A Correlation for the Prediction of Interaction Energy Parameters for Mixtures of Small Molecules

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Low temperature, phase-equilibria data for binary systems containing hydrogen, helium, and neon were used to develop a correlation relating deviations from the geometric mean combining rule for the characteristic energy parameter to the ionization potentials of the component species. With the exception of oxygen systems, this relatively simple relationship correctly predicts published deviations, determined by different methods, for a number of systems within expected uncertainties. It is shown that consideration of attractive forces only, as done by Hudson and McCoubrey, is inadequate for such predictions.

The development of a satisfactory method of relating parameters for unlike molecule interactions to those for like molecule interactions has been hampered in the past by the lack of appropriate data of sufficient accuracy to provide tests for fundamental relationships.

Recent measurements provide data of this type for a complete set of nine binary systems containing hydrogen, helium, and neon, with three different light hydrocarbons as the second component. Equilibrium phase compositions now have been determined for the binary systems: methane with hydrogen (*2, 8, 20, 25*), helium (*15, 21, 43*), and neon (*22*) in the solid-vapor region and, with the exception of neon-methane, in the liquid-vapor region; ethane with hydrogen (*6, 18, 47*), helium (*14, 17*), and neon (*17*) in the liquid-vapor region and for hydrogen-ethane in the solid-vapor region; and ethylene with hydrogen (*19, 47*), helium (*17*), and neon (*17*) in the liquid-vapor and solid-vapor regions. No liquid-phase compositions for the systems neon with ethane or ethylene and helium with ethylene were determined in the above investigations.

These data are particularly valuable below the normal boiling point temperature of the condensable component, where assumptions made to simplify models representing the gas-phase compositions are most nearly satisfied. It was found that for the neon and helium systems, predictions of gas-phase compositions by means of an expression based on the virial equation and commonly used combining rules are in error by as much as an order of magnitude, even though excellent pure component parameters are used.

Prausnitz et al. (*4, 5, 11*) have shown that if the characteristic energy parameter for a binary interaction, derived from the geometric mean of the pure component parameters, is corrected by a coefficient ($1 - k_{12}$), an excellent representation of the mixture data can be obtained. The distance parameter for a mixture, given by a linear average of the pure component parameters, is usually found to be satisfactory, since the results are insensitive to the exact method of averaging.

Thus far, the value of k_{12} has been obtained empirically for each system of interest. The studies of the binary systems of hydrogen, helium, and neon with light hydrocarbons, however, have revealed a definite pattern for the deviations from the geometric mean combining rule, apparently related to some significant difference in the properties of the volatile components. That is, k_{12} values for the helium, neon, and hydrogen systems are approximately 0.4, 0.3, and 0.05, respectively.

Based on these results and others critically selected from the literature, a correlation has been developed relating the deviation from the geometric mean combining rule k_{12} to the ionization potentials of the pure components in the binary mixture.

EXPERIMENTAL VALUES OF k_{12}

A convenient way to represent the gas phase for systems such as these is in the form of enhancement factors, that is, the ratio of partial pressures to the vapor pressure of the condensable component. Enhancement factors (for the case of an incompressible, pure, condensed phase of component 1 and an essentially pure gas phase of component 2) can be represented isothermally with the following expression based on the virial equation of state:

$$\ln(y_1\pi/p_{01}) = v_{01}(\pi - p_{01})/RT + \ln Z_2 - 2\rho_2 B_{12} - 3\rho_2{}^2 C_{122}/2 \quad (1)$$

Owing to assumptions made in the derivation of this expression, it is rigorous only in the solid-vapor region. However, it is also applicable between the triple point and normal boiling point temperatures (where isothermal, liquid-phase compressibility is insignificant) for systems in which the solubility of gas in the liquid is no more than a few percent.

Values of the interaction second virial coefficient B_{12} were obtained for the binary systems of hydrogen, helium, and neon with ethylene, ethane, and methane by a least-squares fit of the data, below the boiling point of the condensable components, to Equation (1). For most of the data, terms containing virial coefficients higher than the third were not needed to obtain a fit within experimental error.

To obtain deviations from the geometric mean combining rule for the energy parameter, these experimental values of B_{12} are compared with those calculated from the Kihara potential model for $k_{12} = 0$ and $k_{12} > 0$ in

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the equation

$$U_{012} = (1 - k_{12})(U_{01}\, U_{02})^{1/2} \qquad (2)$$

As an example, experimental values of B_{12} for the systems hydrogen-ethylene and helium-ethylene are compared in Figure 1 with those calculated from the Kihara potential model, by using parameters determined by Prausnitz and Myers (*41*), with and without appropriate values of k_{12}.

