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Calculation of the thermophysical properties of ground state sodium atoms

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Transport properties of dilute monatomic gases depend on the two body interaction potentials between the atoms. When two ground state sodium atoms interact, they can follow either of two potential energy curves corresponding to the Na_2 molecule in the $X^1\Sigma_g^+$ or the $^3\Sigma_u^+$ state. Transport collision integrals and second virial coefficients of monatomic sodium have been calculated by accurately representing quantum mechanical potential energy curves with the Hulburt–Hirschfelder potential. The generally good agreement of calculated viscosities and second virial coefficients with the available experimental viscosities and with previously calculated virial coefficients provides further evidence that this approach can be used for accurate estimates of thermophysical properties under conditions where experimental data are sparse or unavailable.

I. INTRODUCTION

The properties of sodium vapor are of both theoretical interest and practical importance. Monatomic sodium is important for laser and optical studies since the spectroscopy of the states of sodium are so well known.¹⁻⁴ Small clusters of sodium atoms have been considered as models for investigating catalytic activity.^{5,6} Liquid sodium is used as a coolant in breeder reactors^{7,8} and in heat pipes,⁹ and alkali metal vapor magnetohydrodynamics can be used for the conversion of solar energy to electricity.¹⁰

The purpose of this paper is to report theoretical calculations of the transport properties (viscosity, thermal conductivity, and self-diffusion) and the second virial coefficient of monatomic sodium vapor. The kinetic theory of gases has been used to calculate the transport properties and statistical mechanics has been used to calculate the second virial coefficient. Both approaches depend¹¹ on knowledge of the interaction potential between two sodium atoms (i.e., Na_2) for the molecular states which dissociate to the ground state (2S) atoms. We have previously developed methods for calculating transport properties for any reasonably well-behaved atom–atom interaction potential, including those with interesting features such as multiple extrema.¹²⁻¹⁵ The focus of much of this work has been on predicting the thermophysical properties of gases at high temperatures, where laboratory measurements are not currently feasible. The Hulburt–Hirschfelder (HH) potential,^{16,17} for which the potential parameters can be determined from the spectroscopic constants, has been especially useful for this purpose.

II. INTERACTION POTENTIALS

The interaction of two ground state (2S) sodium atoms results in either the singlet ground $X^1\Sigma_g^+$ state or the excited $^3\Sigma_u^+$ molecular state of the Na_2 dimer. Contributions from both molecular states must be included in transport property and second virial coefficient calculations for the ground state atoms.

The HH potential^{16,17} is probably the best general pur-

pose potential¹⁸⁻²² for representing atom–atom interactions with an attractive minimum. Indeed, it may represent the true potential better¹⁴ than the representation provided by the Rydberg–Klein–Rees²³⁻²⁵ (RKR) potential. For example, it is capable of representing¹²⁻¹⁵ the multiple extrema found²⁶⁻²⁹ in some atom–atom interactions, whereas the RKR potential, which is determined by internuclear separations in the region of the potential well, cannot do this. We have also found³⁰ that differences between the RKR and HH potentials in the well region can often be an indicator of the unusual behavior of a state.

The HH potential depends only on the spectroscopic constants for the well depth, ϵ , the fundamental vibrational frequency, ω_e , the anharmonicity constant, $\omega_e\chi_e$, the rotational constant, B_e , the vibration–rotation coupling constant, α_e , and the equilibrium internuclear separation of the atoms in the dimer, r_e . These constants are known for the singlet state of Na_2 . They are³¹

$$\begin{aligned}\epsilon &= 0.730 \text{ eV} & B_e &= 0.154\,707 \text{ cm}^{-1}, \\ \omega_e &= 159.124 \text{ cm}^{-1} & \alpha_e &= 0.000\,873\,6 \text{ cm}^{-1}, \\ \omega_e\chi_e &= 0.7254 \text{ cm}^{-1} & r_e &= 3.0788 \text{ \AA}.\end{aligned}$$

With these constants, a comparison of the HH potential can be made with the experimental RKR potential³² for the singlet state of the sodium dimer. This is illustrated in Table I. Excellent agreement is seen at all but the smallest internuclear separations. For example, comparison with the available RKR values³² shows a difference of 3% or less for $r > 2.540 \text{ \AA}$.

