Second Virial Coefficients of Helium from the Exp-Six Potential*

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A set of potential constants for the He-He exp-six intermolecular potential has been found which leads to calculated results in good agreement with the experimental second virial coefficients of He^4 both at high and at low temperatures and with the high-temperature viscosity and thermal conductivity data. A table of the second virial coefficients of He^3 and He^4 over the temperature range 0.3°K to 60°K is given. The position of a negative discrete energy as a function of some of the parameters of the exp-six potential has been investigated.

I. INTRODUCTION

RECENTLY we have published[1] the results of our calaulation of the second virial coefficients of He^3 and He^4 with a Lennard-Jones 12–6 intermolecular potential. For two reasons it has seemed desirable to repeat these calculations with a different type potential: (1) Mason,[2] Rice and Hirschfelder,[3] and Mason and Rice[4] have shown that the Lennard-Jones 12–6 potential is not capable of giving as good a representation of the high temperature equation of state and transport data for He^4 as is the exp-six potential (variously known as the Slater-Kirkwood, the modified Buckingham, the Mason-Rice, and the exp-six potential); (2) in the light of the work done recently by Keller[5] on the second virial coefficients of He^4 at low temperatures, it now appears that the true experimental values are distinctly more negative than is indicated by the results of earlier authors. In addition, these new data and re-analyzed older data lead to values of B that are considerably more consistent and are probably more accurate than the second virial coefficients previously published. We first calculated the second virial coefficients of He^4, using the exp-six potential with the constants given by Mason and Rice.[4] Since the calculated B's from this potential were not in good agreement with the low-temperature experimental data, the potential constants were modified in such a way as to preserve the agreement with the high-temperature data and also to give a good fit to the low-temperature second virial coefficients.

II. METHOD

The numerical method used in this work closely parallels that used in reference 1. The following modifications were made:

(1) The radial scaling factor was arbitrarily set at $\rho = 2.77$A in order that the exp-six potential should have a zero at about the same location as that of the 12–6 potential used in reference 1.

(2) The integration pattern was $R = 0.625$ (1/128) 1.5 (1/64) 16, rather than 0.625 (1/128) 1.5 (1/64) 4 (1/32) 8 as used in reference 1. This change resulted in somewhat higher accuracy in the phase shifts for the higher energies.

(3) The pattern of the reduced energy or wave-number parameter q was $q=0$ $(\frac{1}{8})$ 10.5 $(\frac{1}{2})$ 18. The wider spacing was shown to result in no appreciable loss in accuracy in the calculated virials, and the increased range eliminated the necessity for a tail-end correction on the integral for the virials at 50°–60°K.

(4) The junctions of the numerically integrated phase shifts to the Born approximation phase shifts were made uniformly according to the formula $l^* = [aq]$, where $a=3$ for He^4 and $a=4$ for He^3, the square brackets indicate the largest even integer contained in aq, and l^* is the last even l (and l^*+1 the last odd l) for which phase shifts were calculated numerically.

The natural constants used in this work are as follows:

Boltzmann's constant:	$k = 1.380257\times10^{-16}$,
Planck's constant:	$h = 6.62377\times10^{-27}$,
Avogadro's number:	$N_0 = 6.02380\times10^{23}$,
Atomic weight He^4:	4.00390,
Atomic weight He^3:	3.01700.

III. POTENTIALS

The several exp-six potentials used in this work will be designated by $MR1$, $MR2$, etc., and the Lennard-Jones 12–6 potentials used in reference 1 similarly by $LJ1$, $LJ2$, and $LJ2'$. The exp-six potential was taken in the standard form

$$V(r) = \frac{\epsilon}{1-6/\alpha}\left[\frac{6}{\alpha}e^{\alpha(1-r/r_m)} - \left(\frac{r_m}{r}\right)^6\right]. \qquad (1)$$

The constant ϵ (given in this work as ϵ/k °K) is the depth of the potential minimum, r_m is the value of r at the minimum, and α determines the hardness of the repulsive core.