The magnitude of k_{12} values needed to reproduce experimental interaction second virial coefficient values for the systems ethylene with helium, neon, and hydrogen are 0.40, 0.31, and 0.07, respectively. The effect of different values of k_{12} on the calculated values of B_{12} for these systems is shown in Table 1. The experimental B_{12} values for neon-ethylene, not shown in Figure 1, were for two temperatures only, 102° and 122°K.

The experimental B_{12} values for the systems ethane with helium, neon, and hydrogen cover the same temperature range with data for the neon system at 112° and 130°K. In this case, the k_{12} values for the helium-ethane system appear to be temperature dependent. Above 130°K., the values of k_{12} are slightly larger than 0.40; below this temperature, the k_{12} values decrease uniformly toward zero at the lowest temperatures. Nevertheless, between 120° and 150°K., a value of k_{12} equal to 0.40 reproduces the experimental B_{12} values satisfactorily. The k_{12} values for the neon-ethane system also exhibit a relatively strong temperature dependence, that is, 0.38 at 130°K. and 0.24 at 112°K. A k_{12} value of 0.02, however, reproduces the experimental B_{12} values for the hydrogen-ethane system with no apparent temperature dependence.

Based on the difficulty encountered in making phase-equilibria measurements with ethane, particularly at the lower temperatures, the observed temperature dependence of the k_{12} values for helium-ethane and neon-ethane may be due to a consistent, temperature dependent error from some undetected phenomenon, such as sorption in the access lines to the equilibrium cell. It is also possible that the values of the Kihara parameters or the ethane vapor pressure values are not the best for the subject temperature region.

It is interesting to note that the k_{12} values determined from the B_{12} values, with a different method, by Chueh and Prausnitz (*38*) for the helium-methane system (*21*) between 50° and 87°K. exhibit a similar temperature dependence; that is, values of k_{12} vary from 0.45 to 0.35 from high to low temperature with an average value of 0.40. In addition, Chueh and Prausnitz (*4*) find k_{12} values of 0.28 and 0.03 for the neon-methane (*22*) and hydrogen-methane (*20*) systems, respectively. The k_{12} values determined by these authors for the methane systems were used as given, since the same sources of data were used and quantum deviations were accounted for. Chueh and Prausnitz (*39, 40*) also find values of 0.05 for both the hydrogen-ethylene and hydrogen-ethane systems in comparison with the values of 0.07 and 0.02 found here.

TABLE 1. EFFECT OF k_{12} CORRECTION

System	T, °K.	k_{12}	B_{12} (calc.) cc./g.mole	B_{12} (exp.) cc./g.mole
He-C_2H_4	122	0.00	−8.91	
		0.10	−3.75	
		0.20	+1.19	
		0.30	+6.22	
		0.40	+10.74	+13.13
Ne-C_2H_4	122	0.00	−73.87	
		0.10	−58.73	
		0.20	−44.68	
		0.30	−32.26	−30.89
		0.40	−19.84	
H_2-C_2H_4	102	0.00	−116.7	
		0.05	−105.5	
		0.07	−100.4	−99.05
		0.10	−93.9	

Allowing for an uncertainty in the k_{12} values for the helium and neon systems of ±0.05, with the exception of the helium-ethane system below 130°K., nevertheless, results in a pattern of deviations for the helium, neon, and hydrogen systems with the light hydrocarbons of 0.4, 0.3, and 0.05, respectively.

The excellent measurements of Mullins (*34*) on the helium and hydrogen-argon binary systems below the boiling point of argon provide a valuable addition to the information relative to deviations from the geometric mean combining rule. Mullins determined the deviations (k_{12} values) for these systems to be 0.22 and 0.00, respectively, in the same manner as used here. The latter value is in excellent agreement with the value of k_{12} determined from Mullins' data in the present study.

