

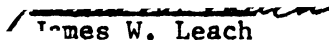
INTERMOLECULAR POTENTIAL COMBINING RULES
UTILIZING CORRESPONDING STATES CORRELATIONS FOR PURE SUBSTANCES
HAVING NONSPHERICAL MOLECULES

by
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NOMENCLATURE

Upper Case Letters

A_1, A_2, A_3	$\sigma_{1ij}^3, \sigma_{2ij}^3$, and ϵ_{ij} , respectively
B	Second virial coefficient
C	Constant; third virial coefficient
D	Fourth virial coefficient
F	Function
I	First ionization potential; configuration integral
K	Kelvin temperature
L	Total number of data points
N	Number of molecules
P	Pressure
R	Gas constant
T	Temperature
U	Total intermolecular potential energy
V	Volume
X	Mole fraction
Z	Compressibility factor

Lower Case Letters

f, g	Functions
h_1, h_2, h_3	Functions
k	Boltzmann's constant
m	Number of dimensions
n	Number of quantities; exponent
r	Position vector length; intermolecular separation distance

u Potential energy for a molecular pair

Greek Letters

α Slope of vapor pressure curve

∂ Partial differential operator

ϵ Energy parameter in potential function

η Angular coordinate

π 3.14159. . .

Π Function; dimensionless group of thermodynamic properties; product

σ Length parameter in potential function

ω Acentric factor

Subscripts and Superscripts

c Critical state; calculated value

i Index

j Index

l Index

m Mixture property

O Trial value

' New function; actual error; correlated parameter

R Reduced value

" Combining rule value

INTRODUCTION

Determining the properties of fluid mixtures is one of the most vexing problems in the application of thermodynamics. Thermodynamic properties of pure components and mixtures may either be measured experimentally or predicted by analytical methods. For pure substances, thermodynamic properties usually can be measured at a sufficient number of conditions to permit accurate interpolation or extrapolation of the data to conditions for which the properties are unknown. However, mixture properties usually must be predicted, as it is a never-ending task to determine the properties experimentally for all the mixtures and mixture proportions of interest.

In general, two approaches have been taken in the prediction of thermodynamic properties of pure substances and mixtures. The prediction of properties by means of equations of state with substance-dependent coefficients was historically the first approach attempted. This approach has the capability of high accuracy, depending upon the number of constants appearing in the equation of state. The empirical equation obtained by Vennix [1] for methane is indicative of the potential accuracy of equations of state in which many constants appear. His equation has 26 constants and predicts pressure or density with a maximum error of less than 0.1 per cent at temperatures above 200° Kelvin.

A disadvantage of the equation of state approach is that all of the constants in the equation of state must be determined for each substance of interest. For mixtures of pure substances, the constants will vary depending on the proportions of each substance in the

mixture. Rules must then be established for calculating the composition dependence of all of the coefficients in order to predict mixture properties.

A second approach employs the principle of corresponding states, which proposes the numerical equality of dimensionless groups of properties of different substances determined at the same values of reduced temperature and reduced volume. A primary advantage of the corresponding states principle is that it requires knowledge of only two or three physical parameters to predict the properties of one substance from the measured properties of another substance. The number of parameters required to predict properties of a substance depends upon the complexity of its molecules. For substances such as the inert gases which have spherically shaped molecules, only two parameters are necessary. For substances with nonspherical, nonpolar molecules it has been determined empirically [2] that three parameters are required to predict thermodynamic properties within 2.5 per cent of experimental data.

The principle of corresponding states has been derived [3] from statistical thermodynamics based on assumptions concerning the forces between molecules. This theoretical basis gives assurance that the corresponding states principle will be applicable at conditions for which it has not been previously tested. Equations of state, however, generally cannot be applied outside of the range for which their constants were initially determined.

Because of its theoretical basis and simplicity, it is believed that the corresponding states principle has more potential than

equations of state for predicting thermodynamic properties. Therefore, this work is concerned solely with evaluating and improving the corresponding states principle.

A mathematical statement of the principle of corresponding states for fluids with spherical molecules is:

$$\Pi_i(T_{Ri}, V_{Ri}) = \Pi_j(T_{Rj} = T_{Ri}, V_{Rj} = V_{Ri})$$

where Π_i and Π_j are dimensionless groups of properties of substances "i" and "j" respectively. Usually the arguments are reduced by the critical properties such that

$$T_{Ri} = T_i/T_{ci}$$

$$V_{Ri} = V_i/V_{ci}$$

From the theoretical derivation of the corresponding states principle [3] based upon statistical mechanics it is known that the reduced parameters should be

$$T_{Ri} = T_i/\epsilon_i$$

$$V_{Ri} = V_i/\sigma_i^3$$

where ϵ_i and σ_i are characteristic constants of the intermolecular potential function. ϵ_i is the minimum value of the intermolecular potential energy, and σ_i is the distance of separation of the molecules for which the intermolecular force is zero. It can be shown [4] that for substances which have spherical molecules

$$\epsilon \propto T_c$$

and

$$\sigma^3 \propto V_c$$

Part of this work is concerned with determining the relationship between the intermolecular parameters and the critical parameters for substances which have nonspherical molecules. Correlations are obtained which relate the intermolecular parameters to critical constants and to a third parameter used in applying the corresponding states principle to substances with nonspherical molecules.

The principle of corresponding states can be applied to predict properties of mixtures if the parameters characterizing the interaction between unlike molecules are known. These interaction parameters are related by combining rules to the parameters which govern the interaction between the like molecules of each pure specie in the mixture. Part of this work is concerned with evaluating and developing the theory for relating interaction parameters to pure component parameters.

Most investigators [5, 6, 10] have studied the nature of intermolecular forces in order to determine the combining rules for the parameters characterizing the intermolecular potential function. One of the most common rules in use for the interaction energy parameter is the geometric mean:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$

For substances with spherical molecules the equivalent interaction critical temperature is

$$T_{cij} = \sqrt{T_{ci} T_{cj}}$$

These equations result from approximations made when considering London dispersion forces between molecules [5]. It is usually assumed that the interaction distance parameter σ_{ij} is given by the simple arithmetic mean of the pure components σ_i and σ_j .

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$

In 1960 Hudson and McCoubrey published [6] work on a combining rule obtained from a more detailed study of the London dispersion forces. Their result is:

$$\epsilon_{ij} = \left\{ \frac{2(I_i I_j)^{1/2}}{I_i + I_j} \right\} \left\{ 2^6 \frac{\sigma_i^3 \sigma_j^3}{(\sigma_i + \sigma_j)^6} \right\} (\epsilon_i \epsilon_j)^{1/2}$$

where I is the ionization potential. Reference [8] reports that the use of the geometric mean combining rules produces errors of 50° Kelvin in the interaction critical temperature. It has also been reported [7, 8, 9] that the Hudson and McCoubrey rule is more accurate than the simple geometric rule in most cases but still is not adequate. Recently Sikora [10] has proposed a new combining rule which was obtained by using a model involving both the attractive and the repulsive forces between molecules. The resulting ϵ_{ij} is:

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2} \left\{ \frac{4(I_j/I_i)}{(1.0 + I_j/I_i)^2} \right\} \left[\frac{2^{13} \left[\frac{\epsilon_j \sigma_j^{12}}{\epsilon_i \sigma_i^{12}} \right]^{1/2}}{\left[1.0 + \left[\frac{\epsilon_j \sigma_j^{12}}{\epsilon_i \sigma_i^{12}} \right] \right]^{1/13}} \right]$$

Preliminary results show that this rule is much improved over the Hudson and McCoubrey rule.

In this study a new empirical combining rule for ϵ_{ij} is determined and is compared with the existing theoretical rules. The new rule is applicable to mixtures of fluids which do not have spherical molecules.

SECTION I

THE INTERMOLECULAR POTENTIAL FUNCTION

The nature of intermolecular forces is not completely understood, but it is known that they arise from several effects acting simultaneously [5]. The repulsive forces are primarily coulombic in nature, whereas the attractive forces are explained as an effect of instantaneous, nonsymmetrical charge distributions in atoms and molecules. These forces may be described by referring to a hypothetical intermolecular potential energy curve in Fig. 1. The intermolecular force is equal to the negative derivative of the potential with respect to the separation distance. The force is zero at the point where the intermolecular potential energy is a minimum. The force is negative or attractive when r is greater than σ and repulsive when r is less than σ .

From statistical thermodynamics, the thermodynamic properties of a fluid are related to its intermolecular potential function through the classical configuration integral, I_N

$$I_N = \int \dots \int_V e^{-U/kT} \prod_{i=1}^N dr_i d\eta_i \quad (1)$$

where r_1, r_2, \dots, r_N and $\eta_1, \eta_2, \dots, \eta_N$ are position coordinates of the N molecules and U is the total intermolecular potential energy computed by summing the intermolecular pair potentials

$$U = \sum_{i < j}^N u_{ij} \quad (2)$$

For example, it may be shown that the thermodynamic pressure is given by

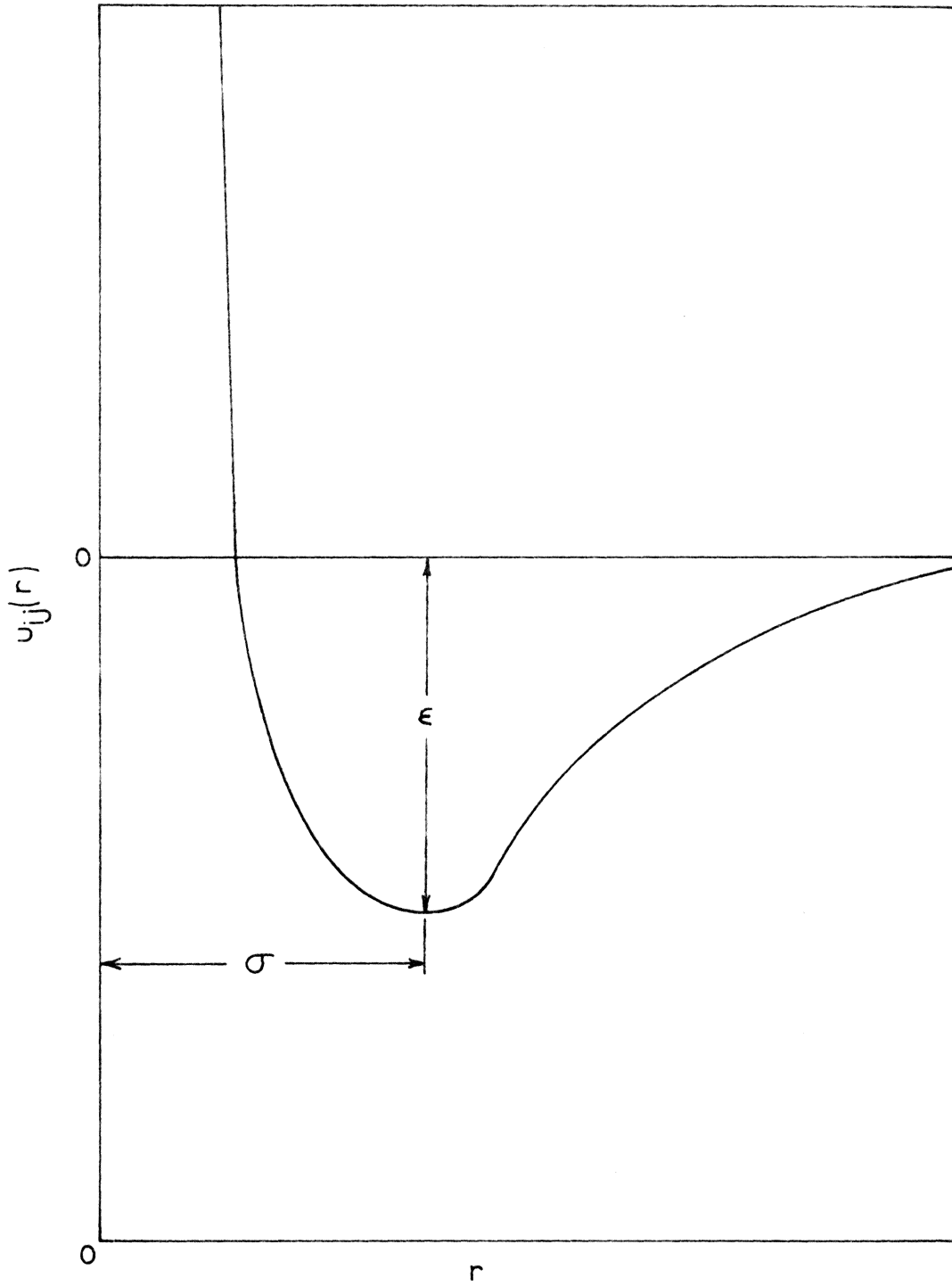


FIG. 1. AN INTERMOLECULAR POTENTIAL FUNCTION

$$P = kT \left(\frac{\partial \ln I_N}{\partial V} \right)_{T,N} \quad (3)$$

Sherwood and Prausnitz have shown [11] that three parameters may be necessary in order to represent the intermolecular potential. They have compared five candidate potentials and found that three-parameter potentials could fit second virial coefficient data within experimental accuracy whereas the two-parameter potentials could not. In addition they found that the three-parameter rectangular well potential shown in Fig. 2 had the lowest rms deviation of the five potentials tested. Although the virial coefficients computed from this potential are in close agreement with experimental values, the intermolecular forces computed from the potential are not believed to be representative of actual intermolecular forces. Since the forces are determined from the derivative of the potential function, it may be seen from Fig. 2 that the rectangular well potential predicts an infinite repulsive force at $r = \sigma_1$, no force between $r = \sigma_1$ and $r = \sigma_2$, and an infinite attractive force at $r = \sigma_2$.

London showed from calculations based on quantum mechanics [12] that the attractive part of the intermolecular potential should be proportional to r^{-6} . This r^{-6} proportionality is used in the attractive portions of the empirical Lennard-Jones and the Sutherland potentials [5], which are both two-parameter potentials. There is no theoretical basis for computing the dependence of the repulsive force on distance of separation. In the Lennard-Jones potential, the term which represents the repulsive force is assumed to be proportional to r^{-12} . Other empirical potential functions assume larger negative

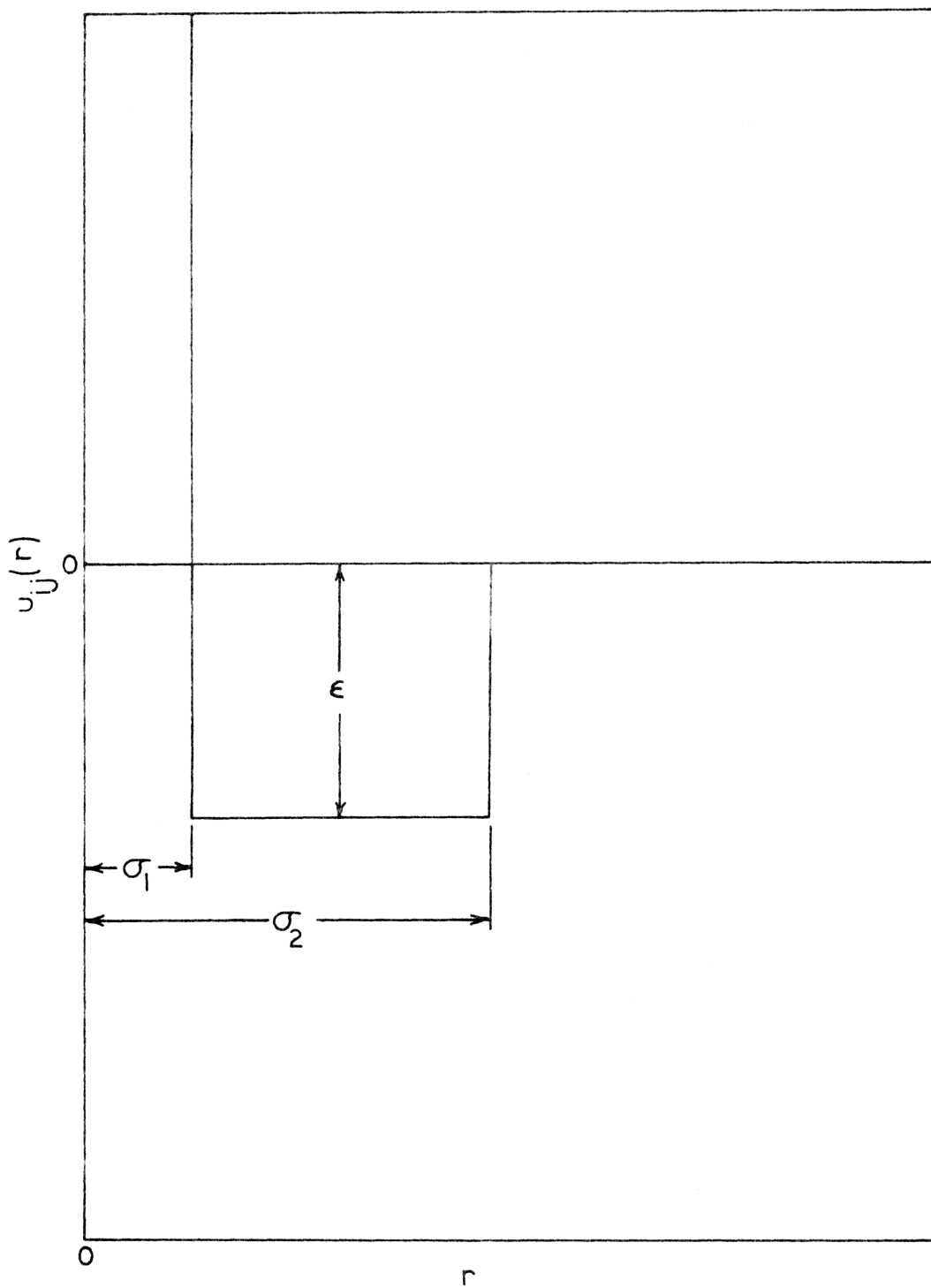


FIG. 2. THE RECTANGULAR WELL POTENTIAL

values for the exponent of the repulsive term. This corresponds to the fact that the repulsive forces are short ranged, and increase rapidly as the molecules are brought closely together.