It is immaterial that this potential has a maximum at $r \ll r_m$ and then approaches minus infinity as r goes

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[1] Kilpatrick, Keller, Hammel, and Metropolis, Phys. Rev. **94**, 1103 (1954).
[2] E. A. Mason, J. Chem. Phys. **22**, 169 (1954).
[3] W. E. Rice and J. O. Hirschfelder, J. Chem. Phys. **22**, 187 (1954).
[4] E. A. Mason and W. E. Rice, J. Chem. Phys. **22**, 522 (1954).
[5] W. E. Keller, preceding paper [Phys. Rev. **97**, 1 (1955)].

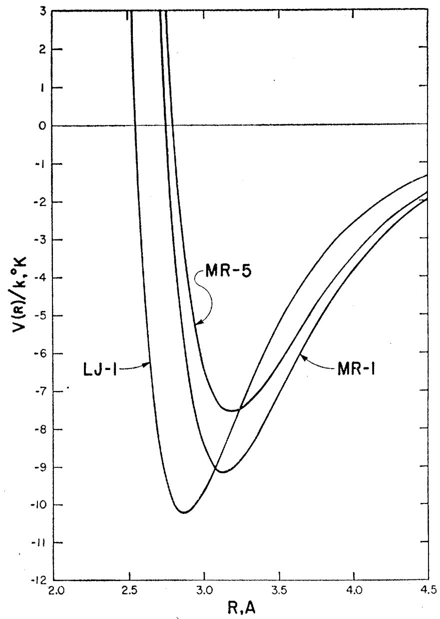

FIG. 1. Potential of interaction of two He atoms.

to zero. The phase shifts are not appreciably affected by the portion of the potential near the origin in the range of potential constants used.

In Table I the potential constants for the various exp-six potentials used in this work are listed, together with the constants of some Lennard-Jones 12–6 potentials and the original theoretical Slater-Kirkwood[6] potential. Figure 1 shows graphically the relation of potentials $LJ1$, $MR1$, and $MR5$.

According to Mason and Rice[4,7] it is necessary that $\alpha=12.4$ in order to preserve the fit to the high-temperature data. In all of the exp-six potentials used in this work this value of α has been used. On the other hand, the values of r_m and ϵ/k are not determined uniquely by the high-temperature data. Mason[7] has very kindly calculated for us several ϵ/k, r_m pairs which result in just as satisfactory a fit to the high-temperature

TABLE I. Potential constants of various exp-six and 12–6 potentials.

	α	ϵ/k, °K	r_m, A
$MR1$	12.4	9.16	3.135
$MR2$	12.4	8.76	3.138
$MR3$	12.4	7.85	3.150
$MR4$	12.4	7.682	3.185
$MR5$	12.4	7.5628	3.1894
$LJ1$		10.22	2.86911
$LJ2$		10.3364	2.86911
$LJ2'$		10.22	2.88541
Slater-Kirkwood	13.54	9.25	2.943

[6] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).
[7] E. A. Mason and W. E. Rice (private communication).

data as does the original set of Mason-Rice[4] constants. These alternative constants satisfy the linear log-log relation,

$$-10.86957 \log r_m + 6.35368 = \log(\epsilon/k). \quad (2)$$

Since the very low-temperature second virial coefficients depend in a different way upon the relative values of r_m and ϵ/k than do the high-temperature virials, it was possible to adjust the low-temperature fit independently of the high-temperature fit.

The original Mason-Rice constants ($MR1$) lead to second virial coefficients for He^4 distinctly too negative in the 2°–4°K temperature range. Mason thereupon suggested the constants of $MR2$, which lead to results still too negative. $MR3$ was estimated by extrapolation from $MR1$ and $MR2$ and is about right but is not quite consistent with Eq. (2) (which was unknown to us at the time). $MR4$ gives nearly the same second virial coefficients as $MR3$ but is consistent with Eq. (2). $MR5$ is our final best potential. All of the figures given for the constants of $MR5$ in Table I are not significant in the sense of being required to fit the experimental data but are given as they were actually used in the calculation of the phase shifts.