In reduced form, the HH potential is given by¹⁵

$$V^*(r^*) = e^{-2a(r^*/d-1)} - 2e^{-a(r^*/d-1)} + \beta(r^*/d-1)^3 \times [1 + \gamma(r^*/d-1)]e^{-2a(r^*/d-1)}, \quad (1)$$

where

$$V^* = \frac{V}{\epsilon} \quad r^* = \frac{r}{\sigma} \quad d = \frac{r_e}{\sigma}.$$

Here, V is the potential energy, r is the internuclear separa-

TABLE I. Comparison of the HH and RKR (Ref. 32) potential energies (V) as a function of internuclear separation (r) for the ground $X^1\Sigma_g^+$ state of Na_2 .

$r(\text{\AA})$	$V(\text{HH})/V(\text{RKR})$	$r(\text{\AA})$	$V(\text{HH})/V(\text{RKR})$
2.449	1.24	3.220	1.00
2.453	1.20	3.333	1.00
2.460	1.14	3.416	1.00
2.475	1.10	3.486	1.00
2.493	1.07	3.549	1.00
2.503	1.04	3.607	1.00
2.540	1.02	3.718	0.98
2.556	1.02	3.770	1.00
2.636	1.00	3.873	1.00
2.661	1.00	4.022	1.00
2.720	1.00	4.070	1.00
2.757	1.00	4.214	1.00
2.802	1.00	4.315	0.97
2.860	1.00	4.418	0.97
2.949	1.00	4.468	0.97

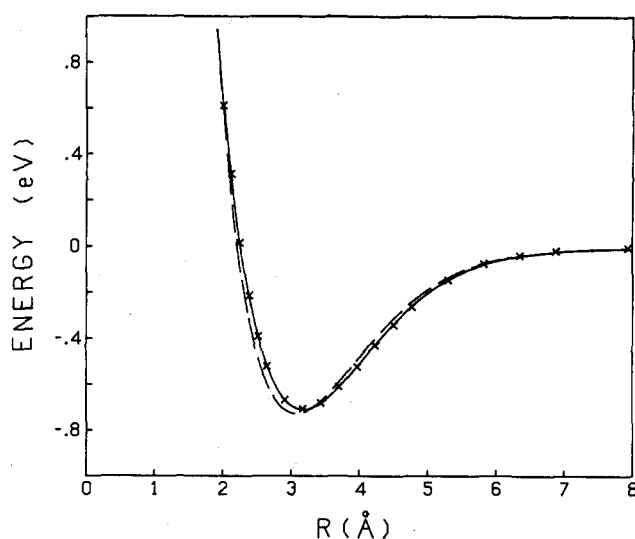


FIG. 1. Fit of H-H potential (solid line) to the *ab initio* results (\times 's) from Ref. 33 for the ground $X^1\Sigma_g^+$ state of Na_2 . For comparison, the dashed line shows the H-H potential based on spectroscopic parameters from Ref. 31.

tion, and σ is the smallest internuclear separation at which the potential is zero (the effective hard sphere diameter). Also, with ϵ' the well depth in cm^{-1} ,

$$a = \frac{\omega_e}{2\sqrt{B_e\epsilon'}}, \quad \beta = ca^3, \quad \gamma = ba,$$

$$c = 1 + a_1 \sqrt{\frac{\epsilon'}{a_0}}, \quad b = 2 - \frac{7/12 - \epsilon'a_2/a_0}{c},$$

$$a_0 = \frac{\omega_e^2}{4B_e}, \quad a_1 = -1 - \frac{\alpha_e\omega_e}{6B_e^2}, \quad a_2 = \frac{5}{4}a_1^2 - \frac{2\omega_e\chi_e}{3B_e}.$$

Alkali metal atoms are subject to considerable polarization and the induced polarizability affects the long-range tail of the potential. Any spectroscopically determined potential (such as the RKR and HH potentials) would be expected to be most accurate in the region of the minimum in the potential well and to provide a less accurate representation of the long-range attractive tail. Fortunately, *ab initio* quantum mechanical calculations of the Na-Na interaction potential can be used to provide information about the longer range part of the potential. The best available calculations for the singlet ground state of Na_2 are those of Konowalow, *et al.*³³ (KRO). It is difficult to estimate the error in their calculations but it is certainly greater than the 1%–3% error that Konowalow and Olson³⁴ estimated for their singlet ground state Li_2 calculation.

