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Classical and quantal calculations of the dimerization constant and second virial coefficient for argon

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Summary. Computations of the second virial coefficient and thermodynamic equilibrium constant for the dimerization of argon are reported. These are based on accurate analytic representations of the Ar–Ar interaction energy. Calculations have been made using classical and quantal statistical mechanics and for the second virial coefficient the JWKB series as well.

Key words: Argon, second virial coefficient – Dimerization of argon – Ar–Ar interaction

1. Introduction

The information reported here is part of an investigation we are conducting into the role of van der Waals complexes in the photochemistry of dense gases and liquids [1]. Of particular concern to us are the concentrations of these loosely bound aggregates. To calculate these concentrations it is necessary to determine not only the thermodynamic equilibrium constants of the various complexes but their fugacities as well. An evaluation of the fugacities requires the calculation of quantities similar to virial coefficients [1, 2].

In our search for approximate means of computing the concentrations of weakly bound complexes, we have found it useful to have available for comparison very accurate calculations for a few simple reference systems. It is in this context that we decided to investigate the van der Waals complexes of argon. In this paper values are reported of the equilibrium constant and second virial coefficient for ^{40}Ar. Classical and quantal calculations have been performed using a very accurate analytical potential for the Ar–Ar interaction.

This subject seems peculiarly appropriate for inclusion in a volume devoted to the memory of Joseph O. Hirschfelder, since the theory upon which our calculations are based was treated with special care and authority in "Molecular Theory of Gases and Liquids" [3]. To acknowledge our indebtedness to this outstanding treatise we have, wherever possible, adopted its notation.

Because the binding energies of van der Waals complexes are so much smaller than those of the more familiar and thoroughly investigated strongly bonded species, uncertainties naturally arise about the applicability of approximations commonly used in dealing with the latter. These include uncertainties about the separability of rotational and vibrational motions and about the suitability of a classical in place of a quantal treatment of the internal, vibrational and rotational degrees of freedom. Also of concern is the sensitivity of the computational output to the accuracy with which the internal-state Hamiltonian (potential energy) is represented. Many of these issues already have been addressed in our recent report [4] on the equilibrium constants for formation of the van der Waals dimers Ar_2 and Mg_2. There it was found that most of the dynamical approximations which work so well for strongly bound species are seriously inadequate when applied to weakly bound complexes. However, at each level of dynamical approximation remarkably good agreement was found between calculations based on classical and quantum mechanics. Although relatively small, the quantal corrections are significant, given the current accuracy of the Ar–Ar interaction potential.

Here we briefly shall review and summarize a portion of our earlier work on the equilibrium constant for dimer formation. This is then combined with a previously unpublished comparison of the classical and quantal second virial coefficients. The former of these is easy to calculate. The latter is not. To calculate the quantal second virial coefficient one must determine not only the bound-state eigenvalues of the two-body Hamiltonian operator but the corresponding set of phase shifts as well. JWKB calculations of the second virial coefficient also are included.

2. Theoretical basis for the calculations

2.1. *Potential energy of* Ar–Ar *interaction*

A number of accurate analytic potentials have been constructed for the Ar–Ar electronic ground state. The experimental data upon which all of these rely come from spectroscopic studies performed by Colbourn and Douglas [5], who resolved a large number of vibrational-rotational levels. These investigators then calculated the corresponding RKR potential and further refined this to reproduce the observed spectra.

The analytic potential used for most of the calculations in the present study is potential 4 of Koide, Meath, and Allnatt [6]. The formula for this potential (in atomic units) is:

$$V(r) = [2.0073(1+0.1r)-1]\exp(-2.1510r+7.2920-4.787r^{-1}+1.724r^{-2}) \\ -[64.4899r^{-6}+1700.27r^{-8}+50160.8r^{-10}]f_{\mathrm{ArAr}}(r) \qquad (2.1)$$

with

$$\begin{aligned} f_{\mathrm{ArAr}}(r) &= \exp[-0.4(9.081r^{-1}-1)^2]; \quad r<9.081 \\ &= 1 \qquad\qquad\qquad\qquad\qquad\; ; \quad r\geqslant 9.081 \end{aligned}$$

Classical second virial coefficients are calculated using two other accurate analytic potentials as described below.

