of diatomic molecules is the Hulburt–Hirschfelder (HH) potential. It has been shown that the HH potential accurately represents experimental RKR potential energy curves [16–21], including those of the oxygen molecule [12], that it can be used to calculate very accurate transport properties, second virial coefficients, and thermodynamic properties [4, 12, 16–21], and that it can be used to accurately fit ab initio quantum mechanical potential energy curves [12, 16, 17, 20, 21].

The HH potential is given by

$$V_{\mathrm{HH}}^* = e^{-2A(r^*/d-1)} - 2e^{-A(r^*/d-1)} + B(r^*/d-1)^3[1 + G(r^*/d-1)]\, e^{-2A(r^*/d-1)} \tag{12}$$

where

$$A = \omega_e/2(B_e\varepsilon)^{1/2}, \qquad B = cA^3, \qquad G = AB$$

$$b = 2 - (7/12 - \varepsilon a_2/a_0)/c, \qquad c = 1 + a_1(\varepsilon/a_0)^{1/2}$$

$$d = r_e/\sigma, \qquad a_0 = \frac{\omega_e^2}{4B_e}$$

$$a_1 = -1 - \frac{\alpha_e\omega_e}{6B_e^2}, \qquad a_2 = \frac{5}{4}a_1^2 - \frac{2\omega_e\chi_e}{3B_e}$$

and ω_e is the fundamental vibrational frequency, $\omega_e\chi_e$ is the anharmonicity constant, B_e is the rotational constant, and α_e is the vibration–rotation coupling constant. Thus V_{HH} depends on these four spectroscopic constants and r_e and ε.

We have previously calculated the transport properties of oxygen atoms using the HH potential to represent the 18 electronic states that dissociate to ground-state atoms. The HH potentials were obtained by making a fit to the accurate quantum mechanical potentials of Saxon and Liu [22]. We now use these same potentials to calculate $B_i(T)$ for each bound electronic state.

4. SEMICLASSICAL CORRECTIONS

In addition, the first two semiclassical corrections to the second virial coefficient, B_I^* and B_{II}^*, have been included in these calculations; i.e. [23],

$$B^*(T^*) = B^{cl,*} + (\Lambda^*)^2 B^{I,*} + (\Lambda^*)^4 B^{II,*} + \cdots \tag{13}$$

where $B^{cl,*}$ is given by Eq. (8), with the subscript "i" deleted after degeneracy averaging, and

$$B^{I,*} = \frac{1}{16\pi^2(T^*)^3}\int_0^\infty e^{-V^*/T^*}\left(\frac{dV^*}{dr^*}\right)^2 (r^*)^2\,dr^* \tag{14}$$

Also,

$$B^{II,*} = -\frac{1}{64\pi^4(T^*)^4}\int_0^\infty e^{-V^*/T^*}\left[\frac{1}{10}\left(\frac{d^2V^*}{dr^{*2}}\right)^2 + \frac{1}{5(r^*)^2}\left(\frac{dV^*}{dr^*}\right)^2 + \frac{1}{9r^*T^*}\left(\frac{dV^*}{dr^*}\right)^3 - \frac{1}{72(T^*)^2}\left(\frac{dV^*}{dr^*}\right)^4\right](r^*)^2\,dr^* \tag{15}$$

and

$$(\Lambda^*)^2 = \frac{h^2}{\sigma^2 m\varepsilon} \tag{16}$$

We also need the reduced first and second derivatives to determine the thermodynamic properties. These are given below:

$$B_1^*(T) = B_1^{\text{cl},*} + (\Lambda^*)^2 B_1^{\text{I},*} + (\Lambda^*)^4 B_1^{\text{II},*} \tag{17}$$

and

$$B_2^*(T) = B_2^{\text{cl},*} + (\Lambda^*)^2 B_2^{\text{I},*} + (\Lambda^*)^4 B_2^{\text{II},*} \tag{18}$$

where

$$B_1^{\text{cl},*} = -\frac{3}{T^*}\int_0^\infty e^{-V^*/T^*} V^*(r^*)^2\,dr^* \tag{19}$$

and

$$B_2^{\text{cl},*} = \frac{6}{T^*}\int_0^\infty e^{-V^*/T^*} V^*(r^*)^2\,dr^* - \frac{3}{(T^*)^2}\int_0^\infty e^{-V^*/T^*}(V^*)^2(r^*)^2\,dr^* \tag{20}$$