We have represented the *ab initio* KRO potential³³ for the singlet ground state by fitting the functional form of the HH potential to it. A nonlinear Nelder-Mead simplex procedure^{35,36} has been adapted to simultaneously fit the four HH parameters a , β , γ , and ϵ for various values of the fifth, σ , using a microcomputer with math co-processor. The results of our fitting procedure are shown as the solid line in Fig. 1, demonstrating excellent agreement over the entire range of the *ab initio* results. Comparison with the spectroscopically determined HH potential, shown by the dashed line in Fig. 1, indicates generally good agreement between the potentials but with some differences similar to those we found earlier for the Li_2 potential.³⁷ The HH parameters for

both the best fit and spectroscopic potentials are given in Table II. It can be seen that the HH parameters are similar, with the physical constants ϵ and r_e for the best fit potential almost identical to the KRO results. Agreement between the potentials is quite good.

The first excited $^3\Sigma_u^+$ state of Na_2 is weakly bound because of the polarizability of the sodium atoms. However, experimentally determined spectroscopic constants are not available for this state. Konowalow *et al.*³³ have calculated an *ab initio* quantum mechanical potential energy curve for the triplet state (KRO2). We have applied our simplex fitting procedure to their *ab initio* values and our results, using the HH potential, are shown in Fig. 2 with an expanded scale plot around the shallow minimum in Fig. 3. The fit is seen to be excellent. The equilibrium separation and the well depth predicted from this fit are given in Table III and compared with some other calculated values.^{33,38,39} Our results are in excellent agreement with the KRO2 results.

III. THERMOPHYSICAL PROPERTIES

The viscosity of a pure gas, η , is given by¹¹

$$\eta = \frac{5}{16} \left(\frac{mkT}{\pi} \right)^{1/2} \frac{1}{\sigma^2 \Omega^{(2,2)*}}, \quad (2)$$

TABLE II. The HH parameters for the ground $X^1\Sigma_g^+$ state of Na_2 as obtained from the spectroscopic constants (Ref. 31) and from a best fit to the KRO potential (Ref. 33).

	Spectroscopy	Best fit	KRO values
a	2.636 1	2.673 3	
β	4.642 8	6.122 2	
γ	1.772 0	1.527 5	
r_e (\AA)	3.078 87	3.186	3.174
ϵ (eV)	0.730	0.713	0.710

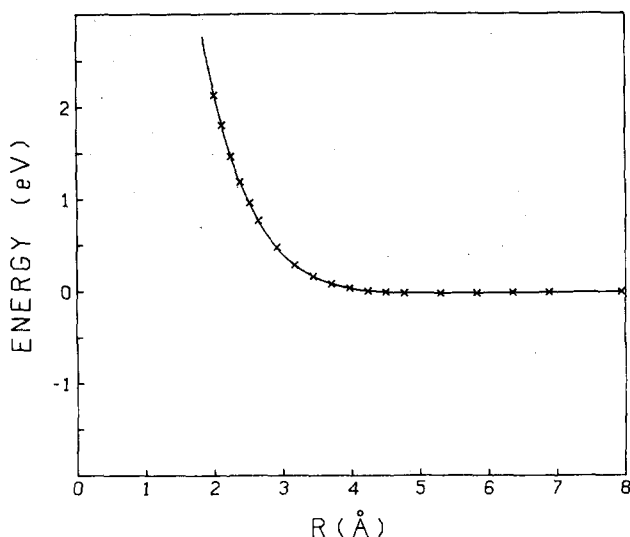


FIG. 2. Fit of the H-H potential (solid line) to the *ab initio* results (×'s) from Ref. 33 for the $^3\Sigma_u^+$ state of Na_2 .

where m is the molecular mass, k is Boltzmann's constant, T is the temperature, and $\sigma^2\Omega^{(2,2)*}$ is the viscosity collision integral. Also, the thermal conductivity of a pure monatomic gas, λ , is given by

$$\lambda = \frac{25}{32} \left(\frac{kT}{\pi m} \right)^{1/2} \frac{c_v}{\sigma^2\Omega^{(2,2)*}} = \frac{15}{4} \frac{k}{m} \eta, \quad (3)$$

where c_v is the specific heat per particle, taken to be $3k/2$ in these calculations. In addition, the self-diffusion coefficient, D , is given by

$$D = \frac{3}{8} \left(\frac{kT}{\pi m} \right)^{1/2} \frac{1}{\rho\sigma^2\Omega^{(1,1)*}}, \quad (4)$$

where ρ is the particle density and $\sigma^2\Omega^{(1,1)*}$ is the diffusion collision integral. The second virial coefficient, B , is given by¹¹

$$B = 2\pi N_0 \int_0^\infty (1 - e^{-V(r)/kT}) r^2 dr, \quad (5)$$

where N_0 is Avogadro's number.