CORRELATION FOR k_{12} PARAMETERS

In order to understand the possible reason for these deviations, it is necessary to study the basis for the geometric mean combining rule. The origin of this rule is found in London's theory of dispersion forces (*16*). Dispersion forces are the main forces of attraction which apply to the interaction of nonpolar molecules with which we are primarily concerned. The dispersion energy ϵ_{12} for the interaction of species 1 with species 2 can be expressed as

$$\epsilon_{12} = (-3/2r^6_{12})\,[\Delta_1\Delta_2/(\Delta_1 + \Delta_2)]\alpha_1{}^0\alpha_2{}^0 \qquad (3)$$

It can be seen from Equation (3), which is also applicable to interactions between like species, that if r_1 is equal to r_2 and Δ_1 is equal to Δ_2, then

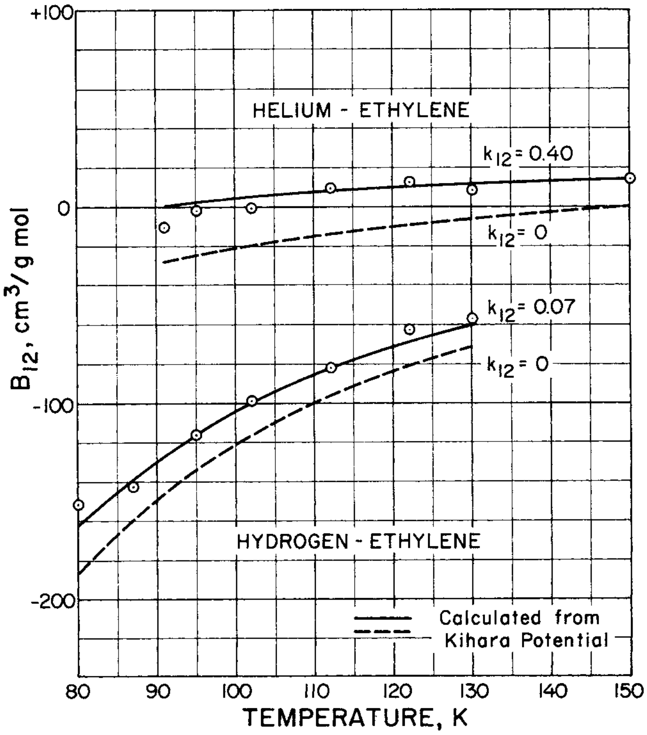

Fig. 1. Comparison of experimental and calculated values of B_{12} for the systems helium-ethylene and hydrogen-ethylene.

TABLE 2. DEVIATIONS FROM GEOMETRIC MEAN COMBINING RULE

System	k_{12} [Equation (5)]	k_{12} (exp.)	k_{12} [Equation (7)]	k_{12} source	Data source	Data temp., °K.
He-CH_4	0.155	0.40	0.361	*38*	*21*	55 to 91
		0.40		*32, 33*	*15*	95 to 185
He-C_2H_4	0.258	0.40	0.416	*	*17*	91 to 150
He-Ar	0.084	0.22	0.237	*34*	*34*	68 to 108
He-Ne	0.006	0.07	0.038	*	*14*	27 to 30
He-Xe	0.202	0.40	0.422	*42*	—	—
He-N_2	0.119	0.25	0.232	*	*48*	90
He-H_2	0.038	0.25-0.35†	0.228	*	*27*	90
Ne-CH_4	0.105	0.28	0.246	*4*	*22*	50 to 87
		0.263		*3*	*3*	123 to 273
Ne-C_2H_4	0.199	0.31	0.293	*	*17*	102 to 122
Ne-Ar	0.047	0.18	0.139	*33*	*45*	84 to 130
		0.141		*3*	*3*	123 to 323
Ne-Kr	0.075	0.20	0.203	*5*	—	—
		0.206		*3*	*3*	148 to 323
H_2CH_4	0.055	0.03	0.049	*4*	*20*	50 to 87
		0.03		*33*	*2*	116 to 172
H_2-C_2H_4	0.137	0.07	0.077	*	*19*	80 to 170
		0.05		*40*	*19*	
H_2-C_2H_6	0.069	0.02	0.056	*	*18*	83 to 190
		0.05		*39*	*18*	
		0.03		*33*	*18*	
H_2-Ar	0.017	0.00	0.001	*	*34*	68 to 108
		0.00		*34*	*34*	
Ar-Kr	0.003	0.014	0.021	*30*	*7*	116
		0.014		*3*	*3*	148 to 323
Ar-N_2	0.005	0.002	0.000	*30*	*36, 44*	84
		0.00		*5*	—	—
		0.001		*3*	*3*	123 to 323
Ar-O_2	0.007	0.014	0.060	*30*	*28, 36*	84
Ar-CO	0.008	0.011	0.017	*30*	*10, 36*	84
		0.014		*3*	*3*	123 to 273
Ar-CH_4	0.013	0.033	0.043	30	*29, 31, 44*	91
		0.063		*3*	*3*	123 to 273
N_2-O_2	0.007	−0.002	0.064	*30*	*1, 36*	78
N_2-CO	0.001	0.009	0.019	*30*	*36, 44*	84
		0.010		*3*	*3*	273
N_2-C_2H_6	0.008	0.05	0.054	*5*	—	—
N_2-Kr	0.002	0.019	0.024	*3*	*3*	148 to 323
N_2-Xe	0.016	0.073	0.079	*3*	*3*	173 to 323
CO-CH_4	0.001	0.018	0.014	*30*	*37, 44*	91
CO_2-C_2H_4	0.003	0.06	0.038	*5*	—	—
CF_4-CH_4	0.043	0.091	0.115	*30*	*9*	111
H_2S-CH_4	—	0.05	0.062	*5*	—	—
H_2S-C_2H_4	—	0.05	0.036	*5*	—	—