In reference 1 an extensive table of the second virial coefficients of helium using $LJ1$, the original de Boer-Michels potential, is given, along with a brief table showing the effect of small variations in these constants ($LJ2$ and $LJ2'$). These data could readily be extrapolated to find a set of Lennard-Jones constants ($LJ3$) yielding results in agreement with the experimental virial data quoted in this paper. The parameter p^2 would be about 22.55. It is quite possible that the true He-He interaction potential is quite different from $MR5$. The evidence for this conclusion is that $LJ3$ and $MR5$, giving essentially the same virial coefficients, differ considerably in form.

IV. RESULTS

A. Second Virial Coefficients

Figure 2 shows some of the phase shifts for He^4 obtained from $MR1$ and $MR5$. The phase shifts for $MR1$ are always more positive than those for $MR5$; however, only when $l=0$ and q is small is this difference large. A system composed of two He^4 atoms interacting according to the $MR5$ potential has no discrete negative energy level; consequently the phase shift is zero at $q=0$. Since this potential very nearly has a discrete level, the phase shifts for $l=0$ increase rapidly to a maximum. The $MR1$ potential, on the other hand, has a discrete level, and phase shifts for $l=0$ start at π and decrease rapidly. The phase shifts for $LJ1$ [shown in reference (1)] are very slightly more negative than those for $MR5$.

The second virial coefficients of He^4 and He^3 (B_{44} and B_{33}) as calculated from potential $MR5$ are given in

TABLE II. Second virial coefficients of He^4 and He^3.

T°K	B_{44} cc/mole	B_{33} cc/mole	T°K	B_{44} cc/mole	B_{33} cc/mole	T°K	B_{44} cc/mole	B_{33} cc/mole
0.3	−2709.0	−490.2	3.5	−96.46	−73.22	10.5	−18.36	−12.78
0.4	−1711.4	−439.7	3.6	−93.18	−70.81	11.0	−16.60	−11.34
0.5	−1206.9	−395.0	3.7	−90.09	−68.52	11.5	−15.00	−10.03
0.6	− 914.1	−356.8	3.8	−87.15	−66.34	12.0	−13.53	− 8.83
0.7	− 727.7	−342.2	3.9	−84.37	−64.26	12.5	−12.18	− 7.72
0.8	− 600.9	−296.3	4.0	−81.73	−62.29	13.0	−10.94	− 6.70
0.9	− 510.1	−272.1	4.1	−79.22	−60.40	13.5	− 9.79	− 5.75
1.0	− 442.4	−251.14	4.2	−76.83	−58.60	14.0	− 8.73	− 4.87
1.1	− 390.2	−232.76	4.3	−74.56	−56.88	14.5	− 7.74	− 4.06
1.2	− 348.9	−216.57	4.4	−72.38	−55.23	15.0	− 6.82	− 3.29
1.3	− 315.3	−202.21	4.6	−68.33	−52.14	15.5	− 5.96	− 2.58
1.4	− 287.62	−189.41	4.8	−64.61	−49.30	16.0	− 5.16	− 1.91
1.5	− 264.33	−177.93	5.0	−61.19	−46.67	17.0	− 3.70	− 0.69
1.6	− 244.48	−167.60	5.2	−58.03	−44.24	18.0	− 2.41	0.39
1.7	− 227.34	−158.25	5.4	−55.11	−41.98	19.0	− 1.26	1.35
1.8	− 212.39	−149.75	5.6	−52.40	−39.87	20.0	0.25	2.21
1.9	− 199.23	−142.01	5.8	−49.88	−37.91	21.0	0.70	2.99
2.0	− 187.54	−134.92	6.0	−47.53	−36.06	22.0	1.53	3.69
2.1	− 177.08	−128.42	6.2	−45.33	−34.34	23.0	2.29	4.33
2.2	− 167.66	−122.42	6.4	−43.26	−32.72	24.0	2.98	4.92
2.3	− 159.14	−116.89	6.6	−41.33	−31.19	25.0	3.62	5.45
2.4	− 151.38	−111.76	6.8	−39.50	−29.75	26.0	4.20	5.94
2.5	− 144.28	−107.00	7.0	−37.78	−28.39	27.0	4.73	6.39
2.6	− 137.76	−102.56	7.2	−36.16	−27.10	28.0	5.22	6.80
2.7	− 131.75	− 98.42	7.4	−34.63	−25.88	29.0	5.67	7.19
2.8	− 126.20	− 94.56	7.6	−33.17	−24.72	30.0	6.09	7.54
2.9	− 121.04	− 90.93	7.8	−31.79	−23.62	35.0	7.80	8.98
3.0	− 116.24	− 87.53	8.0	−30.49	−22.57	40.0	9.02	10.02
3.1	− 111.76	− 84.33	8.5	−27.48	−20.16	45.0	9.92	10.79
3.2	− 107.57	− 81.31	9.0	−24.82	−18.02	50.0	10.61	11.37
3.3	− 103.64	− 78.46	9.5	−22.44	−16.09	55.0	11.13	11.81
3.4	− 99.94	− 75.77	10.0	−20.29	−14.35	60.0	11.53	12.16