Using the transport collision integral program that we

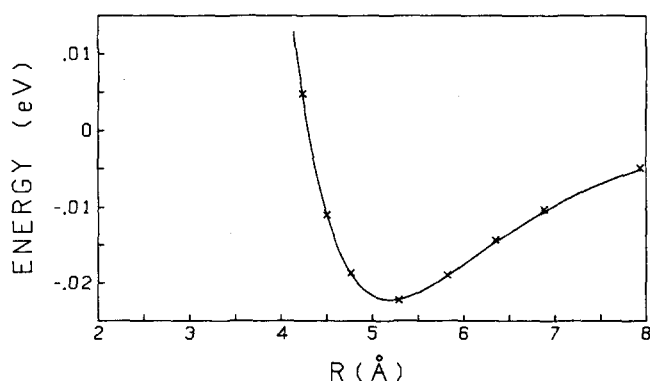


FIG. 3. The same comparison as in Fig. 2, but the energy scale has been expanded to emphasize the fit in the region of the potential well.

TABLE III. Equilibrium separation and well depth for the $^3\Sigma_u^+$ state of Na_2 .

	r_e (Å)	ϵ (eV)
Best fit result	5.199	0.0222
Konowalow <i>et al.</i> (Ref. 33)	5.206	0.0223
Roach (Ref. 38)	5.8	0.011
Bardsley <i>et al.</i> (Ref. 39)	5.3	>0.0055

have developed,^{12,13,15} viscosity collision integrals for monatomic sodium corresponding to interactions along the Na_2 ground state singlet potential energy curve have been calculated both for the HH potential determined by spectroscopy³¹ and for the best fit of the HH function to the *ab initio* KRO results.³³ There is excellent agreement (typically to 1% or better) between the collision integrals obtained from the spectroscopic data and from the *ab initio* results from 600 K to 20 000 K.

The transport collision integrals and the second virial coefficient are obtained by averaging the contributions from the singlet and triplet states according to their degeneracies.⁴⁰ Using the best fits to the KRO potential for the singlet state and the KRO2 potential for the triplet state, we obtained the results for the transport collision integrals shown in Table IV. The transport properties are given in Table V and the second virial coefficients in Table VI. Monatomic sodium vapor becomes important at temperatures above about 1000 K (the normal boiling point⁴¹ of sodium is 1165 K). The first ionization potential⁴¹ is 8.23×10^{-19} J and Na^+ becomes important at temperatures above about 10 000 K.

IV. DISCUSSION

The first theoretical calculation of the transport properties of monatomic sodium were reported by Davies *et al.*³² They essentially used the RKR potential energy curve to represent the singlet ground state and a scaling procedure

TABLE IV. The degeneracy averaged diffusion and viscosity collision integrals (in 10^{-20} m^2) for monatomic sodium as a function of temperature.

T (K)	$\sigma^2\Omega^{(1,1)*}$	$\sigma^2\Omega^{(2,2)*}$
500	26.5800	28.0657
750	22.6174	23.9596
1 000	20.2995	21.7500
1 250	18.6424	20.2945
1 500	17.3177	19.1840
2 000	15.2292	17.4206
2 500	13.6212	15.9717
3 000	12.3319	14.7274
3 500	11.2813	13.6531
4 000	10.4114	12.7315
4 500	9.6800	11.9277
5 000	9.0581	11.2318
6 000	8.0550	10.0877
7 000	7.2846	9.1916
8 000	6.6685	8.4707
9 000	6.1675	7.8711
10 000	5.7448	7.3707

TABLE V. The theoretically calculated viscosity (η), thermal conductivity (λ), and self-diffusion coefficient (D) of monatomic sodium as a function of temperature.