* Means this work; Kihara parameters of Prausnitz and Myers (*41*).

† Experimental k_{12} is based on one data point with large error limits, that is, B_{12} = 12.8 ± 1 cc./g.mole at 90°K. and is included only to show that the k_{12} value is approximately the same as that predicted by the ionization potential correlation of Equation (7).

$$\epsilon_{12} = (\epsilon_1, \epsilon_2)^{1/2} \tag{4}$$

which forms the basis for the geometric mean combining rule.

It has been assumed generally that the ionization potentials of the interacting species are sufficiently close as to be considered equal; however, in many cases this assumption is invalid. Hudson and McCoubrey (*23*) related Equation (3) to the attractive part of the Lennard-Jones 12:6 potential, replacing Δ with I (ionization potential), to obtain

$$\epsilon_{12} = \left\{ \frac{2(I_1 I_2)^{1/2}}{I_1 + I_2} \right\} \left\{ \frac{2^6 \sigma_1{}^3 \sigma_2{}^3}{(\sigma_1 + \sigma_2)^6} \right\} (\epsilon_1 \epsilon_2)^{1/2} \tag{5}$$

The product of ionization potential and collision diameter terms is equivalent to $(1 - k_{12})$ in the notation used here. The above authors have shown that the corrections in (5) make a substantial difference to the values of the interaction virial coefficients, calculated from the data for pure components, for a variety of systems. However, these corrections are inadequate to account for the large deviations observed for systems such as the helium-ethylene system.

It should be noted that repulsive forces also are related to the ionization potentials of the interacting species, as well as to the separation distance (*16*). The short-range contribution can be approximated by the much simplified form

$$\psi^{(\text{val})} = b \cdot \exp\left\{ -\frac{r}{a_o} \left(\frac{2a_o}{e^2} \right)^{1/2} (I_1{}^{1/2} + I_2{}^{1/2}) \right\} \tag{6}$$

The characteristic interaction energy parameter must be determined by the repulsive forces as well as by the attractive forces. It is probable that this is at least part of the reason that the correction terms of Equation (5) are less than adequate. A theoretical treatment of this problem

Table 3. Ionization Potentials, Electron-Volts*

He	24.46	CH_4	13.04 (*35*)
Ne	21.47	C_2H_4	12.2
Ar	15.4 (*24*)	C_2H_6	12.8
Kr	13.9	CO	14.1
Xe	12.08	CO_2	14.4
H_2	15.6	H_2S	10.42
N_2	15.51	CF_4	17.8 (*12*)
O_2	12.5		

* From (*13*) unless noted otherwise.

appears formidable. Thus, an empirical appproach was followed to examine the deviations from the geometric mean rule in this study.

As a result of the comprehensive study of binary systems of hydrogen, helium, and neon with light hydrocarbons (and argon), it has become apparent that the deviations are due, at least in part, to differences in the ionization potentials of the interacting species. This suggested the use of the ionization potential I as a parameter for correlating the deviations from the combining rule. It is found that the value of k_{12} in Equation (2) is best represented by

$$k_{12} = 0.17\,(I_1 - I_2)^{1/2} \ln\left(\frac{I_1}{I_2}\right) \tag{7}$$

where 1 refers to the component with the larger ionization potential. The basic assumption made is that the geometric mean represents the maximum interaction energy, and that k_{12} is always positive.

