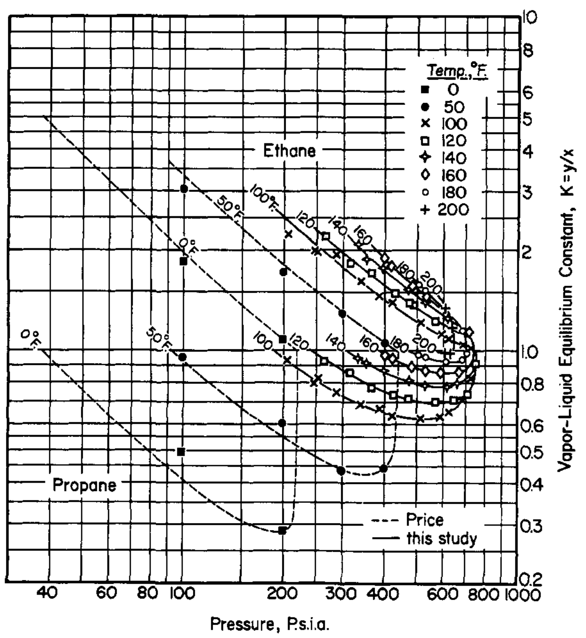

Figure 3. Vapor-liquid equilibrium constants

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for the support which made this study possible. Appreciation is also extended to T.W. Legatski of the Phillips Petroleum Co. for his interest and for the contribution of the hydrocarbons used.

LITERATURE CITED

(1) Barkelew, C.H., Valentine, J.L., Hurd, C.O., *Trans. Am. Inst. Chem. Eng.* **43**, 25 (1947).
(2) Lydersen, A.L., Greenkorn, R.A., Hougen, O.A., Wisconsin Univ. Eng. Exp. Sta., Rept. **4**, October 1955.
(3) Matschke, D.E., Ph.D. dissertation, Northwestern Univ., Evanston, Ill., 1962.
(4) Price, A.R., Ph.D. dissertation, Rice Inst., Houston, Tex., (1957).
(5) Rigas, T.J., Ph.D. dissertation, Northwestern Univ., Evanston, Ill., (1957).
(6) Rigas, T.J., Mason, D.F., Thodos, George, *Ind. Eng. Chem.* **50**, 1297 (1958).
(7) Rigas, T.J., Mason, D.F., Thodos, George, J. CHEM. ENG. DATA **4**, 201 (1959).
(8) Stearns, W.V., George, E.J., *Ind. Eng. Chem.* **35**, 602 (1943).

RECEIVED for review October 9, 1961. Accepted December 19, 1961.

Lennard-Jones Force Constants Predicted from Critical Properties

LEONARD I. STIEL and GEORGE THODOS
The Technological Institute, Northwestern University, Evanston, Ill.

EQUATIONS developed by Hirschfelder, Curtiss, and Bird (*4*) for the calculation of the transport properties of nonpolar gases at moderate pressures have found widespread application. These equations were developed using the Lennard-Jones force potential,

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

as the proper expression of the intermolecular forces between the molecules; and consequently, the equations require the Lennard-Jones force constants, ϵ/κ and σ, for the calculation of viscosity, thermal conductivity, and self-diffusivity. These equations can be expressed as follows:

$$\mu = 2.6693 \times 10^{-5}\,\frac{(MT)^{1/2}}{\sigma^2\Omega^{(2,2)*}[T_N]} \tag{2}$$

$$k = 19.891 \times 10^{-5}\,\frac{(T/M)^{1/2}}{\sigma^2\Omega^{(2,2)*}[T_N]} \tag{3}$$

$$\Delta = 262.80 \times 10^{-5}\,\frac{(T^3/M)^{1/2}}{\pi\sigma^2\Omega^{(1,1)*}[T_N]} \tag{4}$$

where $\Omega^{(1,1)*}[T_N]$ and $\Omega^{(2,2)*}[T_N]$ are tabulated functions of the normalized temperature, $T_N = T/(\epsilon/\kappa)$.