$T(K)$	$\eta(10^{-5} \text{ kg/m s})$	$\lambda(10^{-1} \text{ W/m K})$	$D(10^{-4} \text{ m}^2/\text{s})$
500	1.020	0.1383	0.2305
750	1.463	0.1984	0.4977
1 000	1.861	0.2524	0.8538
1 250	2.229	0.3024	1.299
1 500	2.584	0.3504	1.839
2 000	3.285	0.4456	3.219
2 500	4.006	0.5434	5.030
3 000	4.759	0.6455	7.303
3 500	5.545	0.7521	10.06
4 000	6.357	0.8622	13.32
4 500	7.197	0.9762	17.09
5 000	8.054	1.092	21.39
6 000	9.826	1.333	31.62
7 000	11.65	1.580	44.07
8 000	13.51	1.833	58.81
9 000	15.42	2.092	75.88
10 000	17.36	2.355	95.41

ture^{32,42} was used to estimate the potential energy curve for the triplet state. The minimum in the triplet state potential was not considered in their calculations. Their singlet state results are a few percent lower than ours at the lower temperatures considered and a few percent higher than ours at the higher temperatures. However, their results for the triplet state are about 50% larger than ours at all temperatures. This disagreement is not surprising. Yargin⁴³ has shown that the minimum in the triplet state potential has a substantial effect on the transport properties of alkali metal vapors.

More recently, Smirnov and Chibisov⁴⁴ have calculated the transport collision integrals of monatomic sodium by using an asymptotic hard sphere model. Their averaged viscosity collision integrals and thermal conductivities differ from ours by only a few percent near 1000 K but their singlet state values are about 20% smaller than ours while their triplet state results are about 20% larger than our values. Clearly the good overall agreement is largely fortuitous. Similar results are obtained upon making a comparison with the diffusion collision integrals reported by Smirnov and Chibisov.⁴⁴

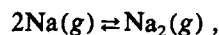
Timrot and Varava⁴⁵ have experimentally measured the viscosity of monatomic sodium at temperatures in the vicini-

TABLE VI. The theoretically calculated second virial coefficient, B , as a function of temperature.

$T(K)$	$B(10^{-3} \text{ m}^3/\text{mol})$	$T(K)$	$B(10^{-3} \text{ m}^3/\text{mol})$
500	-8.041×10^4	3 000	-0.237 3
750	-409.3	3 500	-0.162 7
1000	-31.14	4 000	-0.119 8
1250	-6.932	4 500	-0.092 49
1500	-2.616	5 000	-0.073 77
1750	-1.322	6 000	-0.050 11
2000	-0.796 5	7 000	-0.036 02
2250	-0.536 6	8 000	-0.026 82
2500	-0.389 7	9 000	-0.020 42
2750	-0.298 3	10 000	-0.015 77

ty of 1000 K and Vargaftik and Voshchinin⁴⁶ and Timrot, *et al.*⁴⁷ have measured the thermal conductivity over a similar temperature range. Comparisons with our results are given in Table VII. There is generally good agreement for the viscosity but the agreement for the thermal conductivity is not as good. Since alkali metal vapors undergo dimerization, trimerization, etc. reactions which make very important contributions to the thermal conductivity,^{48,49} extrapolations of experimental thermal conductivity results to the monatomic limit probably do not entirely eliminate the effects of the reactive thermal conductivity.

For the reaction



the second virial coefficient of monatomic sodium is given by⁵⁰

$$B = -K_c, \quad (6)$$

where K_c is the equilibrium constant in concentration units. Using a simple statistical mechanical expression⁵¹ for K_c , the second virial coefficient has been calculated and compared, in the second column of Table VIII, with the results we obtained using Eq. (5). Only the singlet state of Na_2 has been considered, signified by $B^{(1)}$. Clearly the agreement is poor.

Sinanoglu and Pitzer⁵² calculated the thermodynamic properties of monatomic sodium by representing the singlet state of Na_2 with a Rydberg potential. A comparison of their results for $B^{(1)}$ with the results we obtained using Eq. (5) is given in the third column of Table IX. The two sets of results differ by about 10%.

Recently, Mies and Julienne⁵³ have reported calculations of the second virial coefficients of monatomic sodium based on the KRO and KRO2 potentials. A comparison of the results of their quantum mechanical calculations with the results we obtained using Eq. (5) is shown in Table IX. The two sets of results are seen to differ by about 10% at temperatures above 1000 K. This difference is substantially greater than for our calculated second virial coefficients for lithium³⁷ which differed from those of Mies and Julianne by only about 1% at temperatures above 2500 K. Unlike the case for lithium, however, Mies and Julienne used modified

TABLE VII. Comparison of the results of this work with experimental results.

