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The Ideal and Real Gas Heat Capacity of Potassium Atoms at High Temperatures

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Abstract The ideal gas heat capacity, C_p , of potassium atoms is calculated to high temperatures using statistical mechanics. Since there are a large number of electronic energy levels in the partition function (Boltzmann sum) below the first ionization potential, the partition function and C_p will become very large as the temperature increases unless the number of energy levels contributing to the partition function is constrained. Two primary categories of arguments are used to do this. First, at high temperatures, the increased size of the atoms constrains the sum (Bethe method). Second, an argument based on the existence of interacting charged species at higher temperatures is used to constrain the sum (ionization potential lowering method). When potassium atoms are assumed to constitute a real gas that obeys the virial equation of state, the lowest non-ideal contribution to C_p depends on the second derivative of the second virial coefficient, $B(T)$, which depends on the interaction potential energy curves between two potassium atoms. When two ground-state (2S) atoms interact, they can follow either of the two potential energy curves. When a 2S atom interacts with an atom in the first electronically excited (2P) state, they can follow any of the eight potential energy curves. The values of $B(T)$ for the ten states are determined, then averaged, and used to calculate the nonideal contribution to C_p .

Keywords Potassium atoms · Heat capacity · Second virial coefficient

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1 Introduction

The normal boiling point of potassium metal is 1047 K [1] and its vapor pressure is 0.704 bar at 1000 K [1]. The first ionization potential, IP, of potassium vapor is 4.3407 eV [2], corresponding to thermal energy, kT , of 50 371 K. Most atoms are not ionized even at high temperatures. There are a substantial number of potassium atoms in the gas phase over the range of temperatures from 1000 K to 50 000 K.

The heat capacity, C_p^0 , of potassium atoms behaving as an ideal gas is given as a function of temperature to 6000 K in the NIST-JANAF Thermochemical Tables [3]. One of the purposes of this paper is to extend the calculations to higher temperatures. However, as T increases and more excited electronic states contribute to the heat capacity and other thermodynamic properties, the sum over excited states needs to be constrained or the values of C_p^0 become much too large.

In addition, assuming that potassium atoms obey the virial equation of state, the nonideal gas correction to C_p^0 is found through the term depending on the second virial coefficient, $B(T)$.

2 Ideal Gas Heat Capacity

The heat capacity of a mole of atoms is given by [4]

$$C_p^0 = 20.786 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + C_{p,\text{el}}^0 \quad (1)$$

where $C_{p,\text{el}}^0$ is the electronic contribution to the heat capacity, given by

$$C_{p,\text{el}}^0 = \frac{RT}{q_{\text{el}}} \left[T^2 \frac{\partial^2 q_{\text{el}}}{\partial T^2} - \frac{T}{q_{\text{el}}} \left(\frac{\partial q_{\text{el}}}{\partial T} \right)^2 + 2 \frac{\partial q_{\text{el}}}{\partial T} \right] \quad (2)$$

and the electronic partition function, q_{el} , is given by

$$q_{\text{el}} = \sum_i g_i e^{-E_i/kT} \quad (3)$$

where the sum over i is the sum over the electronic states of a potassium atom.

The ground state of a potassium atom is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. The Atomic Spectra Database (ASD) tables [2] list 187 other known electronic states of potassium atoms with energies less than that of the first IP, corresponding to the excitation of the 4s electron only. Results are given to $n = 46$, where n is the value of the principle quantum number (labeling the energy level). However, this list of states is incomplete. For potassium, the degeneracy, g_n , of an energy level is [5] given by

$$g_n = 2n^2 \quad (4)$$

For instance, for $n = 46$, $g_n = 4232$. However, the ASD table [2] lists the energies of only the 46s and 46d states with a total degeneracy of 12. Thus, the energies of 4220

Table 1 Electronic contribution to the heat capacity, $C_{p,\text{el}}^0$ ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), of potassium atoms as a function of temperature

T (K)	JANAF	“FILL”	Bethe	IP-kT
1500	0.015	0.015	0.015	0.015
2000	0.189	0.192	0.189	0.189
3000	2.150	6.315	2.182	2.149
4000	7.559	125.059	8.890	7.481
5000	15.533	195.469	28.941	14.749
6000	24.192	59.460	55.906	22.985
7000		16.419	67.878	19.787
8000		5.636	60.838	20.711
9000		2.367	42.116	19.933
10 000		1.162	27.735	18.199
20 000		0.037	1.291	4.598
30 000		0.009	0.276	1.708
40 000		0.004	0.100	0.857
50 000		0.002	0.055	0.509

$C_{p,\text{el}}^0 = 0$ for $T \leq 1000$ K

states are missing. There is a similar problem for almost all of the other energy levels. In fact, energy listings are complete only for the $n = 4$ and $n = 5$ energy levels [2].

