Second Virial Coefficients of Gases Obeying a Modified Buckingham

(Exp - Six) Potential*

by

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ABSTRACT

The second virial coefficient has been calculated for gases obeying a modified Buckingham potential, (Exp-Six),

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

The results are tabulated over the temperature range kT/ϵ from 0.40 to 400., and for seven values of the parameter α , from 12. to 15. The treatment was entirely classical, and no corrections for quantum effects were made.

A separate paper will present the evaluation of the parameters for specific substances and applications of the results, together with applications of the calculated transport properties given in the preceeding paper.

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L INTRODUCTION

The equation of state of any gas may be written in virial form,

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \cdots \quad , \tag{1}$$

where $B(T)$ is called the second virial coefficient. According to classical statistical mechanics, the second virial coefficient for molecules with central forces is directly related to the energy of interaction between pairs of molecules, $\varphi(r)$, by the integral

$$B(T) = -\frac{2\pi N}{3kT} \int_0^\infty r^3 \frac{d\varphi(r)}{dr} e^{-\varphi(r)/kT} \, dr . \tag{2}$$

Up to the present time, the second virial coefficient has been evaluated[1] for Lennard-Jones type potentials, and, in a few special cases, for potentials containing an exponential repulsion term. The Buckingham potential is more reasonable from a theoretical standpoint than is a potential having an inverse-power repulsion, and is more flexible since it contains three parameters instead of two. Therefore, we have compiled a complete table of the second virial coefficient using the Buckingham potential.

We have taken the Buckingham potential in the following modified form (which we shall henceforth refer to as "Exp-Six") :

$$\varphi(r) = \frac{\epsilon}{1-6/\alpha} \left[\frac{6}{\alpha} e^{\alpha(1-r/r_m)} - \left(\frac{r_m}{r}\right)^6 \right], \; r \geq r_{max} . \tag{3}$$

$$\varphi(r) = \infty, \qquad r < r_{max} . \tag{4}$$

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[1] An extensive table of second virial coefficients for the Lennard-Jones (12 - 6) potential is given by R. B. Bird and E. L. Spotz, University of Wisconsin CM - 599 (1950).

The constants ϵ, r_m, and α characterize the molecular interaction. Here ϵ is the maximum energy of attraction; r_m is the separation at the energy minimum; and α is a measure of the steepness of the repulsive potential. Fig. 1 shows the behavior of $\varphi(r)$. The position of zero potential is σ; its value as a function of α is given in Table 2. The function defined in Eq. (3) would pass through a maximum at r_{max} and then approach $-\infty$ as $r \to 0$. The location and height of the maximum for each α is given in Table 2.

Table 2

Reduced separation σ^* at which the Buckingham potential is zero, location (r_{max}^*) and the height of the maximum, and separation λ taken as the lower limit of the numerical integration.

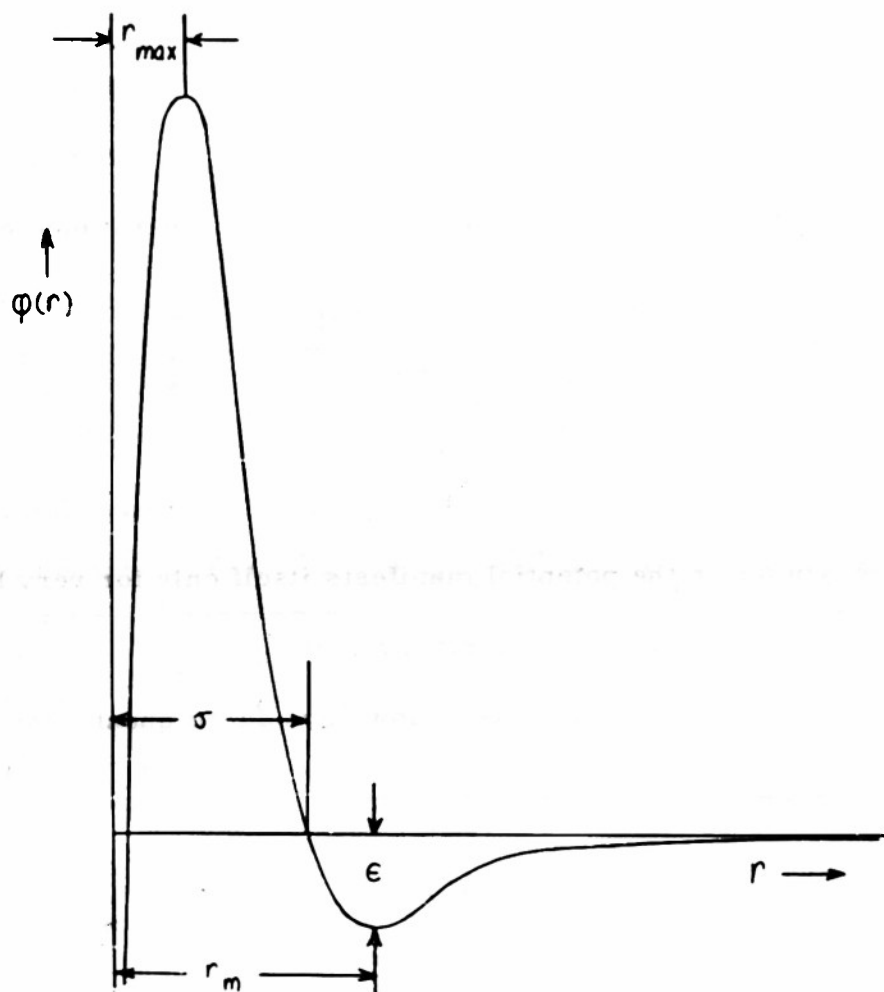| α	σ^*	r_{max}^*	$\varphi^*(r_{max}^*)$	λ
12.0	0.8761 0051	0.3024 7469	1705.4129	.
12.5	0.8798 2937	0.2730 3685	3518.3635	.
13.0	0.8831 9813	0.2469 7188	7110.0863	0.2784
13.5	0.8862 7341	0.2238 1785	1 4114.558	0.3186
14.0	0.8891 0396	0.2031 8787	2 7585.192	0.3442
14.5	0.8917 2672	0.1847 5586	5 3170.123	0.3620
15.0	0.8941 7037	0.1682 4550	10 1221.60	0.3844

Fig 1. The Buckingham potential,

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

as a function of intermolecular separation. The magnitude of $\varphi\,(r_{max})$ relative to ϵ is much reduced in the figure.

Fortunately the height of the maximum is so large for all practical cases that very little error is produced by the anomalous behavior of our modified Buckingham potential in the neighborhood of r_{max}. The original Buckingham potential corresponds to the use of Eq. (3) for all separations. Instead of our modification (Eq. 4) to avoid the anomalous behavior for small separations, Buckingham and Corner[2] use Eq. (3) for separations larger than r_m, hat is $r_m \leq r \leq \infty$ and the following expression for separations less than r_m:

$$\varphi(r) = \frac{\epsilon}{1-6/\alpha}\left[\frac{6}{\alpha} e^{\alpha(1-r/r_m)} - \left(\frac{r_m}{r}\right)^6 e^{-4\left(\frac{r_m}{r}-1\right)^3}\right] . \tag{5}$$

This relation makes the potential unduly complicated. We have found that the effect of the maximum in the potential manifests itself only for very high temperatures and for small values of the parameter α.

It is convenient to introduce the following reduced quantities:

$$r^* = r/r_m . \tag{6}$$

$$\varphi^*(r^*) = \frac{\varphi(r)}{\epsilon} = \frac{1}{1-6/\alpha}\left[\frac{6}{\alpha} e^{\alpha(1-r^*)} - \frac{1}{r^{*6}}\right], r^*_{max} \leq r^* \leq \infty . \tag{7}$$

$$\varphi^*(r^*) = \infty, \quad 0 \leq r^* < r_{max} . \tag{8}$$

$$T^* = kT/\epsilon . \tag{9}$$

$$B^*(\alpha,T^*) = B(T)/b_0 , \quad b_0 = \frac{2}{3}\pi N r_m^3 . \tag{10}$$

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[2] R. A. Buckingham and J. Corner, Proc. Roy. Soc. A189, 118 (1947). According to private correspondence Buckingham and Corner were primarily concerned with interpreting high energy molecular beam scattering which is sensitive to the potential energy for small separations.