The Lennard-Jones force constants required in these equations can be obtained from either second virial coefficients or from viscosity data for gases. Hirschfelder, Bird, and Spotz (*3*) compare force constants obtained from both methods for a number of common substances. Equations 2, 3, and 4 can be applied only to those substances for which experimental *P-V-T* data and/or viscosities are available for the establishment of the force constants. Because of this limitation, several attempts have been made to relate the force constants of a substance to its critical properties. Bird, Stewart, and Lightfoot (*1*) present the following relationships between the Lennard-Jones force constants and the critical properties of a substance, which were developed from semitheoretical considerations:

$$\epsilon/\kappa = 0.77\,T_c \tag{5}$$

and

$$\sigma = 0.841\,v_c^{1/3} \tag{6}$$

Flynn (*2*) has calculated Lennard-Jones force constants from viscosity data for 16 hydrocarbons for which reliable experimental viscosities are available, including the normal paraffins up to nonane, olefins, acetylenes, naphthenes, and aromatics. These values and those determined from viscosity data by Hirschfelder, Curtiss, and Bird (*4*) for 11 nonhydrocarbon substances, including the inert and diatomic gases, carbon dioxide, and carbon tetrachloride, were used to compare the Lennard Jones force constants resulting from Equations 5 and 6. The data used in these calculations are presented in Table I. An average deviation of 20.4% resulted for the temperature force constant, ϵ/κ, and 4.6% for σ, the collision diameter.

Flynn (*2*) has developed the following empirical relationships between force constants and critical constants:

$$\epsilon/\kappa = 1.77\ T_c^{5/6} \tag{7}$$

and

$$\sigma = 0.561\ (v_c^{1/3})^{5/4} \tag{8}$$

Equation 7 was found to reproduce the reported temperature force constants, ϵ/κ, with an average deviation of 10.6% for the 27 substances, while Equation 8 reproduces the reported collision diameters with an average deviation of 3.1%. Although Equations 7 and 8 are thus more accurate in reproducing force constants obtained from experimental viscosity data than Equations 5 and 6, they have the disadvantage of being dimensionally inconsistent. Therefore, in this study a dimensional analysis approach has been utilized in conjunction with the reported force constants for the 27 substances to develop relationships between force constants and critical constants, which are of improved accuracy and which possess dimensional consistency.

DIMENSIONAL ANALYSIS

Since the force constants are known to be essentially independent of temperature and pressure at moderate pressures, it is assumed that ϵ/κ and σ are functions only of the critical temperature, critical pressure, critical volume, molecular weight, and R, the gas constant. The application of the Rayleigh method of dimensional analysis leads to the following development for the temperature force constant:

$$\epsilon/\kappa = \alpha T_c^a P_c^b R^c M^d v_c^e \tag{9}$$

The dimensions involved are mass, length, time, and temperature. The dimensional analysis produces the following values for the exponents:

$a = 1 + c \qquad b = -c \qquad c = c \qquad d = 0 \qquad$ and $\qquad e = -c$

Using these exponents and combining variables,

$$\epsilon/\kappa = \alpha T_c z_c^m \tag{10}$$

where $z_c = P_c v_c / R T_c$ and $m = -c$.

Similarly for the collision diameter

$$\sigma = \beta T_c^f P_c^g R^h M^i v_c^j \tag{11}$$

and from dimensional analysis

$f = h \qquad g = -h \qquad h = h \qquad i = 0 \qquad$ and $\qquad j = \frac{1}{3} - h$

Substituting these values into Equation 11 and combining terms,

$$\sigma = \beta v_c^{1/3} z_c^n \tag{12}$$

where $n = -h$. Thus Equations 10 and 12 are similar to Equations 5 and 6, except that the force constants are now seen to be also dependent on z_c, the critical compressibility factor of the substance.

TREATMENT OF DATA

The reported Lennard-Jones force constants for the 27 gases (*2, 4*) were used to establish the constants α and β and the exponents m and n of Equations 10 and 12. In Figure 1, the quotient $(\epsilon/k)/T_c$ is plotted *vs.* z_c on log-log coordinates for the 27 substances. The best straight-line relationship can be expressed analytically as follows:

$$\epsilon/\kappa = 65.3\ T_c z_c^{18/5} \tag{13}$$

where ϵ/κ and T_c are in degrees Kelvin.

Similarly, in Figure 2 the quotient $\sigma/v_c^{1/3}$ is plotted against z_c on log-log coordinates to give the following relationship:

$$\sigma = 0.1866\ v_c^{1/3} z_c^{-6/5} \tag{14}$$

where v_c is the critical volume in cc./g.-mole and σ is in Angstrom units. Equations 13 and 14 can be combined to produce the following expression.