Table II. The cross second virial coefficient, B_{34}, is probably very nearly as given in reference (1) and was not recalculated. In Fig. 3, these calculated results are shown together with the experimental data (from reference 5). For comparison, a portion of the calculated results from $MR1$ and from $LJ1$ are also shown. Although $MR5$ gives better agreement with the experimental data in the very low and the high temperature region, $LJ1$ (reference 1) is somewhat superior in the middle temperature region.

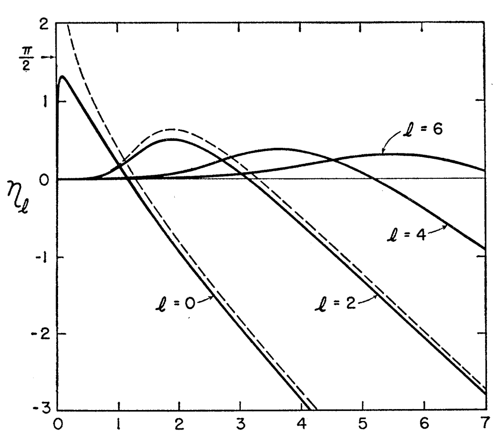

FIG. 2. Phase shifts for He^4; $MR1$ dashed curves, $MR5$ solid curves.

B. Discrete Levels

It was immediately apparent from the behavior of the low energy phase shifts for $MR1$ (He^4) that this system has a low-lying negative discrete energy level. We first determined the exact position of this level and then proceeded to a general investigation of such levels for the exp-six potential. A similar investigation has

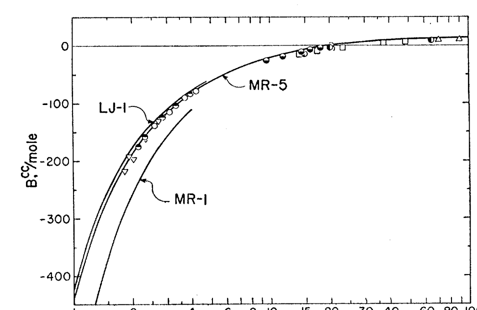

FIG. 3. Second virial coefficient of He^4 *vs* temperature. Experimental points: ◒ W. H. Keesom and W. K. Walstra, Physica **13**, 225 (1947); △ G. P. Nijoff and W. H. Keesom, Leiden Comm. 188b (1927); □ Nijoff, Keesom, and Iliin, Leiden Comm. 188c (1927); ◐ L. Holborn and J. Otto, Z. Physik. **38**, 359 (1926); ▽ J. Kistemaker and W. H. Keesom, Physica **12**, 227 (1946); revised by W. E. Keller, preceding paper [Phys. Rev. **97**, 1 (1955)]; ○ W. H. Keesom and W. K. Walstra, Physica **7**, 985 (1940); revised by W. E. Keller, preceding paper; ◓ W. E. Keller, preceding paper.