In terms of (Exp-Six) potential, values of $B*(\alpha, T*)$ are given in Table 1 for the range $0.40 \leq T* \leq 400.$ and $12.0 \leq \alpha \leq 15.0$.

II. GENERAL FORMULAS

The integral for the second virial coefficient in reduced form is

$$B^*(\alpha, T^*) = - \frac{1}{T^*} \int_0^\infty r^{*3} \frac{d\varphi^*(r^*)}{dr^*} e^{-\varphi^*(r^*)/T^*} dr^* .$$
(11)

Following the procedure of Buckingham and Corner[2] , we have divided the range of integration into two regions of $r*$ separated by the arbitrarily chosen value of the separation, $M(\alpha)$;

$$B^*(\alpha, T^*) = - \frac{1}{T^*} \int_0^{M(\alpha)} r^{*3} \frac{d\varphi^*(r^*)}{dr^*} e^{-\varphi^*(r^*)/T^*} dr^*$$

$$- \frac{1}{T^*} \int_{M(\alpha)}^\infty r^{*3} \frac{d\varphi^*(r^*)}{dr^*} e^{-\varphi^*(r^*)/T^*} dr^* .$$
(12)

Since $M(\alpha)$ is taken to be almost equal to $\sigma(\alpha)$, the two regions of integration correspond roughly to a separation between the large separation where the energy of attraction is dominan⁺ from the small separations where the energy of repulsion prevails. Different sorts of mathematical techniques are used to evaluate the integrals in the two regions. We shall employ the symbol $K(\alpha, T*)$ for the integral from zero to $M(\alpha)$ in Eq. (12) , and $\Gamma(\alpha, T*)$ for the integral from $M(\alpha)$ to ∞ . Then,

$$B^*(\alpha, T^*) = - K(\alpha, T^*) + \Gamma(\alpha, T^*) .$$
(13)

Table 1

The Second Virial Coefficients for the Modified Buckingham Potential

$$B(T) = b_0 B^*(\alpha, T^*)$$

$$T^* = kT/\epsilon$$

$$b_0 = \frac{2}{3}\pi N_0 r_m^3$$

α / T^*	12.0	12.5	13.0	13.5	14.0	14.5	15.0
0.40	-10.347	-10.052	-9.787	-9.548	-9.332	-9.134	-8.953
0.45	-8.060	-7.826	-7.616	-7.427	-7.256	-7.099	-6.956
0.50	-6.536	-6.342	-6.168	-6.012	-5.871	-5.741	-5.623
0.55	-5.455	-5.290	-5.141	-5.008	-4.887	-4.777	-4.676
0.60	-4.653	-4.508	-4.373	-4.262	-4.157	-4.061	-3.973
0.65	-4.035	-3.906	-3.791	-3.688	-3.595	-3.509	-3.431
0.70	-3.546	-3.430	-3.326	-3.233	-3.149	-3.072	-3.002
0.75	-3.149	-3.043	-2.949	-2.864	-2.788	-2.718	-2.654
0.80	-2.822	-2.725	-2.638	-2.560	-2.490	-2.425	-2.366
0.85	-2.547	-2.457	-2.377	-2.304	-2.239	-2.179	-2.125
0.90	-2.313	-2.229	-2.154	-2.087	-2.026	-1.970	-1.919
0.95	-2.111	-2.033	-1.963	-1.899	-1.842	-1.790	-1.742
1.00	-1.9362	-1.8623	-1.7960	-1.7363	-1.6823	-1.6330	-1.5877
1.05	-1.7827	-1.7127	-1.6499	-1.5934	-1.5422	-1.4955	-1.4526
1.10	-1.6470	-1.5805	-1.5208	-1.4671	-1.4184	-1.3740	-1.3332
1.15	-1.5263	-1.4628	-1.4059	-1.3546	-1.3082	-1.2658	-1.2269
1.20	-1.4181	-1.3574	-1.3029	-1.2539	-1.2095	-1.1689	-1.1316
1.25	-1.3208	-1.2625	-1.2103	-1.1632	-1.1206	-1.0816	-1.0455
1.30	-1.2327	-1.1767	-1.1264	-1.0812	-1.0401	-1.0027	-0.9682
1.35	-1.1526	-1.0986	-1.0502	-1.0066	-0.9670	-0.9309	-0.8976
1.40	-1.0795	-1.0274	-0.9806	-0.9385	-0.9002	-0.8653	-0.8332
1.45	-1.0125	-0.9621	-0.9168	-0.8761	-0.8391	-0.8052	-0.7742
1.50	-0.9509	-0.9020	-0.8582	-0.8187	-0.7828	-0.7500	-0.7199
1.55	-0.8941	-0.8467	-0.8041	-0.7657	-0.7309	-0.6990	-0.6698
1.60	-0.8416	-0.7954	-0.7541	-0.7168	-0.6829	-0.6519	-0.6234
1.65	-0.7928	-0.7479	-0.7076	-0.6713	-0.6363	-0.6062	-0.5804

