Lennard-Jones Parameters for Methane

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The virial equation of state has special significance, since it follows rigorously from statistical thermodynamics (*1*). Calculation of the virial coefficients for the equation rests upon the application of a model for intermolecular interactions, that is, a potential function. In general, potential function parameters cannot be derived from theory. It is necessary to develop them by reduction of experimental thermodynamic or transport data.

The Lennard-Jones (6-12) potential is of much interest because of its relative simplicity, applicability to numerous common fluids, and extensive background literature. The writers have developed revised L-J (6-12) constants for methane based on a new treatment of experimental data. Existing constants for methane are reported by Hirschfelder, Curtiss, and Bird (*2*). They were developed originally from an unweighted fit to compressibility data of Michels and Nederbragt (*3*).

The new treatment is based upon Joule-Thomson coefficients. This procedure is an extension of ideas reported by Hirschfelder and Roseveare (*4*). The latter thermodynamic property has a dual advantage. First, it does not degenerate to an ideal gas property as zero pressure is approached. Rather, at the limit, it is a function of the character of the real gas, that is

$$\mu^o = \frac{T[B'(T)] - [B(T)]}{c_p{}^o} \qquad (1)$$

Second, the general coefficient is a function not only of the virial coefficients, but of their first and second derivatives as well. Therefore, it was anticipated that predictions might be very sensitive to values selected for potential function constants. This was found to be the case.

Computations were carried out as a one-dimensional optimization, over a range of pressures from 0 to 150 atm. at constant temperature, with the use of the golden section method. Unimodality was verified by graphical presentation of data derived with an IBM 7040. One major constraint was placed on the optimization. Since the error arising from truncation of the virial equation disappears at zero pressure, the computation was forced to duplicate the Joule-Thomson coefficient exactly at that pressure.

TABLE 1. ISOTHERMAL OPTIMUM L-J PARAMETERS

T, °K.	ϵ/k, °K.	b_o, cc./mole
200	121.10	106.23
210	126.11	96.02
220	131.32	87.42
230	137.90	79.07
240	140.52	75.29
250	140.80	73.86
270	140.37	72.90
280	142.11	71.34
300	145.01	69.23
320	144.71	70.10
350	142.39	73.53
370	140.57	75.98
400	139.99	77.53
420	139.32	79.10
450	138.22	82.30

TABLE 2. COMPARISON OF ERRORS

T, °K.	Ave. abs. error HCB values, %	Ave. abs. error isothermal optimum, %	Ave. abs. error average optimum, %
200	63.64	15.48	53.01
210	51.42	10.94	33.76
220	30.64	6.11	16.48
230	12.26	1.67	2.12
240	5.77	5.08	5.27
250	9.93	7.49	7.54
270	8.91	5.14	5.26
280	6.74	3.77	3.63
300	2.52	1.29	2.11
320	2.28	1.29	2.44
350	3.15	0.37	1.03
370	4.52	0.19	0.35
400	5.23	0.57	0.59
420	6.19	0.90	1.61
450	7.92	1.46	2.65

At a given temperature, a real positive ϵ/k was chosen at random and a reduced temperature was calculated. In turn, reduced virial coefficients and derivatives were calculated. An L-J (6-12) b_o was determined from these and the appropriate experimental Joule-Thomson coefficient at very low pressure, that is

$$b_o = \frac{\mu^o{}_{\text{exp}}\; c_p{}^o}{T^*[B^*]' - [B^*]} \qquad (2)$$

Error was assigned as a sum of absolute differences between experimental data and data predicted with the ϵ/k and b_o set. Computation was repeated, with revised values of ϵ/k, until a minimum error was generated. Data codified by Din (*5*) was the basis of calculation. Table 1 summarizes optimum ϵ/k and associated b_o at several temperatures.