2.2. *Equilibrium constant for dimerization*

The equilibrium constant for the dimerization reaction $2M \rightleftharpoons M_2$ is given by the formula [4]:

$$K(T) = (Z_2^b/V)/(Z_1/V)^2 \tag{2.2}$$

with V denoting the volume of the system. Z_1 is the partition function of a single atom and Z_2^b is the contribution of bound, dimer states to the two-particle partition function.

We assume that the nuclear spins are equal to zero and that only the ground electronic state of the two-atom system is significantly populated. Both of these are appropriate to the case of ^{40}Ar. Consequently, $Z_1 = V\lambda^{-3}$ (with $\lambda^2 = \beta h^2/2\pi m$ and $\beta = 1/k_B T$) and $Z_2^b = 2^{3/2} V \lambda^{-3} Z_2^{b,int}$ with $Z_2^{b,int}$ the internal-state portion of Z_2^b. The equilibrium constant then can be written in the form

$$K(T) = \lambda_r^3 Z_2^{b,int} \tag{2.3}$$

with $\lambda_r = (\beta h^2/2\pi\mu)^{1/2}$ denoting the thermal de Broglie wavelength associated with the reduced mass $\mu = m/2$.

When the relative motion of the nuclei is treated classically, the internal-state part of Z_2^b is given by:

$$(Z_2^{b,int})_{CL} = \frac{1}{2}\left\{\frac{1}{h^3}\int\int_b dr\, dp\, e^{-\beta H}\right\} \tag{2.4}$$

The integral in this formula extends over the bound (b) states of the classical Hamiltonian function $H = p^2/2\mu + V(r)$ associated with the electronic ground state, for which the potential energy is so chosen that $V(\infty) = 0$. The factor of 1/2 appearing in Eq. (2.4) is the symmetry factor due to the indistinguishability of the two identical nuclei. Equation (2.4) can be rewritten as:

$$(Z_2^{b,int})_{CL} = 4\sqrt{\pi}\lambda_r^{-3}\int_\sigma^\infty dr\, r^2 e^{-\beta V(r)}\left\{\frac{\sqrt{\pi}}{2}\operatorname{erf}[-\beta V(r)]^{1/2} - (-\beta V(r))^{1/2} e^{\beta V(r)}\right\} \tag{2.5}$$

so that the corresponding classical approximation to the equilibrium constant becomes:

$$K_{CL}(T) = 4\sqrt{\pi}\int_\sigma^\infty dr\, r^2 e^{-\beta V(r)}\left\{\frac{\sqrt{\pi}}{2}\operatorname{erf}[-\beta V(r)]^{1/2} - (-\beta V(r))^{1/2} e^{\beta V(r)}\right\} \tag{2.6}$$

The parameter σ appearing here is the value of the internuclear separation at which $V(r)$ passes from positive (repulsive) to negative (attractive) values, i.e., $V(\sigma) = 0$.

Because the spins of the ^{40}Ar nuclei are equal to zero, the wave functions of the dimer must be symmetric with respect to interchange of the nuclei. The term symbol for the electronic ground state of Ar is $^1\Sigma_g^+$ and so this state is symmetric with respect to the inversion of the electrons and nuclei through the center of mass. Furthermore, the nuclear spin wave function is symmetric with respect to nuclear interchange. Consequently, the rotational states must be symmetric, that is, the rotational quantum number must be even. The quantal bound state partition function is therefore given by the expression:

$$(Z_2^{b,int})_{QU} = \sum_{J_e}(2J+1)\sum_n e^{-\beta E_{nJ}} \tag{2.7}$$

with $\sum_{J_e}(\cdots)$ indicating a sum over even values of J and where E_{nJ}^- denotes a bound state eigenvalue of the quantal Hamiltonian operator associated with the classical Hamiltonian function H. Recall that the zero of the potential is defined at infinite separation. Therefore, the electronic partition function is unity and the bound state eigenvalues are negative.

2.3. Second virial coefficient

According to Eq. 6.4-1 of Ref. [3], the second virial coefficient of a monatomic gas is given by the formula:

$$B(T) = -\frac{\lambda^6}{2V}(2Z_2 - Z_1^2) = \frac{\lambda^6 Z_1^2}{V^2}\left[\frac{V}{2} - \frac{VZ_2}{Z_1^2}\right] \tag{2.8}$$

with (see previous subsection) $\lambda^6 Z_1^2/V^2 = 1$. The two-particle partition function Z_2 may be decomposed into the sum of the two terms, Z_2^b and Z_2^{unb}, associated with bound and unbound states, respectively. Furthermore, Z_2^{unb} can be written as the sum of Z_2^0 and $(Z_2^{unb} - Z_2^0)$ with Z_2^0 denoting the partition function for two (hypothetical) non-interacting argon atoms. Thus, Eq. (2.8) becomes the sum of three terms:

$$B(T) = B^0(T) + B^b(T) + B^{unb}(T) \tag{2.9}$$

The first of these is:

$$B^0(T) = \frac{V}{2} - \frac{VZ_2^0}{Z_1^2} \tag{2.10}$$

the second virial coefficient for two non-interacting atoms. The second:

$$B^b(T) = -VZ_2^b/Z_1^2 \tag{2.11}$$

immediately can be identified with the negative of the dimerization equilibrium constant $K(T)$, given by Eq. (2.2). Finally:

$$B^{unb}(T) = -\frac{V(Z_2^{unb} - Z_2^0)}{Z_1^2} \tag{2.12}$$

is the contribution to $B(T)$ due to the unbound states of two interacting argon atoms.

We now briefly review the procedures for evaluating B^0, B^b and B^{unb}. The quantal "ideal gas" two-particle partition function Z_2^0 can be written in the form:

$$(Z_2^0)_{QU} = \tfrac{1}{2}\lambda^{-6}\iint d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, W^0(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{2.13}$$

where [cf. Ref. [3], Eq. (6.3-2)]:

$$W^0(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1 \pm \exp[-2\pi r_{12}^2/\lambda^2] \tag{2.14}$$

is the Slater sum for two non-interacting atoms. The upper and lower signs in Eq. (2.14) refer to Bose–Einstein and Fermi–Dirac statistics, respectively. From these formulas it follows that (cf. Ref. [3], Eq. (6.3-8)):

$$B_{QU}^0(T) = \frac{1}{2V}\iint d\boldsymbol{r}_1\, d\boldsymbol{r}_2(1 - W^0) = \mp\frac{1}{2}\int d\boldsymbol{r}_{12}\exp[-2\pi r_{12}^2/\lambda^2] = \mp\frac{1}{16}\lambda_r^3 \tag{2.15}$$

Since $(Z_2^0)_{CL} = \frac{1}{2}Z_1^2$, the classical value of $B^0(T)$ is identically equal to zero, i.e.:

$$B^0_{CL}(T) = 0 \tag{2.16}$$

Furthermore, because $(Z_2^0)_{CL} = \frac{1}{2}Z_1^2$ the quantity $(Z_2^{unb} - Z_2^0)/Z_1^2$ simplifies to $(Z_2^{unb}/Z_1^2 - 1)$. In the classical case it is simpler to recombine Z_2^{unb} and Z_2^b. Then since $(Z_2)_{CL} = \frac{1}{2}\lambda^{-6} \iint d\mathbf{r}_1\, d\mathbf{r}_2 \exp[-\beta V]$ it can be seen that:

$$\begin{aligned} B_{CL}(T) &= -\tfrac{1}{2}V^{-1} \iint d\mathbf{r}_1\, d\mathbf{r}_2 [e^{-\beta V(r_{12})} - 1] \\ &= -2\pi \int_0^\infty dr\, r^2 [e^{-\beta V(r)} - 1] \end{aligned} \tag{2.17}$$

This formula could be combined with $B_{CL} = B^b_{CL} + B^{unb}_{CL} = -K_{CL} + B^{unb}_{CL}$ to generate values of B^{unb}_{CL}.

In the quantal case:

$$\begin{aligned} (Z_2^{unb} - Z_2^0)_{QU} &= 2^{3/2} V \lambda^{-3} \sum_{J_e} (2J+1) \sum_n [e^{-\beta E^+_{nJ}} - e^{-\beta E^0_{nJ}}] \\ &= 2^{3/2} V \lambda^{-3} \sum_{J_e} (2J+1) \int_0^\infty dp\, e^{-\beta p^2/2\mu} \left[\frac{dn_J}{dp} - \frac{dn_J^0}{dp}\right] \end{aligned} \tag{2.18}$$

where dn_J/dp and dn_J^0/dp, respectively, are the densities of states associated with the unbound states of two interacting and two non-interacting atoms. The difference $[dn_J/dp - dn_J^0/dp]$ can be identified (cf. Ref. [3], Eq. 1.7-14) with $\pi^{-1}\, d\eta_J/dp$ where $\eta_J(p)$ denotes the phase shift of the Jth partial wave. Therefore, we find that:

$$B^{unb}_{QU}(T) = -\pi^{-1} \lambda_r^3 \sum_{J_e} (2J+1) \int_0^\infty dp\, e^{-\beta p^2/2\mu} \{d\eta_J(p)/dp\} \tag{2.19}$$

Thus, the quantal second virial coefficient can be identified with the sum of three terms, $B^0(T)$ from Eq. (2.15), $B^b_{QU}(T) = -K(T)$ from Eqs. (2.3) and (2.7), and $B^{unb}_{QU}(T)$ from Eq. (2.19).