In this work two intermolecular potentials are considered in order to determine the relationship between critical and intermolecular parameters as well as to study and develop combining rule theory. The rectangular well potential is considered since it predicts experimental virial coefficients more accurately than any of the other existing intermolecular potential functions. In addition, a new potential function, hereafter referred to as the r^{-6} potential, is studied. The new potential function is shown qualitatively in Fig. 3. The r^{-6} potential is similar to the rectangular well potential excepting the potential fall proportional to $(\sigma_2/r)^6$ starting at σ_2 and extending to an indefinite separation distance corresponding with the London theory.

It is believed that this work is the first to consider three intermolecular parameters in evaluating combining rule theory. It is shown that this permits a significant improvement in the prediction of interaction parameters, particularly when one of the components has non-spherical molecules. It is also shown that the three intermolecular parameters may be related to the critical temperature and volume and to a third thermodynamic property used in the three-parameter corresponding states principle. This makes it possible to predict mixture properties based on three thermodynamic properties measured for each of the pure components in the mixture.

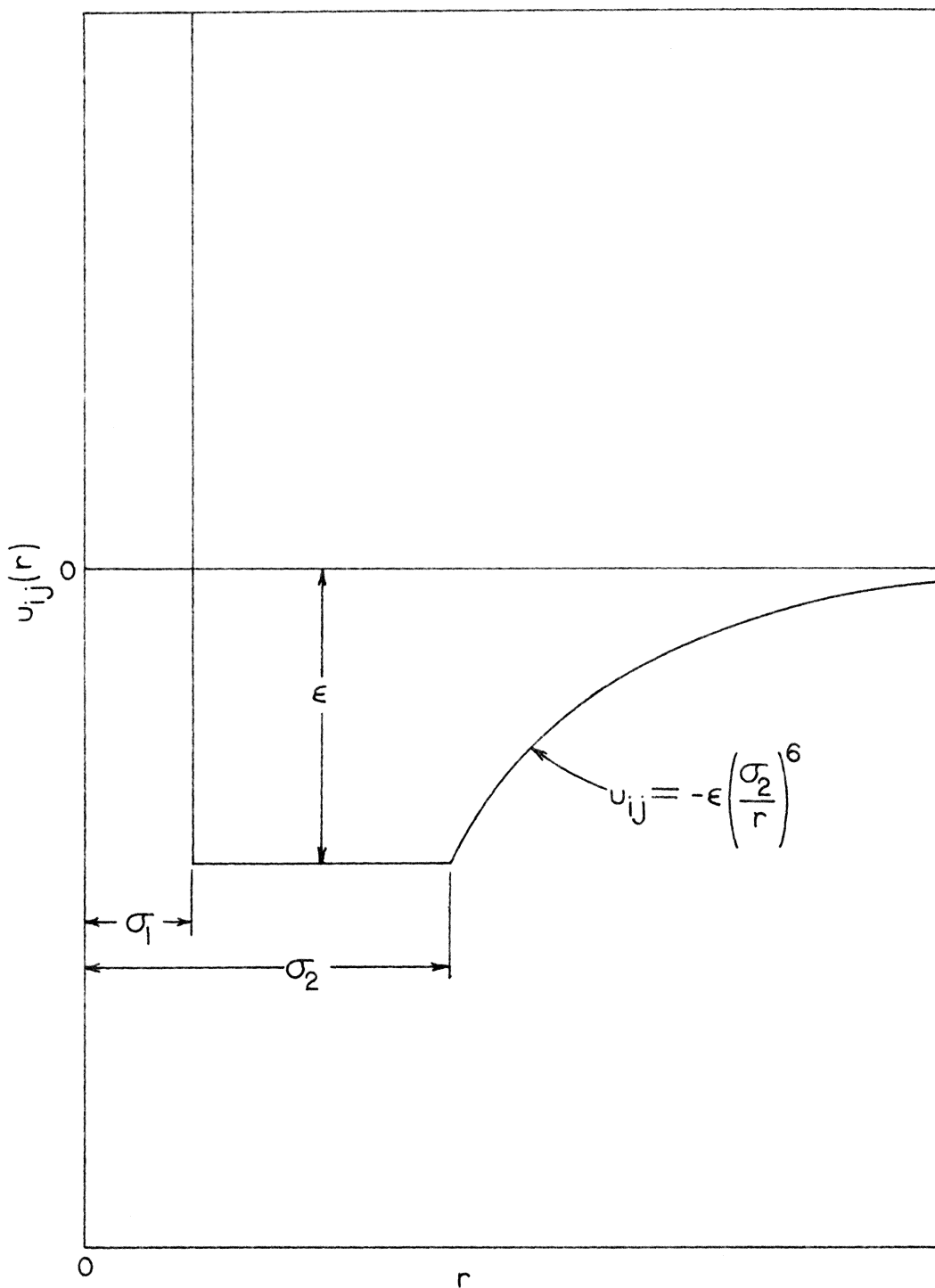


FIG. 3. THE r^{-6} POTENTIAL

SECTION II

THE CORRESPONDING STATES PRINCIPLE

By applying the techniques of dimensional analysis to the thermodynamic and molecular properties of fluids, it can be shown that the number of parameters required in the corresponding states principle is equal to the number of parameters in the intermolecular potential function. This type of analysis has been applied previously [4] to the two-parameter principle of corresponding states, but it is here extended to the three-parameter principle.

The Two-Parameter Principle of Corresponding States

If there are two characteristic parameters in the intermolecular potential, the equation of state of a fluid can be represented as

$$F(kT, P, V/N, \epsilon, \sigma) = 0 \quad (4)$$

where ϵ and σ are the intermolecular parameters discussed in Section I. The Buckingham Π Theorem requires the existence of another equation. This equation is:

$$f(\Pi_1, \Pi_2, \dots, \Pi_{n-m}) = 0 \quad (5)$$

$\Pi_1, \Pi_2, \dots, \Pi_{n-m}$ are dimensionless groups of the n quantities appearing in the equation of state, and m is the number of dimensions appearing in the n quantities. In this case, $n = 5$ and $m = 2$, since only the dimensions of force and length appear in the five quantities. This implies that there are three dimensionless groups in equation 5 which becomes

$$f\left(\frac{PV}{NkT}, \frac{kT}{\epsilon}, \frac{V}{N\sigma^3}\right) = 0 \quad (6)$$

Solving for PV/NkT gives

$$\frac{PV}{NkT} = g\left(\frac{kT}{\epsilon}, \frac{V}{N\sigma^3}\right) \quad (7)$$

When the intermolecular potential has the same functional form for a group of fluids, equation 7 has the same form for all of the fluids in the group, and becomes the statement of the two-parameter corresponding states principle for that group. This equation also indicates that the substances in the group all have the same values of $Z = PV/NkT$ when they have equal values of kT/ϵ and $V/N\sigma^3$. At the critical point,

$$Z_c = \frac{P_c V_c}{NkT_c} = g\left(\frac{kT_c}{\epsilon}, \frac{V_c}{N\sigma^3}\right) \quad (8)$$

The critical point is defined by the two conditions

$$\left. \begin{array}{l} \frac{\partial P}{\partial V} \\ T = T_c \\ V = V_c \end{array} \right| = 0 \quad (9)$$

$$\left. \begin{array}{l} \frac{\partial^2 P}{\partial^2 V} \\ T = T_c \\ V = V_c \end{array} \right| = 0 \quad (10)$$

Simultaneously solving equations 8, 9, and 10:

$$\frac{kT_c}{\epsilon} = C_1 \quad (11)$$

$$\frac{V_c}{N\sigma^3} = C_2 \quad (12)$$

$$\frac{P_c V_c}{NkT_c} = g(C_1, C_2) = C_3 \quad (13)$$

Thus C_1 , C_2 , and C_3 must have the same respective values for each fluid in the group, and all the fluids have the same critical compressibility factor, $P_c V_c / NkT_c$. Substituting equations 11 and 12 into 7 gives

$$\frac{PV}{NkT} = g\left(C_1 \frac{T}{T_c}, C_2 \frac{V}{V_c}\right) = g_1\left(\frac{T}{T_c}, \frac{V}{V_c}\right) \quad (14)$$

which is the usual statement of the two-parameter corresponding states principle.

The Three-Parameter Principle of Corresponding States

As was previously mentioned, only substances with spherically symmetrical molecules obey the two-parameter corresponding states principle. The normal alkane hydrocarbons are examples of compounds with nonspherical molecules which deviate from the two-parameter principle. It has been reported [13] that if a third parameter is included in the principle of corresponding states, the accuracy of correlation is increased by approximately one order of magnitude. The following analysis

indicates how the critical properties and potential parameters are related.

If the intermolecular potential has three characteristic parameters, as do the rectangular well and the r^{-6} potentials, the equation of state is written

$$F(kT, P, V/N, \epsilon, \sigma_1, \sigma_2) = 0 \quad (15)$$

There are still only the two dimensions of force and length appearing in the six quantities, so there are four dimensionless groups involving the six quantities. Equation 7 becomes

$$f\left(\frac{PV}{NkT}, \frac{kT}{\epsilon}, \frac{V}{N\sigma_1^3}, \frac{\sigma_2}{\sigma_1}\right) = 0 \quad (16)$$

and

$$\frac{PV}{NkT} = g\left(\frac{kT}{\epsilon}, \frac{V}{N\sigma_1^3}, \frac{\sigma_2}{\sigma_1}\right) \quad (17)$$

Thus, fluids have the same compressibility factor if their intermolecular potentials have the same functional form and they have the same values of kT/ϵ , $V/N\sigma_1^3$, and σ_2/σ_1 . Applying the conditions at the critical point for this case gives

$$\frac{kT_c}{\epsilon} = h_1\left(\frac{\sigma_2}{\sigma_1}\right) \quad (18)$$

$$\frac{V_c}{\sigma_1^3} = h_2\left(\frac{\sigma_2}{\sigma_1}\right) \quad (19)$$

$$Z_c = h_3(\sigma_2/\sigma_1) \quad (20)$$

where h_1 , h_2 , and h_3 are universal functions. Equations 18 and 19 indicate that it should be possible to correlate kT_c/ϵ and V_c/σ_1^3 with a third parameter. For example, equation 20 could be solved to give σ_2/σ_1 as a function of Z_c . This relationship could then be substituted into equations 18 and 19 to give

$$\frac{kT_c}{\epsilon} = h_1'(Z_c) \quad (21)$$

$$\frac{V_c}{\sigma_1^3} = h_2'(Z_c) \quad (22)$$

σ_2/σ_1 may be empirically related to other third parameters. Among the third parameters that have been suggested [13] is the acentric factor, ω , defined in equation 23.

$$\omega = -\log(P_g/P_c) - 1.000, \quad T_R = 0.7 \quad (23)$$

The symbol P_g is the vapor pressure of the pure substance evaluated at $T/T_c = 0.7$. For those substances having spherically symmetrical molecules, the acentric factor is approximately zero.

Another third parameter is α , the slope of the vapor-pressure curve at the critical temperature. Any of the third parameters discussed above could be used to relate the critical parameters to the molecular parameters. The acentric factor was chosen for this work because it may be measured more accurately experimentally than the other parameters. When this parameter is included, the mathematical

statement of corresponding states is

$$\Pi_i(T_{Ri}, V_{Ri}, \omega_i) = \Pi_j(T_{Rj} = T_{Ri}, V_{Rj} = V_{Ri}, \omega_j = \omega_i) \quad (24)$$

Values of the acentric factor and critical properties along with their respective literature references for the pure substances considered in this research are given in Table I.

Application of Corresponding States Theory

To Properties of Mixtures

Corresponding states theory is utilized in predicting the properties of mixtures by two methods [14]. First is the so-called "one-fluid" model for a mixture which attempts to define conditions such that corresponding states theory is applied to the mixture as if it were a pure substance. This approach requires the definition of pseudocritical properties of mixtures. In the second method, the "multifluid" model, the corresponding states principle is applied to each pure component in the mixture in such a way that the pseudocritical concept is avoided.

The conditions sought in the first model are called "pseudopotentials" and "pseudocriticals." Pseudopotentials are the composition-dependent potential parameters obtained when the form of the intermolecular potential function describing a mixture is assumed to be identical to that describing a pure substance. Pseudocriticals are composition-dependent parameters related to the pseudopotentials which are used in place of T_c and V_c in the corresponding states principle. Pseudocriticals cannot be determined experimentally, since mixtures do not exhibit critical point behavior, as do pure components. Common

TABLE I

PURE SUBSTANCE CRITICAL PROPERTIES AND ACENTRIC FACTORS

Substance Name	Symbol	Substance Code Number	T _c °K	V _c $\frac{CC}{g-mole}$	ω	References
Nitrogen	N ₂	3	126.260	90.080	0.0418	17
Oxygen	O ₂	4	154.780	76.400	0.0252	17
Neon	Ne	6	44.450	41.740	-0.0258	17
Argon	Ar	7	150.720	75.270	-0.0022	17
Krypton	Kr	8	209.410	92.240	0.0046	17
Xenon	Xe	9	289.750	118.800	0.0081	17
Methane	CH ₄	10	191.060	99.000	0.0100	1
Carbon tetrachlo- ride	CCl ₄	11	556.300	275.700	0.1910	8
Tetra- fluoro- methane	CF ₄	12	227.550	146.700	0.2120	17
Carbon Monoxide	CO	13	132.920	93.200	0.0486	17
Carbon Dioxide	CO ₂	14	304.190	94.200	0.2630	17
Acetylene	C ₂ H ₂	15	309.500	113.000	*0.3000	17
Ethylene	C ₂ H ₄	16	283.060	124.000	0.0868	17
Ethane	C ₂ H ₆	17	305.430	148.000	0.0990	17
Propane	C ₃ H ₈	19	369.970	200.000	0.1530	17
n-Butane	C ₄ H ₁₀	20	425.170	255.000	0.2010	17

*Estimated value

Table I (continued)

Substance Name	Symbol	Substance Code Number	T _c °K	V _c $\frac{\text{CC}}{\text{g-mole}}$	ω	References
iso-Butane	C ₄ H ₁₀	21	408.140	263.000	0.1860	17
n-Pentane	C ₅ H ₁₂	22	469.780	311.000	0.2524	17
neo-Pentane	C(CH ₃) ₄	23	433.760	303.000	0.1980	17
iso-Pentane	C ₅ H ₁₂	24	461.000	308.000	0.2169	17
n-Hexane	C ₆ H ₁₄	25	507.900	368.000	0.3033	17
n-Heptane	C ₇ H ₁₆	27	540.160	426.000	0.3499	17
n-Octane	C ₈ H ₁₈	28	569.400	486.000	0.3945	17
Propylene	C ₃ H ₆	29	365.100	181.000	0.1430	17
1-Butene	C ₄ H ₈	30	419.600	241.000	0.1278	17
Benzene	C ₆ H ₆	37	562.610	260.000	0.2120	17
Sulfur Hexafluoride	SF ₆	41	318.700	194.000	0.2100	8
Ammonia	NH ₃	43	405.500	72.500	0.2530	2
Perfluoro- n-Pentane	C ₅ F ₁₂	54	419.000	490.000	0.4340	18
Perfluoro- n-Hexane	C ₆ F ₁₄	55	447.900	575.000	0.4690	18

practice is to define the pseudocriticals in terms of the critical parameters of the pure components in the mixture by means of pseudocritical equations. Equation 25 is an example of a pseudocritical equation for a binary mixture.

$$T'_c = X_1^2 T_{ci} + 2X_1X_j T_{cij} + X_j^2 T_{cj} \quad (25)$$

The symbol, X, represents the mole fraction of each component and T_{cij} is the interaction critical temperature. There are several different forms for the pseudocritical equations, but the correct form has yet to be discovered.

In the second method of applying the theory of corresponding states to mixtures the properties are predicted by treating the mixture as a solution of the pure components. One approach in the treatment of the solution employs the virial equation of state for mixtures, equation 26, and the definition of the second virial coefficient of a mixture, equation 27.

$$Z_m = 1.0 + \frac{B_m}{V} + \frac{C_m}{V^2} + \frac{D_m}{V^3} + \dots \quad (26)$$

In equation 26, the virial coefficients are computed from corresponding states. For example, B_m is given by

$$B_m = \sum_{i=1}^n \sum_{j=1}^n X_i X_j B_{ij} \left(\frac{kT}{\epsilon_{ij}} \right) \quad (27)$$

where B_{ij} is a universal function of kT/ϵ_{ij} which may be predicted from pure component data.

A common approximation that is made is to assume that all of the

mixture properties can be determined from equations similar to equation 27. For example, the compressibility factor is assumed to be given by

$$Z_m = X_i^2 Z_i + 2X_i X_j Z_{ij} + X_j^2 Z_j \quad (28)$$

where Z_{ij} is predicted by means of the corresponding states principle from pure component data.