$T(K)$	$\eta(\text{this work})/$ $\eta(\text{Ref. 45})$	$\lambda(\text{this work})/$ $\lambda(\text{Ref. 46})$	$\lambda(\text{this work})/$ $\lambda(\text{Ref. 47})$
700		0.93	0.75
727	0.94		
800		0.91	0.78
803	0.94		
900		0.90	0.81
923	0.94		
977	0.94		
1000		0.86	0.83
1046	0.93		
1100		0.86	0.85
1200		0.85	0.87
1300		0.83	0.89

TABLE VIII. Comparisons of the second virial coefficient, $B^{(1)}$, for monatomic sodium.

$T(K)$	Eq. (5)/Eq. (6)	Eq. (5)/(Ref. 52)
1 000	1.03	0.77
1 500	1.18	0.84
2 000	1.28	0.86
2 500	1.33	0.87
3 000	1.34	0.88
4 000	1.27	0.88
5 000	1.16	0.90
7 000	0.94	0.89
9 000	0.75	0.90
10 000	0.68	0.90

well depths for the Na_2 potentials of Konowalow *et al.*,³³ making them about 6% more attractive for their calculations.⁵⁴ This modification can account for most of the observed difference between our results and theirs (as verified by our own calculations with a 6% deeper well). This is also shown in Table IX. Differences at lower temperatures for sodium are not as great as we found for lithium,³⁷ suggesting that the differences here may be primarily due to quantum mechanical effects.

The principal source of error in the calculations presented in this paper should be in the quantum mechanical calculations of the Na_2 singlet and triplet state potential energy curves. There is a rough rule-of-thumb⁵⁵ that an error of a factor of 2 in the potential leads to an error of 20%–40% in the transport collision integrals. Clearly these *ab initio* potentials are in error by much less than this. Our previous experience based on thermophysical property calculations for several other gaseous systems^{14,15,30,37,56} and our generally good agreement with experimental viscosities⁴⁵ and previously calculated^{52,53} second virial coefficients for monatomic sodium suggest that the transport properties given in Table V are in error by 10% or less from 1000 K to 4000 K.

TABLE IX. Comparison of the second virial coefficients, B , obtained using Eq. (5) with those obtained by Mies and Julienne (Refs. 53, 54).^a

$T(K)$	Eq. (5)/(Ref. 53)	$T(K)$	Eq. (5)/(Ref. 53)
500	0.41, 1.06	2100	0.82, 1.01
600	0.47, 1.05	2200	0.83, 1.01
700	0.53, 1.04	2300	0.84, 1.01
800	0.58, 1.03	2400	0.84, 1.01
900	0.61, 1.03	2500	0.85, 1.01
1000	0.65, 1.02	2600	0.85, 1.01
1100	0.68, 1.02	2700	0.86, 1.01
1200	0.70, 1.02	2800	0.86, 1.01
1300	0.72, 1.02	2900	0.86, 1.01
1400	0.74, 1.01	3000	0.87, 1.01
1500	0.76, 1.01	3500	0.88, 1.02
1600	0.77, 1.01	4000	0.89, 1.02
1700	0.79, 1.01	4500	0.90, 1.02
1800	0.80, 1.01	5000	0.90, 1.02
1900	0.81, 1.01	5500	0.91, 1.03
2000	0.82, 1.01	6000	0.91, 1.03

^a The first entry at each temperature is the result obtained by using the value of ϵ obtained from a best fit to the Konowalow potentials (Ref. 33) (see Tables II and III) and the second entry is the result obtained when ϵ is increased by 6% as done by Mies and Julienne. (Refs. 53, 54).

At lower temperatures, one might expect contributions from quantum mechanical effects. However, our agreement with experimental transport properties and quantum mechanically calculated second virial coefficients is about as good below 1000 K as at higher temperatures. Thus there is probably an error of 10% or less at temperatures as low as 500 K.

Excited electronic states begin to contribute to the thermophysical properties at temperatures above^{53,57} about 4000 K. However, the potential energy curves of low-lying excited states are similar to the ground state potential energy curve (the r_e values, in particular, being similar^{31,33}). Thus the contribution to the transport properties from the excited states are expected to be similar to the contribution from the ground state⁵⁸ and the estimated error of 10% or less is probably appropriate to about 10 000 K, where ionization becomes important. Since the virial coefficients depend on the details of the potential in a more sensitive way than the transport properties,⁵⁶ we estimate the error at temperatures between 4000 K and 10 000 K to be 15% or less.

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