An alternative to this is the JWKB series:

$$B_{JWKB}(T) = B_{CL}(T) + B^0_{QU}(T) + B^{(1)}(T) + B^{(2)}(T) + \cdots \tag{2.20}$$

which Uhlenbeck and Beth [7] obtained by using Kirkwood's [8] expansion (in powers of the Planck constant) of the Slater sum for interacting particles. Here, B_{CL} and B^0 are given by Eqs. (2.17) and (2.15), respectively, and (cf. Ref. [3], Eqs. (6.5-5) and (6.5-6)):

$$B^{(1)}(T) = 2\pi \frac{\hbar^2}{m} \frac{\beta^3}{12} \int_0^\infty dr\, r^2\, e^{-\beta V(r)} [V'(r)]^2 \tag{2.21}$$

$$\begin{aligned} B^{(2)}(T) = -2\pi \left(\frac{\hbar^2}{m}\right)^2 \frac{\beta^4}{120} \int_0^\infty dr\, r^2\, e^{-\beta V(r)} \Big\{ &[V''(r)]^2 + \frac{2}{r^2}[V'(r)]^2 \\ &+ \frac{10\beta}{9r}[V'(r)]^3 - \frac{5\beta^2}{36}[V'(r)]^4 \Big\} \end{aligned} \tag{2.22}$$

Table 1. Classical (CL) and quantal (QU) dimerization constants (in cm³/mol) for the KMA potential

	T (K)				
	100	200	300	400	500
CL	130.2	36.54	18.54	11.64	8.165
QU	130.4	36.89	18.76	11.79	8.276

wherein $V'(r) = dV/dr$ and $V''(r) = d^2V/dr^2$. In the JWKB case, as in the classical situation, it is simpler not to separate the bound and unbound contributions to the two particle partition function.

3. Computational results

3.1. Equilibrium constant

The classical equilibrium constant of Eq. (2.6) has been calculated for the KMA potential. Numerical values are presented in Table 1.

The eigenvalues E_{nJ}^- needed to evaluate the quantal equilibrium constant (see Eqs. (2.3) and (2.7)):

$$K_{QU}(T) = (\beta h^2/2\pi\mu)^{3/2} \sum_{J_e} (2J+1) \sum_n e^{-\beta E_{nJ}^-} \tag{3.1}$$

were obtained by using the renormalized Numerov method of Johnson [9] to solve the radial Schrödinger equation:

$$\frac{d^2\psi_{nJ}}{dr^2} - \frac{2\mu}{\hbar^2}\left[V(r) + \frac{J(J+1)\hbar^2}{2\mu r^2} - E_{nJ}^-\right]\psi_{nJ} = 0 \tag{3.2}$$

The calculated eigenvalues agree very well (within a few parts per thousand) with the five experimentally observed $J = 0$ eigenvalues. The eigenvalues we calculated for two different Lennard–Jones 6-12 potentials failed badly to reproduce accurately the experimental results and the equilibrium constants calculated for these potentials differed markedly (from 6–16%) from those associated with the KMA potential. These and other details of our equilibrium constant calculations have been reported elsewhere [4].

Quantal equilibrium constants for the KMA potential are presented in the second row of Table 1.

3.2. Second virial coefficient

3.2.1. Classical calculations. We have calculated the classical second virial coefficient directly from Eq. (2.17), using the trapezoidal rule integration procedure with a step size of 0.004 Bohr. The integrations were truncated at values of r (usually on the order of 1000 Bohr) for which the integrand had become negligibly small. Calculations were performed using three accurate analytical representations of the Ar–Ar interaction, namely, the KMA potential of Eq. (2.1) and two others, designated by their originators as HFDTCS2 [10] and