The missing states should be accounted for in the calculation of C_p^0 . This is done by using the “FILL” procedure, i.e., the missing states are assumed to have the energy of the highest observed state for that value of n [5]. This procedure has been used in a number of high-temperature monatomic gas calculations; see, e.g., [4–8].

It seems as if this procedure is subject to considerable error. For $n = 46$, it requires estimating the energy of 4220 of the 4232 states. However, the 46s state has an energy of 4.333 577 12 eV and the 46d state has an energy of 4.334 154 94 eV, showing a very small difference [2]. Other states in the $n = 46$ energy level should have nearly the same energies, reducing the error made by approximating the energies. At lower values of n , the differences in the energies of the states, and thus the error introduced by using the “FILL” procedure, will be greater.

When the “FILL” procedure is used to calculate q_{el} and $C_{p,\text{el}}^0$ as a function of T , the results shown in the third column of Table 1 are obtained. These appear to be unreasonable at intermediate temperatures, i.e., it is very unlikely that $C_{p,\text{el}}^0$ is $195 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 5000 K. The results in the second column are from the NIST-JANAF Thermochemical Tables [3].

3 Constraining the Sum over Energy Levels

It is to be expected that when the number of energy levels contributing to q_{el} becomes large, then $C_{p,\text{el}}^0$ will become large. In fact, in principle, as for the hydrogen atom, there are an infinite number of bound state electronic energy levels below the ionization limit [5].

The sum over n needs to be constrained so that $C_{p,\text{el}}^0$ is constrained. One method for doing this was originally suggested by Bethe [9]. As n increases, the size of the atom increases, and it can be shown, e.g., [4], that the maximum value of n , called n_{max} , that contributes to q_{el} , is given by

$$n_{\text{max}} = 2.4561T^{1/6} \quad (5)$$

at 1 bar pressure. This approach has been used in a number of calculations; see, e.g., [4, 5, 8, 10–14]. The values of n_{max} as a function of T are given in the second column of Table 2, and the results for $C_{p,\text{el}}^0$ are given in the fourth column of Table 1.

The second method commonly used for constraining the sum over n is to use the fact that, as the energy associated with energy level n becomes close to the IP, some atoms will be ionized, and spectroscopic studies show that this has the effect of lowering the IP of the remaining neutral atoms [5, 10, 15–17]. This is due to the stabilization of an ion that occurs since it is surrounded by other charged particles that align themselves so that charged particles with the opposite sign dominate among nearest neighbors, providing a net attractive interaction. This is the basis of the Debye–Huckel theory.

Perhaps the easiest way to illustrate this is to use the arguments of Myers, et al. [18]. For the equilibrium between atom A and its singly charged ion, i.e.,



where the symbol e represents an electron, they show that the equilibrium constant, K_p , is given by [18]

$$K_p = \frac{\left(\frac{Q_+}{\gamma_+^{3/2}}\right)\left(\frac{Q_e}{\gamma_e^{3/2}}\right)}{Q_A} e^{-IP/RT} \quad (6)$$

where the Debye–Huckel theory has been used for the charged species, the Q 's are the molecular partition functions, and the γ 's are the activity coefficients. Since

$$0 \leq \gamma \leq 1$$

the value of K_p is larger than it would be if there was no ionization, i.e., the ionization in effect lowers IP.

If the Landau length, i.e., the distance of the closest approach during an electron–electron collision [10], is taken to be the appropriate distance between a charged particle and its surrounding ionic atmosphere [19], then it can be shown that n_{max} can be obtained from [10]

$$E_{n_{\text{max}}} = \text{IP} - kT \quad (7)$$

This approach, called the “IP – kT” method here, has been used in a number of calculations; see, e.g., [4–8, 18, 20, 21]. The values of n_{max} as a function of T for

Table 2 Maximum value of n , n_{\max} , contributing to q_{el} as a function of temperature

$T(K)$	Bethe	IP-KT
1500	8	10
2000	8	8
3000	9	7
5000	10	5
10 000	11	4
15 000	12	4
20 000	12	4
30 000	13	4
50 000	14	4

potassium atoms are given in the third column of Table 2, and the results for $C_{p,\text{el}}^0$ are given in the fifth column of Table 1.