Both of the methods for predicting mixture properties described above require knowledge of the interaction critical properties T_{cij} and V_{cij} . In general, combining rules for calculating the interaction criticals may be obtained by merely substituting the relationships between the criticals and the potentials into the combining rules for the potential parameters. If this is done, assuming mixtures involving only interactions between spherical molecules, the following combining rules are obtained from those given in the Introduction:

$$V_{cij} = \left(\frac{v_{ci}^{1/3} + v_{cj}^{1/3}}{2} \right)^3 \quad (29)$$

$$T_{cij} = \sqrt{T_{ci} T_{cj}} \quad (30)$$

$$T_{cij} = \frac{(2)^6 v_{ci} v_{cj}}{(v_{ci}^{1/3} + v_{cj}^{1/3})^6} \left\{ \frac{2(I_i I_j)^{1/2}}{I_i + I_j} \right\} (T_{ci} T_{cj})^{1/2} \quad (31)$$

$$T_{cij} = (T_{ci} T_{cj})^{1/2} \left\{ \frac{4(I_j/I_i)}{(1.0 + I_j/I_i)^2} \right\} \left\{ \frac{(2)^{13} \left(\frac{T_{ci} v_{ci}^4}{T_{ci} v_{ci}^4} \right)^{1/2}}{\left[1.0 + \left(\frac{T_{ci} v_{ci}^4}{T_{ci} v_{ci}^4} \right)^{1/13} \right]^{13}} \right\} \quad (32)$$

SECTION III

THE SECOND VIRIAL COEFFICIENT AND THE INTERMOLECULAR POTENTIAL

One of the most direct methods of calculating the intermolecular potential parameters for like or unlike molecular interactions utilizes experimental values of the second coefficient in the virial equation of state. The virial equation of state for a mixture is:

$$Z_m = \frac{P_m V_m}{R T_m} = 1 + \frac{B_m}{V} + \frac{C_m}{V^2} + \frac{D_m}{V^3} + \dots \quad (33)$$

where Z_m is the compressibility factor, and B_m , C_m , and D_m are the second, third, and fourth virial coefficients respectively. For a mixture of n components, the second virial coefficient is given by

$$B_m = \sum_{i=1}^n \sum_{j=1}^n X_i X_j B_{ij}(T) \quad (34)$$

From statistical mechanics [15] it is known that

$$B_{ij}(T) = 2\pi \int_0^{\infty} (1 - e^{-u_{ij}(r)/kT}) r^2 dr \quad (35)$$

where $u_{ij}(r)$ is the intermolecular pair potential energy for molecules of species "i" and "j" respectively. Equation 35 provides a means for computing the parameters in the intermolecular potential if experimental second virial coefficient data is available over a wide range of temperature.

It is also possible to express the third or higher virial coefficients in terms of the intermolecular potential by considering interactions of three or more molecules. However, this information is not

as useful for studying intermolecular forces since the experimental data for the third and higher virial coefficients is not as accurate as that for the second virial coefficient, and the theory for computing the forces between more than two molecules is not completely understood.

To determine the intermolecular force constants from equation 35, it is necessary to assume the functional form of the potential function and evaluate the integral in terms of the force constants. If the rectangular well potential is assumed, equation 35 becomes

$$B_{ij} = 2\pi \left[\int_0^{\sigma_{1ij}} (1 - e^{-\infty/kT}) r^2 dr + \int_{\sigma_{1ij}}^{\sigma_{2ij}} (1 - e^{\epsilon_{ij}/kT}) r^2 dr + \int_{\sigma_{2ij}}^{\infty} (1 - e^{0/kT}) r^2 dr \right]$$

performing the integration,

$$B_{ij} = 2\pi \left[\frac{\sigma_{1ij}^3}{3} + (1 - e^{\epsilon_{ij}/kT}) \left(\frac{\sigma_{2ij}^3 - \sigma_{1ij}^3}{3} \right) + 0 \right]$$

or,

$$B_{ij} = \frac{2\pi}{3} \left[\sigma_1^3 + (e^{\epsilon_{ij}/kT} - 1) (\sigma_{1ij}^3 - \sigma_{2ij}^3) \right] \quad (36)$$

The derivation of B_{ij} for the r^{-6} potential is rather lengthy and is not given here, but it is given in Appendix A.

An iterative least-squares curve fitting technique described in Appendix B is used to calculate the parameters σ_{1ij} , σ_{2ij} , and ϵ_{ij} from experimental data for the second virial coefficient.

An extensive search of the literature has been conducted to find pure component and interaction second virial coefficients. Since more than one thousand data points of pure and interaction second virial coefficients were found, it is impractical to list each value. Table II gives the number of data points, the temperature range, the virial coefficient range, and the literature references for each pure substance and mixture considered in this study.

Table II does not list all existing compounds. A particular substance may not be included in Table II for at least one of the following reasons. First, there is little or no data for the second virial coefficient. Second, the critical properties of the compound have not been determined. Third, it is known from quantum mechanics that the molecule of the element or compound is too small to be accurately studied with classical mechanics.

The intermolecular parameters calculated for the rectangular well and the r^{-6} potentials from the pure component second virial coefficient data, along with the rms deviation of predicted virial coefficients, are listed in Table III.

TABLE II
DATA SUMMARY

Mixture Number	Number of Values	Reduced* Temperature Range		B _{ij} or B _{ij} CC/g-mole		References
		Low	High	Low	High	
3	38	.959	5.925	-113	+24.740	19,20,21,22, 24
6	16	2.770	9.520	0.100	13.094	20,32
7	151	0.533	5.793	-285.100	19.480	20,21,41,38,39, 40,33,34,35,36, 37
8	87	.514	4.170	-386.670	17.190	38,39,41,42,31, 37,43,44
9	48	.598	3.359	-368.320	14.220	39,45,31,46,47, 48
10	80	.568	3.261	-364.990	9.660	37,22,49,31,50, 51,52,53,54
12	30	1.200	2.958	-110.000	23.600	54,55
13	14	.926	3.183	-122.840	10.164	56,31
41	5	.983	1.234	-253.000	-145.000	54
29	15	0.832	1.133	-329.000	-166.000	74
4	13	.581	2.088	-245.000	- 12.000	21,25,26,27,28, 29,30,31
19	37	.671	1.542	-579.000	89.000	65,89,22,31

*For Mixtures, $T_R = T/\sqrt{T_{ci} T_{cj}}$

Table II (continued)

Mixture Number	Number of Values	Reduced* Temperature Range		B_{ij} or B_{ij} CC/g-mole		References
		Low	High	Low	High	
11	4	.567	.617	-1445.000	-1120.000	8
16	18	.930	1.673	- 172.800	- 42.800	60,61,27
15	8	.872	1.367	- 198.000	- 64.000	90,91
17	49	.704	1.713	- 340.630	- 60.000	63,64,65,53,22
24	41	.593	1.026	-1390.000	- 377.000	70,71
23	29	.699	1.264	- 900.400	- 216.000	22,54,70
30	12	.725	1.001	- 606.000	- 295.000	74
21	6	.844	1.252	- 414.000	- 191.600	22
20	37	.666	1.348	- 846.000	- 159.000	89,66,65,22,67
22	43	.635	1.220	-1194.000	- 244.000	89,68,69,70,54
25	38	.587	.932	-1984.000	- 530.000	89,66,72
27	32	.580	1.154	-3735.000	- 399.000	66,89,65,73
28	10	.655	1.726	-2122.000	-1518.000	89
37	80	.525	.894	-1525.000	- 460.000	75,68,73,76,77,8, 78,79

*For Mixtures, $T_R = T/\sqrt{T_{c1} T_{c2}}$

Table II (continued)

Mixture Number	Number of Values	Reduced* Temperature Range		B_{ij} or B_{ij} CC/g-mole		References
		Low	High	Low	High	
54	9	.734	.915	-1360.000	- 716.000	69
14	70	.701	2.877	- 310.000	+ 122.000	57,58,59,60,62, 22,31
43	13	.674	1.413	- 345.000	- 44.000	65,91
55	9	.687	.858	-1922.000	-1047.000	69
6 + 19	3	1.935	2.325	28.070	26.080	31
7 + 19	3	1.051	1.263	- 98.760	- 70.180	31
3 + 19	3	1.148	1.379	- 85.740	- 58.790	31
3 + 17	5	1.414	2.602	- 65.400	5.900	85
3 + 20	5	1.330	2.061	- 84.000	- 2.300	22,86
3 + 22	2	1.224	1.265	- 103.000	- 85.000	86,87
3 + 25	3	1.177	1.276	- 112.000	- 79.000	87
7 + 25	5	1.060	1.224	- 130.000	- 100.000	87
10 + 22	11	0.995	1.705	- 222.000	- 46.000	22,88
10 + 20	17	1.046	2.011	- 183.000	- 29.200	88,22,66

*For Mixtures, $T_R = T/\sqrt{T_{ci} T_{cj}}$

Table II (continued)

Mixture Number	Number of Values	Reduced* Temperature Range		B_{11} or B_{1j} CC/g-mole		References
		Low	High	Low	High	
10 + 17	7	1.131	1.545	-111.900	- 56.000	88,85
10 + 19	14	1.121	1.922	-139.000	- 34.800	88,85,22
10 + 25	4	0.957	1.198	-261.000	-153.000	88
7 + 8	27	0.608	1.819	-236.160	- 23.430	41,31,37
8 + 9	4	0.703	1.109	-229.540	- 94.710	31
8 + 10	18	0.593	1.366	-297.200	- 58.000	31,37
9 + 13	2	0.882	1.392	-138.700	- 52.490	31
9 + 10	3	0.736	1.161	-219.770	- 90.690	31
8 + 13	5	0.738	1.637	-183.130	- 34.650	31
7 + 13	5	0.870	1.930	-122.810	- 18.480	31
7 + 9	5	0.829	1.546	-141.240	- 36.740	31
7 + 3	10	0.652	2.343	-195.000	- 6.160	20,83
6 + 13	5	1.602	3.554	- 14.710	+ 12.230	31
6 + 10	5	1.336	2.964	- 17.960	+ 12.420	31

*For Mixtures, $T_R = T/\sqrt{T_{c1} T_{c2}}$

Table II (continued)

Mixture Number	Number of Values	Reduced* Temperature Range		B_{ij} or B_{ij} CC/g-mole		References
		Low	High	Low	High	
6 + 9	5	1.526	2.847	- 6.620	+ 15,740	31
6 + 8	6	1.536	3.349	- 12.490	+ 12.130	31
6 + 7	9	1.100	3.948	- 35.300	+ 12,150	20,83
6 + 3	9	1.201	4.314	- 31,000	+ 14,960	20,83
3 + 9	4	0.905	1.690	-125,430	- 27,150	31
3 + 8	6	0.911	1.987	-119,580	- 17,080	31
13 + 14	2	1.110	1.358	- 88,980	- 58,440	31
10 + 12	16	1.310	2.989	- 62,070	+ 18,880	7
9 + 14	2	0.752	0.920	-185,080	-124,730	31
8 + 14	2	0.884	1.082	-120,270	- 82,240	31
7 + 14	3	1.042	1.276	- 74,780	- 50,620	31
7 + 10	19	0.631	1.616	-233,100	- 35,200	37,31
37 + 27	5	0.840	0.913	-668,000	-523,000	73
3 + 14	8	1.139	2.032	- 77,450	- 17,700	31,22

*For Mixtures, $T_R = T/\sqrt{T_{c1} T_{c2}}$

Table II (continued)

Mixture Number	Number of Values	Reduced* Temperature Range		B_{ij} or B_{ij} CC/g-mole		References
		Low	High	Low	High	
3 + 37	3	1.137	1.175	-122.000	-108.000	87
7 + 24	2	1.131	1.169	- 94.000	- 78.000	86
6 + 14	3	1.919	2.349	3.820	+ 6.250	31
10 + 23	8	1.053	1.400	-165.000	- 78.000	54
10 + 44	5	1.269	1.593	- 85.000	- 33.000	54
10 + 21	6	1.233	1.830	-125.500	- 40.400	22
14 + 17	7	1.020	1.676	-103.000	- 26.000	85
14 + 19	6	0.927	1.523	-154.500	- 42.000	22
43 + 15	5	0.912	1.195	-240.000	-134.000	91
17 + 29	4	1.131	1.430	-146.000	- 82.300	22
10 + 14	7	1.290	2.119	- 63.600	- 8.400	22
17 + 19	4	0.887	1.110	-274.000	-165.000	88
17 + 20	4	0.827	1.025	-362.000	-215.000	88
17 + 22	4	0.787	0.985	-448.000	-272.000	88

*For Mixtures, $T_R = T/\sqrt{T_{ci} T_{cj}}$

Table II (continued)

Mixture Number	Number of Values	Reduced* Temperature Range		B ₁₁ or B _{1j} CC/g-mole		References
		Low	High	Low	High	
17 + 25	4	0.757	0.947	- 540.000	-319.000	88
19 + 20	4	0.752	0.941	- 540.000	-316.000	88
19 + 22	4	0.715	0.895	- 671.000	-399.000	88
19 + 25	4	0.688	0.861	- 822.000	-478.000	88
20 + 22	4	0.667	0.835	- 928.000	-540.000	88
20 + 25	4	0.645	0.803	-1111.000	-650.000	88
14 + 20	4	1.050	1.328	- 130.600	- 65.000	22
22 + 54	3	0.694	0.864	- 969.000	-625.000	22
22 + 55	3	0.671	0.838	-1180.000	-643.000	22
22 + 25	3	0.662	0.764	-1229.000	-838.000	88
22 + 54	3	0.694	0.864	- 969.000	-625.000	22
22 + 55	3	0.671	0.838	-1184.000	-643.000	22

*For Mixtures, $T_R = T/\sqrt{T_{c_i} T_{c_j}}$

TABLE III

POTENTIAL PARAMETERS FROM $B_{ij}(T)$ DATA

Substance Number	r^{-6} Potential				Rectangular Well Potential			
	σ_1 cm/mole ^{1/3}	σ_2 cm/mole ^{1/3}	ϵ/k °K	rms cc/mole	σ_1 cm/mole ^{1/3}	σ_2 cm/mole ^{1/3}	ϵ/k °K	rms cc/mole
3	2.767	3.038	173.7	0.59	2.750	4.261	102.1	0.55
7	2.605	3.160	145.0	2.32	2.568	4.282	99.8	2.33
8	2.813	3.409	201.4	2.14	2.759	4.583	140.9	2.17
9	3.073	3.663	291.3	1.26	3.030	4.990	196.4	1.31
10	2.854	3.334	210.5	3.26	2.794	4.480	144.0	3.39
12	3.495	3.596	353.9	3.43	3.454	4.984	209.4	2.10
13	2.840	3.249	152.1	.17	2.820	4.529	94.3	0.17
4	2.624	3.113	155.7	4.15	2.566	4.185	107.4	4.15
39	3.120	3.317	443.2	.15	3.041	4.503	267.7	0.16
19	3.756	4.071	522.1	7.52	3.592	5.347	345.0	7.55
16	3.479	4.471	191.7	.70	3.460	6.264	125.1	0.70
17	3.246	3.762	350.4	5.64	3.154	5.033	239.2	5.60
38					5.344	7.262	415.1	18.73
23	4.538	4.649	743.0	13.20	4.238	6.012	452.3	13.26

Table III (continued)

Substance Number	r^{-6} Potential				Rectangular Well Potential			
	σ_1 cm/mole ^{1/3}	σ_2 cm/mole ^{1/3}	ϵ/k °K	rms cc/mole	σ_1 cm/mole ^{1/3}	σ_2 cm/mole ^{1/3}	ϵ/k °K	rms cc/mole
30	4.004	4.100	754.8	3.72	3.614	5.138	477.2	3.70
20	3.695	3.767	902.7	8.37	3.234	4.591	583.5	8.55
22	3.970	4.067	980.3	10.79	3.275	4.752	667.1	10.98
6					1.989	2.367	109.7	0.16
41					4.895	1.031	68.4	1.92
15					2.441	3.256	503.2	3.99
25					3.577	4.825	822.2	30.49
54					5.171	6.308	639.0	10.36
14					2.607	3.355	469.7	8.99
43					2.039	2.651	789.8	2.45

SECTION IV

CORRELATION OF POTENTIAL PARAMETERS WITH CRITICAL PROPERTIES AND THE ACENTRIC FACTOR

To establish interdependence among the three parameters of each potential and the constants T_c , V_c , and ω for each pure substance, a three-step procedure was used.