Also,

$$B_1^{\text{I},*} = -3B^{\text{I},*} + \frac{1}{16\pi^2(T^*)^4}\int_0^\infty e^{-V^*/T^*}\left(\frac{dV^*}{dr^*}\right)^2 V^*(r^*)^2\,dr^* \tag{21}$$

and

$$B_2^{\text{I},*} = 12B^{\text{I},*} - \frac{1}{2\pi^2(T^*)^4}\int_0^\infty e^{-V^*/T^*} V^*\left(\frac{dV^*}{dr^*}\right)^2 (r^*)^2\,dr^* - \frac{1}{16\pi^2(T^*)^5}\int_0^\infty e^{-V^*/T^*}(V^*)^2\left(\frac{dV^*}{dr^*}\right)^2(r^*)^2\,dr^* \tag{22}$$

In addition,

$$B_1^{\text{II},*} = -4B^{\text{II},*} - \frac{1}{64\pi^4(T^*)^5}\int_0^\infty e^{-V^*/T^*} V^*\left[\frac{1}{10}\left(\frac{d^2V^*}{dr^{*2}}\right)^2 + \frac{1}{5(r^*)^2}\left(\frac{dV^*}{dr^*}\right)^2 + \frac{1}{9r^*T^*}\left(\frac{dV^*}{dr^*}\right)^3 - \frac{1}{72(T^*)^2}\left(\frac{dV^*}{dr^*}\right)^4\right](r^*)^2\,dr^* \tag{23}$$

and

$$
\begin{aligned}
B_2^{\mathrm{II},*} ={}& \frac{1}{16\pi^4(T^*)^4}\int_0^\infty e^{-V^*/T^*}\left[\frac{1}{10}\left(\frac{d^2V^*}{dr^{*2}}\right)^2+\frac{1}{5(r^*)^2}\left(\frac{dV^*}{dr^*}\right)^2\right.\\
&\left.+\frac{1}{9r^*T^*}\left(\frac{dV^*}{dr^*}\right)^3-\frac{1}{72(T^*)^2}\left(\frac{dV^*}{dr^*}\right)^4\right]\left[-5+\frac{5V^*}{2T^*}-\frac{(V^*)^2}{4(T^*)^2}\right]\\
&\times(r^*)^2\,dr+\frac{1}{288\pi^4(T^*)^5}\int_0^\infty e^{-V^*/T^*}\left(\frac{dV^*}{dr^*}\right)^3\left[-\frac{1}{r^*}+\frac{1}{4T^*}\left(\frac{dV^*}{dr^*}\right)\right]\\
&\times\left[5-\frac{V^*}{T^*}\right](r^*)^2\,dr^*+\frac{1}{2304\pi^4(T^*)^6}\int_0^\infty e^{-V^*/T^*}\left(\frac{dV^*}{dr^*}\right)^4(r^*)^2\,dr^*
\end{aligned}
\tag{24}
$$

5. RESULTS AND CONCLUSIONS

Results calculated for some thermodynamic properties using the second virial coefficient method are given in Tables I and II along with comparisons with the JANAF Thermochemical Tables [24] and with results obtained by Balakrishnan [25] and by Browne [8]. The quantum mechanical corrections have also been included in our calculations. These contribute less than 1% to the virial coefficients and thermodynamic properties. The results presented here are very similar to those determined previously [26] by using the HH potential to fit the available RKR potentials for the bound states of O_2 and ignoring quantum mechanical effects. The sets of results from Refs. 24 and 25 for C_{P}^{0} and $H_{\mathrm{T}}^{0}-H_{\mathrm{O}}^{0}$, both obtained by summing over the vibrational–rotational energy levels, are nearly the same.

