below that of many of the liquids of interest. It was this circumstance which necessitated the alteration of the range of the refractometer described in the preceding paragraph. Even with this range extension it was necessary to use formamide as a secondary reference for measuring the refractive index of carbon tetrachloride, dichloracetic acid and hydrazine.

Bayen's dispersion data for water at 17.7° was corrected to 25° using his temperature dependence of refractive index. These values were then used as standards for measuring the dispersion of formic acid and the 8 molar urea solution. In order to obtain the refractive index of the sodium bromide solutions at 25° the refractometer was first calibrated at 18° using water *vs.* sodium bromide. The sample temperature was then raised to 25° and the calibration (which is independent of temperature) used to determine the difference in refractive index of water and sodium bromide solutions.

Solvents. The solvents used were of the best grade obtainable commercially and were not purified further except for the dioxane and ethylene dichloride which were distilled. The urea was recrystallized once from ethanol. Refractive indices were measured at 25° at the sodium D line with an Abbe refractometer and were: formic acid 1.3692, 8 molar urea 1.3993, *p*-dioxane 1.4191, furan (at 18°) 1.4196, methylene chloride 1.4209, dimethylformamide 1.4273, 2-chlorethanol 1.4392, chloroform 1.4421, ethylene dichloride 1.4423, formamide 1.4431, hydrazine 1.4686, dichloroacetic acid 1.4692.

RESULTS

Table II records the refractive index (at 25°) and Lorentz correction factors of fourteen solvents as a function of wavelength. Blank spaces in the table indicate that absorption of light at the given wavelength was too great to permit measurement. A sharp cutoff in transmitted light as an absorption region is approached is a disadvantage of the hollow prism method.

A short extrapolation of the results of Table II was made for comparison with our measured sodium D line values. Excluding formamide and dichloroacetic acid, the average deviation between the measured and extrapolated values was .0007. But the extrapolated values were .0033 too large for formamide and .0044 too small for dichloroacetic acid. However, even a decrease of .0044 in the refractive index of dichloroacetic acid will only lead to about a 0.3 per cent decrease in the calculated Lorentz correction.

Thus, it would appear that in spite of the many corrections required in obtaining ultraviolet refractive indices with a differential refractometer, the results are quite satisfactory for Lorentz corrections. On the other hand, it would be desirable to have a simpler, absolute method available. For this purpose an ordinary table spectrometer with a fluorescent eyepiece would probably useful as far as the transmission cutoff of glass.

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Estimation of Lennard-Jones Potential Energy Parameters from Liquid Densities

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McKinley has shown that the smoothed-potential cell model for the liquid state is a satisfactory basis for correlating the temperature dependence of the density of nonpolar molecules along the saturated liquid curve from 0° K. to approximately 0.8 of the critical temperature. This paper shows that such a correlation gives estimates of both the energy parameter and the distance parameter in the Lennard-Jones bireciprocal pair-potential energy relationship. The parameters obtained in this way give satisfactory estimates of the second virial coefficients for molecules in the gas phase. Thus, with a single, empirical, potential energy function, the equation of state of the gas phase can be correlated with that of the liquid phase at low pressures.

THIS PAPER investigates the possibilities for correlating by a single pair-potential energy function the volumetric behavior of pure polyatomic molecules in both the gas phase and the liquid phase at low pressures. For this purpose, the Lennard-Jones bireciprocal pair-potential energy function and the smoothed-potential cell model for the liquid state were chosen. These devices lead to empirical relationships that demonstrate such a correlation. In this model (*11*), the pressure P, temperature T, and density x in units of V^* ($x = V^*/V$) are related in the following way:

$$P = \frac{-zE^*m}{6(m/n-1)V}\left[Cx^{n/3} - Dx^{m/3}\right] + kT/V\alpha$$

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where m and n are attraction and repulsion exponents, respectively, on the reciprocal intermolecular distance in the Lennard-Jones potential energy function. This pair-potential energy function is preferred over others, such as the Morse function (*8*), because of its flexibility in four adjustable parameters, m, n, R^*, and E^*.