4 Potassium Atoms as a Real Gas

Assume that potassium atoms obey the virial equation of state, i.e., [22]

$$\frac{PV}{RT} = 1 + \frac{B(T)}{RT}P + \frac{C(T) - B(T)^2}{(RT)^2}P^2 + \dots \tag{8}$$

where $B(T)$ is the second virial coefficient, and $C(T)$ is the third virial coefficient. The virial equation has been written as a power series in pressure, since this form is convenient for calculating C_p . For a gas obeying the virial equation of state, C_p is given by [22,23]

$$C_p = C_p^0(\text{IG}) - T \frac{d^2B(T)}{dT^2}P - D(T)P^2 + \dots \tag{9}$$

where $C_p^0(\text{IG})$ is the ideal gas result, and

$$D(T) = \frac{1}{RT^2} (C - B^2) + \frac{1}{2R} \frac{d^2C}{dT^2} - \frac{1}{R} \left(\frac{dB}{dT} \right)^2 - \frac{B}{R} \frac{d^2B}{dT^2} - \frac{1}{RT} \frac{dC}{dT} + \frac{2B}{RT} \frac{dB}{dT}.$$

The third term on the right side in Eq. 9 involves $C(T)$. Now $B(T)$ depends on two-body interactions between potassium atoms, but $C(T)$ depends on the interactions among three potassium atoms. There are rigorous results for many two-body interactions between potassium atoms but not for three-body interactions. Thus, this work considers only the contribution from the second term on the right side in Eq. 9.

Classically, $B_{\text{cl}}(T)$ is given by [24]

$$B_{\text{cl}}(T) = 2\Pi \int_0^\infty \left(1 - e^{-V(R)/kT} \right) R^2 dR \tag{10}$$

where “cl” denotes the classical contribution to $B(T)$, R is the distance between two interacting potassium atoms, and $V(R)$ is the interaction potential energy. Semiclassical corrections to $B_{\text{cl}}(T)$ are obtained by expanding in powers of Planck’s constant [24]. The resulting expressions are lengthy and given elsewhere [24, 25].

5 Electronic States and $B(T)$

The potential $V(R)$ depends on the electronic state associated with the atom–atom interaction, i.e., on the electronic state of K_2 . When two ground-state (^2S) atoms interact, they can interact along two potential energy curves, the ground $\text{X}^1\Sigma_{\text{g}}^+(1)$ and the excited $^3\Sigma_{\text{u}}^+(1)$ states. When a ground-state atom interacts with an atom in the first excited (^2P) electronic state, they can interact along eight potential energy curves: the $^1\Sigma_{\text{g,u}}^+$, $^3\Sigma_{\text{g,u}}^+$, $^1\Pi_{\text{g,u}}$, and $^3\Pi_{\text{g,u}}$ gerade/ungerade pairs of states [26]. The percentages of potassium atoms in the lowest ^2P excited state are $8 \times 10^{-9} \%$ at 1000 K, 2.3 % at 5000 K, and 13.7 % at 10 000 K. Thus, interactions between two ^2P atoms play a small role at 5000 K and have become somewhat important above 10 000 K. Such interactions have not been included in these calculations, since accurate potential energy curves for these interactions are not available. As will be seen, nonideal effects essentially vanish above 10 000 K.

Nine of the ten electronic states are bound. Only the $^3\Sigma_{\text{u}}^+(2)$ state is repulsive [27]. The symbols (1) and (2) are used to distinguish between states with the same term symbol.

