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Second Virial Coefficients from the Gaussian-Six Intermolecular Potential

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A two-parameter Gaussian-Six intermolecular potential function,

$$E(r) = \frac{e^2}{r}\left[1 + \frac{\operatorname{erf}(2^{-1/2}\beta r) - 2\operatorname{erf}(\beta r)}{1 - \exp(-\beta^2 r^2/2)} - \frac{(2/\pi)^{1/2}\beta r - 4\operatorname{erf}(\beta r/2)}{\exp(\beta^2 r^2/2) - 1}\right] - \frac{C'}{r^6}$$

was used to calculate the reduced second virial coefficients of gases for the following parametric values: $T^* = [kT/\beta e^2] = 0.0005(0.0005)0.0125$ and $K = [C'\beta^5/e^2] = 1.00(0.05)2.00(0.20)3.00$. The intermolecular potential parameters, β and C'/e^2, were determined from the experimental data on second virial coefficients for argon, krypton, xenon, nitrogen, carbon dioxide, methane, ethane, propane, and ethylene. Comparison with experimental data indicates that the Gaussian-Six potential function is a slight improvement over the Lennard-Jones (6, 12) potential function in the lower temperature range for nonpolar, spherical molecules.

BECAUSE OF THE uncertainties associated with both the inverse power and the exponential forms of the repulsive potential, consideration of other functional forms is desirable, preferably those having theoretical bases. One such expression for the repulsion potential has been developed from quantum mechanics by Jansen (*12*). Jansen's model is based on the following assumptions and simplifications (*12*): Only single interatomic exchange of electron pairs is taken into account. Effects due to exchange of two or more pairs of electrons between the same two atoms are therefore not considered. Contributions due to coupling of inter- and intraatomic exchange are neglected. The electron charge distribution of an atom has spherical symmetry.

Three atoms are considered, and a summation is made over single-exchange effects between all possible pairs of electrons having parallel spin. This total effect is then replaced by exchange between one effective electron on each atom. The charge distribution for the effective electron is expressed in the Gaussian form

$$\rho(r) = (\beta^3\pi^{-3/2})\exp(-\beta^2 r^2) \qquad (1)$$

in which $\rho(r)$ is the charge density at a distance, r, from the nucleus while β is a parameter.

Based on the model just described, Jansen has developed an expression for the triatomic, first-order, many-body interaction. By considering only the two nearest-neighbor atoms, a and b, and ignoring the effect of the third, distant atom, the expression for a pair interaction is simplified to the form

$$(H_{ab})^0/e^2 = \frac{1}{r} - \frac{1}{1-\Delta_{ab}^2}\left[2G_{au(b)} - 2\Delta_{ab}G_{ab(a)} - A_{abab} + A_{aabb}\right] \qquad (2)$$

where e is the electron charge, or 4.802×10^{-10} statcoulomb. For a Gaussian distribution of electron charge as given by Equation 1, the integrals occurring in Equation 2 for the first-order perturbation Hamiltonian, $(H_{ab})^0$, are listed in Table I as given by Jansen (*12*).

The first-order Hamiltonian is the sum over single-exchange effects between all possible pairs of electrons of two atoms; thus, it can be interpreted as the repulsive energy. Then, the first-order London dispersion force, the inverse sixth-power attraction potential ($-C'r^{-6}$) is superimposed into Jansen's first-order repulsive energy function to constitute the proposed intermolecular potential function. Thus, the Gaussian-Six potential function is given by the form

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Table I. List of Integrals for $(H_{ab})^0$ (*12*)

Integral	Value for Gaussian Distribution[a]
$\Delta_{ab}{}^2$	$\exp(-\beta^2 r^2/2)$
$G_{aa(b)}$	$(2\beta\pi^{-1/2})F(\beta^2 r^2)$
$G_{ab(a)}$	$(2\beta\pi^{-1/2})\ \Delta_{ab}F(\beta^2 r^2/4)$
A_{abab}	$\beta(2/\pi)^{1/2}\ F(\beta^2 r^2/2)$
A_{aabb}	$\beta(2/\pi)^{1/2}\,\Delta_{ab}{}^2$

[a] F denotes integral, $F(x) = (x)^{-1/2}\int_0^{x^{1/2}} \exp(-y^2)dy$.

$$E(r) = \frac{e^2}{r}\left[1 + \frac{\operatorname{erf}(2^{-1/2}\beta r) - 2\operatorname{erf}(\beta r)}{1 - \exp(-\beta^2 r^2/2)} - \frac{(2/\pi)^{1/2}\beta r - 4\operatorname{erf}(\beta r/2)}{\exp(\beta^2 r^2/2) - 1}\right] - \frac{C'}{r^6} \tag{3}$$

A plot of the reduced potential function is shown in Figure 1 for K = 1, 2, and 3, with K representing the attractive parameter and defined as

$$K = C\beta^5,\ C = C'/e^2,\ \text{and}\ R = \beta r \tag{4}$$

The Gaussian-Six description of the intermolecular potential energy is similar to that given by the Buckingham potential, with $E(r)$ approaching negative infinity as r approaches zero and going through a maximum at some small molecular separation, denoted $r_{\max}$. To eliminate this spurious maximum, the intermolecular potential function as given by Equation 3 is approximated following the procedure of Rice and Hirschfelder (*25*) in using the modified Buckingham potential. This modification imposes the limitation

$$E(r) = \infty \text{ for } 0 \le r < r_{\max} \tag{5}$$

while $E(r)$ is given by Equation 3 for $r \ge r_{\max}$. The Gaussian-Six potential function as given by Equation 3 and 5 is used to calculate second virial coefficients, and these calculated values are compared with experimental second virial coefficient data to evaluate the adequacy of this potential.

CALCULATION OF SECOND VIRIAL COEFFICIENT

Substituting the expression given in Equations 3, 4, and 5 for the Gaussian-Six potential into the expression for the reduced second virial coefficient, $B^*(T^*)$, derived from the statistical mechanics (*8*), one obtains

$$B^*(T^*) = \tfrac{1}{3} R_{\max}^3 + \int_{R_{\max}}^{\infty} R^2 \left\{ 1 - \exp\left(-\frac{1}{RT^*}\left[1 + \frac{\operatorname{erf}(2^{-1/2}R) - 2\operatorname{erf}(R)}{1 - \exp(-R^2/2)} - \frac{(2/\pi)^{1/2}R - 4\operatorname{erf}(R/2)}{\exp(R^2/2) - 1}\right] - \frac{K}{R^5}\right)\right\} dR \tag{6}$$

where $B^* = B/(2\pi N/\beta^3)$, $T^* = kT/(\beta e^2)$, $R = \beta r$, and $K = C\beta^5$. $R_{\max}$ denotes the smallest R which is a solution of $dE(R)/dR = 0$. In Equation 6 if one analyzes the ratio

$$(-K/R^5)/\left[1 + \frac{\operatorname{erf}(2^{-1/2}R) - 2\operatorname{erf}(R)}{1 - \exp(-R^2/2)} - \frac{(2/\pi)^{1/2}R - 4\operatorname{erf}(R/2)}{\exp(R^2/2) - 1}\right]$$

one will find that the ratio increases rapidly with increasing R (at R = 10, the ratio is in the order of magnitude of 10^{15}). Hence, beyond $(R_{\max} + 9)$, the repulsive portion of the potential will be eliminated from Equation 6, which will not produce significant error in the results, inasmuch as five significant figures are adequate.

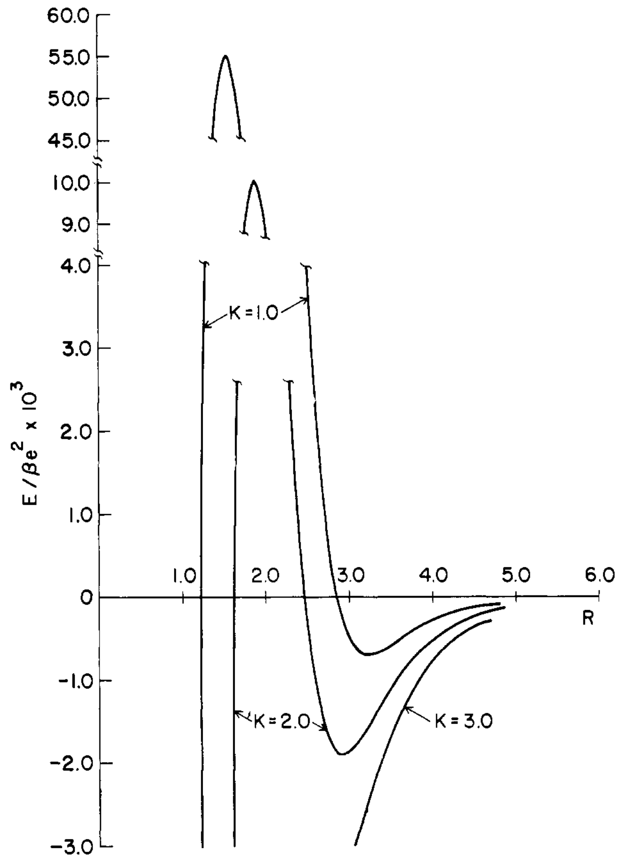

Figure 1. Reduced Gaussian-Six potential functions

The exponential term in the second integral is expanded into a power series and integrated. Following this modification, Equation 6 yields

$$B^*(T^*) = \tfrac{1}{3} R_{\max}^3 + \int_{R_{\max}}^{R_{\max}+9} R^2\left\{1 - \exp\left[\frac{-1}{RT^*}\left(1 + \frac{\operatorname{erf}(2^{-1/2}R) - 2\operatorname{erf}(R)}{1 - \exp(-R^2/2)} - \frac{(2/\pi)^{1/2} - 4\operatorname{erf}(R/2)}{\exp(R^2/2) - 1} - \frac{K}{R^5}\right)\right]\right\}dR - \sum_{j=1}^{\infty}\left(\frac{K}{T^*}\right)^j/[(6j-3)j!(R_{\max}+9)^{6j-3}] \tag{7}$$

A Fortran program for an IBM 7040 digital computer was written to evaluate Equation 7. For the calculation of $B^*(T^*)$ with the desired accuracy of five significant figures, the following procedure was employed in evaluating Equation 7: $R_{\max}$ was computed from Equation 7 using a halving technique which determined the smallest R at which $dE(R)/dR$ was within $\pm 10^{-6}$ of zero. The integral occurring in Equation 7 was evaluated by a Simpson's rule technique using 180 strips of width 0.05 in R. The first four terms of the series in Equation 7 were evaluated, as the series converges so rapidly that the evaluation of the first four terms was sufficient to give the desired accuracy. These results are presented in Table II.

Table II. Second Virial Coefficients from the Gaussian-Six Potential Function

T^*	K = 1.00	1.20	1.30	1.50	1.80	2.0	3.0
0.000500	−29.295128	−45.524610	−56.101237	−84.917383	−163.810422	−267.966528	−17562.086400
0.005000	2.843606	1.885270	1.377616	0.294301	−1.544774	−2.951219	−9.791323
0.010000	3.306520	2.726439	2.420359	1.773910	0.723305	−0.013947	−1.903365

The first value of $B^*(T^*)$ presented in Table II is converted to dimensional form [$B(T)$ in cubic centimeters per mole] to illustrate the procedure of conversion. From Table II,

$$\begin{aligned} T^* &= 0.00050 \\ K &= 1.00 \\ B^* &= -29.295 \end{aligned}$$

A value must be specified for the β parameter, such as $\beta = 0.50A^{-1}$.

Then

$$C = K/\beta^5 = 1.00/(0.50A^{-1})^5 = 32.0A^5$$

and

$$T = \beta e^2 T^*/k$$

$$= \frac{0.50\ A^{-1}(4.803 \times 10^{-10}\ \text{statcoulomb})^2(5 \times 10^{-4})}{1.380 \times 10^{-16}(\text{erg}/^\circ\ \text{K.})(10^8\ A/\text{cm.})}$$

$$= 41.79\ (\text{statcoulomb}^2/\text{cm.})(^\circ\ K./\text{erg})$$

$$= 41.79^\circ\ K.$$

Thus

$$B = B^*(2\pi N/\beta^3)$$

$$= \frac{-29.295(2.0)(3.1416)(6.025 \times 10^{23}\ \text{mole}^{-1})}{(0.50\ A^{-1})^3(\text{cc.}/10^{24}A^3)}$$

$$= -887.2\ \text{cc./mole}$$

DETERMINATION OF POTENTIAL PARAMETERS OF GASES

To assess the adequacy of the Gaussian-Six potential, it is necessary to determine the values of the β and C parameters which reproduce the experimental second virial coefficient data for various gases. The reduced second virial coefficients as presented in Table II were converted to dimensional form by specifying various values for β and evaluating $B(T)$, T, and C. Thus, calculated $B(T)$ *vs.* T results were obtained and plotted for various values of the β and C parameters. The experimental $B(T)$ *vs.* T data for nine gases were plotted and compared with the series of calculated curves to obtain an estimate of the β and C values which give the best fit for each gas. The β and C values were then refined for each gas to minimize the standard deviation between calculated and experimental values of $B(T)$. In this manner, the parameters were determined for nine gases: argon, krypton, xenon, nitrogen, carbon dioxide, methane, ethane, propane, and ethylene. The values for the β and C parameters for these nine gases are shown in Table III with the standard deviation of estimate, number of data points, and the temperature range of data points used in the determination for each gas.

A representative plot of the second virial coefficient *vs.* temperature is presented in Figure 2 for krypton with the experimental data points. Results for the Lennard-Jones (6, 12) potential using the potential parameters determined by Tee, Gotoh, and Stewart (*27*) are also presented for comparison in Table III.

RESULTS AND CONCLUSIONS

The reproducibility of second virial coefficients using the Gaussian-Six potential is satisfactory for gases whose molecules are nonpolar and essentially spherical. The results for argon, krypton, xenon, nitrogen, and methane are in good agreement with experimental values over a wide temperature range as indicated by the deviations (Table III). Results for carbon dioxide are also good except at low temperatures, where sublimation effects are involved. As would be expected, considerable deviation resulted between calculated and experimental values for the higher order hydrocarbons. These larger molecules violate the assumption incorporated in the Gaussian-Six potential of spherical electron charge distribution. The results show that the Gaussian-Six potential appears to accommodate a better fit over a wide range of temperatures than the Lennard-Jones (6, 12) potential in reproducing the second virial coefficients of spherical and nonpolar molecules. The larger standard deviation of estimate for ethane may result from the uncertainty on measured data from Euckens and Parts (*6*).

Table III. Potential Parameters Determined by Second Virial Coefficient Analysis for Gaussian-Six and Lennard-Jones (6–12) Potential Functions (27)

				Gaussian-Six Potential				Lennard-Jones (6–12) Potential			
Gas	Temp. Ranges, ° K.	No. of Data Used	Omitted Data	β, $A.^{-1}$	C, A^5	$K = C\beta^5$	Std. dev., cc./mole	σ, A.	ϵ/k (° K.)	Std. dev., cc./mole	Source of Data
Ar	84.79–873.16	54	. . .	0.77	4.60	1.245	1.35	3.499	118.13	1.98	(*7, 10, 17, 20, 30*)
Kr	107.55–873.16	42	. . .	0.64	14.74	1.583	4.32	3.846	162.74	4.43	(*2, 7, 29, 30*)
Xe	273.16–973.16	32	. . .	0.54	41.2	1.892	0.81	4.100	222.32	0.94	(*1, 19, 30*)
N_2	80.00–673.16	38	. . .	0.75	4.77	1.132	2.32	3.694	96.26	1.50	(*4, 10, 11, 21, 23*)
CO_2	262.66–873.16	41	273° K. (*14*)	0.52	48.5	1.844	2.96	4.416	192.25	3.34	(*3, 14, 18, 24*)
CH_4	125.2 –623.29	33	108° K. (*28*)	0.64	14.1	1.514	3.55	4.010	142.87	3.73	(*5, 26, 28*)
C_2H_6	191.86–523.16	33	. . .	0.40	192.4	1.970	14.26	5.220	194.14	13.39	(*6, 9, 13, 22*)
C_3H_8	295.4 –570.46	29	. . .	0.36	366.0	2.214	8.89	5.711	233.28	8.53	(*9, 15*)
C_2H_4	263.16–473.16	19	. . .	0.50	60.1	1.878	1.34	4.433	202.52	1.88	(*3, 16*)

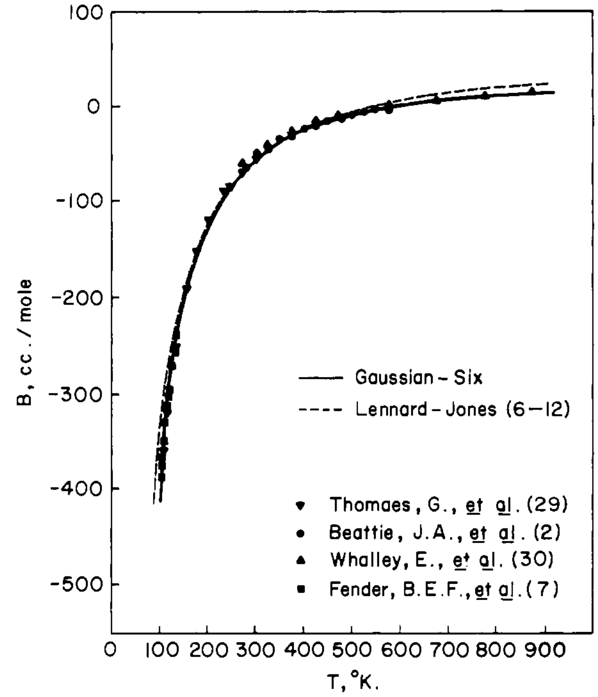

Figure 2. Experimental and calculated values of second virial coefficients as a function of temperature for krypton

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NOMENCLATURE

B = second virial coefficient
B^* = reduced second virial coefficient
C = attractive parameter for Gaussian-Six potential
C' = attractive constant for generalized Lennard-Jones potential
e = charge of an electron, 4.802×10^{-10} statcoulomb
E = intermolecular potential energy of interaction
G_{ab} = integral defined in Table I.
$(H_{ab})^0$ = first order perturbation Hamiltonian
k = Boltzmann constant, $1.380 \times 10^{\times 16}$ erg/° K.
K = reduced parameter for Gaussian-Six potential defined in Equation 14
N = Avogadro's number, 6.0247×10^{23} mole^{-1}
r = intermolecular separation
R = reduced intermolecular separation
T = absolute temperature
T^* = reduced temperature
β = repulsive parameter for Gaussian-Six potential
ϵ = maximum energy of attraction for Lennard-Jones (6, 12) potential
ρ = charge density
σ = intermolecular separation corresponding to zero energy for Lennard-Jones (6, 12) potential

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