Table 2. Second virial coefficients (in cm^3/mol) calculated according to the classical mechanical Eq. (2.17). Three accurate analytic representations of the Ar–Ar interaction potential have been used. These are indicated as follows; KMA refers to Eq. (2.1), *I* to the HFDTCS2 potential of Ref. [10] and *II* to the EHFACE2 potential of Ref. [11]. The experimental values are taken from Ref. [12]

	T (K)				
	100	200	300	400	500
B_{CL} (KMA)	−184.02	−48.340	−15.438	−1.0343	6.8698
B_{CL} (I)	−183.91	−48.289	−15.441	−1.0736	6.8075
B_{CL} (II)	−184.11	−48.363	−15.452	−1.0546	6.8385
B_{EXP}	-185.5 ± 1	-47.6 ± 1	-15.6 ± 0.5	-0.9 ± 0.5	7.3 ± 0.5

EHFACE2 [11]. The calculations were converged to at least six significant figures so that the results displayed in Table 2 are accurate to all displayed figures. The tabular entries labeled B_{EXP} are experimental values compiled by Dymond and Smith [12].

A glance at Table 2 reveals that the differences among the classical virial coefficients associated with these three potential energy functions are small compared to the uncertainties of the experimental data. It is reasonable to expect that the numerical values of the quantal and JWKB second virial coefficients for these three potentials also will differ very little one from the other. Consequently, we have limited our quantal and JWKB calculations to the KMA potential of Eq. (2.1) for which we previously have computed the classical and quantal dimerization constants, cf. Table 1.

3.2.2. Quantal calculations. The bound-state contribution to the quantal second virial coefficient is, as previously observed, given by the dimerization constant $K_{QU} = -B^b_{QU}$. To determine the contribution associated with unbound states it is necessary to calculate the elastic scattering phase shifts $\eta_J(p)$ from the radial Schrödinger equation for a large number of rotational states (partial waves) and a large range of collision energies. To accomplish this we once again have used the renormalized Numerov method. Details of the procedure used to obtain the phase shifts are reported in a separate communication [13] along with calculated values of the cross section for Ar–Ar elastic collisions. Here our attention will be confined to calculational details directly related to the second virial coefficient.

When trapezoidal rule integration and finite difference differentiation are applied to Eq. (2.19), it becomes:

$$B^{unb}_{QU} = -\pi^{-1}\lambda_r^3 \sum_{J_e=0}^{J_{MAX}} (2J+1) \sum_{i=0}^{N_p-1} \exp[-\beta p^2_{i+1/2}/2\mu][\eta^{i+1}_J - \eta^i_J] \quad (3.3)$$

Here the index i is the label of a momentum (p) grid point and N_p is the total number of these points. η^0_J is specified below.

Our computational procedure produces values of the phase shifts, modulo π, i.e., values restricted to the range $(-\pi/2, \pi/2)$. Thus, a computed phase shift will vary smoothly with momentum until its value reaches $\pm\pi/2$, at which point its value jumps abruptly by $\mp\pi$ to the other end of the interval. These artificial jumps must be incorporated into the factors $\eta^{i+1}_J - \eta^i_J$ of (3.3). If the momentum step size is sufficiently small, the occurrence of these jumps can be anticipated and taken into account. Difficulties arise in the neighborhoods of resonances, for as the energy passes through a resonance the value of the phase shift will execute a *real* jump on the order of π. The widths of the argon shape resonances that we have observed vary dramatically. Some are quite broad and therefore can be resolved by the procedure just described, using a momentum grid appropriate to obtain accurate results for the smooth portion of the phase shift. However, others are so awesomely sharp that there is no hope of locating them directly by the straightforward procedure of stepping along a reasonable momentum grid. Therefore, some real jumps of π easily can be overlooked. To correct for this, Eq. (3.3) is replaced with the modified formula:

$$B_{QU}^{unb} = -\pi^{-1}\lambda_r^3 \sum_{J_e=0}^{J_{MAX}} (2J+1) \left[\sum_{i=0}^{N_p-1} \exp(-\beta p_{i+1/2}^2/2\mu)(\eta_J^{i+1} - \eta_J^i) + \pi \sum_{k=1}^{n_J^r} \exp(-\beta E_{Jk}^r) \right] \tag{3.4}$$

Here n_J^r is the number of unresolved resonances for the Jth partial wave and E_{Jk}^r is the energy at which the kth of these occurs. The methods we have used to obtain the values of these quantities will now be described.