σ_1 Correlation Procedure

In this step an expression involving the previously calculated distance parameter, σ_1 , was plotted against the acentric factor for each pure component. The resulting plots for each potential were similar, so only the plot for the rectangular well potential is shown in Fig. 4. It will be noticed that there is considerable scatter in V_c/σ_1^3 , when plotted in this manner. A possible explanation for this scatter may be found by examining equation 36, the expression for B_{ij} for the rectangular well potential. For $T < \epsilon_{ij}/k$, the second term in square brackets is much larger than the σ_1^3 term so that it is difficult to determine σ_1 from low temperature virial coefficient data. At high temperatures the virial coefficient is sensitive to the value of σ_1^3 . A similar situation occurs for the r^{-6} potential. Thus in order to determine σ_1^3 precisely, high temperature virial coefficient data are required. Table II shows that many of the substances which deviate greatly from the line $V_c/\sigma_1^3 = 4.25$ have data with a relatively low ($0.5 < T/T_c < 1.5$) reduced temperature range. Therefore, it is believed that the deviation of the computed points from the correlation is due to insufficient data, not to the influence of additional parameters which should be included in the correlation. Taking this into

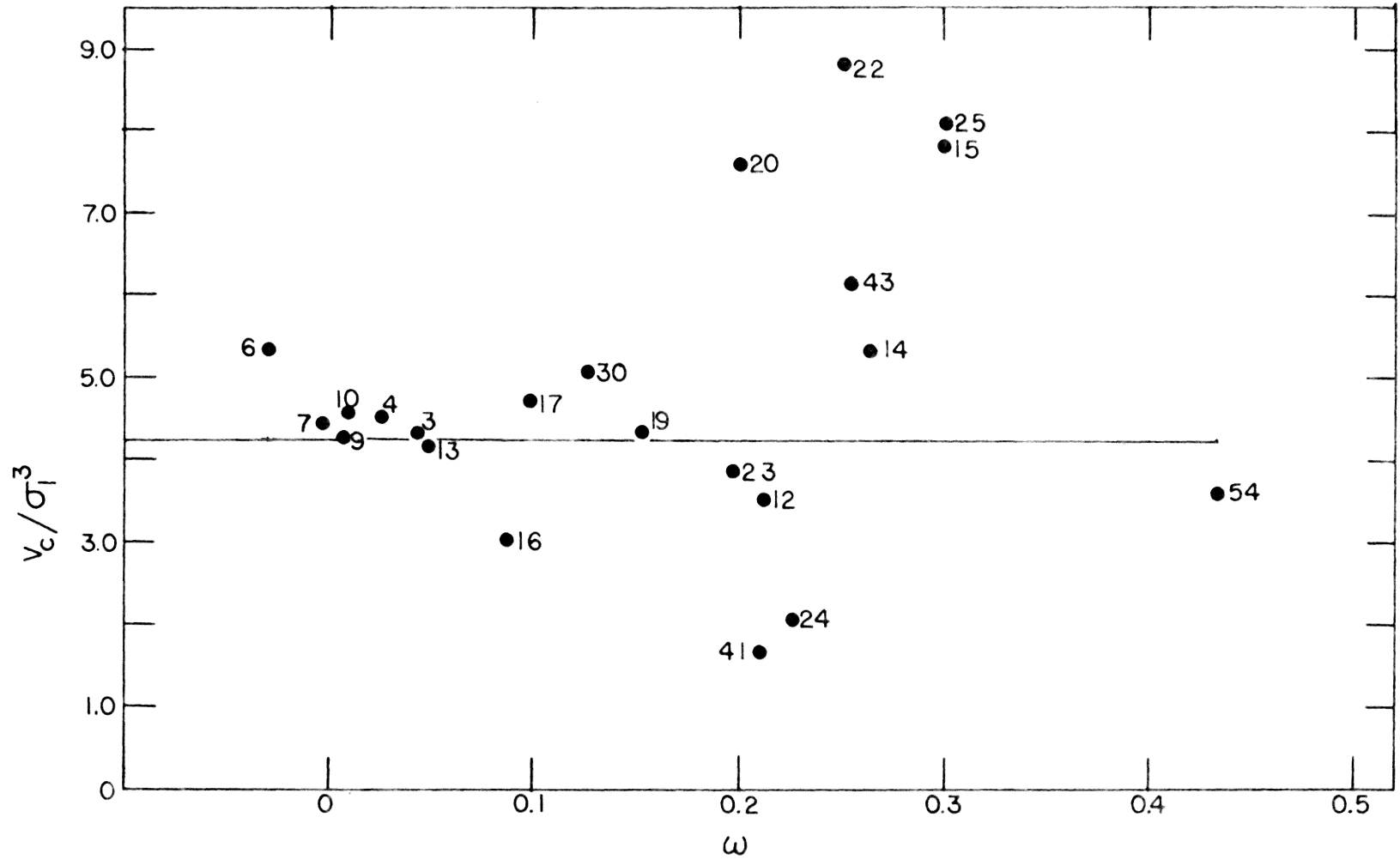


FIG. 4. CORRELATION OF σ_1 FOR RECTANGULAR WELL POTENTIAL

consideration, it was decided to assume that σ_1 is independent of ω and is given by $\sigma_1' = (V_c/4.25)^{1/3}$.

Next, the potential parameters σ_2 and ϵ were recalculated for each potential while σ_1 was held constant at $(V/4.25)^{1/3}$. The results showed that fixing σ_1 did not increase the error in the predicted virial coefficient above what is considered to be due to experimental error, and that the scatter in the computed σ_2 and ϵ data was reduced significantly.

σ_2 Correlation Procedure

With σ_1 fixed, σ_2 and ϵ were computed using the iterative least squares technique. The values computed for σ_2 were then examined to determine whether they could be correlated with the acentric factor. After several trial graphs, it was determined that, if $\log(\sigma_2/\sigma_1 - 1)$ were graphed versus $\log(1 + \omega)$, a straight line could reasonably be drawn through the calculated points as shown in Fig. 5 and Fig. 6.

The straight line drawn through the rectangular well calculated parameters has the mathematical expression given in equation 37.

$$\sigma_2' = (V_c/4.25)^{1/3} [1.0 + 0.66 (1 + \omega)^{-3.40}] \quad (37)$$

The deviation from this line for the two fluorocarbon compounds C_5F_{12} and C_6F_{14} appeared with all attempts to correlate σ_2 . This could be due to experimental error or to the influence of a fourth parameter.

A straight line may be drawn through the calculated parameters of the r^{-6} potential as well, but with not quite so high a degree of confidence. The equation of this line is:

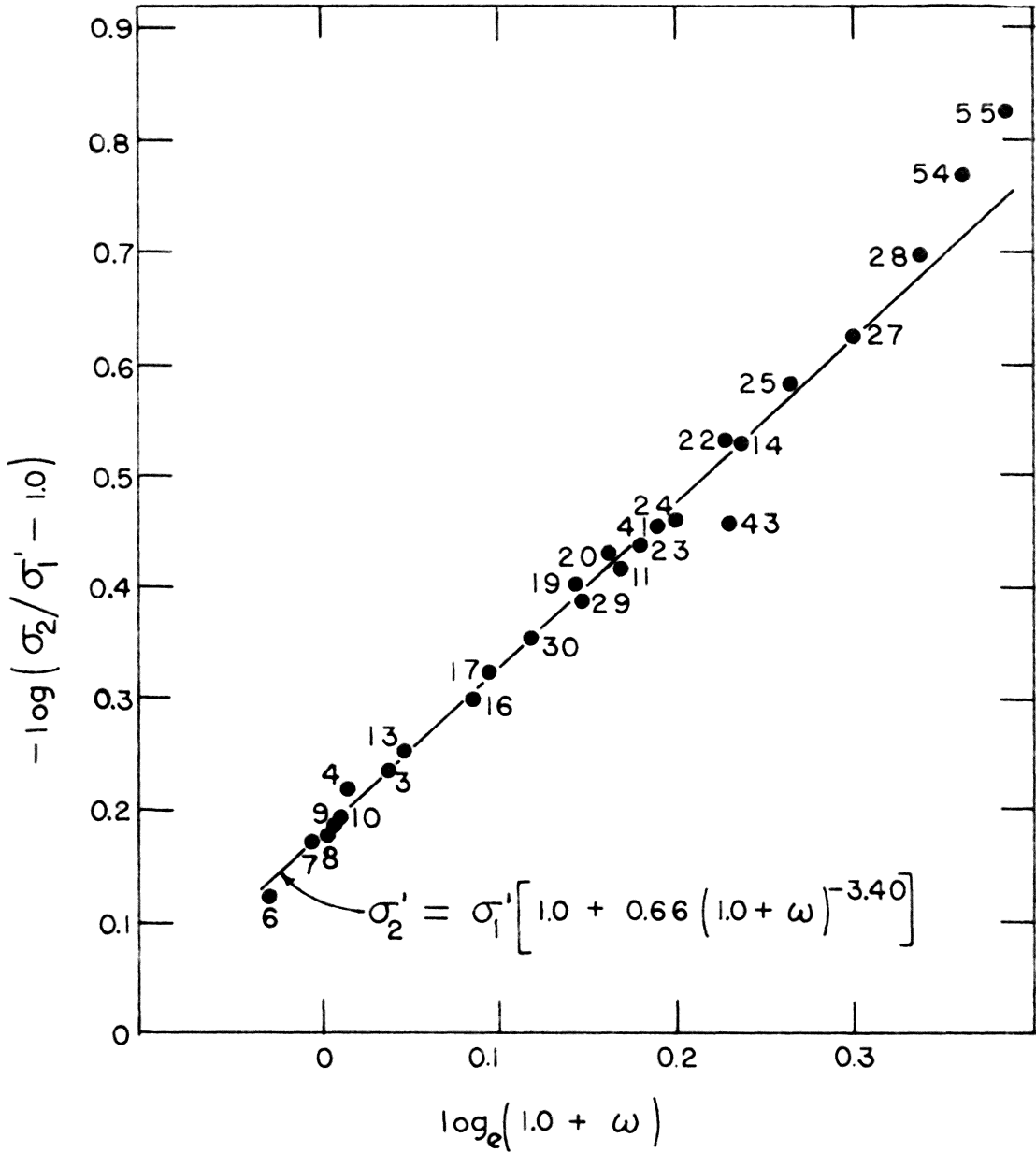


FIG. 5. CORRELATION OF σ_2 FOR RECTANGULAR WELL POTENTIAL

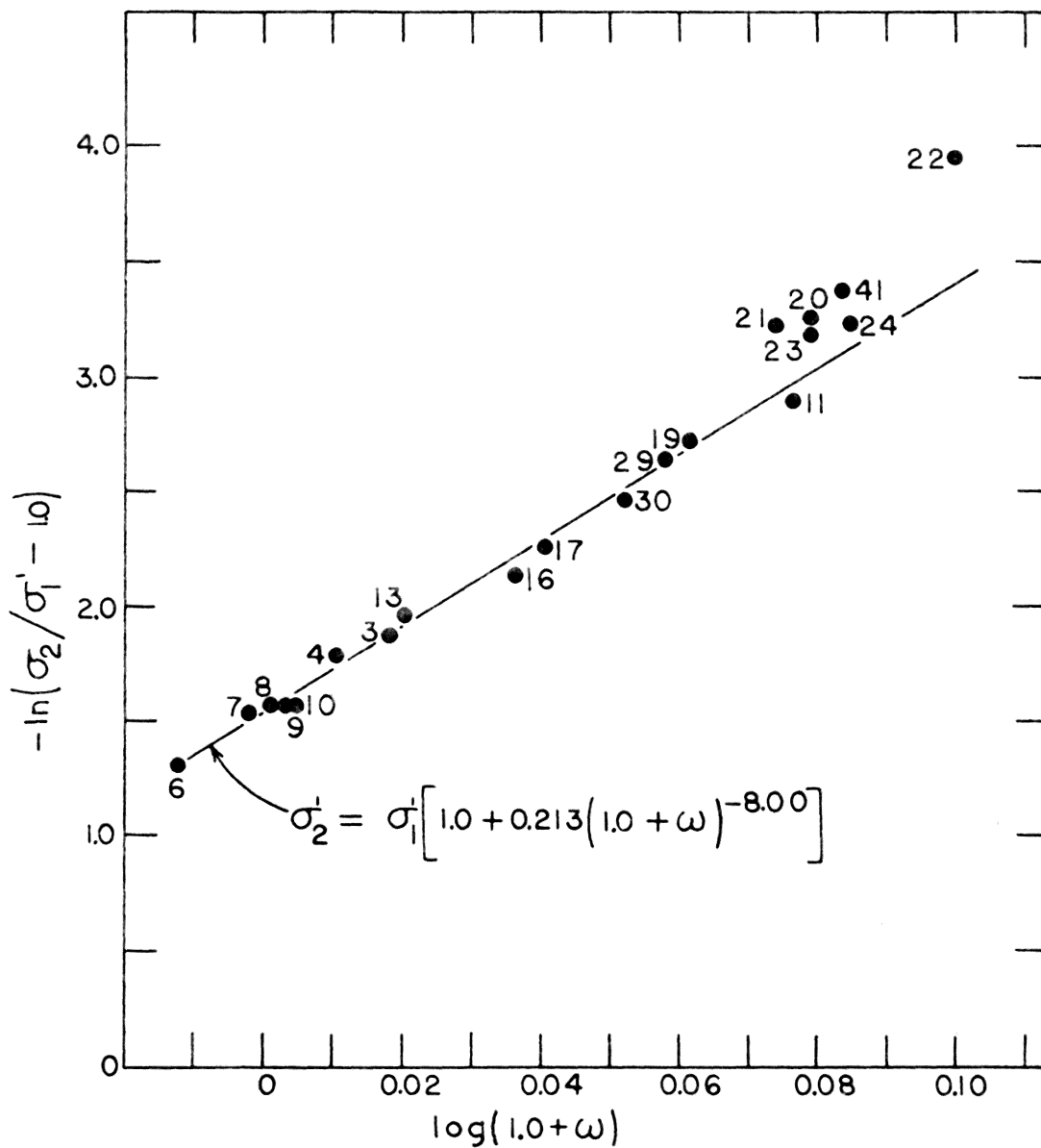


FIG. 6. CORRELATION OF σ_2 FOR r^{-6} POTENTIAL

$$\sigma_2' = \sigma_1' [1.0 + 0.213(1.0 + \omega)^{-8.00}] \quad (38)$$

There seems to be a definite curvature to the points in the upper portion of the curve. This deviation may be the result of the same unknown phenomena causing the deviation from the line drawn in the rectangular well graph.

Before the third correlation procedure was attempted, σ_2 was fixed along with σ_1 for each potential and ϵ was again calculated. As a result of this action, the rms deviation was usually increased by more than 10 per cent.

ϵ Correlation Procedure

For the rectangular well potential, the ratio of the new ϵ to kT_c was plotted versus ω as shown in Fig. 7. Most of the calculated points fall near the straight line

$$\epsilon' = T_c (0.66 + 2.73\omega)k \quad (39)$$

Again, the compounds C_5F_{12} and C_6F_{14} deviate from the line.

A slightly different plot was used for correlating for the r^{-6} potential. It was found that the line

$$\epsilon' = T_c [0.970 + 9.0667 \log_{10}(1.0 + \omega)]k \quad (40)$$

represented the data, but with considerable scatter as shown in Fig. 8.

Table IV presents a comparison of the final correlated parameters of each potential. The rms deviation given by the Pitzer and Curl correlation is also presented in Table IV. Table IV should be compared with Table III which shows the resulting potential parameters when all

