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Thermodynamic Properties of Nitrogen Molecules at High Temperatures[1]

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Calculations of the second virial coefficients and their derivatives for the Hulburt–Hirschfelder (HH) and other accurate interaction potentials are used to determine the thermodynamic properties of nitrogen at high temperatures. Unlike the usual methods employing partition functions, which are most accurate at low temperatures where the energy levels are precisely known, the virial coefficient method depends on integrating over potential energy functions which provide a useful description of energies even near the top of the potential well, a region where the vibrational–rotational energy levels are not readily accessible. This makes this method particularly useful for predicting high-temperature properties outside the range of laboratory measurements and beyond the useful limits of the partition function approach. In the present work, we use the virial coefficient method to predict the heat capacities and enthalpies of nitrogen up to 25,000 K.

KEY WORDS: enthalpy; heat capacity; high temperatures; nitrogen; virial coefficients.

1. INTRODUCTION

This paper presents theoretical calculations of the thermodynamic properties of molecular nitrogen at high temperatures. Accurate high-temperature gas-phase thermophysical properties are essential for understanding, modeling, and/or predicting many important processes. Knowledge of the high-temperature thermophysical properties of molecular nitrogen is important in understanding upper atmospheric chemistry [1], for understanding and predicting the ablation process of heat shields [2–8], and for

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predicting the heating rates at aircraft and spacecraft surfaces [9–12], especially during atmospheric entry. The method we use for these calculations is based on numerical evaluation of the second virial coefficients and their derivatives using accurate interaction potentials for the various electronic states of N_2. These results are then degeneracy averaged over the contributing states [13].

2. THE PARTITION FUNCTION APPROACH

The usual way in which thermodynamic properties are calculated is via the partition function [14]. For 1 mol of an ideal diatomic gas the partition function, Q, is written as

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

where N_0 is Avogadro's number, the q's signify contributions to the partition functions of a single molecule from the various degrees of freedom, and the subscripts nu, tr, and in denote nuclear, translational, and internal contributions to the partition function, respectively. The various thermodynamic properties depend on the derivatives of Q or the derivatives of $\ln(Q)$ [14].

The international partition function, q_{in}, consists of contributions from the electronic, vibrational, and rotational degrees of freedom. The contributions from vibration and rotation in each electronic state vary since the spectroscopic constants for each electronic state [14] are different. The vibrational–rotational partition function in the nth electronic state, q_n, is given by

$$q_n=\sum_{v,j} g_j \exp(-\varepsilon^n_{v,j}/kT) \tag{2}$$

where v is the vibrational quantum number, j is the rotational quantum number, g_j is the rotational degeneracy, $\varepsilon^n_{v,j}$ is the rotational–vibrational energy in electronic state n, k is Boltzmann's constant, and T is the temperature. The result for q_{in} is obtained by summing over all electronic states; i.e. [14],

$$q_{\mathrm{in}}=\sum_{n} q_n g_n \exp(-\varepsilon_n/kT) \tag{3}$$

where g_n is the electronic degeneracy and ε_n is the energy at the minimum of the nth electronic potential energy curve.

At low and intermediate temperatures, the vibrational–rotational energy is given quite accurately for most diatomic molecules by the expression [14]

$$\frac{\varepsilon^n_{v,j}}{hc}=\left(v+\frac{1}{2}\right)\omega^n_e+j(j+1)\,B^n_e-\left(v+\frac{1}{2}\right)^2\omega_e\chi^n_e-j^2(j+1)^2\,D^n$$
$$-\left(v+\frac{1}{2}\right)j(j+1)\,\alpha^n_e \qquad (4)$$

where h is Planck's constant, c is the speed of light, ω^n_e is the fundamental vibrational frequency, B^n_e is the rotational constant, $\omega_e\chi^n_e$ is the anharmonicity constant, D^n is the centrifugal stretching constant, and α^n_e is the vibration–rotation coupling constant, all in cm^{-1} for the nth electronic state. The experimental spectroscopic constants are known for one or more electronic states for most diatomic molecules [15, 16].

The first two terms in Eq. (4) account for harmonic oscillation and rigid rotation, respectively, and the last three terms are correction terms due to anharmonic oscillation, nonrigid rotation and vibration-rotation coupling, respectively. Explicit useful expressions for the partition function for this model are available [14, 17]. These expressions are commonly used to obtain the thermodynamic data found in several sources such as the JANAF thermochemical tables [18] and elsewhere [19].

At high temperatures high v and j states are populated and Eq. (4) does not accurately represent the vibrational–rotational energy levels [20–23] for such states. Thus both the partition function and any thermodynamic properties calculated by using Eq. (4) are incorrect for diatomic molecules at high temperatures. At such temperatures, more accurate results [20–24] for the partition function and the thermodynamic properties can be obtained by calculating the second virial coefficient, B, for two interacting atoms and then calculating the partition function and thermodynamic properties [14]. This is the procedure we use in the present work.

3. THERMODYNAMIC CALCULATIONS USING VIRIAL COEFFICIENTS

The virial coefficient method is based on treating all of the different molecular species that may exist as an imperfect monatomic gas described by the virial equation of state with nonideal behavior due to both the interactions between the atoms and excluded volume effects. This is a cluster approach to the problem and clusters containing larger species than diatomic molecules can also be treated [14, 25–29].

For the system of interest in this paper, consider the equilibrium between nitrogen atoms and nitrogen molecules, i.e.,

$$2\mathrm{N}(g) \rightleftarrows \mathrm{N}_2(g) \tag{5}$$

The equilibrium constant for this reaction can be written as

$$K_p = \frac{K_c}{RT} = \frac{1}{kT} \frac{q(\mathrm{N}_2)/V}{\{q(\mathrm{N})/V\}^2} \tag{6}$$

where K_p is the equilibrium constant in terms of pressure, K_c is the equilibrium constant in concentration units, V is the volume of the system, $q(\mathrm{N})$ is the partition function for N, and $q(\mathrm{N}_2)$ is the partition function for N_2. We can also show that [25]

$$B(T) = -K_c \tag{7}$$

where $B(T)$ is the second virial coefficient. Classically, $B(T)$ is given by [14]

$$B(T) = 2\Pi \mathrm{N}_0 \int_0^\infty [1 - e^{-V(r)/kT}]\, r^2\, dr \tag{8}$$

Here r is the separation between the nitrogen atoms and $V(r)$ is the potential energy of the molecule. Since $q(\mathrm{N})$ depends only on mass, temperature, and volume, Eqs. (6), (7), and (8) can be used to find $q(\mathrm{N}_2)$ in terms of the potential. The result is [20, 23]

$$q(\mathrm{N}_2) = -B(T) \left(\frac{2\Pi m_{\mathrm{N}} kT}{h^2}\right)^3 \frac{V}{\mathrm{N}_0}\, g_0^2(\mathrm{N})\, e^{-D_0/kT} \tag{9}$$

where m_{N} is the mass of a nitrogen atom, $g_0(\mathrm{N})$ is the degeneracy of the ground electronic state of the atom, and D_0 is the spectroscopic dissociation energy for the ground electronic state of N_2. The zero of energy is taken to be the molecule in its lowest vibrational–rotational energy level.

At high temperatures, excited electronic states of the atoms and molecules contribute to the partition function. In this case, $B(T)$ is calculated using [21]

$$B(T) = \frac{\sum_i B_i(T)\, g_i(\mathrm{N}_2)\, e^{-E_i/kT}}{(\sum_j g_j(\mathrm{N})\, e^{-E_j/kT})^2} \tag{10}$$

where i denotes a sum over molecular states, j denotes a sum over atomic states, $g_i(\mathrm{N}_2)$ represents the electronic degeneracies of N_2, $g_j(\mathrm{N})$ represents the electronic degeneracies of N, E_i is the energy of a molecule in electronic state i, E_j is the energy of an atom in electronic state j, and B_i is the second virial coefficient for the ith potential energy curve of N_2.

It is usually more convenient to work in terms of the reduced virial coefficients, $B^*(T^*)$, which are defined by

$$B(T) = b_0 B^*(T^*) \tag{11}$$

where

$$B^*(T^*) = 3\int_0^\infty [1 - e^{-V^*(r^*)/T^*}]\, r^{*2}\, dr^* \tag{12}$$

and

$$r^* = \frac{r}{\sigma} \qquad V^* = \frac{V}{\varepsilon} \qquad T^* = \frac{kT}{\varepsilon}$$

Here σ is the effective rigid sphere diameter, ε is the depth of the potential energy well, and b_0 is the rigid sphere second virial coefficient, given by

$$b_0 = \frac{2\Pi}{3}\sigma^3 \tag{13}$$

Thus $q(N_2)$ can be written in terms of $B^*(T^*)$ and the thermodynamic properties are given by [23]

$$H_T^0 - H_O^0 = RT(4 + B_1^*/B^*) \tag{14}$$

and

$$C_p^0 = R\{4 + 2B_1^*/B^* + B_2^*/B^* - (B_1^*/B^*)^2\} \tag{15}$$

where

$$B_n^* = (T^*)^n \left(\frac{d^n B^*}{dT^{*n}}\right) \tag{16}$$

4. INTERACTION POTENTIALS FOR N_2

Equations (14) and (15) are useful for calculating the thermodynamic properties of N_2 only if we have accurate potentials for the ground electronic state and for several excited electronic states. We have recently developed a technique [30, 31] for calculating the thermophysical properties of diatomic molecules by using the Hulburt–Hirschfelder (HH) potential. This potential is based on the spectroscopic constants and is probably the most accurate general–purpose atom–atom potential [32, 33]. We have previously demonstrated that it accurately mimics experimental RKR potential energy curves [11, 12, 34–37] and that it can be used to calculate very accurate transport properties and second virial coefficients [34–36]. It is also possible to use this potential form to fit ab initio quantum mechanical potential energy curves very accurately [11, 35–37].

We have previously calculated the transport properties of nitrogen atoms [11] by accurately representing either spectroscopic (HH) or quantum mechanical potential energy curves for the four electronic states of N_2 that dissociate to ground state (^4S) atoms; the $X^1\Sigma_g^+$, $A^3\Sigma_u^+$, $^5\Sigma_g^+$, and $^7\Sigma_u^+$ states. In the present work we apply these potential energy curves in calculating the thermodynamic properties of N_2. Furthermore, enough spectroscopic data is available for excited electronic states of N_2 to allow us to include many additional electronic states that contribute to the thermodynamic properties of N_2 at high temperatures. Thus we can accurately represent the potentials needed at temperatures up to 25,000 K for N_2 and accurately calculate the second virial coefficient, and derivatives, needed to obtain the thermodynamic properties. This procedure is inherently more accurate at high temperatures than the procedure involving summations over the vibrational and rotational energy levels.

Table I lists the 16 bound electronic states of N_2 that we have used in our calculations. They are listed in order of increasing energy at the minimum in the potential. A diagram of the potential energy curves is shown in Fig. 1. For most states, the six spectroscopic constants required for the HH potential are readily available [16, 38–41] and we have directly used these to obtain the appropriate potentials. However, in the case of the $^5\Sigma_g^+$ and $^7\Sigma_u^+$ states, the ab initio quantum mechanical potentials were used, as described previously [11]. The $E^3\Sigma_g^+$ state was fit with the Morse potential since the spectroscopic constants required to use the HH potential are not available.

At 25,000 K, the states in Table I comprise 94 % of the occupied states (based on an equilibrium calculation using 34 states). The second virial coefficients, and their derivatives, have been calculated for the states listed in Table I by using the HH and Morse potentials. The virial coefficients and their derivatives were calculated by using the Gauss–Kronrod integrator in the QUADPACK software collection [42] and also by using a procedure developed previously [43, 44]. Agreement is excellent.

Table I. States of N_2 Included in These Calculations

State	D_e (10^{19} J)[a]	Dissociation products[b]	Ref. No.[c]
$X^1\Sigma_g^+$	15.87	$^4S+{}^4S$	16
$A^3\Sigma_u^+$	5.808	$^4S+{}^4S$	16
$B^3\Pi_g$	7.845	$^4S+{}^2D$	16
$W^3\Delta_u$	7.808	$^4S+{}^2D$	38, 39
$B'^3\Sigma_u^-$	8.434	$^4S+{}^2P$	16
$a'^1\Sigma_u^-$	9.969	$^2D+{}^2D$	16
$a^1\Pi_g$	9.756	$^2D+{}^2D$	16
$w^1\Delta_u$	9.186	$^2D+{}^2D$	16
$^5\Sigma_g^+$	0.1634	$^4S+{}^4S$	12
$^7\Sigma_u^+$	0.008437	$^4S+{}^4S$	12
$G^3\Delta_g$	2.221	$^4S+{}^2D$	38, 40
$C^3\Pi_u$	1.982	$^4S+{}^2D$	16, 38
$E^3\Sigma_g^+$	0.6468	$^4S+{}^2D$	16, 38
$C'^3\Pi_u$	0.1432	$^4S+{}^2D$	38, 41
$b'^1\Sigma_u^+$	4.804	$^2D+{}^2D$	16, 38
$H^3\phi_u$	2.507	$^2D+{}^2D$	16, 38

[a] D_e is the electronic dissociation energy.

[b] The atomic states to which the molecular state dissociates.

[c] Sources for the spectroscopic constants used for these calculations.