COMPARISON OF PREDICTED AND EXPERIMENTAL k_{12} VALUES

A graphical comparison is shown in Figure 2 between representative, experimental k_{12} values and those predicted from Equation (7). Table 2 gives a more extensive comparison of experimental k_{12} values for thirty binary systems with those predicted by Equations (5) and (7).

Table 4. Collision Diameters for Lennard-Jones 12:6 Potential*

He	2.56 (Quant)	CH_4	3.82
Ne	2.75	C_2H_4	4.52
Ar	3.41	C_2H_6	3.95
Kr	3.60	CO	3.76
Xe	4.10	CO_2	4.49
H_2	2.93 (Quant)	H_2S	—
N_2	3.70	CF_4	4.70
O_2	3.58		

* From second virial coefficients (*16*).

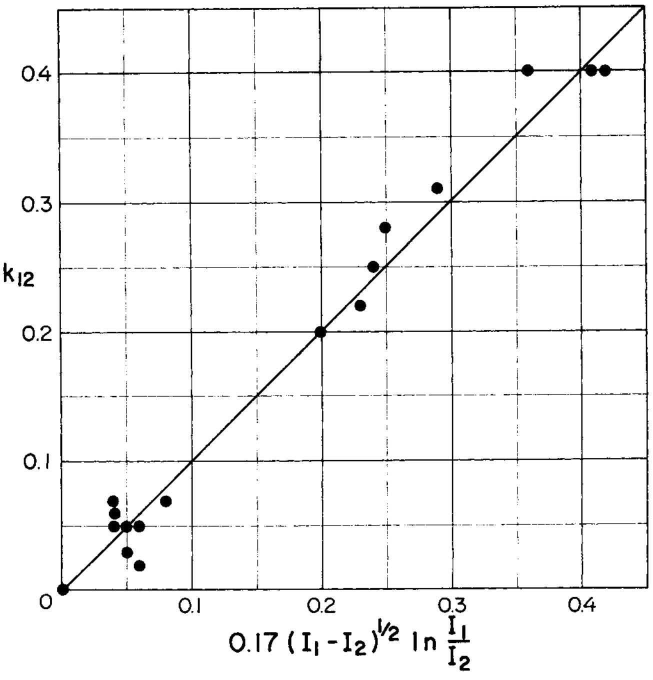

Fig. 2. Correlation of deviations from the geometric mean combining rule with ionization potentials.

Represented in Table 2 are systems having various combinations of similar and dissimilar component properties such as critical temperature, molecular size (and, to some extent, shape), and ionization potential. In addition, k_{12} values determined in different ways and from different properties are represented. The properties evaluated include liquid solution excess properties (*30*), Henry's constants from gas solubility (*32*, *33*), and interaction second virial coefficients from gas-phase volumetric data (*3*, *48*) or phase-equilibria data (*34*), as evaluated here and by Chueh and Prausnitz (*4*, *5*). Where possible, quantum corrections were considered in the present study in evaluation of gas-phase data to obtain k_{12} values.

Generally, k_{12} values for the same system from different sources are in good agreement. However, the experimental k_{12} values given in Table 2 for the systems helium-nitrogen and helium-argon are quite different from those given by Chueh and Prausnitz (*5*). These authors give 0.16 and 0.05 for the helium-nitrogen and -argon systems, respectively. The difference might be resolved by comparison of the data evaluated in the two studies. This has not been done, as yet, since no reference was given for the sources of data they used. However, the data used in the present work were carefully surveyed, and the values of k_{12} listed in Table 2 for these systems are probably the better values.

Discrepancies also were found between k_{12} values for hydrogen systems reported by Brewer (*3*) and those obtained from other sources. For example, Brewer reports a k_{12} value of -0.021 for hydrogen-argon compared with 0.00 from the data of Mullins (*34*). In contrast, we found a k_{12} value of $+0.01$ from Brewer's hydrogen-argon interaction second virial coefficient at 123.15°K. (−150°C.) using the Kihara model with quantum corrections. It was noted that Brewer obtained effective mixture characteristic temperatures for the hydrogen systems by fitting the interaction second virial coefficients to a correlating equation obtained from pure nitrogen, argon, carbon monoxide, neon, methane, and krypton, and the actual critical parameters of these species. The k_{12} values of the hydrogen systems, however, were obtained by using pseudocritical parameters. Brewer's k_{12} values for hydrogen systems were not included in Table 2. However, with more careful data reduction, k_{12} values for those systems also would be a valuable addition.