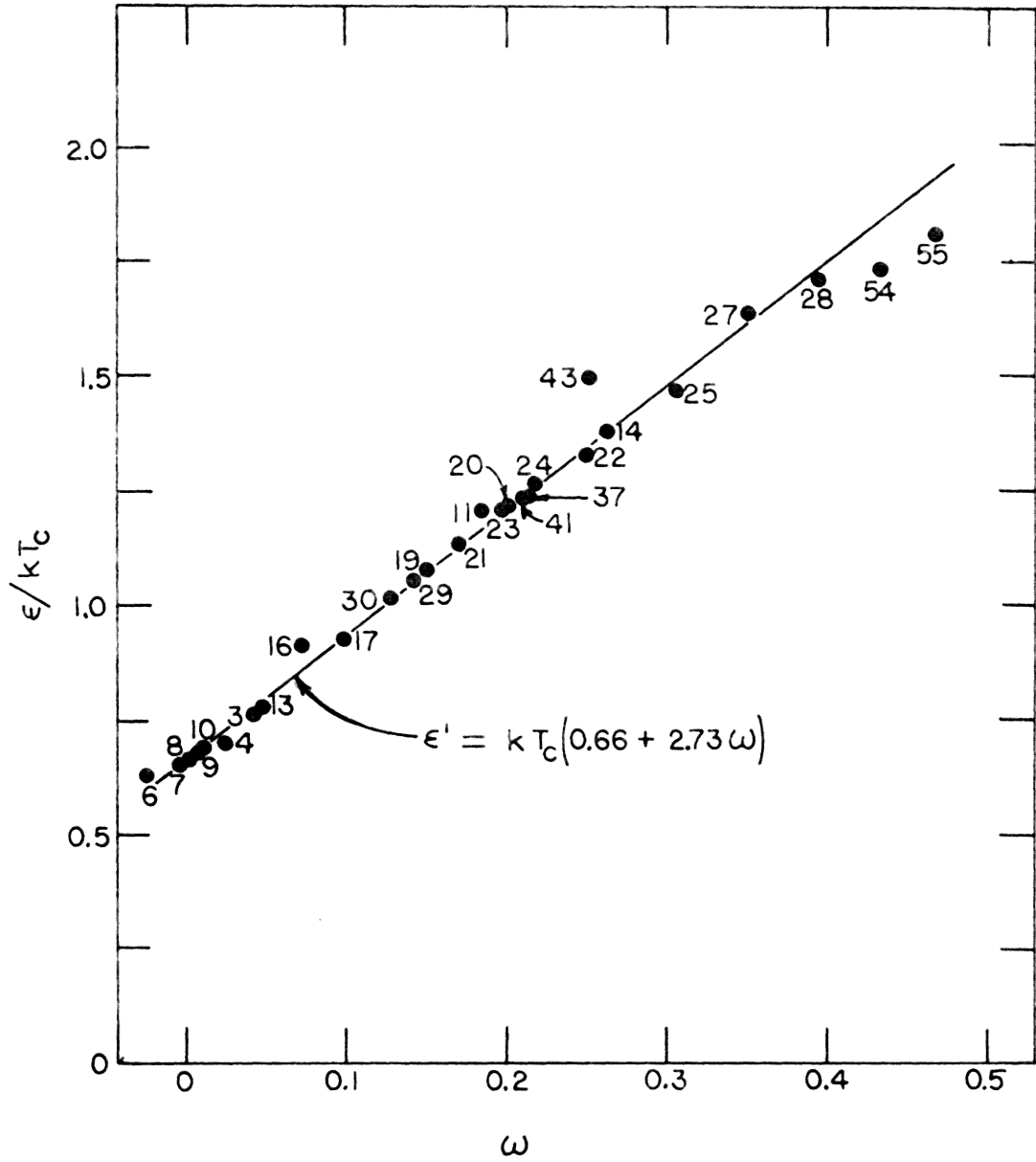


FIG. 7. CORRELATION OF ϵ FOR RECTANGULAR WELL POTENTIAL

$$(\sigma_1 = \sigma_1', \sigma_2 = \sigma_2')$$

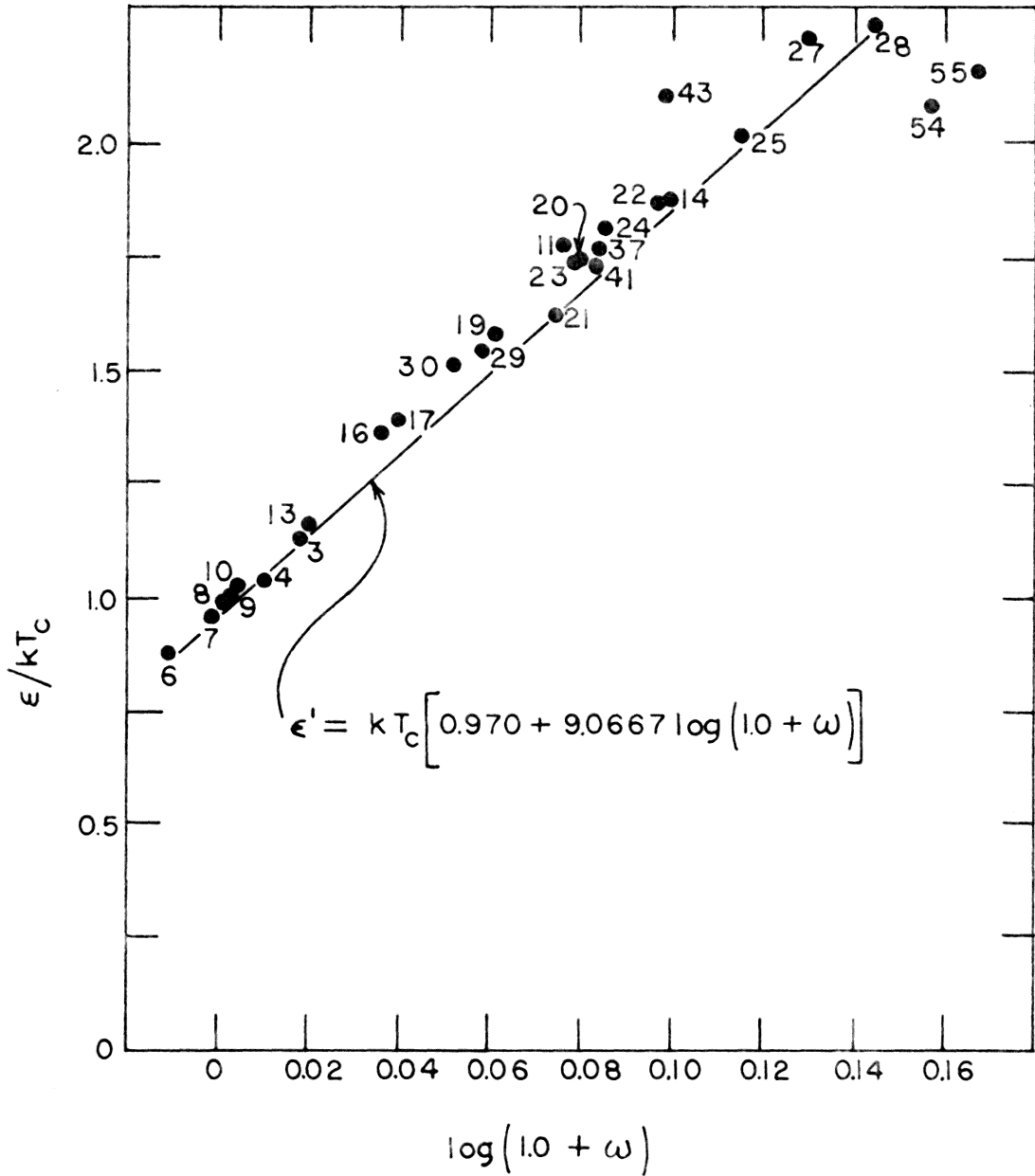


FIG. 8. CORRELATION OF ϵ FOR r^{-6} POTENTIAL
($\sigma_1 = \sigma_1'$, $\sigma_2 = \sigma_2'$)

TABLE IV

COMPARISON OF CORRELATED POTENTIAL PARAMETERS

Substance Number	Curl and Pitzer (13) rms cc/mole	r^{-6} Potential				Rectangular Well Potential			
		σ_1 cm/mole	σ_2 cm/mole	ϵ/k °K	rms cc/mole	σ_1 cm/mole	σ_2 cm/mole	ϵ/k °K	rms cc/mole
3	1.14	2.767	3.192	143.7	1.25	2.767	4.357	96.7	1.13
6	6.80	2.142	2.704	39.0	.99	2.142	3.686	28.3	1.37
7	4.34	2.607	3.172	143.3	3.36	2.607	4.340	97.9	2.85
8	9.80	2.789	3.362	207.1	2.24	2.789	4.602	140.8	2.33
9	2.65	3.035	3.641	290.5	1.62	3.035	4.984	197.4	1.37
10	7.55	2.856	3.418	195.4	5.21	2.856	4.678	132.3	4.18
12	8.02	3.256	3.405	372.8	10.42	3.256	4.374	281.0	2.80
13	1.00	2.800	3.207	153.9	.87	2.799	4.371	103.5	2.12
41	3.42	3.574	3.740	551.9	5.94	3.574	4.808	397.9	7.10
29	9.84	3.492	3.748	565.7	18.86	3.492	4.955	384.7	6.17
4	4.70	2.620	3.077	161.0	8.04	2.620	4.208	108.1	11.82
19	1.07	3.610	3.857	584.2	19.41	3.610	5.079	398.8	11.00
11	113.83	4.018	4.229	988.2	226.54	4.018	5.482	673.8	92.75
16	4.21	3.079	3.415	384.2	10.70	3.079	4.610	257.4	3.97

Table IV (continued)

Substance Number	Curl and Pitzer (13) rms cc/mole	r^{-6} Potential				Rectangular Well Potential			
		σ_1 cm/mole	σ_2 cm/mole	ϵ/k °K	rms cc/mole	σ_1 cm/mole	σ_2 cm/mole	ϵ/k °K	rms cc/mole
15	7.09	2.985	3.063	588.9	17.41	2.985	3.792	457.2	6.28
17	8.24	3.266	3.592	420.1	9.99	3.266	4.829	282.1	8.65
24	29.57	4.169	4.354	839.0	82.03	4.169	5.581	584.0	32.84
23	22.17	4.147	4.355	749.9	36.74	4.147	5.627	521.5	17.34
30	451.20	3.842	4.155	636.3	45.28	3.842	5.526	426.8	9.30
21	31.69	3.955	4.171	662.3	18.64	3.955	5.417	465.0	32.26
20	12.09	3.915	4.107	737.6	26.11	3.915	5.301	515.2	12.17
22	26.11	4.183	4.330	878.1	18.15	4.183	5.467	627.8	26.86
25	43.61	4.424	4.537	1024.9	45.46	4.424	5.610	748.2	48.11
27	264.49	4.645	4.735	1179.6	257.10	4.645	5.751	884.4	226.01
28	35.81	4.854	4.926	1257.8	180.18	4.854	5.888	970.3	122.70
37	46.69	3.940	4.121	1000.9	83.35	3.940	5.293	691.9	53.87
54	122.66	4.867	4.925	889.6	426.84	4.867	5.810	728.0	238.45
14	10.31	2.809	2.901	570.3	12.20	2.809	3.647	421.1	9.31
43	29.12	2.574	2.664	861.7	46.85	2.574	3.363	613.7	43.10
55	325.79	5.134	5.184	988.4	678.94	5.134	6.050	812.8	429.52

three parameters are free in the curve fitting technique.

Table IV shows that the r^{-6} correlations for the nonspherical molecules are not as accurate as the rectangular well parameters. The rectangular well potential compares closely to the Pitzer and Curl values. For these reasons, it was decided not to consider the r^{-6} potential in the work toward determining the best combining rules.

SECTION V

DETERMINATION OF EMPIRICAL COMBINING RULES

FOR BINARY MIXTURES

As was discussed in Section III, intermolecular potential parameters for the interaction of unlike molecules may be obtained from curve fits of interaction second virial coefficient data. This is carried out in precisely the same manner as for determining the pure component potential parameters. The values of the interaction potential parameters, σ_{11j} , σ_{21j} , and ϵ_{1j} , obtained are listed in Table V. The iterative curve fitting technique would not converge for those mixtures which have no values listed. The work described in this section was done in order to find combining rules for the unlike interaction potential parameters which would approximate the values calculated from the interaction second virial coefficients.

The interaction virial coefficient data employed to compute the interaction potential parameters generally are not as accurate as the data for pure components. The reason for this is that the interaction virial coefficient data cannot be measured directly, but must be calculated from data measured for the mixture combined with data measured for the pure components of the mixture. For example, if the virial coefficient for a binary mixture is measured for a known mixture composition, then equation 34 may be solved to determine the interaction virial. The result is:

$$B_{ij}(T) = [B_m - X_1^2 B_1 - X_j^2 B_j] / 2X_1 X_j \quad (41)$$

Thus it may be seen that the interaction virial is subject to errors

TABLE V

UNCORRELATED INTERACTION RECTANGULAR WELL PARAMETERS

Mix. Code Num.	σ_{11j}	σ_{21j}	ϵ_{1j}/k	rms	Mix. Code Num.	σ_{11j}	σ_{21j}	ϵ_{1j}/k	rms
7+8	2.808	5.043	88.5	1.80	10+17	2.302	3.365	344.6	1.23
8+9	3.059	5.161	142.3	.56	10+19	2.518	3.447	432.1	2.35
8+10	2.773	4.636	133.6	.99	10+21	3.140	4.281	367.4	1.52
9+13	2.894	4.721	129.9	0.00	14+19	3.102	4.288	355.2	3.08
9+10	2.982	4.960	149.9	0.00	15+43	3.208	4.792	345.6	.73
8+13	2.777	4.677	105.0	0.14	10+14	2.876	4.104	244.2	.06
7+13	2.702	4.545	88.8	0.11	17+19	3.689	5.369	299.7	.50
7+9	2.758	4.550	137.0	0.48	17+22	3.942	5.627	360.9	1.63
7+3	2.858	5.537	52.8	.95	17+25	5.874	10.616	113.7	4.21
6+13	2.411	3.568	63.1	.02	19+20	4.224	5.758	404.7	.46
6+10	2.490	3.906	53.5	.07	19+22	4.096	5.651	447.4	1.35
6+9	2.541	3.448	101.0	.32	19+25	5.058	6.861	389.9	2.84
6+7	2.373	4.755	25.1	.12	20+22	4.275	5.762	513.9	1.31
3+9	2.978	4.958	111.5	.08	14+20	1.622	2.064	1040.3	.36
3+8	2.863	5.133	80.4	.17	3+20	3.556	4.759	263.9	.45
13+14	2.570	4.077	172.9	.00	3+37	4.250	5.522	274.2	.41
10+12	3.184	4.973	142.2	.06	7+24	4.147	4.598	507.7	.00
9+14	2.969	4.817	189.5	.00	10+22	2.835	3.423	639.0	5.43
8+14	2.446	4.082	190.6	.00	10+20	2.606	3.398	527.8	3.32
7+10	2.573	4.318	117.4	7.11					
3+17	2.589	2.944	535.0	2.23					
3+14	2.806	5.558	73.8	1.31					

in the mixture virial, the mixture composition, and the pure component virials.

Since the interaction virial coefficients, generally, are not as accurate as the pure component virials, the interaction parameters computed from them cannot be correlated as readily as the parameters computed from pure component data. In this work it was found that the existing data is not of sufficient quality to permit evaluation of individual combining rules for all three molecular parameters. However, it was found that if one of the parameters is fixed according to existing theory, then the other two parameters can be determined and correlated in terms of pure component data.

Combining Rule for σ_{1ij}

As a first step in finding a combining rule for σ_{1ij} , it was decided to test the rule given by equation 29. When the correlation for σ_1 is applied to this rule, the result is

$$\sigma''_{1ij} = (\sigma'_{1i} + \sigma'_{1j})/2 \quad (42)$$

This rule results from assuming that the repulsive forces between molecules become significant at separation distances for which the electrons of adjacent molecules are very close together. For interactions between like molecules, this distance corresponds to twice the radius of the molecules. Thus σ_1 is approximately twice the radius of the molecule. For interactions between unlike molecules, the separation distance corresponding to physical contact of the electrons is the sum of the molecular radii. Substituting $\sigma_1/2$ for the molecular radius gives equation 42. The interaction parameters

from the $B_{ij}(T)$ data were plotted versus equation 42 in Fig. 9. To discuss the points in Fig. 9 it is convenient to divide them into three groups.

The first group of points represents those mixtures in which only interactions of spherically symmetrical molecules occur. The interaction σ_{1ij} term computed for these mixtures generally fall on the line representing equation 42. Experimental data usually exists over a wide range of temperature for these substances.

The second group are representative of mixtures in which there are interactions of spherically symmetrical and long-chain hydrocarbon molecules. These points generally fall below the line given by equation 42. For some of these points the value of σ_{1ij} is much less than the value of σ_1 of the component of the mixture with the smaller molecules. Since there is no theoretical explanation for this, it is believed that part of the deviation of the points from the line representing equation 42 is due to errors in the experimental data. None of the experimental data for this group of mixtures is for high temperatures.

The points which have large σ_{1ij} and are above the line correspond to mixtures in which there are interactions between long-chain hydrocarbon molecules. The value of σ_{1ij} computed for some of the substances is larger than the value of σ'_{1i} for either of the molecules which are interacting. This is believed to be due to experimental error since none of the data for these substances are measured at high temperatures.

Since all of the experimental data which covers a substantial range of temperature is represented fairly accurately by equation 42,

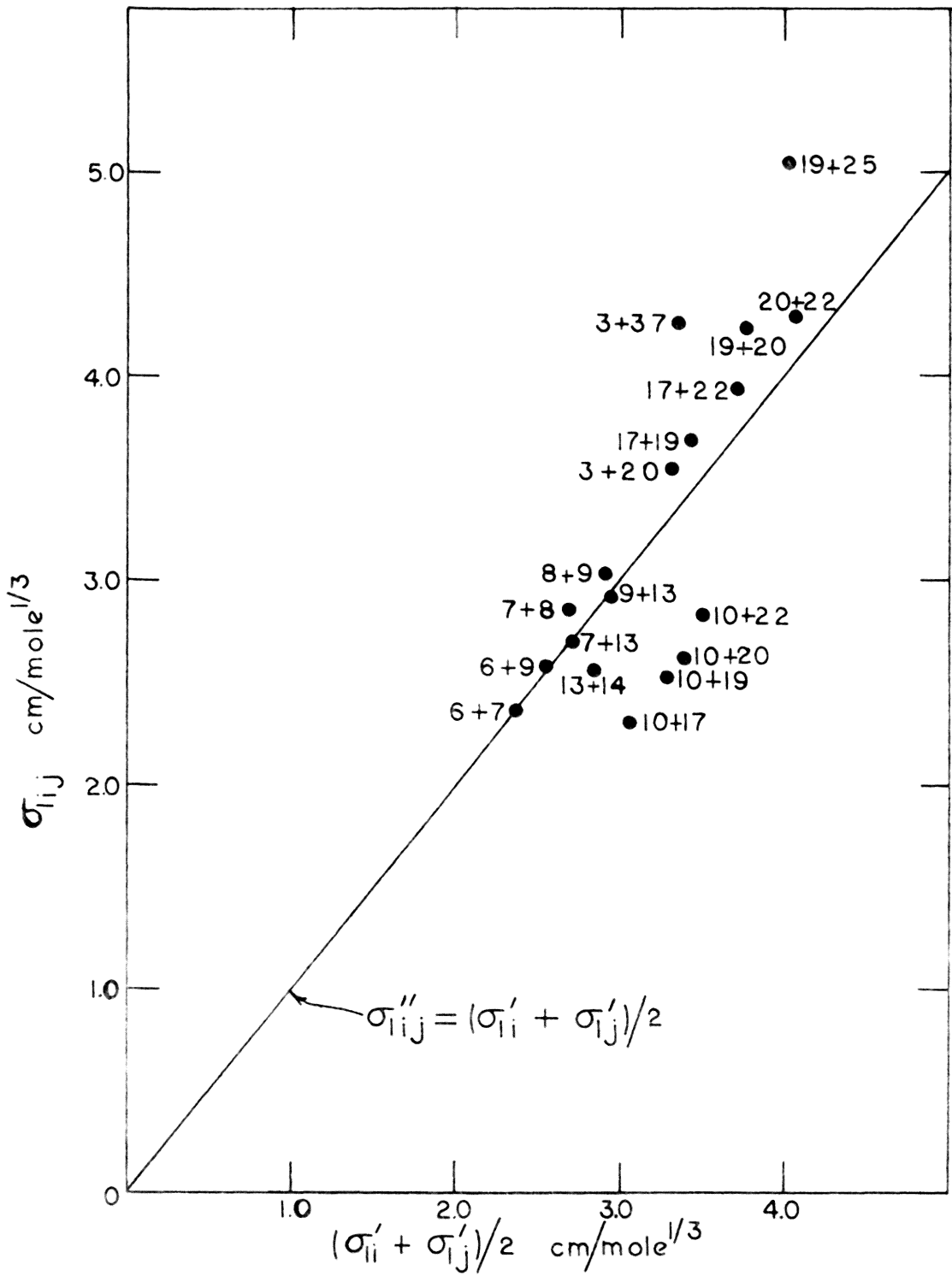


FIG. 9. σ_{ij} CORRELATION FOR RECTANGULAR WELL POTENTIAL (selected representative points)

it was decided to fix σ_{1ij} according to this equation and to recalculate σ_{2ij} and ϵ_{ij} . The results showed that this did not increase the error in the predicted interaction virial coefficient significantly. Table VI illustrates this fact by comparing the two curve fits of a mixture from the second group.

Combining Rules for σ_{2ij} and ϵ_{ij}

It was discovered that the choice of combining rule for σ_{2ij} had a marked effect on the ability to find a combining rule for ϵ_{ij} . For this reason the description of the work done in determining the empirical combining rule for ϵ_{ij} must be presented along with the work done in finding the σ_{2ij} combining rule.

One may choose the form of equation 42 as a possible form for the σ_{2ij} combining rule. When this is done equation 43 results.

$$\sigma_{2ij}'' = (\sigma_{2i}' + \sigma_{2j}')/2 \quad (43)$$

Figure 10 shows the correlation of this combining rule with values of σ_{2ij}' , calculated from the data when σ_{1ij} was fixed at $(\sigma_{1i}' + \sigma_{1j}')/2$. Equation 43 represents most of the points in Fig. 10.

In Appendix C an expression for the ϵ_{ij} combining rule is developed for three-parameter potentials. In this development only the long-range attractive forces between molecules are considered, and the forces are considered to be proportional only to the distance of separation. The result of this development is:

$$\epsilon_{ij}'' = \sqrt{\epsilon_i \epsilon_j} \left(\frac{\sqrt{\sigma_{2i}' \sigma_{2j}'}}{\sigma_{2ij}'} \right)^n \quad (44)$$

TABLE VI
METHANE - PENTANE INTERACTION

$T_R = T/\sqrt{T_{c_i} T_{c_j}}$	B_{ij} cc/mole	Deviation From B_{ij}	
		$\sigma_{lij} = 2.83$	$\sigma''_{lij} = \frac{\sigma'_{li} + \sigma'_{lj}}{2} = 3.52$
1.00	-222	-3.30 cc/mole	0.42 cc/mole
1.08	-190	11.96	11.15
1.16	-148	4.65	2.22
1.26	-107	-6.12	-8.51
1.48	- 67	-1.88	-1.14
1.70	- 46	3.27	8.09

rms = 5.43 cc/mole rms = 6.02 cc/mole

$\epsilon_{ij}/k = 639^\circ\text{K}$ $\epsilon_{ij}/k = 419^\circ\text{K}$

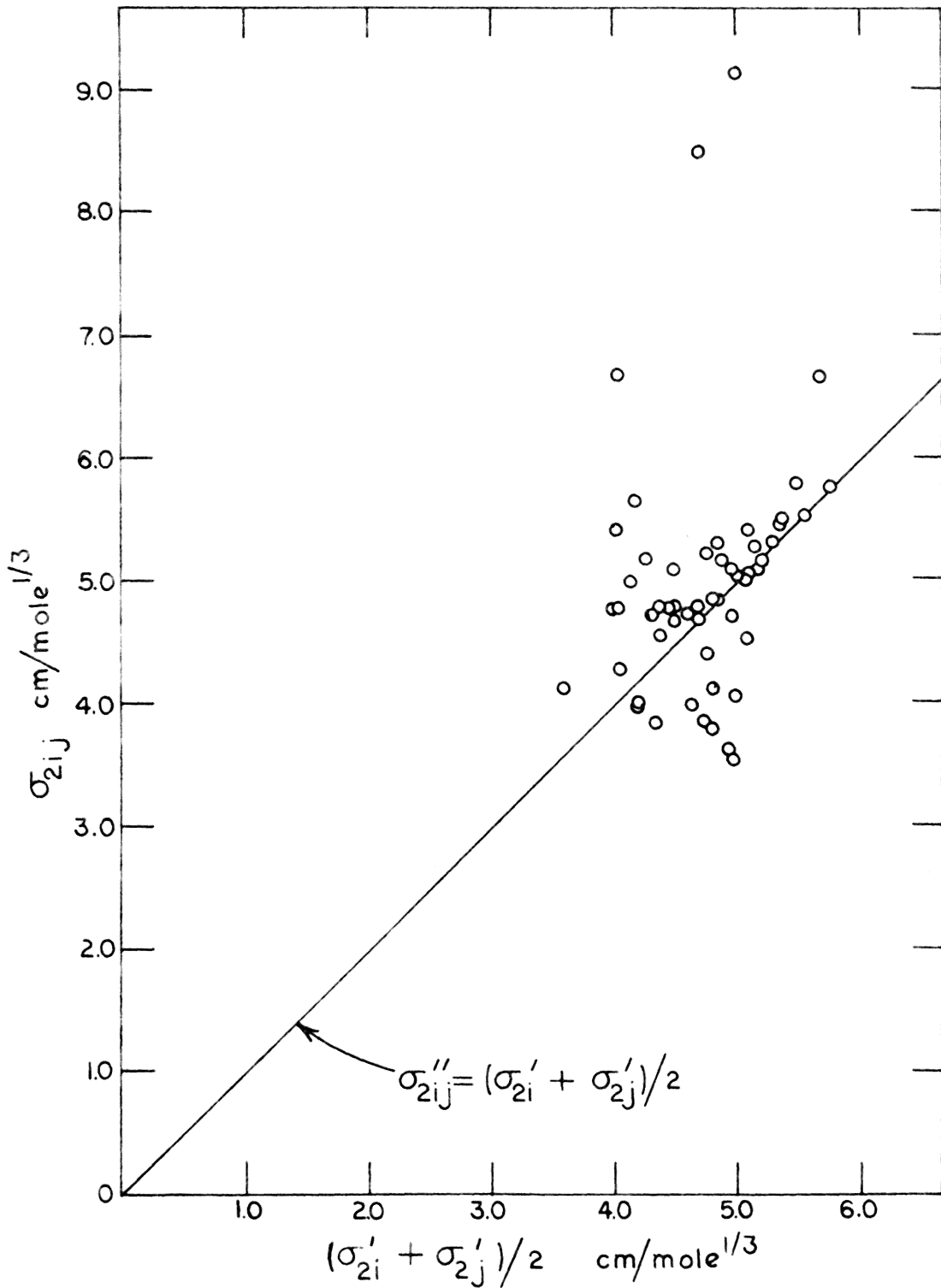


FIG. 10. TEST OF EQUATION 43 FOR σ_{2ij}''

where n is to be found empirically. This result should be compared with that of Hudson and McCoubrey [6]:

$$\epsilon''_{ij} = \sqrt{\epsilon_i \epsilon_j} \left(\frac{\sqrt{\sigma_i \sigma_j}}{\sigma_{ij}} \right)^6 \left\{ \frac{2(I_i I_j)^{1/2}}{I_i + I_j} \right\} \quad (45)$$

which was obtained by considering London dispersion forces.

Data for the ionization potentials appearing in equation 45 are not available for all of the substances studied in this work. Table VII shows values of the terms containing the ionization potentials for several mixtures for which data could be found in the literature. From Table VII it may be seen that the correction to the combining rule due to this term is very small.

The ionization potential term is neglected altogether in this work. Since this term is always less than unity, the combining rule of this work should always produce results which are slightly larger than the actual values.

When equation 43 is used to fix σ_{21j} and equation 42 is used to fix σ_{1ij} while ϵ_{ij} is calculated from the data for unlike pairs, the resulting ϵ_{ij} may be used to determine the n in equation 44. Figure 11 is a plot of $\log(\epsilon_{ij}/\sqrt{\epsilon'_i \epsilon'_j})$ versus $\log(\sqrt{\sigma'_{2i} \sigma'_{2j}}/\sigma_{2ij})$. Only mixtures with at least five data points are plotted in Fig. 11. Unfortunately, the points in Fig. 11 cannot be represented by a single straight line. It was found that much of the scatter in this data could be removed by changing the σ_{21j} combining rule.

Employing equation 29 as the form of the σ_{1ij} combining rule and equation 37 as an example of the correlated pure component σ'_2 , an

TABLE VII
THE IONIZATION POTENTIAL CORRECTION FACTOR

Substance <u>i</u>		Substance <u>j</u>		$\frac{2\sqrt{I_j I_i}}{I_j + I_i}$
Chemical Symbol	I_i [92] e.v.	Chemical Symbol	I_j [92] e.v.	
CH ₄	12.60	C ₂ H ₆	11.50	.9990
CH ₄	12.60	C ₃ H ₈	11.10	.9980
CH ₄	12.60	C ₄ H ₁₀	10.63	.9964
CH ₄	12.60	C ₅ H ₁₂	10.35	.9952
C ₃ H ₈	11.10	C ₄ H ₁₀	10.63	.9998
Ar	15.76	Ne	21.56	.9878
Xe	12.13	Kr	13.996	.9974
O ₂	12.50	N ₂	15.50	.9942
Ne	21.56	C ₆ H ₁₄	10.18	.9335

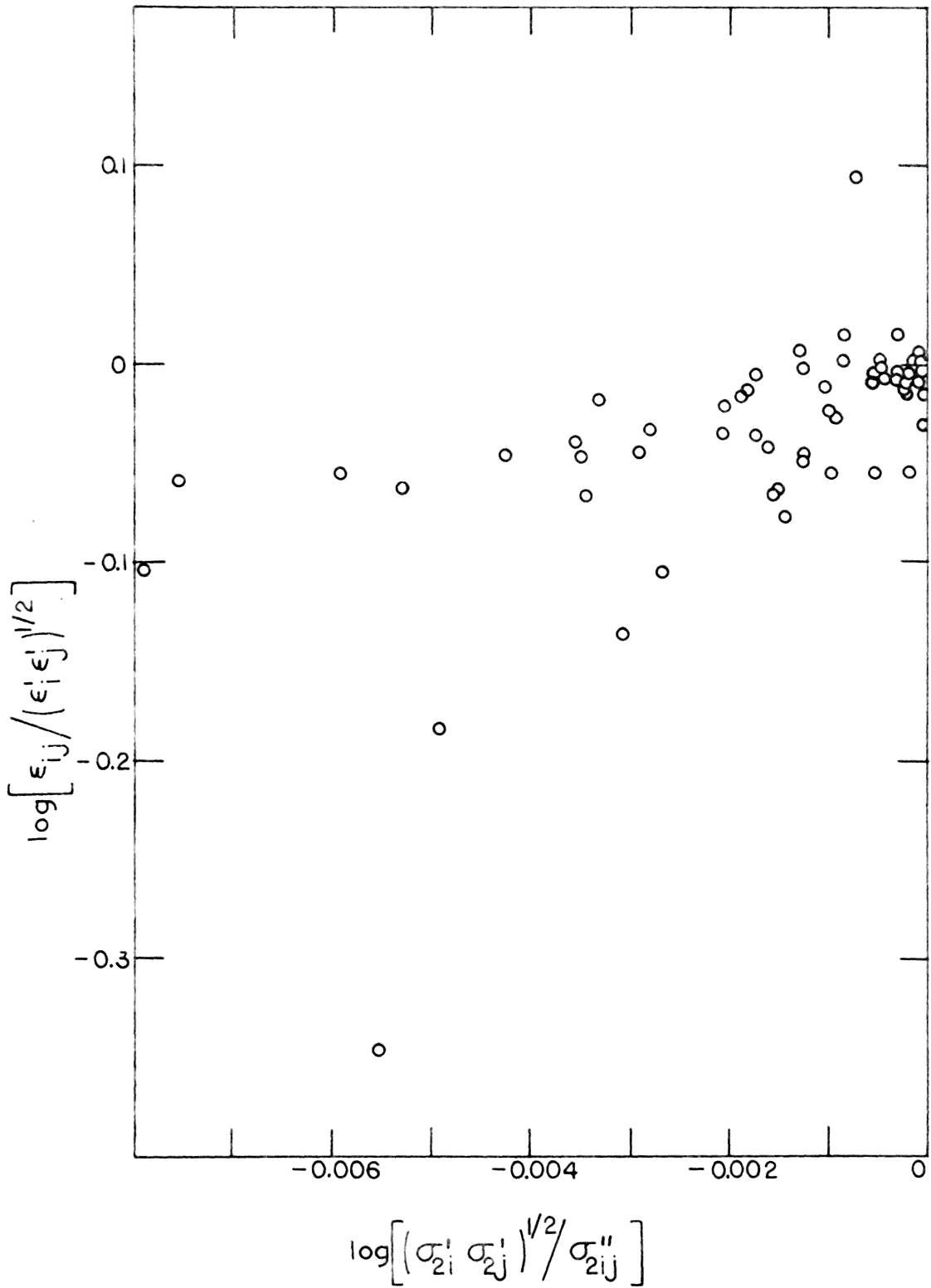


FIG. II. ϵ_{ij}/k FOR σ_{2ij}'' FROM EQUATION 43

alternative form of the combining rule for σ_{2ij} can be obtained. Equation 37 relates σ_2 to σ_1 for pure substances.

$$\sigma'_{2i} = \sigma'_{1i} [1.0 + 0.66 (1.0 + \omega)^{-3.40}] \quad (37)$$

If this equation is assumed to be valid for mixtures, one obtains:

$$\sigma''_{2ij} = \sigma_{1ij} [1.0 + 0.66 (1.0 + \omega_{ij})^{-3.40}]$$

Writing equation 29 for σ_{1ij} gives

$$\sigma''_{2ij} = [1.0 + 0.66 (1.0 + \omega_{ij})^{-3.40}] (\sigma'_{1i} + \sigma'_{1j})/2 \quad (46)$$

In order to apply equation 46, it is necessary to assume values for ω_{ij} . Calculations were made based on the following assumption:

$$\omega''_{ij} = (\omega_i + \omega_j)/2 \quad (47)$$

Table VIII compares the values of σ_{2ij} , calculated from the data when σ_{1ij} was fixed, with the values of σ_{2ij} calculated from equation 43 and equation 46. There is not enough difference between the values of equation 43 and equation 46 to show graphically, but the difference in values has a decided effect on a new c_{ij} .