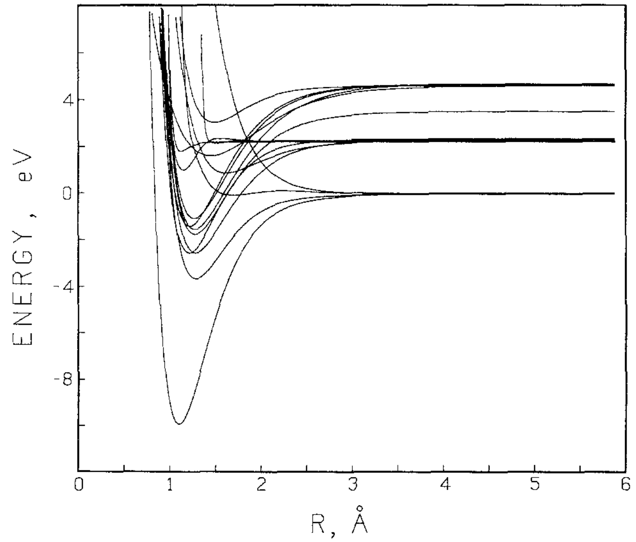

Fig. 1. Potential energies of 16 electronic states of nitrogen as a function of internuclear separation. The states are listed in Table I.

5. RESULTS AND CONCLUSION

Results for the thermodynamic properties are given in Table II along with comparisons with previous results from Balakrishnan [19]. The results for C_p^0 and $H_T^0 - H_O^0$ from Refs. 18 and 19 are nearly the same. At the lowest temperatures our results, using the $B(T)$ method, differ by a few percent from those obtained using Eq. (4). Since Eq. (4) should represent the energy levels of N_2 accurately at low temperatures, the results in Ref. 19 are likely to be more accurate here. At intermediate temperatures (e.g., 7000 K) there is only about a 1 % difference between the two methods. Much of this difference is probably due to the classical approximation used to calculate $B(T)$. The good agreement of results at low and intermediate temperatures indicates that the potential energy curves we use are accurate.

Table II. Thermodynamic Properties of N_2

	cal · mol^{-1}		kcal · mol^{-1}	
T(K)	$C_P^{0\,a}$	$C_P^{0\,b}$	$[H_T^0 - H_O^0]^a$	$[H_T^0 - H_O^0]^b$
2,000	9.012	8.594	14.578	15.487
3,000	9.053	8.841	23.609	24.222
4,000	9.094	8.958	32.681	33.125
5,000	9.143	9.033	41.799	42.116
6,000	9.204	9.100	50.972	51.173
7,000	9.296	9.200	60.220	60.307
8,000	9.448	9.387	69.958	69.577
9,000	9.691	9.725	79.196	79.104
10,000	10.037	10.268	89.140	89.065
11,000	10.481	11.046	99.570	99.684
12,000	10.979	12.043	110.60	111.19
13,000	11.474	13.204	122.30	123.77
14,000	11.898	14.437	134.65	137.54
15,000	12.196	15.630	147.55	152.52
16,000	12.331	16.679	160.85	168.60
17,000	12.299	17.505	174.33	185.61
18,000	12.114	18.064	187.79	203.29
19,000	11.806	18.354	201.06	221.37
20,000	11.412	18.400	213.98	239.60
21,000	10.969	18.248	226.46	257.76
22,000	10.505	17.947	238.44	275.68
23,000	10.044	17.547	249.89	293.23
24,000	9.601	17.092	260.81	310.35
25,000	9.184	16.612	271.22	326.98

[a] Results obtained in this work.

[b] Results given in Ref. 19.

At high temperatures the results obtained by the two methods begin to diverge substantially, with differences up to 50 % at 20,000 K. We believe that the primary reason for these large differences at high temperatures is that the partition function method based on Eq. (4) does not accurately reproduce the vibrational and rotational energy levels at high values of the quantum numbers.

The accuracy of the virial coefficient approach depends on the accuracy of the potentials used and the accuracy of the classical approximation for $B(T)$, which should be excellent at high temperatures [25]. We have previously compared [11] our HH potentials for N_2 with the RKR potentials [38] for the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states and find them to be in excellent agreement, especially at the values of r which contribute most significatly to the virial coefficients [34, 45, 46]. We have also performed comparisons with the RKR potential [38] for the excited $b'^1\Sigma_u^+$ state (which dissociates to two excited state atoms) and find very good agreement. These results demonstrate that the HH potential accurately models the "true" potential energy curves for N_2.

Other results from our previous calculations of the virial coefficients for lithium [35] and sodium [36] using the HH potential are in excellent agreement with careful quantum mechanical calculations of the second virial coefficient [25]. Also, our calculations of the second virial coefficient of argon [34] using the HH potential show excellent agreement with Kestin and co-workers' [47] comprehensive correlation of experimental results at temperatures above 1500 K. Based on these considerations, we estimate the errors in the results we report using the virial coefficient method in the present work to be 10% or less.

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