already been carried out for the Lennard-Jones 12–6 potential.[8]

A very simple technique was used. With the aid of the numerical integration system already on hand, very little time was required to integrate directly the wave equation out to a large value of R and to adjust the initial estimate of the negative eigenvalue on the basis of the behavior of the wave function. This process was continued until the eigenvalue was determined with sufficient accuracy.

TABLE III. Discrete levels for He^4, exp-six potential, $\alpha=12.4$.

ϵ/k, °K	$r_m(\epsilon/k)^{\frac{1}{2}}$	q^-	E^-/k, °K
	$r_m=3.0$A		
8.639887	8.818105	0.000000	0.000000
8.8	8.899437	0.0166	−0.00044
9.0	9.000000	0.04102	−0.00266
9.2	9.099450	0.06354	−0.00637
9.4	9.197826	0.086029	−0.011684
9.6	9.295161	0.108398	−0.018551
10.0	9.486834	0.152777	−0.036850
	$r_m=3.2$A		
7.593743	8.818159	0.000000	0.000000
7.7	8.879638	0.0132	−0.00027
7.8	8.937114	0.02539	−0.00102
7.9	8.994221	0.03662	−0.00212
8.0	9.050966	0.04932	−0.00384
8.4	9.274480	0.097142	−0.014898
8.8	9.492733	0.144500	−0.032965
	$r_m=3.4$A		
6.726675	8.818184	0.000000	0.000000
7.0	8.995553	0.03467	−0.00190
7.2	9.123159	0.06079	−0.00583
7.6	9.373154	0.111517	−0.019634

[8] J. E. Kilpatrick and M. F. Kilpatrick, J. Chem. Phys. 19, 930 (1951).

It is convenient to give our results in terms of the reduced parameter q^-,

$$q^-=[-(2\mu/\hbar^2)\rho^2E^-]^{\frac{1}{2}}, \tag{3}$$

where μ is the reduced He^4 mass, $\rho=2.77$A, and E^- is the negative energy level. All of the following results are for a pair of He^4 atoms, since the physically realistic range of potential constants cannot result in a discrete level for He^3.

The potential $MR1$ has a discrete level at $q^-=0.146498$ or $E^-/k=-0.033883°$; $MR2$ at $q^-=0.101961$ or $E^-/k=-0.016413°$; and $MR4$ at $q^-=0.0020$ or $E^-/k=-0.000006°$. $MR3$ and $MR5$ have no discrete level.

It is of some interest to note that, since $LJ3$ (very nearly the equivalent of $MR5$ in terms of the very low-temperature second virial coefficient) definitely has a low-lying discrete level, the question of whether He^4 really has a discrete level is still open.

Table III shows the location of the discrete level for a number of r_m, ϵ/k pairs, always with $\alpha=12.4$. In the study of discrete levels for the Lennard-Jones potential,[8] it was found that q^- was very nearly linear in $r_m(\epsilon/k)^{\frac{1}{2}}$. This same relationship is valid for the exp-six potential. The value of $r_m(\epsilon/k)^{\frac{1}{2}}$ for $q^-=0$ is very nearly constant; the three curves ($r_m=3.0$, 3.2, and 3.4A) of q^- *vs* $r_m(\epsilon/k)^{\frac{1}{2}}$ are essentially straight and have almost the same slopes.