The ionization potentials and collision diameters employed in calculating k_{12} values from Equations (5) and (7) are given in Tables 3 and 4, respectively. Except for the three cases noted, ionization potentials were taken from the "Handbook of Chemistry and Physics" (*13*). Collision diameters are those listed by Hirschfelder et al. (*16*), determined from second virial coefficients.

The experimental values of k_{12} depend for their accuracy on the accuracy of the experimental data and on the applicability of pure component parameters, in the theoretical expression employed, to the temperature range of interest. The accuracy of the k_{12} values calculated from

Equation (7) depends entirely on the accuracy of reported ionization potentials, and a survey of the literature reveals a few significant discrepancies. Other values of ionization potentials were noted for components, such as methane (*46*), 12.99 electron v., and tetrafluoromethane (*49*), 14.21 electron v., which either support or refute selection of the values given in Table 3. Thus, the choice was not completely unambiguous. It is expected that the values of k_{12}, both the experimental values and those calculated from Equation (7), may be in error by as much as ± 0.05, at least for the larger values. This would explain the small amount of scatter in Figure 2.

The accuracy of k_{12} values calculated from Equation (5), the Hudson and McCoubrey formulation, depends on the accuracy of reported collision diameters, as well as ionization potentials. However, the resultant values of k_{12} are relatively insensitive to these uncertainties, since both correction terms are ratios of geometric and arithmetic averages.

The deviations from the geometric mean rule predicted by Equation (5) clearly are inadequate to account for the large k_{12} values observed for systems such as helium-xenon or helium-hydrogen. These systems are mentioned specifically, since the first pair has large differences in both ionization potentials and collision diameters, and the second pair has a large difference in ionization potentials but a very small difference in collision diameters.

On the other hand, the k_{12} values predicted by Equation (5) are too large for systems, such as the hydrogen-ethylene and hydrogen-argon systems, where differences in the ionization potentials are very small, but where the differences in collision diameters are large.

As a comparison, Equation (7) predicts k_{12} values of the correct magnitude for all of the above-mentioned systems. With the exception of the two oxygen systems, differences between k_{12} values predicted by Equation (7) and experimental values for the other systems included in Table 2 are within expected uncertainties.

SUMMARY

As a result of the observed pattern of deviations from the geometric mean combining rule, it was possible to develop a correlation between the values of k_{12} and the ionization potentials of the components in a number of binary mixtures. This relationship, though in need of refinement as more reliable data become available, offers a good approximation of the k_{12} needed to predict gas-phase properties of binary systems, particularly those containing helium and neon, for which little or no data are available.

NOTATION

a_o = the radius of the first Bohr orbit
B = second virial coefficient, cc./g. mole
b = constant, defined by Equation (6)
C = third virial coefficient, (cc./g. mole)^2
e = charge on the electron
I = ionization potential, electron v.
k_{12} = constant representing deviation from the geometric mean for U_{012}
p_0 = vapor pressure, atm.
v_0 = molal volume of condensed phase, cc./g. mole
R = gas constant
r = separation of molecular centers
T = temperature, °K.
U_0 = maximum, negative, potential energy for the Kihara intermolecular potential function
y = mole fraction in gas phase
Z = compressibility factor

Greek Letters

α^0 = static polarizability
ϵ = dispersion energy
Δ = approximately equal to the ionization potential
π = total pressure, atm.
ρ = gas density, g.mole/cc.
$\psi^{(val)}$ = short-range repulsive force

Subscripts

1 = component 1
2 = component 2

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Virial Coefficients and Critical Properties of Perfluorohexanes

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Compressibility measurements of the gas phase are reported for the compounds n-C_6F_{14}, 2-$CF_3C_5F_{11}$, 3-$CF_3C_5F_{11}$, 2,3-$(CF_3)_2C_4F_8$, and cyclo C_6F_{12}. The measurements range from 1 to 18 atm. pressure and from 80° to 180°C. Second and third virial coefficients and critical properties have been calculated and are reported.

In order that various intermolecular potential energy functions might be studied for large nonpolar molecules, compressibility measurements have been made for five perfluorohexanes. From these measurements the second and third virial coefficients have been calculated and the vapor pressures and critical properties obtained. Measurements on four of these compounds have been made by Cecil (*1*) in the low temperature range. