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labelled L.-J. in Fig. 1. Equation (15) is equivalent to taking $\epsilon_{12} = \epsilon_{11}^{1/2}\,\epsilon_{22}^{1/2}$.

The success of this result suggests by analogy the Lorentz combination for B_{012} and square-root combination for A_{012}/B_{012} and c_{12}/B_{012} of Eq. (5), since B_0 is analogous to $2\pi N\sigma^3/3$ and A_0/RB_0 to θ. Thus:

$$B_{12} = B_{012}\left[1 - \frac{A_{012}}{B_{012}RT} - \frac{c_{12}}{B_{012}T^3}\right], \quad (16)$$

where Eq. (8A) is used for the B_{012} outside the parenthesis, and equations similar to Eq. (7) for (A_{012}/B_{012}) and (c_{12}/B_{012}). Using in Eq. (16) the values of the equation of state constants given in Table III we find

$$B_{12}\ (\text{liter/mole}) = 0.09906 \\ -68.02/T - 117 \times 10^4/T^3. \quad (17)$$

Values from this equation give the curve labelled V shown in Fig. 1. It is the best of the combination rules for computing B_{12} from the equation of state.

Determination of the Lennard-Jones Parameters from Second Virial Coefficients

Tabulation of the Second Virial Coefficient*

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Values of $B/(2\pi N\sigma^3/3)$ to four decimal places as a function of θ/T are computed from $\theta/T = 0.20$ to 1.00 for a Lennard-Jones (6, 12) potential. The equation $B/(2\pi N\sigma^3/3)$ $= (\theta/T)^{\frac{1}{4}}[1.064 - 3.602(\theta/T)]$ computes the tabulated values fairly well. Thus σ and θ can be determined from experimental B values by plotting $BT^{\frac{1}{4}}$ against $1/T$ and finding the slope and intercept of the best straight line through the points. For methane and n-butane this method gave parameters that computed B values agreeing with observed values within the experimental uncertainty.

IN the preceding paper[1] second virial coefficients derived from a Lennard-Jones (6, 12) potential were applied to the compressibility data on methane, n-butane, and mixtures of these two gases. Let:

$$W(r) = \lambda r^{-12} - \mu r^{-6} \\ = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6],$$

where

$$\epsilon = \mu^2/4\lambda, \\ \sigma^6 = \lambda/\mu.$$

The second virial coefficient B (cc/mole) becomes:

$$\frac{B}{\beta} = \sqrt{2}\left(\frac{\theta}{T}\right)^{\frac{1}{4}}\left[\Gamma\left(\frac{3}{4}\right)\right. \\ \left. - \sum_1^\infty \frac{2^{n-2}}{n!}\Gamma\left(\frac{2n-1}{4}\right)\left(\frac{\theta}{T}\right)^{n/2}\right], \quad (1)$$

where

$$\theta = \epsilon/k, \\ \beta = 2\pi N\sigma^3/3;$$

and N is the Avogadro number, σ is in cm, ϵ in ergs, and k the Boltzman constant in ergs/°K, so that θ is in °K. Any other consistent set of units may, of course, be used.

To compute the values of B/β given in Table I as a function of θ/T we set $y = 2(\theta/T)^{\frac{1}{2}}$ and computed the function for values of y increasing by

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[1] J. A. Beattie and W. H. Stockmayer, J. Chem. Phys. 10, 473 (1942).

TABLE I. Lennard-Jones second virial coefficients.

$$W(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

$$B/\beta = \sqrt{2}\left(\frac{\theta}{T}\right)^{\frac{1}{4}}\left[\Gamma(\tfrac{3}{4}) - \sum_{1}^{\infty} {}_n \frac{1}{4n!}\Gamma\left(\frac{2n-1}{4}\right)2^n\left(\frac{\theta}{T}\right)^{n/2}\right]; \quad \theta=\epsilon/k, \quad \beta=2\pi N\sigma^3/3$$

θ/T	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
					B/β					
0.20	+0.2434	+0.2185	+0.1933	+0.1677	+0.1417	+0.1154	+0.0887	+0.0617	+0.0345	+0.0070
0.30	− .0207	− .0487	− .0770	− .1056	− .1344	− .1635	− .1929	− .2225	− .2523	− .2823
0.40	− .3126	− .3431	− .3738	− .4047	− .4359	− .4673	− .4989	− .5307	− .5628	− .5951
0.50	− .6276	− .6604	− .6933	− .7264	− .7597	− .7932	− .8270	− .8610	− .8952	− .9296
0.60	− .9643	− .9992	−1.0343	−1.0696	−1.1051	−1.1408	−1.1767	−1.2129	−1.2493	−1.2859
0.70	−1.3228	−1.3599	−1.3972	−1.4347	−1.4724	−1.5103	−1.5485	−1.5870	−1.6257	−1.6646
0.80	−1.7037	−1.7431	−1.7828	−1.8227	−1.8628	−1.9032	−1.9438	−1.9846	−2.0256	−2.0669
0.90	−2.1084	−2.1502	−2.1923	−2.2346	−2.2772	−2.3201	−2.3632	−2.4065	−2.4501	−2.4939
1.00	−2.5380									

TABLE II. Deviations of B/β computed by Eqs. (2) and (3) from the values listed in Table I.

θ/T	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
				$\Delta(B/\beta)$					
Table I—Eq. (2)	−0.0041	+0.0010	+0.0007	−0.0002	−0.0004	±0.0000	+0.0004	−0.0006	−0.0041
Table I—Eq. (3)	+ .0136	− .0084	− .0129	− .0079	+ .0014	+ .0103	+ .0153	+ .0128	± .0000

increments of 0.05 from 0.8 to 2.2, that is for θ/T from 0.16 to 1.21. In order to construct a table for even values of θ/T in the range $(\theta/T)=0.20$ to 1.00 the approximate equation

$$\frac{B}{\beta} = 0.71875 - 2.131899\frac{\theta}{T} - 1.120795\left(\frac{\theta}{T}\right)^2 \quad (2)$$

was used together with a deviation plot. Deviations of the values computed by Eq. (2) from those of Table I are given in Table II.

Table I covers the region from the critical to the Boyle temperature for all gases, and thus covers the experimentally accessible range for all except the permanent gases.

Another approximate equation, while not as accurate as Eq. (2), is particularly suited for a rapid estimate of θ and β and hence of λ and μ.

It was found that the equation

$$\frac{B}{\beta} = \left(\frac{\theta}{T}\right)^{\frac{1}{4}}\left[1.064 - 3.602\frac{\theta}{T}\right] \quad (3)$$

reproduces the values in Table I as closely as B is known for many gases. (See Table II for the deviations.) Consequently from a plot of the experimental values of $BT^{\frac{1}{4}}$ against $1/T$ we can determine β and θ very quickly since $-3.602\beta\theta^{5/4}$ is the slope and $1.064\beta\theta^{\frac{1}{4}}$ the intercept on the $BT^{\frac{1}{4}}$ axis at $1/T=0$ of the best straight line through the experimental points. This procedure was followed in obtaining θ and β for methane and n-butane. Second virial coefficients determined from these values of θ and β agreed with the observed values within the experimental uncertainty.