First to be considered is the procedure for determining the number, n_J^r, of unresolved J-wave resonances. The phase shift at zero energy is given by [14, 15]:

$$\eta_J(0) = N_J^b \pi \tag{3.5}$$

with N_J^b denoting the number of bound states of the Jth partial wave, i.e., the number of bound states associated with the effective potential $V_J(r) = V(r) + \hbar^2 J(J+1)/2\mu r^2$. Because the KMA potential becomes strongly repulsive as r tends to zero, Levinson's theorem [14, 15] is inapplicable and therefore cannot be used to determine the high energy limit of the phase shift. To obtain this information we have developed a new computational procedure. For a given choice of J and the highest energy of interest, we integrate the radial Schrödinger equation, using both the KMA potential and the potential $V(r) = 0$. The numbers of nodes and the phases of these two wavefunctions at the largest value of r determine what we shall call the "absolute phase shift." The difference between the value of this absolute phase shift and the phase shift determined by stepping along the momentum grid is directly proportional to n_b^r, the number of resonances that were missed.

The sharpest resonances are difficult to locate even when one knows that they are present. Thus, the phase shift calculated on a seemingly reasonable grid may fail to reveal the presence of the resonance. To find latent resonances of this sort we rely upon a fundamental characteristic of resonances [16]. As the momentum (energy) reaches the value associated with a particular shape resonance, the wavefunction suddenly will acquire an additional node within the metastable well. Therefore, a plot of the number of nodes versus momentum will exhibit a sudden jump by one in the immediate vicinity of a resonance. Using this as a guide, one can expand the momentum scale over a narrow range in order to resolve all but the very sharpest resonances. This is the method we have used to locate shape resonances of Ar–Ar collisions that were too narrow to find by stepping along the momentum grid. The energies of all the resonances of the KMA potential are given in Table 3. Further details concerning the absolute phase shifts are reported elsewhere [13].

Table 3. Resonance energies (in cm^{-1}) of the KMA potential. The energies marked with asterisks (*) were resolved using the momentum grid for the momentum integration and therefore were not included in the factor $\pi \sum_k \exp(-\beta E^r_{Jk})$ of Eq. (3.4)

J	E (cm^{-1})	J	E (cm^{-1})
10	0.408	34	2.309, 15.539
14	0.417	36	9.237, 21.324*
16	1.854	38	16.436, 26.881*
20	2.170	40	6.966, 23.863
22	4.705	42	15.817, 31.444
24	1.475	44	24.985, 39.038
26	5.285	46	34.440
28	9.212	48	44.019
30	4.560, 13.22*	50	54.019
32	9.964	52	63.939

The accuracy of B^{unb}_{QU} calculated according to Eq. (3.4) is determined by the number of partial waves (J_{MAX}) as well as by the momentum grid and the position grid used in integrating the radial Schrödinger equation. The appropriate choices of the momentum and position grids, themselves, are dependent on which partial wave (J) is being considered. The step sizes of the r grid were taken to be $dr = 0.34130 \times 10^{-2}$ Bohr ($J = 0-100$), $dr = 0.26545 \times 10^{-2}$ Bohr ($J = 102-400$) and $dr = 0.22753 \times 10^{-2}$ Bohr ($J = 402-600$).

Because the range of the effective potential $V_J(r)$ is so great, it is extremely difficult to integrate the Schrödinger equation at low energies and nonzero values of J. However, this low energy range contribution to the second virial coefficient becomes progressively smaller with increasing J. To cope with this problem, a larger maximum value of the r coordinate has been used at low energies. Specifically, the range of r extends from 1–197 Bohr at high energy and from 1–591 Bohr at low energy. The dividing line between these ranges of low and high energy has been chosen to lie at an energy equal to the value of the J-dependent effective potential $V_J(r)$ at 50 Bohr. Contributions from energies less than the value of $V_J(r)$ at 500 Bohr were discarded. The errors produced by these difficulties at low energy are very slight.

The appropriate momentum grids are sensitively dependent on the value of J. For small values of J the contributions to B^{unb}_{QU} are due mostly to lower energies. As J increases, contributions from higher energies become relatively more important. Also, for a given partial wave and a specified value of the computational accuracy, different momentum step sizes may be appropriate to different ranges of energy. Therefore, we have divided the total energy range arbitrarily into three selected parts, to each of which are associated minimum and maximum energies. Within each of these subdivisions a fixed momentum step size has been used. This is illustrated by Table 4, which contains a complete listing of the momentum grids used in our calculations.