Table 1 (Continued)

x							
1.70	-0.7475	-0.7037	-0.6645	-0.6291	-0.5969	-0.5675	-0.5404
1.75	-0.7052	-0.6625	-0.6242	-0.5897	-0.5583	-0.5296	-0.5031
1.80	-0.6657	-0.6240	-0.5866	-0.5529	-0.5222	-0.4941	-0.4683
1.85	-0.6287	-0.5880	-0.5514	-0.5184	-0.4884	-0.4609	-0.4357
1.90	-0.5940	-0.5542	-0.5184	-0.4861	-0.4567	-0.4298	-0.4050
1.95	-0.5614	-0.5224	-0.4873	-0.4557	-0.4269	-0.4005	-0.3763
2.0	-0.5307	-0.4924	-0.4581	-0.4271	-0.3988	-0.3730	-0.3492
2.1	-0.4744	-0.4376	-0.4045	-0.3746	-0.3474	-0.3224	-0.2995
2.2	-0.4241	-0.3885	-0.3565	-0.3276	-0.3013	-0.2772	-0.2550
2.3	-0.3788	-0.3443	-0.3134	-0.2854	-0.2600	-0.2366	-0.2151
2.4	-0.3379	-0.3045	-0.2744	-0.2473	-0.2225	-0.1999	-0.1789
2.5	-0.3007	-0.2683	-0.2391	-0.2127	-0.1886	-0.1665	-0.1461
2.6	-0.2669	-0.2353	-0.2068	-0.1811	-0.1577	-0.1361	-0.1163
2.7	-0.2359	-0.2051	-0.1774	-0.1523	-0.1294	-0.1083	-0.0889
2.8	-0.2075	-0.1774	-0.1503	-0.1258	-0.1034	-0.0828	-0.0638
2.9	-0.1813	-0.1519	-0.1254	-0.1014	-0.0795	-0.0593	-0.0407
3.0	-0.1572	-0.1283	-0.1024	-0.0789	-0.0574	-0.0377	-0.0194
3.1	-0.1348	-0.1066	-0.0811	-0.0580	-0.0370	-0.0176	-0.0003
3.2	-0.1141	-0.0863	-0.0614	-0.0387	-0.0180	0.0010	0.0186
3.3	-0.0948	-0.0675	-0.0430	-0.0207	-0.0004	0.0184	0.0357
3.4	-0.0768	-0.0500	-0.0258	-0.0039	0.0161	0.0345	0.0516
3.5	-0.0600	-0.0336	-0.0098	0.0117	0.0314	0.0496	0.0664
3.6	-0.0442	-0.0183	0.0051	0.0264	0.0458	0.0637	0.0803
3.7	-0.0295	-0.0039	0.0192	0.0401	0.0593	0.0770	0.0933
3.8	-0.0156	0.0096	0.0324	0.0530	0.0719	0.0894	0.1055
3.9	-0.0026	0.0223	0.0448	0.0652	0.0838	0.1011	0.1170
4.0	0.0097	0.0343	0.0564	0.0766	0.0951	0.1121	0.1279
4.1	0.0212	0.0455	0.0674	0.0874	0.1056	0.1225	0.1381
4.2	0.0322	0.0562	0.0779	0.0976	0.1156	0.1323	0.1477
4.3	0.0425	0.0663	0.0877	0.1072	0.1250	0.1415	0.1568
4.4	0.0523	0.0758	0.0970	0.1163	0.1340	0.1503	0.1655
4.5	0.0616	0.0848	0.1058	0.1249	0.1425	0.1586	0.1736
4.6	0.0704	0.0934	0.1142	0.1331	0.1505	0.1665	0.1814
4.7	0.0787	0.1016	0.1222	0.1409	0.1581	0.1740	0.1888
4.8	0.0867	0.1093	0.1297	0.1483	0.1654	0.1811	0.1958
4.9	0.0943	0.1167	0.1369	0.1554	0.1723	0.1879	0.2025
5.	0.1015	0.1237	0.1438	0.1621	0.1789	0.1944	0.2088
6.	0.1581	0.1788	0.1976	0.2147	0.2305	0.2451	0.2586
7.	0.1955	0.2152	0.2331	0.2495	0.2645	0.2785	0.2916
8.	0.2215	0.2406	0.2578	0.2736	0.2882	0.3017	0.3144
9.	0.2403	0.2587	0.2755	0.2909	0.3051	0.3183	0.3307

Table 1 (Continued)

10.	0.2540	0.2721	0.2885	0.3036	0.3175	0.3305	0.3427
20.	0.2937	0.3102	0.3252	0.3392	0.3522	0.3643	0.3758
30.	0.2904	0.3065	0.3213	0.3350	0.3478	0.3598	0.3712
40.	0.2811	0.2971	0.3118	0.3254	0.3381	0.3502	0.3616
50.	0.2712	0.2872	0.3018	0.3154	0.3282	0.3402	0.3517
60.	0.2619	0.2778	0.2924	0.3060	0.3188	0.3308	0.3423
70.	0.2534	0.2692	0.2838	0.2974	0.3101	0.3222	0.3337
80.	0.2456	0.2614	0.2759	0.2895	0.3023	0.3144	0.3259
90.	0.2385	0.2543	0.2688	0.2824	0.2951	0.3073	0.3188
100.	0.2320	0.2477	0.2623	0.2758	0.2886	0.3007	0.3123
200.	0.1877	0.2034	0.2177	0.2312	0.2438	0.2560	0.2676
300.	0.1624	0.1780	0.1921	0.2053	0.2178	0.2298	0.2413
400.	0.1444	0.1600	0.1740	0.1870	0.1994	0.2113	0.2228
0.78125	-2.937	-2.837	-2.748	-2.668	-2.595	-2.528	-2.468
1.5625	-0.8806	-0.8335	-0.7912	-0.7531	-0.7185	-0.6869	-0.6578
3.125	-0.1295	-0.1014	-0.0760	-0.0531	-0.0321	-0.0128	-0.0050
6.25	0.1688	0.1893	0.2078	0.2247	0.2403	0.2547	0.2681
12.5	0.2753	0.2927	0.3085	0.3230	0.3365	0.3491	0.3610
25.	0.2935	0.3098	0.3247	0.3385	0.3513	0.3634	0.3748

In the range $M(\alpha) \le r^* \le \infty$, $|\varphi^*(r^*)| \le 1$ and T^* varies from 0.40 to 400., the exponential function, $\exp(-\varphi^*(r^*)/T^*)$, can be expanded in powers of the argument and the series converges rapidly. This expansion is used in evaluating $\Gamma(\alpha, T^*)$ and permits the removal of the reduced temperature from under the integral sign:

$$\Gamma(\alpha, T^*) = -\frac{1}{T^*} \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{1}{T^*}\right)^n J_n(\alpha), \tag{14}$$

where

$$J_n(\alpha) = \int_{M(\alpha)}^{\infty} r^{*3} \frac{d\varphi^*(r^*)}{dr^*} \left[\varphi^*(r^*)\right]^n dr^*. \tag{15}$$

For $12.0 \le \alpha \le 15.0$, the expansion converges sufficiently rapidly for the present purposes when $M(\alpha)$ is the largest integer multiple of 0.005 less than $\sigma^*(\alpha)$. This choice of M is convenient in preliminary hand computations because it avoided interpolation in the numerical tables of the exponential function. The coefficients $J_n(\alpha)$ have alternating signs so that Eq. (14) can be rewritten in the form:

$$\Gamma(\alpha, T^*) = -\sum_{n=0}^{\infty} \frac{|J_n(\alpha)|}{n!} T^{*-n-1} . \tag{16}$$

It is in the range of integration of $K(\alpha, T^*)$ that our modification of the Buckingham potential enters into the calculations. $K(\alpha, T^*)$ may be rewritten as

$$K(\alpha, T^*) = -3 \int_{0}^{M(\alpha)} r^{*2} \left[1 - e^{-\varphi^*(r^*)/T^*}\right] dr^* + M^3 \left[1 - e^{-\varphi^*(M)/T^*}\right] . \tag{17}$$

Setting the potential equal to ∞ for separations smaller than r_{max},

$$K(\alpha, T^*) = -3 \int_0^{r^*_{max}} r^{*2} \, dr^* - 3 \int_{r^*_{max}}^{M(\alpha)} r^{*2} \left[1 - e^{-\varphi^*(r^*)/T^*} \right] dr^*$$

(18)

$$+ M^3 \left[1 - e^{-\varphi^*(M)/T^*} \right].$$

III. NUMERICAL INTEGRATIONS

In evaluating $K(\alpha, T^*)$, it is certainly satisfactory to ignore the quantity $\exp \left[-\varphi^*(r^*)/T^* \right]$ in the integrand for separations smaller than r_1^*, where this exponential function is equal to 4×10^{-7} for $T^* = 400$. For $13.0 \leq \alpha \leq 15.0$, the function actually is this small for certain separations, $r_1^*(\alpha)$. In actual practice, the lower limit of numerical integration of the complete integrand was $\mathcal{H}(\alpha)$, which is a separation smaller than $r_1^*(\alpha)$ such that $(M - \mathcal{H})$ is an integer multiple of 0.0032. This value of $\mathcal{H}$ was chosen so as to facilitate preliminary hand computations. For $\alpha = 12.0$ and 12.5, the complete integrand was used for the entire range between r_{max}^* and M, so that $\mathcal{H}$ and r_{max}^* are the same. The separations $\mathcal{H}$ are given as a function of α in Table 2. Having introduced $\mathcal{H}(\alpha)$, in order to shorten the range of numerical integration, we may write:

$$K(\alpha, T^*) = -\mathcal{H}^3 + M^3 \left[1 - e^{-\varphi^*(M)/T^*} \right] - 3 \int_{\mathcal{H}}^{M} r^{*2} \left[1 - e^{-\varphi^*(r^*)/T^*} \right] dr^*.$$

(19)

The eight-strip Newton-Cotes quadrature formula of the closed type was used to evaluate the integral appearing in $K(\alpha, T^*)$ in the following temperature ranges.

$12.5 \leq T^* \leq 400$. Sixteen integration strips covering the range of separations from $\chi'(\alpha)$ to $M(\alpha)$ were taken for $T^* = 400.$, $200.$, $100.$, $50.$, $25.$, and 12.5. The error arising in the course of this integration was estimated by repeating the integration with strips of half the usual width. The errors for several pairs of values of α and T^* both within and out of this temperature range are shown in Table 3. The error taken to be maximum for the present temperature range is 6×10^{-5}.

Table 3

Error of the sixteen-strip integration of $K(\alpha, T^*)$, the small-separation part of the integral in the second virial coefficient, $B^*(\alpha, T^*)$.

α / T^*	12.0		15.0	
	B^*	error	B^*	error
400.	0.1444	8.7×10^{-7}		
12.5			0.3610	0.000057
6.25	0.1688	0.00013	0.2681	0.00023
3.125	-0.1295	0.00025	0.0050	0.00045
1.5625	-0.8806	0.00029	-0.6578	0.00057
0.78125	-2.937	0.00019	-2.468	0.00050
0.390625		0.000016		0.000022
0.40	-10.347		-8.953	

$1.5625 \leq T^* \leq 8$. Thirty-two strips were taken for $T^* = 8.$, 6.25, $4.$, 3.125, $2.$, and 1.5625. The exponential function in the integrand was neglected through the first 16 strips, with no error resulting except at $T^* = 8.$,

where the maximum error (at $\alpha = 12.0$) was 6×10^{-8} out of a total B*-value of 0.2215 .

$0.80 \leq T* \leq 1.50$ Thirty-two strips were taken for $T* = 0.80$ to 1.50 by steps of 0.10. The exponential in the integrand was neglected in the first 24 strips, with a maximum resulting error, at $T* = 1.50$ and

$\alpha = 12.0$, of 3.5×10^{-5} out of $B* = -0.9509$.

$0.40 \leq T* \leq 0.75$ Sixteen strips were taken for $T* = 0.40$ to 0.75 by steps of 0.05 . The exponential was neglected in the first 14 strips, with a maximum resulting error of 0.00033 for $T*$ slightly above the range (0.78125) and

$\alpha = 12.0$, where $B* = -2.937$.

In the four temperature ranges, the errors in $K(\alpha, T*)$ which are quoted above are maximum values, which are taken to be typical for the respective ranges in estimating the total error in $B*(\alpha, T*)$.

For the range of α mentioned above, and for all n , it was found that no significant error (less than one part in 10^7) is introduced in evaluating the coefficients $J_n(\alpha)$, by neglecting the repulsive part of the potential for separations larger than $\Lambda(\alpha) = M(\alpha) + 2.48$. The integrand formed from the attractive potential alone is then integrated analytically and Eq. (15) becomes:

$$J_n(\alpha) = (-1)^n \frac{\Lambda^{-3-6n}}{n + \frac{1}{2}} + \int_M^\Lambda r^{*3} \frac{d\varphi^*(r^*)}{dr^*}\left[\varphi^*(r^*)\right]^n dr^*.$$

$$(20)$$

The eight-strip Newton-Cotes quadrature formula of the closed type was used to evaluate the integral in $J_n(\alpha)$. Beginning at $M(\alpha)$, 32 strips of width 0.005, then 32 strips of width 0.01, and finally 40 strips of width 0.05 were taken. The greatest error for any set of eight strips was 5.4×10^{-7} in the first eight strips for $\alpha = 12.0$ and $n = 0$, out of a total $J_0(12.0) = 0.9657716$. This error was taken to be typical for $J_0(\alpha)$; the errors for other values of n were too small to be apparent in the eight-digit arithmetic employed in these calculations. The corresponding error in $B*$ is $5.4 \times 10^{-7} T*^{-1}$.

$K(\alpha, T*)$ and $J_n(\alpha)$ having been computed for various arguments, it was necessary only to perform a summation to obtain $B*(\alpha, T*)$, which was to be tabulated. $\Gamma(\alpha, T*)$ was evaluated up to $n = 10$. For $T* = 0.390625$ and $\alpha = 12.0$ the tenth term in Γ was larger than for any other set of parameters, -ing 2.4×10^{-4}. A rough extrapolation indicated the eleventh term to be about 5×10^{-5}. For $T* = 0.78125$ and $\alpha = 12.0$, the tenth term was $1.? \times 10^{-7}$. Thus, the largest errors in $B*$ introduced by cutting off the summation at $n = 10$ are found in the lowest temperature range, where they are an order of magnitude smaller than the errors in $K(\alpha, T*)$. The errors arising from the numerical integration employed in evaluating $J_n(\alpha)$ are likewise smaller than the errors in the K-function, even where the former errors are at their largest.

IV. INTERPOLATIONS

The numerical integrations described above afforded values of B^* (α, T^*) for $T^* = 0.40$ to 0.75 by steps of 0.05, 0.78125, 0.80, to 1.50 by steps of 0.10, 1.5625, $2.$, 3.125, $4.$, 6.25, $8.$, 12.5, $25.$, $50.$, $100.$, $200.$, and 400. For other values of T^*, various interpolation schemes were used to determine B^*, with the aim of producing a more complete table, in which an uncertainty of about one part per thousand was desired.

The values of B^* for $T^* = 300.$ were found by linear interpolation, with $\log_{10} T^*$ being considered the argument of the function B^*. The corresponding error for the Lennard-Jones $(12 - 6)$ potential was 0.067%; a slightly greater computational error would be expected for the present potential, because of the greater curvature of B^* as a function of T^* in this temperature range.