DENSITY VS. TEMPERATURE, $T_R < 0.8$

At zero pressure, the density and the temperature are related, according to the above expression, by

$$(kT/zE^*)\ (-\mathrm{K}) = [Cx^{n/3} - Dx^{m/3}]\alpha \tag{1}$$

in which $\alpha = 1 - x^{1/3}/s$ and $(\mathrm{K}) = 6(n - m)/mn$. It is known empirically (*12*) for nonpolar molecules, and has been shown (*10*) to hold for numerical solutions of Equation 1 for 6,12 and 7,28 Lennard-Jones pair-potential energy functions that mass density d or the molar volume V vary with temperature over the whole saturated liquid range up to approximately $T/T_c = 0.8$ for nonpolar liquids according to

$$d^2/M^2 = 1/V^2 = A - BT \tag{2}$$

where A and B are positive constants characteristic of each substance. That is Equation 2 correlates the liquid density at essentially zero pressure. The molar volume V_0 at absolute zero of temperature is $A^{-0.5}$, so that Equation 2 may be written as

$$V^{-2} = V_0^{-2}[1 - (B/A)T] \tag{3}$$

A list of empirical values of A and B obtained from liquid density in the range $100° < T < 400°$ K. is given in Table I.

Values of V_0 obtained from Equation 2 (Table II) compare quite satisfactorily (within approximately 0.5%) with values estimated by other methods of extrapolation to absolute zero.

The theoretical significance of A and B according to the smoothed-potential cell model may be obtained in the following way. Equation 1 may be rearranged as

$$(D\alpha x^{m/3}) + (kT/zE^*)(-\mathrm{K}) = \alpha Cx^{(n-6)/3}(x^2)$$

The factor x^2 has been taken out of the repulsion term rather than the attraction term because A is a positive number. Division by the coefficient on x^2 gives

$$(D/C)x^{(m-n+6)/3} + \left(\frac{kT}{zE^*}\right)(-\mathrm{K})\ \frac{x^{(6-n)/3}}{\alpha C} = x^2 \tag{4}$$

Comparison of Equation 4 with Equation 2 identifies A and B as

$$A \equiv V_0^{-2} = (D/C)\ [x^{(m-n+6)/3}/(V^*)^2] \tag{5}$$

$$B = (k/zE^*)(\mathrm{K})\ [x^{(6-n)/3}/\alpha C(V^*)^2] \tag{6}$$

so that

$$B/A = (k/E^*)\ (\mathrm{K})\ [1/zD\beta] \tag{7}$$

where

$$\beta = \alpha x^{m/3} \tag{8}$$

When Equations 5 and 6 are combined to eliminate the factor $x^{(6-n)/3}/C(V^*)^2$, the nearest neighbor number z may be computed by Equation 7 from n, m, E^*/k, s, and D for the particular pair-potential energy function using the ratio $A|B$ for each molecule. Thus

$$z = 1/D\beta Y, \tag{9}$$

where

$$Y = (B/A)(E^*/k)/\mathrm{K} = 1/zD\beta. \tag{10}$$

The potential energy parameters, n, m, E^*/k and R^*, have been calculated for several polyatomic molecules by McKinley (*10*) using the method of Hamann and Lambert (*7*). These are tabulated in Table *III*. Values for the dimensionless number Y have been computed from these parameters and listed in Table III. Y is characteristic of the m, n potential with values of 1.1 to 1.3 for the 6,n potentials and 1.5 for the 7,n potentials.

Values of z calculated by Equation 9 for densities x in the ordinary liquid region range form 6 to 12, which are reasonable values for the number of nearest neighbors. The model is not accurate in this respect, however, since z decreases with increasing density. This is a trend opposite to that expected in reality.

Table I. Empirical Constants A and *B* in Equation 2 for some Nonpolar Molecules[a] and *7,28* Parameters Obtained from these Constants

Molecule	A, 10^{-4} mole^2 × cc.$^{-2}$	B, 10^{-7} mole^2 × cc.$^{-2}$ × °K.$^{-1}$	E^*/k, °K.	$(R°)^3$ A.^{3}
Propane	3.3907	7.1771	456	164
n-Butane	2.0983	3.777	536	205
n-Pentane	1.4451	2.367	589	250
Neopentane	1.4289	2.585	533	250
n-Hexane	1.0588	1.6173	633	292
2-Methylpentane	1.0459	1.6094	627	294
3-Methylpentane	1.0754	1.6423	632	288
2,3-Dimethylbutane	1.0624	1.6135	635	296
n-Heptane	0.8081	1.1648	669	334
n-Octane	0.6345	0.8726	702	378
n-Nonane	0.5121	0.6774	729	420
Cyclohexane	1.4571	2.0505	684	248
Methylcyclohexane	1.0423	1.4601	689	294
Benzene	2.1561	3.0345	685	204
F-Propane[b]	1.5343	3.419	433	242
F-n-Butane	0.9815	1.958	483	303
F-n-Pentane	0.6907	1.277	522	360
F-n-Hexane	0.5088	0.8750	561	420
F-2-Methylpentane	0.5230	0.8886	568	415
F-3-Methylpentane	0.5234	0.8960	564	413
F-2,3-Dimethylbutane	0.5505	0.9380	566	403
F-n-Heptane	0.3841	0.630	587	485
F-Cyclopentane	0.9220	1.6740	531	310

[a] Liquid density data for hydrocarbons (*1*) and for fluorocarbons (*12*). [b] F stands for Perfluoro.

Table II. Densities of the Liquid Phase at Low Pressure, Extrapolated to Absolute Zero of Temperature

	n-C_5H_{12}	n-C_7H_{16}	n-C_8H_{18}	n-C_9H_{20}
Equation 2	0.8673	0.9007	0.9098	0.9178
Ref. (*5*)	0.8706	0.9050	0.9162	0.9250
	0.8751	0.9140	0.9119	0.9250

Table III. Parameters for Spherical and Quasispherical Molecules (*10*)

	m	n	E^*/k, °K.	R^*, A.	Y	$\gamma^* = A^{0.5}(R^*)^3$ Moles × Cm.$^{-3}$ × A.^{3}
Argon, Ar	6	12	120	3.84	1.22	2.67
Fluorine, F_2	6	18	154.2	3.88	1.19	3.10
Oxygen, O_2	6	17	152.6	3.70	1.29	2.41
Methane, CH_4	6	12	144	4.32	1.11	2.82
F-Methane, CF_4	7	21	276.4	4.99	1.55	3.12
Ethane, C_2H_6	6	16	275	5.045	1.11	3.17
Neopentane, $C(CH_3)_4$	7	21	465.6	6.39	1.48	3.10
Carbontetrachloride, CCl_4	7	28	683.2	6.44	1.50	3.61

The number $A^{-0.5} \equiv V_0$ is proportional to the cube of the equilibrium separation R^* or R^0 for the isolated pair interaction:

$$(R^*)^3 = \gamma^* V_0 \qquad (R^0)^3 = \gamma^0 V_0 \qquad (11)$$

In Table III, column 7, values of γ^* have been calculated for the molecules studied by McKinley (*10*). The reduced volume $1/\gamma^*$ at absolute zero is not the same for all of these molecules since they do not follow the same *m,n* potential.

POTENTIAL ENERGY PARAMETERS FROM LIQUID DENSITIES

It is fairly well established on an empirical basis (*7, 10*) that the thermodynamic behavior of simple polyatomic molecules in the gas phase corresponds essentially to that expected of a Lennard-Jones *m,n* potential energy function with $m > 6$ and $n > 12$. Such a function, particularly the exponents of 21 and 28 found in many cases for the repulsion term, is not valid at close intermolecular separations—*i.e.*, less than R^*. This function is, nevertheless, a useful empirical expression. The parameters estimated by applying Equations 10 and 11 to the density of nonpolar liquid as it varies with temperature give E^*/k and R^* values, which in turn give estimates of the second virial coefficients for the gas phase. Thus, the same empirical pair-potential energy function approximates the density behavior, over limited ranges of pressure and temperature, for both the liquid and the gas phase.

Using $Y = 1.5$ for the 7,*n* potentials, and $Y = 1.2$ for the 6,*n* potentials from Table III, E^*/k in °K. is obtained by Equation 10, and (R^*) or $(R^0)^3$ in A.^{3} is obtained by Equation 11 with the following values of K Y and γ^* (or γ^0), respectively.

m	6	7	7
n	12	21	28
K	0.5	0.571	0.643
K Y	0.60	0.86	0.965
γ^*	2.7	3.1	3.6
γ^0	1.9	2.5	3.0

Table I, columns 4 and 5, gives the parameters calculated by Equation 10 and 11 from A and B values of various molecules for which experimental second virial coefficients are available. Only 7,28 parameters are listed. Those for other *m,n* potentials may be obtained by comparing the coefficients K Y and γ^* or γ^0 in Equations 10 and 11.

CORRELATION OF SECOND VIRIAL COEFFICIENTS WITH LIQUID DENSITIES

The second virial coefficient $\underline{B}_2$ for the gas phase may be calculated with the potential energy parameters from tables of $\underline{B}_2^*$ *vs.* T^*. These reduced functions are defined for each *m,n* potential as

$$\underline{B}_2^* \equiv \underline{B}_2/b_0 \qquad b_0 \equiv 2\Pi N(R^0)^3/3 \qquad T^* = T/(E^*/k) \qquad (12)$$

Values of $\underline{B}_2$ calculated by Equation 12 using E^*/k and $(R^0)^3$ from Table I are compared in Table IV with experimental values of $\underline{B}_2$ taken from the literature. *A priori*, it is not known which set of *m,n* values fits best. It is too much to expect that a single set will apply to all polyatomic molecules. However, the calculated values agree surprisingly well with the experimental values for many of the larger molecules using the 7,28 potential function. The agreement on this basis is particularly noteworthy for n-C_5H_{12}, n-C_6H_{14}, C_6H_6, n-C_4F_{10}, and n-C_5F_{10}. For the smaller molecules, C_3H_8 and C_4H_{10}, the 7,21 potential is more satisfactory.

The correlation of liquid densities with second virial coefficients may be made in an interesting, alternate and equivalent manner by considering A/B and $A^{-0.5}$, respectively, as a characteristic temperature and volume for each substance and considering corresponding states. Any set of molecules, each of which interacts with a like molecule by the same *m,n* potential function, should have the same reduced virial coefficient, $\underline{B}_2 A^{-0.5}$, at the same reduced temperature, TB/A. In Figure 1, such a correlation is presented for the experimental data on $\underline{B}_2$. This figure shows that there is a strong correlation between the behavior of liquid densities as described by the smoothed-potential model and the behavior of the gas phase, as it is represented by $\underline{B}_2$.

Table IV. Second Virial Coefficients, Calculated from Estimated Parameters of Table I

	T, °K.	$-\underline{B}_2$, cc./G. Mole Exptl.	7,21	7,28
C_3H_8 (*9*)	300	391	350	450
	350	275	255	320
	400	203	190	230
n-C_4H_{10} (*9*)	300	715	630	800
	350	492	450	570
	400	364	340	420
n-C_5H_{12} (*9*)	300	1200		1190
	350	800		850
	400	575		635
n-C_6H_{14} (*9*)	320	1580		1420
	350	1220		1160
	400	850		870
n-C_8H_{18} (*4, 9*)	400	1700		1420
	473	1089	790	980
	500	937	700	870
	573	653	520	640
C_6H_6 (*2, 4*)	340.3	1046	830	1050
	363.0	900	700	890
	393.1	729	600	750
	435	590	490	610
	544	356	300	370
C_3F_8 (*3*)	243	936	730	930
	346	357	350	415
	423	218	230	260
n-C_4F_{10} (*14*)	283.16	1030	850	1070
	303.04	900	730	920
	323.21	774	640	800
n-C_5F_{12} (*6*)	307.6	1360	980	1260
	330.6	1100	840	1080
	337.4	1036	810	1030
	350.9	934	750	940
	372.8	811	650	830
	383.1	717	620	775
n-C_6F_{14} (*6*)	307.7	1922		1720
	329.8	1676		1470
	338.0	1579		1380
	350.8	1416		1290
	372.3	1145		1120
	382.9	1049		1060

The curves for the three *m,n* potential functions were obtained from tables of $\underline{B}_2^*$ *vs.* T^* for each *m,n* by combining Equations 10, 11, and 12. Thus:

$$\underline{B}_2 A^{0.5} = 1.26\gamma^0 \underline{B}_2^* \qquad TB/A = \text{K}\, Y\, T^* \qquad (13)$$

The Lennard-Jones parameters m and n increase gradually with increasing molecular size. The $\underline{B}_2$ data for normal octane is not well represented by the 7,28 potential function and even less satisfactorily by smaller *m,n* values.

DISCUSSION

In demonstrating such a correlation, the authors do not mean to suggest that an accurate, universal, potential energy function may be established in this way from liquid and gas density data. The potential energy functions and the model used are too crude for this purpose. Over small

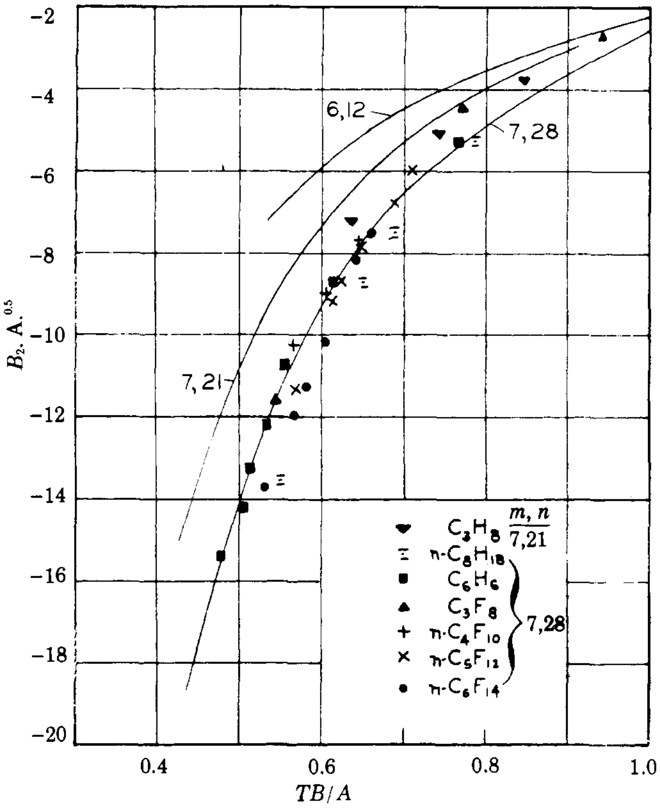

Figure 1. Second virial coefficients for the gas state correlated by characteristic temperatures and volumes for liquid state

temperature ranges, the second virial coefficient may be fitted equally well by many different potential energy functions. The parameters E^*, R^*, m, and n, obtained from gas data will, in general, be quite different from those found in the above way by starting with liquid data.

The approach suggested here is that Y and γ^0 or γ^* have values characteristic of the m,n function, so that when Y and γ are chosen, m and n are fixed. E^*/k and R^*, computed from gas density by means of $\underline{B}_2$ or from liquid density by means of A and B, are to be essentially the same characteristic values of the pair interaction function in the liquid model and in the gas model. It is demonstrated that in this context the 7,28 Lennard-Jones function is a more generally useful one than the 6,12 function for complex polyatomic molecules.

Except for molecular beam scattering experiments, there is no direct experimental observation that will give the actual intermolecular, potential energy function. These functions in Table III, for polyatomic molecules upon which these calculations are based, were obtained from the Hamann and Lambert pair-interaction model using reasonable interaction parameters for the constituent atoms. They thus represent a consistent set of parameters. The only molecule that can be handled by this method to yield the 7,28 function is CCl_4. Thus the values of Y and of γ^0 and γ^* for 7,28 are available only for this molecule. However, Y for other molecules yielding 7,n functions by the Hamann and Lambert method have Y values equal essentially to 1.5, found for CCl_4. By adjusting γ values for particular molecules, the deviations noted for Figure 1 may be reduced arbitrarily to give a better approach to coincidence of experimental data with a particular m,n curve.

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NOMENCLATURE

A, B = constants in density-temperature relationship, (gram mole)^2 cc.$^{-2}$, (gram mole)^2 cc.$^{-2}$ ° K.$^{-1}$
$\underline{B}_2^*$ = reduced second virial coefficient
$\underline{B}_2$ = second virial coefficient, cc./gram mole
b_0 = characteristic molar volume, $2\Pi N(R^0)^3/3$
C, D = lattice summation constants
d = liquid density, grams/cc.
E^* = negative of minimum molecular pair-potential energy
k = Boltzman constant
M = molecular weight, grams/mole
m,n = attraction and repulsion exponents, respectively, on R^{-1} in Lennard-Jones m,n pair-potential energy function
N = Avogadro's number
P = pressure
R^* = distance between molecular centers at minimum pair-potential energy, A.
R^0 = distance between molecular centers when pair-potential energy = 0 and $R < R^*$, A.
s = R^*/R^0
T = absolute temperature, ° K.
T^* = reduced temperature, $T/(E^*/k)$
T_R = T/T_c, T_c = critical temperature
V = molar volume, cc./gram mole
V^* = molar volume when $R = R^*$, cc./gram mole
V_0 = molar volume at 0° K., cc/gram mole
x = V^*/V
Y = dimensionless number defined by Equation 10
z = number of nearest neighbor molecules
α = $1 - x^{1/3}/s$
β = defined by Equation 8
γ^* = $(R^*)^3/V_0$
γ^0 = $(R^0)^3/V_0$
κ = $6(n - m)/mn$

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