Figure 12 is identical to Fig. 11 except that Fig. 12 shows values which were calculated from the data when σ_{2ij} was fixed according to equation 46. The plotting symbols with a diametral line are interactions involving carbon dioxide, all of which deviate from the general trend. The values are approximately represented by a line through the origin with a slope of $n = 23$. This slope was chosen from a larger plot on which only interactions of spherical molecules were

TABLE VIII
 COMPARISON OF σ_{2ij} AND σ''_{2ij} VALUES

Mixture Components	σ_{2ij} cm/mole	σ''_{2ij} Eq. 46	σ''_{2ij} Eq. 43
7 + 8	4.761	4.471	4.471
8 + 9	4.813	4.793	4.793
8 + 10	4.728	4.640	4.640
9 + 13	4.795	4.668	4.677
9 + 10	4.879	4.831	4.831
8 + 13	4.725	4.481	4.487
7 + 13	4.548	4.353	4.356
7 + 9	4.745	4.664	4.662
7 + 3	4.817	4.346	4.348
6 + 13	4.263	4.039	4.029
6 + 10	3.994	4.193	4.182
6 + 9	3.879	4.349	4.335
6 + 8	5.638	4.153	4.144
6 + 7	4.780	4.018	4.013
6 + 3	6.677	4.031	4.021
3 + 9	4.671	4.662	4.670
3 + 8	4.746	4.475	4.479
13 + 14	4.808	3.935	4.009
10 + 12		4.466	4.526
9 + 14	4.720	4.174	4.315
8 + 14	4.974	4.005	4.125
7 + 14	5.173	3.886	3.994

Table VIII (continued)

Mixture Components	σ_{21j} cm/mole	σ''_{21j} Eq. 46	σ''_{21j} Eq. 43
7 + 10	4.664	4.510	4.509
27 + 37	5.093	5.514	5.522
6 + 19		4.415	4.383
7 + 19	8.463	4.711	4.709
3 + 17	3.956	4.596	4.593
3 + 19		4.723	4.718
3 + 14	5.398	3.924	4.002
3 + 20	4.119	4.835	4.829
3 + 22	3.620	4.913	4.912
3 + 25	4.045	4.977	4.983
3 + 37	3.832	4.828	4.825
7 + 24	3.547	4.967	4.960
7 + 25	9.135	4.956	4.975
10 + 22	4.515	5.047	5.073
10 + 20	5.094	4.974	4.990
10 + 17	5.225	4.747	4.754
10 + 19	5.290	4.868	4.878
10 + 25	5.065	4.471	4.471
10 + 23	5.068	5.152	5.153
10 + 41	3.874	4.703	4.743
10 + 21	5.041	5.041	5.048
6 + 14		3.591	3.667
14 + 17	5.163	4.176	4.238

Table VIII (continued)

Mixture Components	σ_{2ij} cm/mole	σ''_{2ij} Eq. 46	σ''_{2ij} Eq. 43
14 + 19	4.546	4.324	4.363
15 + 43	4.113	3.579	3.578
17 + 29	5.149	4.891	4.892
10 + 14	3.952	4.042	4.163
17 + 19	4.896	4.954	4.954
17 + 20	5.042	5.064	5.065
17 + 22	5.287	5.142	5.148
17 + 25	5.252	5.206	5.220
19 + 20	5.103	5.189	5.190
19 + 22	5.393	5.270	5.273
19 + 25	5.425	5.335	5.345
20 + 22	5.501	5.383	5.384
20 + 25	5.800	5.451	5.456
14 + 20	4.372	4.454	4.474
22 + 54	6.635	5.620	5.639
22 + 55	5.761	5.737	5.759
22 + 25	5.537	5.537	5.539

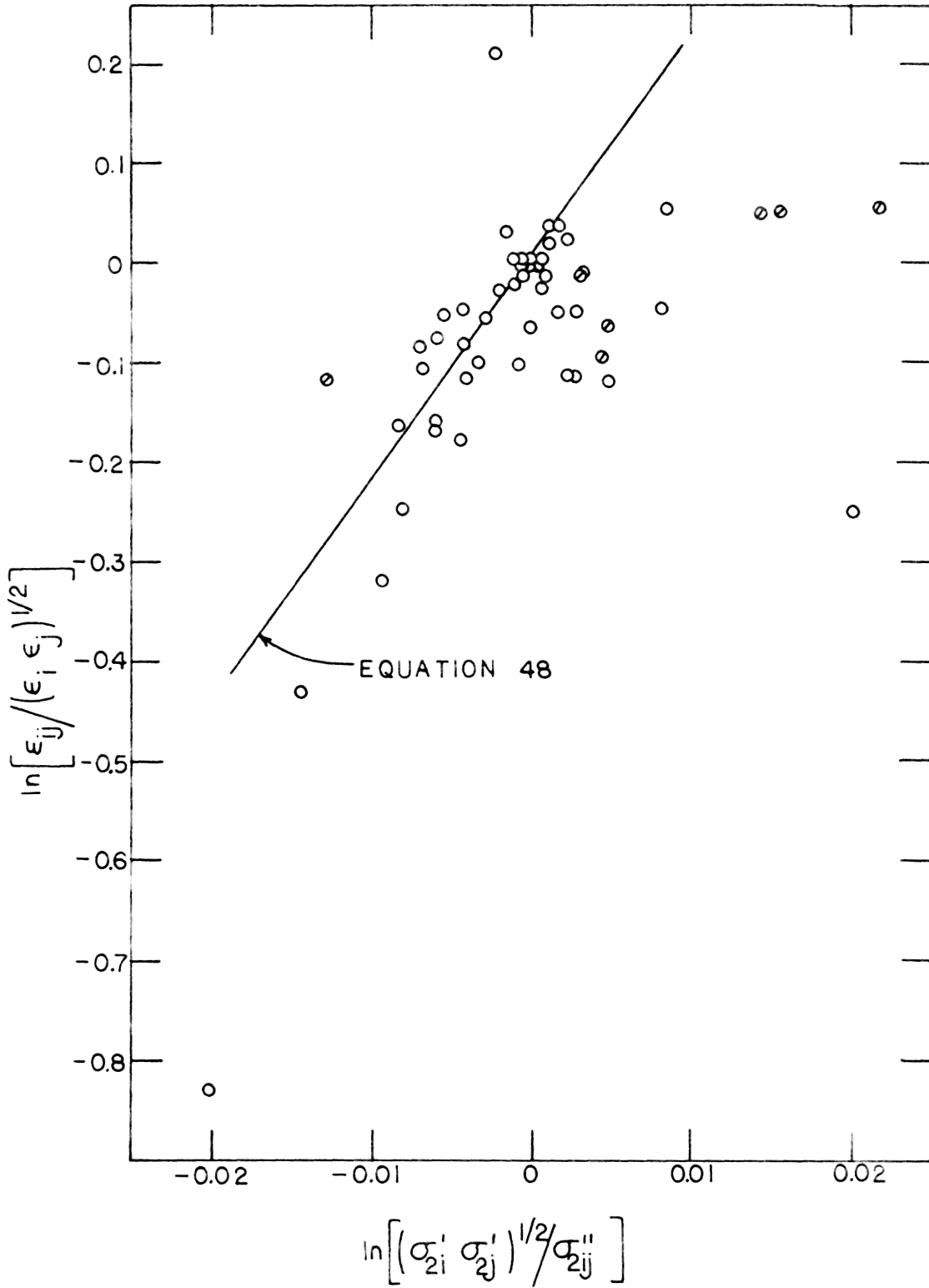


FIG. 12. ϵ_{ij} FOR σ_{2ij}'' FROM EQUATION 46

considered. The values plotted in Figs. 11 and 12 are listed in Table IX. The resulting combining rule for ϵ_{ij} is

$$\epsilon''_{ij} = \sqrt{\epsilon'_i \epsilon'_j} \left(\frac{\sqrt{\sigma''_{2i} \sigma''_{2j}}}{\sigma_{2ij}} \right)^{23} \quad (48)$$

Table X presents a comparison of the ratio, $\epsilon''_{ij}/\sqrt{\epsilon'_i \epsilon'_j}$, for the Hudson and McCoubrey rule, the Sikora rule, and equation 48. The data values of the ratio for σ''_{2ij} given by equations 43 and 46 are also listed. The per cent error between each ratio and its corresponding data value are listed below each $\epsilon''_{ij}/\sqrt{\epsilon'_i \epsilon'_j}$ ratio.

TABLE IX

VALUES INVOLVING ϵ_{ij} AND σ''_{2ij} FOR DETERMINING n IN FIGURES 11 AND 12

Mixture Components	σ''_{2ij} From Eq. 43		σ''_{2ij} From Eq. 46	
	$\log_{10} \left[\frac{\sqrt{\sigma'_{2i} \sigma'_{2j}}}{\sigma''_{2ij}} \right]$	$\log_{10} \left[\frac{\epsilon_{ij}}{\sqrt{\epsilon'_i \epsilon'_j}} \right]$	$\ln \left[\frac{\sqrt{\sigma'_{2i} \sigma'_{2j}}}{\sigma''_{2ij}} \right]$	$\ln \left[\frac{\epsilon_{ij}}{\sqrt{\epsilon'_i \epsilon'_j}} \right]$
7 + 8	-0.00018	-0.0068	-0.00055	-0.0160
8 + 9	-0.00034	-0.0082	-0.00088	-0.0192
8 + 10	-0.00001	-0.0017	-0.00005	-0.0041
9 + 13	-0.00093	-0.0298	-0.00004	-0.0627
9 + 10	-0.00021	-0.0068	-0.00046	-0.0154
8 + 13	-0.00014	-0.0127	+0.00091	-0.0259
7 + 13	-0.00000	-0.0070	+0.00060	-0.0144
7 + 9	-0.00103	-0.0249	-0.00284	-0.0587
7 + 3	-0.00000	-0.0155	+0.00049	-0.0344
6 + 13	-0.00157	-0.0679	-0.00618	-0.1649
6 + 10	-0.00307	-0.1353	-0.00965	-0.3199
6 + 9	-0.00491	-0.1824	-0.01451	-0.4308
6 + 8	-0.00267	-0.1023	-0.00821	-0.2425
6 + 7	-0.00144	-0.0757	-0.00452	-0.1781
6 + 3	-0.00151	-0.0645	-0.00590	-0.1564
3 + 9	-0.00098	-0.0371	-0.00052	-0.0804
3 + 8	-0.00016	-0.0112	+0.00065	-0.0228
13 + 14	-0.00178	-0.0035	+0.01453	+0.0487
10 + 12	-0.00790	-0.1022	+0.01273	-0.0527
9 + 14	-0.00527	-0.0615	+0.02126	-0.0515
8 + 14	-0.00293	-0.0447	+0.02275	-0.0186

Table IX (continued)

Mixture Components	σ''_{2ij} From Eq. 43		σ''_{2ij} From Eq. 46	
	$\log_{10} \left[\frac{\sqrt{\sigma'_{2i} \sigma'_{2j}}}{\sigma''_{2ij}} \right]$	$\log_{10} \left[\frac{\epsilon_{ij}}{\sqrt{\epsilon'_i \epsilon'_j}} \right]$	$\ln \left[\frac{\sqrt{\sigma'_{2i} \sigma'_{2j}}}{\sigma''_{2ij}} \right]$	$\ln \left[\frac{\epsilon_{ij}}{\sqrt{\epsilon'_i \epsilon'_j}} \right]$
7 + 14	-0.00164	-0.0424	+0.02355	-0.0140
7 + 10	-0.00031	-0.0089	-0.00097	-0.0213
27 + 37	-0.00037	-0.0001	+0.00061	+0.0040
6 + 19	-0.00555	-0.3452	-0.02017	-0.8232
7 + 19	-0.00134	-0.0426	-0.00339	-0.0990
3 + 19	-0.00128	-0.0485	-0.00413	-0.1153
3 + 17	-0.00057	-0.0098	-0.00207	-0.0251
3 + 14	-0.00171	-0.0053	+0.01562	+0.0505
3 + 20	-0.00209	-0.0309	-0.00605	-0.0754
3 + 22	-0.00279	-0.0344	-0.00676	-0.0803
3 + 25	-0.00346	-0.0472	-0.00668	-0.1044
3 + 37	-0.00205	-0.0201	-0.00551	-0.0488
7 + 24	-0.00342	-0.0674	-0.00958	-0.1607
7 + 25	-0.00357	-0.0401	-0.00427	-0.0796
6 + 14	-0.00001	-0.1426	+0.02078	-0.2504
10 + 22	-0.00132	+0.0035	+0.00207	+0.0237
10 + 20	-0.00085	+0.0131	+0.00115	+0.0398
10 + 17	-0.00005	+0.0067	+0.00120	+0.0194
10 + 19	-0.00037	+0.0137	+0.00131	+0.0381
10 + 23	-0.00185	-0.0189	-0.00411	-0.0431
10 + 41	-0.00004	-0.0307	+0.00836	-0.0431
10 + 21	-0.00117	+0.0117	-0.00144	+0.0309

Table IX (continued)

Mixture Components	σ''_{21j} From Eq. 43		σ''_{21j} From Eq. 46	
	$\log_{10} \left[\frac{\sqrt{\sigma'_{21} \sigma'_{21}}}{\sigma''_{21j}} \right]$	$\log_{10} \left[\frac{\epsilon_{ij}}{\sqrt{\epsilon'_i \epsilon'_j}} \right]$	$\ln \left[\frac{\sqrt{\sigma'_{21} \sigma'_{21}}}{\sigma''_{21j}} \right]$	$\ln \left[\frac{\epsilon_{ij}}{\sqrt{\epsilon'_i \epsilon'_j}} \right]$
10 + 25	-0.00179	+0.0137	+0.00360	+0.0544
14 + 17	-0.00425	-0.0471	+0.00500	-0.0611
14 + 19	-0.00592	-0.0555	-0.00464	-0.0994
15 + 43	-0.00078	+0.0928	-0.00226	+0.2125
17 + 29	-0.00004	-0.0013	+0.00012	-0.0023
10 + 14	-0.00336	-0.0185	+0.02158	+0.0543
17 + 19	-0.00014	+0.0029	-0.00025	+0.0069
17 + 20	-0.00047	+0.0025	-0.00078	+0.0066
17 + 22	-0.00083	+0.0002	-0.00070	+0.0037
17 + 25	-0.00122	-0.0012	-0.00009	+0.0045
19 + 20	-0.00010	+0.0013	-0.00015	+0.0032
19 + 22	-0.00030	-0.0015	-0.00004	-0.0017
19 + 25	-0.00054	-0.0025	+0.00047	-0.0014
20 + 22	-0.00005	-0.0022	+0.00011	-0.0045
20 + 25	-0.00017	-0.0057	+0.00054	-0.0110
14 + 20	-0.00755	-0.0586	-0.01277	-0.1196
22 + 54	-0.00020	-0.0543	+0.00283	-0.1159
22 + 55	-0.00056	-0.0542	+0.00246	-0.1145
22 + 25	-0.00004	-0.0033	+0.00015	-0.0070

TABLE X

COMPARISON WITH COMBINING RULES OF OTHER INVESTIGATORS

Mixture Code Number	<u>Hudson and McCoubrey</u>		<u>Sikora</u>		<u>This Work</u>		<u>Computed $\epsilon_{1j}/\sqrt{\epsilon_{1j}\epsilon_{1j}}$</u>	
	$\epsilon''_{1j}/\sqrt{\epsilon_{1j}\epsilon_{1j}}$	per cent error	$\epsilon''_{1j}/\sqrt{\epsilon_{1j}\epsilon_{1j}}$	per cent error	$\epsilon''_{1j}/\sqrt{\epsilon_{1j}\epsilon_{1j}}$	per cent error	σ''_{21j} equation 43	σ''_{21j} equation 46
3 + 6	0.96201	10.46	0.84993	- 1.39	0.87311	2.09	0.86190	0.85520
3 + 7	0.99732	3.36	0.99719	3.35	1.01129	4.67	0.96490	0.96620
3 + 8	0.99995	2.61	0.99653	2.26	1.01513	3.85	0.97450	0.97750
6 + 7	0.97149	15.65	0.88442	5.29	0.90123	7.69	0.84000	0.83690
7 + 8	0.99656	1.24	0.98754	0.32	0.98742	0.34	0.98440	0.98410
7 + 9	0.98281	4.10	0.94270	- 0.15	0.93686	-0.65	0.94410	0.94300
7 + 10	0.99376	1.45	0.98305	0.35	0.97799	-0.10	0.97960	0.97900
8 + 10	0.99958	0.37	0.99965	0.38	0.99873	0.28	0.99590	0.99590
10 + 17	0.98663	- 2.84	0.95939	- 5.53	1.02785	0.81	1.01550	1.01960
10 + 19	0.95972	- 7.00	0.89076	-13.69	1.03062	-0.80	1.03200	1.03890
10 + 20	0.92840	- 9.92	0.81787	-20.64	1.02674	-1.33	1.03060	1.04060
10 + 22	0.89715	-11.01	0.75091	-25.51	1.04877	2.42	1.00810	1.02400
10 + 25	0.86717	-15.99	0.69099	-33.06	1.08624	2.87	1.03220	1.05590

SECTION VI

EMPIRICAL COMBINING RULES FOR INTERACTION

CRITICAL PROPERTIES AND THE ACENTRIC FACTOR

The correlations given in Section IV for the pure component data may be used with the combining rules given in Section V to find combining rules for the interaction critical properties and ω . It has already been assumed that

$$\omega''_{ij} = (\omega_i + \omega_j)/2.0 \quad (47)$$

Substituting $\sigma'_{li} = (V_{ci}/4.25)^{1/3}$ into equation 42 gives the familiar combining rule for V_{cij} :

$$V_{cij} = (V_{ci}^{1/3} + V_{cj}^{1/3})^3/8.0 \quad (29)$$

For the rectangular well potential T_{cij} will be given in terms of equation 39. Substituting equations 37 and 39 into equation 48 gives:

$$T_{cij} = \left\{ \frac{\left(\frac{V_{ci}^{1/3} V_{cj}^{1/3}}{V_{cij}^{1/3}} \right) \sqrt{ \frac{[1.0+0.66(1.0+\omega_i)]^{-3.40} [1.0+0.66(1.0+\omega_j)]^{-3.40}}{[1.0+0.66(1.0+\omega''_{ij})]^{-3.40}} } \right\}^{23} \quad (49)$$

$$\times \frac{\sqrt{T_{ci} T_{cj}} (0.66 + 2.73 \omega_i) (0.66 + 2.73 \omega_j)}{(0.66 + 2.73 \omega''_{ij})}$$

SECTION VII

CONCLUDING REMARKS

The three-parameter corresponding states correlation in terms of potential parameters for pure substances is remarkably accurate. Table IV gives the rms deviations from the second virial coefficient data for both the Pitzer and Curl correlation and the present potential parameter correlations. The rectangular well potential correlations compare favorably with those of Pitzer and Curl. It has not yet been determined why the r^{-6} potential failed to be as precise as the rectangular well.