The values of B^* for $T^* = 90.$, $80.$, $70.$, $60.$, $40.$, $30.$, and $20.$ were interpolated by Everett's method, with argument $\log_{10} T^*$. The corresponding error in $B^*(20)$ for the $(12 - 6)$ potential was 0.014% and the largest of the other errors was 0.0056% for $T^* = 70$. The resulting $B^*(20)$ values were averaged with those found by a curve-fitting method described below.

The values of B^* for T^* in the range 1.60 to $20.$ were found by fitting the formula,

$$B^* = \sum_{i=-3}^{3} k_i (T^*)^i \, ,$$

(21)

to several sets of known points in the range $T* = 0.78125$ to $200.$, excluding the evenly-spaced points between 0.80 and 1.50. For $\alpha = 12.0$, the coefficients k_i were computed for several sets of known points, as indicated in Table 4. The interpolated values obtained from various sets of starting points are compared in the table (* indicates that the interpolated point is in an interval adjacent to the middle point of the range of known points; ** indicates the $B*(20)$ computed by Everett's method). The discrepancies for $\alpha = 15.0$ were found to be about the same as those for $\alpha = 12.0$ shown in the table. Following a scrutiny of Table 4, it was decided to use the known set $T* = 3.125$ to $50.$ for interpolating $B*$ for $T* = 7.$ to $20.$ The known set 1.5625 to 12.5 was employed for interpolating in the range 3.2 to 6.0, and the known set 0.78125 to 6.25 for interpolating in the range 1.60 to 3.1. The $B*$-value obtained in this way should be accurate to one in the fourth decimal place.

The values of $B*$ for $T* = 0.85$ to 1.55 by steps of 0.10 were found by curve-fitting the formula,

$$B* = \sum_{i=-2}^{2} k_i(T*)^i , \qquad (22)$$

to the five points in each of the two known ranges: $T* = 0.8$ to 1.2 by steps of 0.1, and $T* = 1.2$, 1.3, 1.4, 1.5, and 1.5625; and interpolating the unknown points within these ranges. When the formula was fitted to all possible five-point ranges including $T* = 0.95$ and 1.25, for the extreme values of α, each of the unknown points was an interior point of four different ranges. The discrepancies among the four calculated values of $B*$ for each of these pairs of values of α and $T*$ were at most 3×10^{-6}.

Table 4

Interpolated Values of the reduced second virial coefficient for $\alpha = 12.0$, obtained by a curve-fit from the values at several sets of known points.

Set T^*	6.25 to 200.	3.125 to 50.	2. to 25.	1.5625 to 12.5	1. to 8.	0.78125 to 6.25	0.390625 to 3.125
20.	0.293578*	0.293594	0.294351	0.286059	(of. 0.29378**)		
10.	0.254128	0.254024*	0.253981	0.254050	0.253128		
7.	0.195410	0.195521*	0.195530*	0.195522	0.195552	0.194388	
5.	0.104235	0.101484	0.101453*	0.101467*	0.101441	0.101659	
3.5		-0.060005	-0.059967	-0.059975*	-0.059968*	-0.059992	
2.5		-0.299797	-0.300806	-0.300738	-0.300763*	-0.300719*	-0.294767
1.75			-0.704730	-0.705212	-0.705178	-0.705204*	-0.705825
1.2			-1.406624	-1.41693	-1.41830	-1.41804	-1.41714*

At higher temperatures, the error of interpolation was less (6×10^{-7} discrepancy between two interpolated values of $B*$ for $T* = 1.45$), whereas for $T* = 0.85$, the low-temperature boundary of the range, the greatest discrepancy among three interpolated values was 1×10^{-4}.

To summarize the computational errors present in the final values of $B*(\alpha, T*)$: For $0.40 \le T* \le 0.75$, the error (which arises in K) is 0.0003; for $0.80 \le T* \le 400.$, the sum of the interpolation errors and the errors in $K(\alpha, T*)$ may be as great as 0.0002; except that, at $T* = 300.$, the larger error of interpolation may raise the total uncertainty to 0.0003.

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