Values of the L-J parameters for temperature between 230° and 450°K. were averaged to give a single set descriptive of the entire array. Resulting ϵ/k and b_o were 140.99°K. and 74.95 cc., respectively. Table 2 is a comparison of errors based upon predictions with the L-J parameters of reference 2, the local isothermal optimums and the average optimum of this work (140.99°K. and 74.95 cc.). Errors are reported as the difference between predicted and experimental values of the Joule-Thomson coefficient referred to the experimental value. The average optimum set recommended above is not as good as the local optimums applied to their individual isotherms. However, it compares well in most cases and is significantly better than the earlier set of reference 2 in all except one case. Errors were calculated for isothermal volumetric data also. All differences were small and the variations between the three types of L-J parameters could not be deemed significant.

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An Observation Concerning Pulse Testing of Flow Systems

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Several authors (*1* to *4*) have listed the advantages of the pulse testing technique over those of other similar methods for experimentally determining the residence time distribution and dynamic response of a flow system. One advantage often mentioned is that when one uses the pulse testing technique, measurements of the tracer concentration are made at two points instead of one, and the shape of the input pulse is not assumed. Another advantage which results from using two measurement points, and which to our knowledge has not been previously pointed out, is described below.

Consider the case where an experiment is to be carried out to determine the residence time distribution $E(\theta)$ of a flow system by injecting a unit impulse (or delta function) input of tracer at the inlet of the system and then measuring the outlet tracer concentration as a function of time. The final recorded trace of the outlet concentration will actually be the combined responses of the flow system and the measurement and recording system.

In Laplace transform notation, what one wishes to find is $\overline{E}(s)$; what one actually gets is $\overline{E}'(s) = \overline{E}(s)\overline{M}(s)$. Here $\overline{E}(s)$ is the Laplace transform of the residence time distribution or, equivalently, the transfer function of the flow system, and $\overline{M}(s)$ is the transfer function of the measuring device and the recorder. In this case, the only way to eliminate the influence of instrument dynamics, represented here by $\overline{M}(s)$, is to make a separate experimental measurement of those dynamics and then divide the transformed impulse response curve $\overline{E}'(s)$ by the measured transfer function of the instruments.

Consider now the case where $\overline{E}(s)$ is to be determined with the pulse testing technique. $\overline{E}(s)$ is given by

$$\overline{E}(s) = \frac{\overline{Y}(s)}{\overline{X}(s)} \tag{1}$$

where $\overline{X}(s)$ and $\overline{Y}(s)$ are the Laplace transforms of the input and output pulses, respectively. In this case, one wants $\overline{X}(s)$ and $\overline{Y}(s)$, but one gets $\overline{X}'(s)$ and $\overline{Y}'(s)$ where

$$\overline{X}'(s) = \overline{X}(s)\overline{M}_1(s) \tag{2}$$

and

$$\overline{Y}'(s) = \overline{Y}(s)\overline{M}_2(s) \tag{3}$$

$\overline{M}_1(s)$ and $\overline{M}_2(s)$ are the transfer functions of the instruments. Hence instead of $\overline{E}(s)$ one actually gets $\overline{E}'(s)$ where

$$\overline{E}'(s) = \frac{\overline{Y}'(s)}{\overline{X}'(s)} = \frac{\overline{Y}(s)}{\overline{X}(s)}\,\frac{\overline{M}_2(s)}{\overline{M}_1(s)} = \overline{E}(s)\,\frac{\overline{M}_2(s)}{\overline{M}_1(s)} \tag{4}$$

The advantage of the pulse testing technique that we wish to emphasize is that one can take steps to insure that

$$\frac{\overline{M}_2(s)}{\overline{M}_1(s)} = 1 \tag{5}$$

This makes it unnecessary to make corrections in the observed response of the system. Even if $\overline{M}_1(s)$ and $\overline{M}_2(s)$ are slightly different, their presence as a ratio in Equation (4) nearly always produces sufficient tendency toward cancellation, so that a separate experiment to evaluate and compensate for instrument dynamics is unnecessary. In our work (*5*), in which the pulse testing technique with radioactive P-32 as a tracer was used to investigate liquid mixing on distillation trays, it was found that off-the-shelf scintillation probes and rate meters satisfied Equation (5) without modification.

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