These grids in r and p produce individual partial wave contributions to B^{unb}_{QU} with accuracies that vary from 3 to 4 significant figures for the highest values of J to 5 or more significant figures at the lowest values of J. Because the contributions from large values of J tend to be smaller than those from lower values of J, the sums of these contributions should be accurate to 4 or 5

Table 4. Momentum Grids. The energies are reported in Hartree units (one hartree = $2.195 \times 10^5\ \mathrm{cm}^{-1} = 27.21$ eV). The symbol N_p indicates the number of momentum steps within the specified range of energy

	E_{min}	E_{max}	N_p
$J = 0$	0	0.5 (−5)	200
	0.5 (−5)	0.25 (−2)	300
	0.25 (−2)	0.5 (−1)	400
$J = 2$–6	0	0.5 (−5)	200
	0.5 (−5)	0.25 (−2)	300
	0.25 (−2)	0.5 (−1)	300
$J = 8$	0	0.5 (−5)	200
	0.5 (−5)	0.25 (−2)	200
	0.25 (−2)	0.5 (−1)	300
$J = 10$–18	0	0.1 (−2)	600
	0.1 (−2)	0.1 (−1)	250
	0.1 (−1)	0.5 (−1)	100
$J = 20$–38	0	0.125(−2)	600
	0.125(−2)	0.1 (−1)	250
	0.1 (−1)	0.5 (−1)	100
$J = 40$–58	0	0.15 (−2)	400
	0.15 (−2)	0.1 (−1)	250
	0.1 (−1)	0.5 (−1)	100
$J = 60$–78	0	0.3 (−2)	300
	0.3 (−2)	0.1 (−1)	200
	0.1 (−1)	0.5 (−1)	100
$J = 80$–400	0	0.3 (−2)	300
	0,3 (−2)	0.1 (−1)	100
	0.1 (−1)	0.5 (−1)	100
$J = 402$–600	0	0.3 (−2)	100
	0.3 (−2)	0.1 (−1)	100
	0.1 (−1)	0.5 (−1)	100

significant figures. To illustrate the relative magnitudes of the contributions from different ranges of J, values of the partial sum:

$$I_p(J_{MIN}, J_{MAX}) = \sum_{J_e = J_{MIN}}^{J_{MAX}} (2J+1) \left[\sum_{i=1}^{N_p} \exp(-\beta p_{i+1/2}^2 / 2\mu)(\eta_J^{i+1} - \eta_J^i) + \pi \sum_{k=1}^{n_J^r} \exp(-\beta E_{Jk}^r) \right] \tag{3.6}$$

are presented in Table 5.

This leads quite naturally to the question of convergence with respect to the value of J_{MAX}. Information relevant to this issue is shown in Table 6. The systematic error due to truncation of the J sum appears to be about 0.05 cm^3/mol at $T = 500$ K and about 0.02 cm^3/mol at $T = 100$ K. At the higher temperatures this truncation is clearly the largest source of error. At the lower temperatures the error caused by J-sum truncation decreases in relative importance and becomes comparable in magnitude to other sources of error.

According to Eq. (2.9), B_{QU} equals the sum of B^0, $B_{QU}^b = -K_{QU}$ and B_{QU}^{unb}. Values of B^0 are given in Table 7. The combination of these with the best values

Table 5. The dimensionless partial sums $I_p(J_{MIN}, J_{MAX})$ defined by Eq. (3.6)

	T (K)				
$J_{MIN} - J_{MAX}$	100	200	300	400	500
0–58	1487.1	−5258.8	−12862.	−20264.	−27275.
60–78	1865.7	3531.0	3316.3	1977.3	17.745
80–100	680.83	2237.9	3200.9	3265.0	2579.1
102–200	466.81	2006.0	4195.1	6371.5	8105.4
202–300	43.321	178.87	416.01	763.11	1222.6
302–400	10.460	42.463	96.944	174.93	277.52
402–500	3.7080	15.027	34.117	61.187	96.450
502–600	1.6305	6.6510	15.066	26.948	42.366

Table 6. Convergence of B_{QU}^{unb}, in units of cm^3/mol, with respect to J_{MAX}

	T (K)				
J	100	200	300	400	500
0–400	−52.010	−11.053	3.5993	11.009	15.396
0–500	−52.053	−11.113	3.5243	10.922	15.298
0–600	−52.071	−11.140	3.4912	10.883	15.254

Table 7. Second virial coefficients and contributions thereto in cm^3/mol. Calculations based on the KMA potential