$$(\epsilon/\kappa)\ \sigma^3 = 0.424\ T_c v_c \tag{15}$$

This relationship is essentially identical to that presented

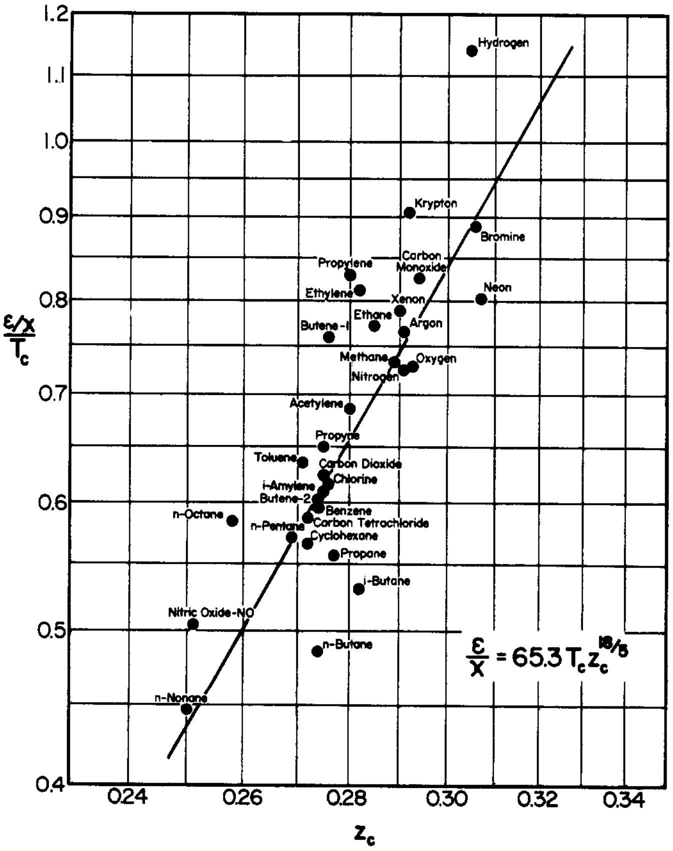

Figure 1. Relationship between $(\epsilon/k)/T_c$ and z_c

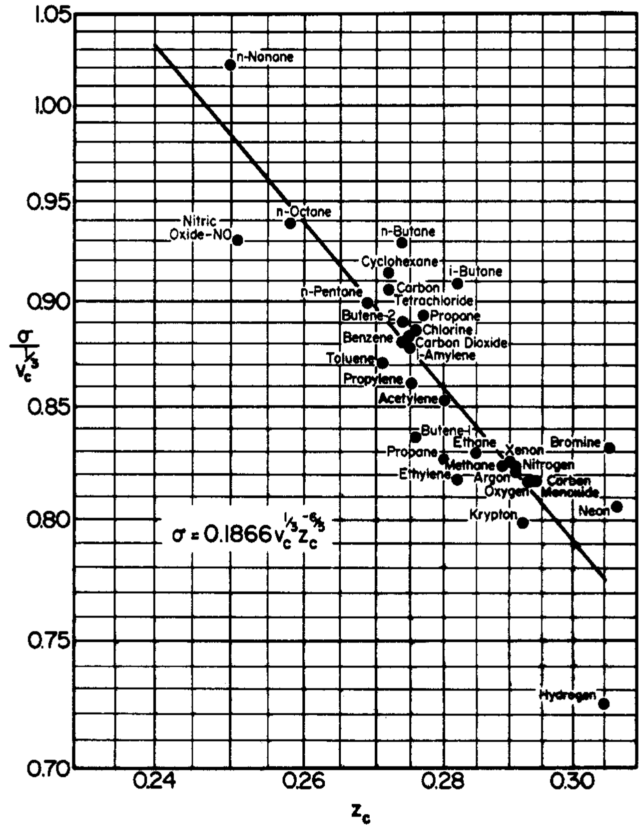

Figure 2. Relationship between $\sigma/v_c^{1/3}$ and z_c

Table I. Lennard-Jones Force Constants, Critical Constants, and Deviations

	z_c	T_c, ° K.	v_c, Cc./ G.-Mole	ϵ/κ, ° K. Literature[a]	ϵ/κ, ° K. Present study	ϵ/κ, ° K. % Dev.	σ, A. Literature[a]	σ, A. Present study	σ, A. % Dev.
Monatomic Gases									
Argon	0.291	151.2	75.22	116	116	0.00	3.465	3.454	0.32
Krypton	0.292	209.4	92.29	190	163	14.21	3.61	3.683	2.02
Xenon	0.290	289.8	119.47	229	218	4.80	4.055	4.055	0.00
Diatomic Gases									
Nitrogen	0.291	126.2	90.1	91.5	97.2	−6.23	3.681	3.659	0.60
Oxygen	0.293	154.8	74.4	113	122	−7.96	3.433	3.422	0.32
Carbon monoxide	0.294	133.0	93.1	110	106	3.64	3.706	3.676	0.81
Nitric oxide	0.251	180	58	91	81	10.99	3.599	3.780	5.03
Chlorine	0.276	417.2	124	257	264	−2.72	4.400	4.325	1.70
Bromine	0.306	584	135	520	538	−3.46	4.268	3.956	7.31
Carbon dioxide	0.275	304.2	94.24	190	191	−0.53	3.996	3.986	0.25
Carbon tetrachloride	0.272	556.4	276	327	335	−2.45	5.881	5.766	1.96
Hydrocarbons									
Methane	0.289	191.1	99.01	140	143	−2.14	3.808	3.814	0.16
Ethane	0.285	305.5	148.1	236	218	7.63	4.384	4.447	1.44
Propane	0.277	370.0	200.4	206	237	−15.05	5.240	5.087	2.92
n-Pentane	0.269	469.8	311.0	269	272	−1.12	6.099	6.111	0.20
n-Octane	0.258	569.4	490.1	333	282	15.32	7.407	7.483	1.03
n-Nonane	0.250	595.4	540	266	265	0.38	8.302	7.975	3.94
Ethylene	0.282	283.1	123.6	230	194	15.65	4.066	4.234	4.13
Propylene	0.280	365.0	180.6	303	246	18.81	4.670	4.859	4.05
Butene-1	0.276	419.6	239.7	319	266	16.61	5.198	5.439	4.64
Butene-2	0.274	430	235.7	259	267	−3.09	5.508	5.439	1.25
i-Amylene	0.275	464.8	293.0	283	291	−2.83	5.829	5.816	0.22
Acetylene	0.280	309.2	112.7	212	208	1.89	4.114	4.144	0.73
Propyne	0.275	401.2	165.7	261	252	3.45	4.742	4.818	1.60
Cyclohexane	0.272	553.2	308.3	313	333	−6.39	6.143	5.971	2.80
Benzene	0.274	562.2	260.4	335	349	−4.18	5.628	5.624	0.07
Toluene	0.271	594.0	317.7	377	353	6.37	5.932	6.079	2.48
					Av.	6.59		Av.	1.93

[a] Values for hydrocarbons (2), for nonhydrocarbons (4).