At lower temperatures our results for C_{p}^{0}, obtained using the virial coefficient method, are within a few percent of results obtained using the spectroscopic partition function approach; Eq. (1). Since Eq. (1) should represent the energy levels of O_2 accurately at low tempratures, the results in Refs. 24 and 25 are likely to be more accurate at these temperatures. At intermediate temperatures, there is only about a 1% difference between the two methods. This good agreement of results at low and intermediate temperatures indicates that the potential energy curves of Saxon and Liu [22] are quite accurate. Our previous calculations [12] of the transport properties of oxygen atoms, which were in good agreement with other good-quality calculations, tested the inner part of Saxon and Liu's potentials. The calculation of virial coefficients and their derivatives, presented here, tests the longer-range part of the potentials.

Table I. C_p^0(cal · mol^{-1}) of O_2

T (K)	This work	JANAF [24]	Balakrishnan [25]	Browne [8]
1,000	8.69	8.34	8.33	8.33
2,000	9.23	9.03	9.02	9.02
3,000	9.47	9.55	9.53	9.52
4,000	10.0	9.93	9.90	9.93
5,000	10.3	10.2	10.2	10.3
6,000	10.5	10.3	10.6	10.6
7,000	10.8		11.2	10.9
8,000	10.6		12.0	11.1
9,000	10.2		12.9	11.2
10,000	9.80		13.9	11.3
11,000	9.34		14.7	11.3
13,000	8.45		15.6	11.2
15,000	7.68		15.7	10.9
17,000	7.06		15.2	10.5
19,000	6.58		14.7	10.1
21,000	6.18		14.1	9.65
23,000	5.86		13.7	9.21
25,000	5.58		13.3	8.81

Table II. $H_T^0 - H_O^0$ (kcal · mol^{-1}) of O_2

T (K)	This work	JANAF [24]	Balakrishnan [25]	Browne [8]
1,000	9.35	7.50	7.50	7.50
2,000	15.8	16.2	16.2	16.2
3,000	27.4	25.5	25.5	25.5
4,000	35.1	35.3	35.2	35.2
5,000	47.2	45.3	45.2	45.4
6,000	57.6	55.6	55.6	55.9
7,000	68.4		66.4	66.7
8,000	78.9		77.9	77.8
9,000	89.2		90.2	88.9
10,000	99.2		104	100
11,000	109		118	112
13,000	127		148	134
15,000	143		179	156
17,000	157		209	178
19,000	171		238	198
21,000	184		266	218
23,000	196		293	237
25,000	207		319	255

At high temperatures, the results obtained by the two methods disagree substantially, with large differences in the heat capacity and differences in the enthalpy of about 50% at 25,000 K. The same trends were observed in our calculations on N_2 [4], although the comparative difference between the two methods for N_2 is smaller. This is thought to arise from the greater well depth for the ground state of N_2 compared to that of O_2, which results in the reduced temperature (T^*) for O_2 being substantially higher than for N_2 at 25,000 K.

It should also be noted that our results for O_2 are in better agreement with those of Browne [8], who used the virial coefficient method for the $X^3\Sigma_g^-$ ground state of O_2 (representing the potential energy curve with a Morse potential) and he included contributions from excited states by using a method that is essentially the spectroscopic method. As one would expect, his results are intermediate between results obtained using the virial coefficient method and the usual statistical thermodynamic method. Balakrishnan [25] also noted the difference between his results and those of Browne [8].

We believe that the large difference between the virial coefficient and spectroscopic methods at high temperatures reflects the inherent differences in the accuracy of these methods under these conditions. Here the virial coefficient method depends on integrating over the potential energy functions, which can provide an accurate description of energies near the top of the potential well, where accurate vibrational–rotational energy levels required for the usual statistical thermodynamic method are not readily accessible. This makes the virial coefficient method a useful alternative for predicting high-temperature thermodynamic properties beyond the range of laboratory measurements.

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