The experimental [28] electronic dissociation energy, D_{e} ; the experimental [29] spectroscopic constants ω_{e} ; the fundamental vibrational frequency, $\omega_{\text{e}}\chi_{\text{e}}$; the anharmonicity constant, B_{e} ; the rotational constant and α_{e} ; the vibration–rotation coupling constant; and the experimental [30] value of R_{e} ; the equilibrium internuclear separation are known for the $\text{X}^1\Sigma_{\text{g}}^+(1)$ state. These same six constants are also known for the $^3\Sigma_{\text{u}}^+(1)$ state [31]; the $^1\Pi_{\text{u}}$ state [30]; the $^1\Pi_{\text{g}}$ state [32]; the $^1\Sigma_{\text{u}}^+$ state [33]; and the $^3\Pi_{\text{u}}$ state [33] of K_2 . These constants can be used to completely determine the Hulbert–Hirschfelder (HH) potential [34, 35], which may be the most accurate general purpose potential for representing bound state atom–atom interactions. It usually finds excellent agreement with “experimental” Rydberg–Klein–Rees (RKR) potential energy curves [36–38] for many atom–atom and atom–ion interactions; see, e.g., [39–43]. Certainly, it is the easiest potential to use to accurately represent such interactions.

The HH potential, V_{HH}^* , has the reduced form: [34, 35]

$$V_{\text{HH}}^*(R^*) = e^{-2Ax} - 2e^{-Ax} + Bx^3(1 + Gx)e^{-2Ax} \quad (11)$$

where

$$\begin{aligned} x &= \frac{R^*}{d} - 1 & V_{\text{HH}}^* &= \frac{V}{D_{\text{e}}} & R^* &= \frac{R}{\sigma} & d &= \frac{R_{\text{e}}}{\sigma} \\ c &= 1 + a_1\sqrt{\frac{D_{\text{e}}}{a_0}} & b &= 2 - \frac{\frac{7}{12} - D_{\text{e}}a_2/a_0}{c} \end{aligned}$$

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

$$A = \frac{\omega_e}{2\sqrt{B_e D_e}} \quad B = cA^3 \quad G = bA$$

and σ is the effective rigid sphere diameter, i.e., the value of R at which V goes to zero. The HH potential has been used for the six states mentioned above.

For the $^1\Sigma_g^+(2)$, $^3\Sigma_g^+$, and $^3\Pi_g$ states, experimental values of the spectroscopic constants are not available. However, theoretical values for D_e , R_e , and ω_e are available [44]. These values are used to determine the constants A and d in the HH potential. The values of the constants B and G are taken to be zero, in which case the HH potential becomes the Morse potential which is not nearly as accurate as the HH potential.

The theoretical potential energy curve for the repulsive $^3\Sigma_u^+(2)$ state [27] has been fit with the exponential repulsive potential, $V_{ER}(R)$, with the form

$$V_{ER}(R) = Ae^{-BR} \tag{12}$$

where the constants A and B are not the same as for the HH potential.

Calculations of $B(T)$, $B'(T)$, and $B''(T)$ have been carried out for each of the ten states discussed above; the classical and first three semiclassical contributions have been included. The results must be degeneracy averaged [45]. The degeneracy averaged second derivative of the second virial coefficient is given by

$$\left(\frac{d^2 B(T)}{dT^2}\right)_{DA} = \frac{\sum_j \left(\frac{d^2 B_j(T)}{dT^2}\right) g_j(K_2) e^{-E_j(K_2)/kT}}{\left(\sum_i g_i(K) e^{-E_i(K)/kT}\right)^2} \tag{13}$$

where j labels the electronic states of K_2 . This result is used to calculate the nonideal contribution to C_p , called $C_{p,NI}$ [23]:

$$C_{p,NI} = -TP \left(\frac{d^2 B(T)}{dT^2}\right)_{DA} \tag{14}$$

Results for $C_{p,NI}$ are given in Table 3.

6 Discussion

Again, it is necessary to constrain the sum over states in the partition function so that the electronic contribution to the ideal gas heat capacity does not become unacceptably large as shown in the third column of Table 1. Both the Bethe and the IP-kT methods constrain the sum over states and reduce $C_{p,el}^0$. The IP-kT method reduces the value of $C_{p,el}^0$ more than the Bethe method. The same result was found for sodium atoms [4]. This is to be expected since, as shown in Table 2, the number of energy levels, n , contributing to the sum in the electronic partition function becomes less for the IP-kT method as T increases while n becomes larger for the Bethe method as T increases.

Table 3 Non-ideal contribution to the heat capacity of potassium atoms, $C_{p,NI}$ ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)

$T(K)$	$C_{p,NI}$	$T(K)$	$C_{p,NI}$
1000	43.552	8000	-0.280
1500	2.101	9000	-0.219
2000	0.394	10 000	-0.165
2500	0.115	15 000	-0.042
3000	0.004	20 000	-0.016
3500	-0.081	25 000	-0.009
4000	-0.160	30 000	-0.007
4500	-0.231	35 000	-0.006
5000	-0.288	40 000	-0.006
6000	-0.345	45 000	-0.007
7000	-0.332	50 000	-0.007

Intuitively, it is reasonable to expect that n would increase as T increases but, as shown in the fourth column of Table 1, the values of $C_{p,el}^0$ are still quite large, perhaps unreasonably so, when the Bethe method is used but much smaller when the IP-kT method is used. The same trend was found for sodium [4] and unpublished work for oxygen atoms by these authors shows much higher results for $C_{p,el}^0$ using the Bethe method than using the IP-kT method.

It also seems reasonable to assume that the Bethe method is superior for calculating $C_{p,el}^0$ for neutral atoms at high temperatures than the IP-kT method since the latter method depends on arguments involving ionization. In fact, in his monograph in 1978 [5], Downey claimed that the Bethe procedure would be used for neutral atoms in future updates of the JANAF Thermochemical Tables; this claim is underlined in his monograph. However, as is clear from Table 1 here and Table 3 in Ref. [4], the IP-kT procedure was used in the 1998 edition of the JANAF Thermochemical Tables [3]. These authors assume that NIST researchers found that the results for $C_{p,el}^0$ for many atoms were larger than acceptable when the Bethe method was used, and we suggest that the results in the fifth column of Table 1 are the most satisfactory results for $C_{p,el}^0$ for potassium atoms at high temperatures.

One might be concerned about the “bump” in the IP-kT values in Table 1 at 7000 K, 8000 K, and 9000 K. This is a consequence of the fact that n_{\max} is discrete; for example, if n_{\max} is found to be 6.94, then the “rule” is [5] to round it off to 6. Downey [5] warns about this effect and suggests that some smoothing procedure is required before the results are used.

No matter which procedure is used to calculate $C_{p,el}^0$ for potassium atoms, the ASD values [2] for the electronic energy states, combined with the “FILL” procedure, are sufficient for calculations to 50 000 K since the value of n_{\max} is never larger than the value of n for which ASD information is available [2]. This may not be true for all atoms. In such cases, an approximation for the energy of the required unknown states can be obtained by assuming that the states are hydrogen-like and including them in the summation or by using the Rydberg or Rydberg–Ritz formulas [46].

Table 4 Comparison of the HH and RKR [30] potentials for the ground $X^1\Sigma_g^+$ state of K_2 for $R < R_e$

v^a	$R(\text{\AA})$	H/R^b	v^a	$R(\text{\AA})$	H/R^b
60	2.902	1.04	12	3.3429	1.01
55	2.925	1.03	11	3.3631	1.01
50	2.950	1.03	10	3.3845	1.01
45	2.978	1.03	9	3.4072	1.01
40	3.012	1.03	8	3.4316	1.01
35	3.051	1.02	7	3.4578	1.00
30	3.096	1.02	6	3.4864	1.00
25	3.149	1.02	5	3.5178	1.00
20	3.212	1.01	4	3.5529	1.00
17	3.2560	1.01	3	3.5930	1.00
16	3.2718	1.01	2	3.6406	1.00
15	3.2884	1.01	1	3.7009	1.00
14	3.3057	1.01	0	3.7922	1.00
13	3.3238	1.01			

$R_e = 3.92433 \text{ \AA}$ [30]
 $D_e = 4450.674 \text{ cm}^{-1}$ [28]
^a The symbol v represents the vibrational quantum number
^b The symbol H/R represents the ratio of the HH potential energy to the RKR potential energy

Consider the nonideal contribution, $C_{p,NI}$, to the heat capacity for potassium atoms. The results at 1000 K (Table 3) are clearly much too large to be correct, and the results at 1500 K may also be too large. A similarly inappropriately large value for $C_{p,NI}$ at 1000 K was found for sodium atoms [4]. It is likely that the primary reason for this is that the semiclassical expansion fails at lower temperatures, and therefore, a full quantum mechanical calculation of $B(T)$, involving the evaluation of phase shifts for the various potentials [24], is required.