It was determined that ϵ is not strictly proportional to T_c , but in fact also depends upon the value of the third parameter. It has been reported [16] that the potential parameters, ϵ and σ , are slowly changing functions of temperature. The potential parameters in this work are average values which were determined over a temperature range. In general, the reduced temperature range of the second virial coefficient data varied from substance to substance; consequently, the average potential parameters are subject to some uncertainty. Leach [4] has determined that the temperature dependence of the potential parameters may be correlated in terms of the acentric factor, ω , and the critical compressibility factor, Z_c . This temperature dependence of ϵ and σ were not considered in this study, but it should be considered in future work with intermolecular potential parameter correlations.

Table X compares the ϵ_{ij} combining rules of Hudson and McCoubrey, Sikora, and this work in terms of the size of the correction applied

to the geometric mean rule for ϵ_{ij}'' . It should be noted that the rectangular well parameter, σ_{1ij}'' , is the proper σ to use in the Hudson and McCoubrey combining rule as well as in the Sikora rule. σ_{1ij}'' , like σ in the Lennard-Jones potential is directly proportional to V_c . The proportionality constants are, of course, not the same, but a different proportionality constant does not change the value given by the combining rules. The ϵ_{ij} combining rule determined in this work is based upon the use of σ_{2ij}'' obtained with $\omega_{ij}'' = (\omega_i + \omega_j)/2.0$.

One of the results of the comparison in Table X is that the rule determined in this work is inferior to the Sikora rule for interactions of spherical molecules, but is usually superior to the Hudson and McCoubrey rule. For interactions involving at least one nonspherical molecule, the new rule has accuracy which exceeds that of the other two rules. Table X lists only those mixtures for which there were at least five experimental values of $B_{ij}(T)$. There are some interesting mixtures involving nonspherical-nonspherical interactions which have only four experimental values, and are not listed in Table X. The new combining rule predicts the values of ϵ_{ij} of mixtures of the normal alkanes with maximum error of 4.0 per cent.

The fact that the exponent of the correction term can be approximated by $n = 23$ does not necessarily imply the characteristics of the actual intermolecular potential. This is especially true, since the repulsive part of the intermolecular potential was completely ignored in the derivation of equation 43.

A detailed study of the properties of mixtures which involve interactions between nonspherical molecules is hindered by the small

quantity of second virial coefficient data for the mixtures and for the pure components. Some of the points which deviate from the line for $n = 23$ in Fig. 12 are mixtures for which there are less than five measurements for the second virial coefficient. It is difficult to be confident in parameters obtained from so few measurements, especially when the temperature range is small. More experimental data are needed for mixtures involving interactions of both spherical and non-spherical molecules.

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APPENDIX A

DERIVATION OF AN EXPRESSION FOR $B_{ij}(T)$ OF THE r^{-6} POTENTIAL

An expression for the second virial coefficient of the r^{-6} potential may be derived in the same manner as the rectangular well potential. Let

$$B = B_{ij}(T)$$

and

$$u = u_{ij}(r)$$

where

$$u = \begin{cases} \infty, & 0 < r \leq \sigma_1 \\ -\epsilon, & \sigma_1 < r < \sigma_2 \\ -\epsilon(\sigma_2/r)^6, & r > \sigma_2 \end{cases}$$

From statistical thermodynamics:

$$B = -2\pi \int_0^{\infty} [e^{-u/kT} - 1] r^2 dr \quad (A1)$$

For the r^{-6} potential:

$$B = -2\pi \left\{ \int_0^{\sigma_1} [e^{-\infty} - 1] r^2 dr + \int_0^{\sigma_2} [e^{\epsilon/kT} - 1] r^2 dr + \int_{\sigma_2}^{\infty} [e^{-u/kT} - 1] r^2 dr \right\} \quad (A2)$$

The first two integrals in equation A2 are easily evaluated. The last term in equation A2 may be integrated by utilizing a series expansion for the exponential term

$$e^X = 1 + \frac{X}{1!} + \frac{X^2}{2!} + \frac{X^3}{3!} + \frac{X^4}{4!} + \dots \quad (A3)$$

For this case

$$e^{\left[\frac{\epsilon}{kT} \left(\frac{\sigma_2}{r} \right)^6 \right]} - 1.0 = \frac{\epsilon}{kT} \left(\frac{\sigma_2}{r} \right)^6 + \frac{1}{2} \left(\frac{\epsilon}{kT} \right)^2 \left(\frac{\sigma_2}{r} \right)^{12} + \frac{1}{6} \left(\frac{\epsilon}{kT} \right)^3 \left(\frac{\sigma_2}{r} \right)^{18} + \dots \quad (A4)$$

Substituting equation A4 into the integral in equation A2 and performing the integration gives

$$\int_{\sigma_2}^{\infty} \left[e^{\frac{\epsilon}{kT} \left(\frac{\sigma_2}{r} \right)^6} - 1 \right] r^2 dr = - \left[\left(\frac{\epsilon}{kT} \right) \frac{\sigma_2^6}{3r^3} + \left(\frac{\epsilon}{kT} \right)^2 \frac{\sigma_2^{12}}{(2)(9) r^9} + \left(\frac{\epsilon}{kT} \right)^3 \frac{\sigma_2^{18}}{(6)(15) r^{15}} + \dots \right]_{\sigma_2}^{\infty} \quad (A5)$$

Substituting the limits of integration:

$$\int_{\sigma_2}^{\infty} \left[e^{\frac{\epsilon}{kT} \left(\frac{\sigma_2}{r} \right)^6} - 1 \right] r^2 dr = \sigma_2^3 \left[\frac{1}{3} \left(\frac{\epsilon}{kT} \right) + \frac{1}{(2)(9)} \left(\frac{\epsilon}{kT} \right)^2 + \dots \right]$$

$$+ \frac{1}{(6)(15)} \left(\frac{\epsilon}{kT} \right)^3 + \dots \quad (A6)$$

Checking the magnitude of the terms reveals that 13 terms must be included in equation A6 in order to determine B within 0.0002 cubic centimeters per gram-mole. Finally,

$$B = -2\pi \left\{ -\frac{\sigma_1^3}{3} + (e^{\epsilon/kT} - 1) \left(\frac{\sigma_2^3}{3} - \frac{\sigma_1^3}{3} \right) \right. \quad (A7)$$

$$\left. + \sigma_2^3 \left[a_1 \left(\frac{\epsilon}{kT} \right) + a_2 \left(\frac{\epsilon}{kT} \right)^2 + \dots + a_{13} \left(\frac{\epsilon}{kT} \right)^{13} \right] \right\}$$

where,

$$a_1 = 1/3$$

$$a_2 = 1/18$$

$$a_3 = 1/90$$

$$a_4 = 1/504$$

$$a_5 = 1/3240$$

$$a_6 = 1/23760$$

$$a_7 = 1/196560$$

$$a_8 = 5.511464 \cdot 10^{-7}$$

$$a_9 = 5.403390 \cdot 10^{-8}$$

$$a_{10} = 4.834617 \cdot 10^{-9}$$

$$a_{11} = 3.976505 \cdot 10^{-10}$$

$$a_{12} = 3.02562 \cdot 10^{-11}$$

$$a_{13} = 2.141213 \cdot 10^{-12}$$

APPENDIX B

ITERATIVE NONLINEAR CURVE FITTING

The second virial coefficient is an exponential function of temperature as can be seen by examining equation 35 which can be derived with the use of statistical thermodynamics. When a particular intermolecular potential function is chosen for $u_{ij}(r)$, an equation such as equation 36 for the rectangular well potential results.

$$B_{ij}(T) = \frac{2\pi}{3} \left[\sigma_{1ij}^3 + \left(e^{\epsilon_{ij}/kT} - 1 \right) (\sigma_{1ij}^3 - \sigma_{2ij}^3) \right] \quad (B1)$$

The purpose of this appendix is to present the technique used to determine the intermolecular potential parameters, σ_{1ij}^3 , σ_{2ij}^3 , and ϵ_{ij} , from experimental values of the second virial coefficient.

To determine the best values of the potential parameters for a particular analytical expression such as equation B1, it is necessary to examine the error, e'_1 , in the computed values of the second virial coefficient at temperature T_1 .

$$e'_1 = B_{c1} - B_1 \quad (B2)$$

where B_{c1} is the value calculated from equation B1 and B_1 is the experimental value. If B_{c1} from equation B1 is substituted into equation B2, the error becomes

$$e'_1 = \frac{2\pi}{3} \left[\sigma_{1ij}^3 + \left(e^{\epsilon_{ij}/kT} - 1 \right) (\sigma_{1ij}^3 - \sigma_{2ij}^3) \right] - B_1 \quad (B3)$$

Equation B3 can be written in the functional form

$$e'_1 = e'_1(A_1, A_2, A_3) \quad (B4)$$

where

$$A_1 = \sigma_{1ij}^3 \quad (B5)$$

$$A_2 = \sigma_{2ij}^3 \quad (B6)$$

$$A_3 = \epsilon_{ij} \quad (B7)$$

From equation B4 and the rules of differential calculus, the derivative of e'_1 may be expressed as in terms of its partial derivatives with respect to the variables as in equation B8.

$$de'_1 = \frac{\partial e'_1}{\partial A_1} dA_1 + \frac{\partial e'_1}{\partial A_2} dA_2 + \frac{\partial e'_1}{\partial A_3} dA_3 \quad (B8)$$

where, from equation B3

$$\frac{\partial e'_1}{\partial A_1} = \frac{2\pi}{3} [e^{\epsilon_{ij}/kT}] \quad (B9)$$

$$\frac{\partial e'_1}{\partial A_2} = \frac{2\pi}{3} [e^{\epsilon_{ij}/kT} - 1] \quad (B10)$$

$$\frac{\partial e'_1}{\partial A_3} = \frac{2\pi}{3} \left[\frac{1}{kT} e^{\epsilon_{ij}/kT} (\sigma_{1ij}^3 - \sigma_{2ij}^3) \right] \quad (B11)$$

If there are initial estimates of A_1 , A_2 , and A_3 which are close to the values of A_1 , A_2 , and A_3 which will be finally determined, then equation B3 becomes an estimate for de'_1 . The differentials dA_1 , dA_2 ,

and dA_3 are the estimates of the corrections which must be applied to the initial estimates of A_1 , A_2 , and A_3 . By definition, dA_1 , dA_2 , and dA_3 are infinitesimally small if de'_1 has its correct value. The object of the least-squares method which follows is to minimize the sum of squares of the errors in the predicted virial coefficient. A problem arises because the error cannot be evaluated until the coefficients A_1 , A_2 , and A_3 are known. However, the error can be estimated if trial values are assumed for the coefficients. The approximate equation for the error is

$$e'_1(A_1, A_2, A_3) \approx e'_1(A_{10}, A_{20}, A_{30}) + de'_1 \quad (B12)$$

where the subscript 0 refers to the trial values. The function to be minimized is

$$Y = \sum_{l=1}^L (e'_1 + de'_1)^2 \quad (B13)$$

An iterative solution is required, since the error is computed in an approximate manner. Substituting equation B8 into equation B13 gives

$$Y = \sum_{l=1}^L \left(e'_1 + \frac{\partial e'_1}{\partial A_1} dA_1 + \frac{\partial e'_1}{\partial A_2} dA_2 + \frac{\partial e'_1}{\partial A_3} dA_3 \right)^2 \quad (B14)$$

For this summation to be a minimum, the partial derivative with respect to each of the A 's must be equal to zero. Applying this first to A_1 gives

$$\frac{\partial Y}{\partial dA1} = \frac{\partial}{\partial dA1} \sum_1^L \left(e_1' + \frac{\partial e_1'}{\partial A1} dA1 + \frac{\partial e_1'}{\partial A2} dA2 + \frac{\partial e_1'}{\partial A3} dA3 \right)^2 \quad (B15)$$

Differentiating each term in the sum

$$\frac{\partial Y}{\partial dA1} = 2 \sum_1^L \left(e_1' + \frac{\partial e_1'}{\partial A1} dA1 + \frac{\partial e_1'}{\partial A2} dA2 + \frac{\partial e_1'}{\partial A3} dA3 \right) \frac{\partial e_1'}{\partial A1} \quad (B16)$$

Setting the derivative equal to zero in order to determine the

$$\sum_1^L \left(e_1' + \frac{\partial e_1'}{\partial A1} dA1 + \frac{\partial e_1'}{\partial A2} dA2 + \frac{\partial e_1'}{\partial A3} dA3 \right) \frac{\partial e_1'}{\partial A1} = 0 \quad (B17)$$

Since $dA1$, $dA2$, and $dA3$ are not dependent on 1, they may be removed from the summation and the summation may be rearranged to give

$$dA1 \sum_1^L \left(\frac{\partial e_1'}{\partial A1} \right)^2 + dA2 \sum_1^L \left(\frac{\partial e_1'}{\partial A1} \right) \left(\frac{\partial e_1'}{\partial A2} \right) + dA3 \sum_1^L \left(\frac{\partial e_1'}{\partial A1} \right) \left(\frac{\partial e_1'}{\partial A3} \right) = - e_1' \frac{\partial e_1'}{\partial A1} \quad (B18)$$

In a similar manner, two other equations may be obtained

$$dA1 \sum_1^L \left(\frac{\partial e_1'}{\partial A1} \right) \left(\frac{\partial e_1'}{\partial A2} \right) + dA2 \sum_1^L \left(\frac{\partial e_1'}{\partial A2} \right)^2 + dA3 \sum_1^L \left(\frac{\partial e_1'}{\partial A2} \right) \left(\frac{\partial e_1'}{\partial A3} \right) = - e_1' \frac{\partial e_1'}{\partial A2} \quad (B19)$$

$$dA1 \sum_1^L \left(\frac{\partial e'_1}{\partial A1} \right) \left(\frac{\partial e'_1}{\partial A3} \right) + dA2 \sum_1^L \left(\frac{\partial e'_1}{\partial A2} \right) \left(\frac{\partial e'_1}{\partial A3} \right) + dA3 \sum_1^L \left(\frac{\partial e'_1}{\partial A3} \right)^2 = - e'_1 \frac{\partial e'_1}{\partial A3} \quad (B20)$$

Equations B18, B19, and B20 may be solved simultaneously for the corrections dA1, dA2, and dA3. These corrections may then be added to the estimated values of A1, A2, and A3 to obtain new estimates. The calculations are repeated until the corrections are as small as desired. It should be emphasized that the technique may not converge on the "best" values of A1, A2, and A3, if the initial estimates are not close to the "best" values.

APPENDIX C

THE FORM OF THE ϵ_{ij} COMBINING RULE

It is possible to determine a simple form for the combining rule by considering the attractive forces between two dissimilar molecules. The attractive force is assumed to be a function of the distance of separation, as in equation C1.

$$F_{ij} = - \frac{P_i P_j}{r^{n+1}} \quad (C1)$$

where P_i and P_j are some constant molecular properties of the two molecules. If ϵ_{ij} is assumed to be the value of the intermolecular potential at σ_{2ij} as in the r^{-6} potential, then

$$\epsilon''_{ij} = \int_{\infty}^{\sigma_{2ij}} - \frac{P_i P_j}{r^{n+1}} dr \quad (C2)$$

Performing the integration:

$$\epsilon''_{ij} = \frac{P_i P_j}{n \sigma_{2ij}^n} - 0 = \frac{P_i P_j}{n \sigma_{2ij}^n} \quad (C3)$$

A similar equation can be derived for the interaction between like molecules. The result is:

$$\epsilon_i = \frac{P_i^2}{n \sigma_{2i}^n} \quad (C4)$$

also,

$$\epsilon_j = \frac{P_j^2}{n \sigma_{2j}^n} \quad (C5)$$

Solving for P_i and P_j :

$$P_i = \sqrt{\epsilon_i n \sigma_{2i}^n} \quad (C6)$$

$$P_j = \sqrt{\epsilon_j n \sigma_{2j}^n} \quad (C7)$$

Substituting equations C6 and C7 into equation C3 gives

$$\epsilon''_{ij} = \frac{\sqrt{\epsilon_i n \sigma_{2i}^n} \sqrt{\epsilon_j n \sigma_{2j}^n}}{n \sigma_{2ij}^n} \quad (C8)$$

Simplifying and rearranging:

$$\epsilon''_{ij} = \sqrt{\epsilon_i \epsilon_j} \left(\frac{\sqrt{\sigma_{2i} \sigma_{2j}}}{\sigma_{2ij}} \right)^n \quad (C9)$$

Equation C9 is the form assumed for ϵ''_{ij} in this work.

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INTERMOLECULAR POTENTIAL COMBINING RULES UTILIZING
CORRESPONDING STATES CORRELATIONS FOR PURE SUBSTANCES
HAVING NONSPHERICAL MOLECULES

by

David C. Chrisman

Abstract

Second virial coefficient data for many pure substances with both spherical and nonspherical molecules are used to determine the characteristic parameters of two different three-parameter potential functions. Parameters for the rectangular well potential function and a new function, called the r^{-6} potential, are calculated from the data by means of a nonlinear, least squares curve fitting technique. Correlations are given for the potential parameters of each substance in terms of its critical temperature, critical volume, and acentric factor. The accuracy of these correlations is near to that of the Pitzer and Curl equations.

The three-parameter correlations for pure substances are used in a new set of combining rules for calculating interaction potential parameters of mixtures. The new combining rules obtained represent empirical correlations of potential parameters calculated from interaction second virial coefficient data for mixtures. The potential parameters calculated from the new rules are compared with those obtained from the data as well as those calculated from other combining rules now being used. The combining rules presented in this work give much improved results for mixtures involving substances with nonspherical molecules.