by Flynn (2) and shown by him to reproduce accurately the product $(\epsilon/\kappa)\sigma^3$ resulting from reported force constants. Equation 15 indicates that the products of the temperature force constant, ϵ/κ, and the cube of the collision diameter, σ, is independent of the critical compressibility factor.

RESULTS AND CONCLUSIONS

Temperature force constants were calculated using Equation 13 for the 27 gases included in this study and produced an average deviation of 6.6% from the corresponding reported values. Similarly, collision diameters were calculated from Equation 14, with a resulting average deviation of 1.9% for these substances. The average deviations for both force constants for the individual substances are included in Table I.

Thus, the results of this study indicate that the use of the critical compressibility factor, z_c, produces relationships between force constants and critical constants which are dimensionally consistent and more accurate than previous proposed relationships.

NOMENCLATURE

a, b, c, d, e = exponents for Equation 9
f, g, h, i, j = exponents for Equation 11
k = thermal conductivity, cal./sec. cm. ° K.
m = exponent for Equation 10
M = molecular weight
n = exponent for Equation 12
P_c = critical pressure
r = intermolecular separation
R = gas constant
T = absolute temperature, ° K.
T_c = critical temperature, ° K.
T_N = normalized temperature, $T/(\epsilon/\kappa)$
v_c = critical volume, cc./g.-mole
z_c = compressibility factor at critical point, P_cv_c/RT_c

Greek Letters

α = constant for Equation 9
β = constant for Equation 11
Δ = self-diffusivity, sq. cm./sec.
ϵ = maximum energy of attraction for Lennard-Jones potential, ergs
κ = Boltzmann constant, 1.3805×10^{-16} ergs/° K.
μ = viscosity, g./cm. sec.
π = pressure, atm.
σ = collision diameter for Lennard-Jones potential, A.
$\phi(r)$ = Lennard-Jones potential
$\Omega^{(1,1)*}[T_N]$ = collision integral function for self-diffusivity
$\Omega^{(2,2)*}[T_N]$ = collision integral function for viscosity and thermal conductivity

LITERATURE CITED

(1) Bird, R.B., Stewart, W.E., Lightfoot, E.N., "Transport Phenomena," p. 22, Wiley, New York, 1960.
(2) Flynn, L.W., M.S. thesis, Northwestern Univ., Evanston, Ill. (1960).
(3) Hirschfelder, J.O., Bird, R.B., Spotz, E.L., *Chem. Revs.* **44**, 205 (1949).
(4) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.

RECEIVED for review September 6, 1961. Accepted December 15, 1961.