At 1000 K, the ground $X^1\Sigma_g^+(1)$ of K_2 contributes 99.92 % to $B''_{DA}(T)$, i.e., it almost completely determines $C_{p,NI}$. A comparison of the HH and RKR [30] potential energy curves is shown in Table 4 and 5. Agreement is very good with an average error of 0.93 %. References [29, 31] give RKR results at higher values of the vibrational quantum number, v , than are given in Ref. [30]. Agreement between the HH and RKR results in these cases is as good, or better, than the agreement shown in Tables 4 and 5. The very good agreement indicates that $C_{p,NI}$ has been calculated quite accurately at this temperature, using the semiclassical approach, giving credence to the assumption that the unacceptably large result for $C_{p,NI}$ is due to the failure of the semiclassical approach.

At 1000 K and temperatures up to 3000 K, Table 3 shows that $C_{p,NI}$ is positive, but it is negative at 3500 K and higher temperatures. At 1000 K, $B''(T)$ is negative for all states except the repulsive $^3\Sigma_u^+(2)$ states which has negligible effect on $B''_{DA}(T)$. Thus, $B''_{DA}(T)$ is negative, and $C_{p,NI}$ is positive.

However, at higher temperatures, excited states no longer have a negligible effect on $B''_{DA}(T)$ and $B''(T)$ becomes positive for several states. For instance, at 5000 K, the ground $X^1\Sigma_g^+(1)$ state contributes only 32.93 % to $B''_{DA}(T)$ while the $^3\Pi_u$ contributes 28.79 %, and the repulsive $^3\Sigma_u^+(2)$ state contributes 22.06 %. Four other states contribute more than 1 %. The effect of this is to make $B''_{DA}(T)$ positive and $C_{p,NI}$ negative. RKR results are available [33] for

Table 5 Comparison of the HH and RKR [30] potentials for the ground $X^1\Sigma_g^+$ state of K_2 for $R > R_e$

v^a	$R(\text{\AA})$	H/R^b	v^a	$R(\text{\AA})$	H/R^b
0	4.0662	1.00	14	4.8500	0.99
1	4.1771	1.00	15	4.8908	0.99
2	4.2572	1.00	16	4.9312	0.99
3	4.3248	1.00	17	4.9712	0.99
4	4.3852	1.00	20	5.090	0.99
5	4.4408	1.00	25	5.287	0.99
6	4.4930	1.00	30	5.488	0.99
7	4.5426	1.00	35	5.699	0.99
8	4.5901	1.00	40	5.924	0.98
9	4.6360	1.00	45	6.173	0.99
10	4.6807	1.00	50	6.455	0.99
11	4.7242	0.99	55	6.787	0.99
12	4.7668	0.99	60	7.197	0.99
13	4.8087	0.99			

$R_e = 3.92433 \text{\AA}$ [30]

$D_e = 4450.674 \text{ cm}^{-1}$ [28]

^a The symbol v represent the vibrational quantum number

^b The symbol H/R represents the ratio of the HH potential energy to the RKR potential energy

Table 6 Comparison of the HH and RKR [33] potentials for the $^3\Pi_u$ state of K_2 for $R < R_e$

v^a	$R(\text{\AA})$	H/R^b	v^a	$R(\text{\AA})$	H/R^b
24	3.0944	1.02	11	3.3052	1.01
23	3.1074	1.02	10	3.3271	1.01
22	3.1208	1.02	9	3.3504	1.01
21	3.1346	1.01	8	3.3753	1.00
20	3.1488	1.01	7	3.4021	1.00
19	3.1635	1.01	6	3.4313	1.00
18	3.1788	1.01	5	3.4633	1.00
17	3.1946	1.01	4	3.4990	1.00
16	3.2111	1.01	3	3.5398	1.00
15	3.2282	1.01	2	3.5881	1.00
14	3.2461	1.01	1	3.6492	1.00
13	3.2649	1.01	0	3.7416	1.00
12	3.2845	1.01			

$R_e = 3.875 \text{\AA}$ [33]

$D_e = 7524.4 \text{ cm}^{-1}$ [33]

^a The symbol v represents the vibrational quantum number

^b The symbol H/R represents the ratio of the HH potential energy to the RKR potential energy

the $^3\Pi_u$ state, and comparisons with the HH results are shown in Tables 6 and 7. The agreement is excellent. Thus, two states that contribute 61.72 % to $B''_{DA}(T)$ at 5000 K are represented very accurately with an average error of 0.80 %.