	T (K)				
	100	200	300	400	500
B_{CL}	−184.02	−48.340	−15.438	−1.0343	6.8698
B_{QU}	−182.49	−48.030	−15.270	−0.9089	6.9784
B_{JWKB}	−182.57	−48.081	−15.321	−0.9640	6.9185
B^0	−2.2424(−3)	−7.9279(−4)	−4.3154(−4)	−2.8029(−4)	−2.0056(−4)
$B^{(1)}$	1.4931	0.26934	0.12175	7.3554(−2)	5.1017(−2)
$B^{(2)}$	−1.6171(−2)	−9.7523(−4)	−2.3798(−4)	−9.4030(−5)	−4.7282(−5)

of B_{QU}^{unb} from Table 6 and the values of K_{QU} from Table 1 has produced the values of B_{QU} presented in Table 7.

3.2.3. JWKB calculations. In the JWKB method the quantal second virial coefficient is expressed in terms of the classical second virial coefficient, B^0, and a series of quantal corrections, ordered in ascending, even powers of the Planck constant. The first and second of these quantal corrections, given by Eqs. (2.21) and (2.22), have been evaluated by trapezoidal rule integration. These integrals were converged with respect to the step size in r and truncation of the upper limit of integration. The results are accurate to at least 3 or 4 significant figures.

Values of $B^{(1)}$ and $B^{(2)}$ are presented in Table 7, along with values of B_{CL} and B^0. $B^{(1)}$ is 2 to 3 orders of magnitude smaller than B_{CL} and $B^{(2)}$ is 2 to 3 orders of magnitude smaller than $B^{(1)}$. As expected, both of these quantal corrections diminish in size as the temperature rises. At the higher temperatures the values of B^0 fall between those of $B^{(1)}$ and $B^{(2)}$ but at $T = 100$ K B^0 is smaller than $B^{(2)}$. The Table 7 entries labeled B_{JWKB} refer to sums of the contributions B_{CL}, B^0, $B^{(1)}$ and $B^{(2)}$, cf. Eq. (2.20).

3.2.4. Comparison of classical, quantal and JWKB *results.* By comparing the classical second virial coefficients of Table 7 with the corresponding quantal and JWKB quantities, we see that the correction due to quantum mechanics ranges from 0.1 cm^3/mol or less at the higher temperatures to more than 1 cm^3/mol at the lower temperatures. Although this correction is relatively small compared to B_{CL}, it is large in comparison with the differences among the B_{CL} values computed for several accurate analytic representations of the Ar–Ar interaction potential, see Table 2. Therefore, the accuracy with which this potential is known is sufficient to make the quantum mechanical effects significant.

It is interesting to compare the quantal and JWKB entries in Table 7. The discrepancies at the higher temperatures can be blamed upon errors due to truncation of the sum over partial wave contributions to B_{QU}^{unb}. Therefore, it is reasonable to expect that the JWKB results are the more accurate at high temperatures.

The cause of the discrepancies at lower temperature is less easy to identify. The partial wave truncation does not seem to account for all of the discrepancy, and the numerical error in evaluating the JWKB integrals should be negligible. Furthermore, truncation of the asymptotic, JWKB series would seem to be an unlikely source of errors as large as the discrepancies appearing in Table 7. The remaining possibility is of a numerical error in B_{QU} other than the systematic error due to truncation of the partial wave sum. This possibility cannot be dismissed out of hand since the differences between the low temperature values of B_{QU} and B_{JWKB} are, indeed, of about the same magnitude as the maximum numerical error anticipated in the calculation of B_{QU}. Without doing further calculations we are unable to say with certainty whether B_{QU} or B_{JWKB} is the more accurate at the lower temperatures included in Table 7.

To the best of our knowledge, the only previous quantal calculation of a second virial coefficient is deBoer and Michels' [17] study of helium. Our calculations for argon are much more accurate than theirs due to the much more modern calculational facilities that we had at our disposal. However, it is important to remember that for Ar and the temperature range considered here the much less costly JWKB calculations have produced estimates of the second virial coefficient that are likely to be just as accurate as the quantal estimates. It is amazing that the relatively simple JWKB expressions account so well for the quantum corrections considering that bound states and resonances contribute quite significantly to the quantum results.

As the Ar potentials become even better and more accurate experimental data become available, it may be worthwhile to refine the quantal calculations in order to sort out the discrepancies we have found between the quantal and JWKB results.

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