The situation is quite different, however, for the repulsive $^3\Sigma_u^+(2)$ state. The theoretical calculations in Ref. [27] have been fit with the exponential repulsive potential, but the fit has much less of an exponential curve than the author has usually found for repulsive states. The curve is not linear, but it does not deviate a great deal from linearity. In addition, the four values of $V(R)$ at the lowest values of R were not used

Table 7 Comparison of the HH and RKR [33] potentials for the $^3\Pi_u$ state of K_2 for $R > R_e$

v^a	$R(\text{\AA})$	H/R^b	v^a	$R(\text{\AA})$	H/R^b
0	4.0168	1.00	13	4.7283	0.99
1	4.1268	1.00	14	4.7655	0.99
2	4.2057	1.00	15	4.8020	0.99
3	4.2718	1.00	16	4.8378	0.99
4	4.3304	1.00	17	4.8730	0.99
5	4.3841	1.00	18	4.9077	0.99
6	4.4341	1.00	19	4.9418	0.99
7	4.4813	1.00	20	4.9755	0.98
8	4.5262	1.00	21	5.0088	0.98
9	4.5693	0.99	22	5.0417	0.98
10	4.6108	0.99	23	5.0742	0.98
11	4.6511	0.99	24	5.1065	0.98
12	4.6902	0.99			

$R_e = 3.875 \text{\AA}$ [33]

$D_e = 7524.4 \text{ cm}^{-1}$ [33]

^a The symbol v represents the vibrational quantum number

^b The symbol H/R represents the ratio of the HH potential energy to the RKR potential energy

in the exponential fit. They are not consistent with the other data, and Valance and Tuan [27] suggest that this may be due to a pseudo-crossing with another $^3\Sigma_u$ state. Of course, it is not surprising that an exponential function becomes much less curved if the first four values, where the curve is most pronounced, are not included in the calculation.

It would be unreasonable not to expect that there is considerable error in the potential energy curve [27] for the $^3\Sigma_u^+(2)$ state. There is a rough rule of thumb that an error of a factor of two in the potential leads to an error of 20 % to 40 % in the calculation of transport collision integrals [47]. One would expect that a similar argument would hold for the calculation of virial coefficients. However, at temperatures at which the contribution of the repulsive $^3\Sigma_u^+(2)$ state to $C_{p,NI}$ becomes important, the value of $C_{p,NI}$ is quite small. Thus, it is realistic to be suspicious of the results in Table 3 for which $C_{p,NI}$ is negative.

It is possible that the change in sign of $C_{p,NI}$ is mirrored in the change in pressure from that of an ideal gas due to potassium atom interactions. The virial equation can be rewritten in its usual form as an expansion in inverse powers of the molar volume [22]:

$$P = \frac{RT}{V} + \frac{B(T) RT}{V^2} + \dots \tag{15}$$

The second term on the right in Eq. 15 is the lowest order nonideal contribution to P . At 2000 K, where $B_{DA}(T)$ is less than zero, the contribution of this term is $-1.643 \times 10^{-7}b$ and, at 2500 K, where $B_{DA}(T)$ is greater than zero, the contribution of this term is $+9.848 \times 10^{-8}b$. The effect of nonideality on P does mirror the effect on $C_{p,NI}$. Notice that the lowest order nonideal effect is much less for the pressure than for the heat capacity.

7 Conclusions

Despite the fact that, conceptually, the Bethe method appears to be superior to the IP–kT method for constraining the sum over energy levels that contribute to $C_{p,\text{el}}^0$ at high temperatures, from a practical point of view the IP–kT method appears to more reliably assure that the values of $C_{p,\text{el}}^0$ are reasonable at high temperatures. It is probably the “method of choice” for high temperature calculations of $C_{p,\text{el}}^0$ for atoms.

For potassium atoms, the IP–kT method and the “FILL” procedure, combined with information in the ASD tables [2], are sufficient to calculate $C_{p,\text{el}}^0$ to 50 000 K.

The HH and RKR potential energy curves for the bound states of K_2 are in very good agreement but errors in representing the repulsive $^3 \sum_u^+(2)$ state mean that there may be considerable error in the calculation of $C_{p,\text{NI}}$ at temperatures where this state makes a significant contribution to $C_{p,\text{NI}}$.

Semiclassical calculations, even when the first three semiclassical terms are included in the calculation, do not appear to be adequate to calculate $C_{p,\text{NI}}$ below approximately 2000 K for either K_2 or Na_2 . A full quantum mechanical approach appears to be required.

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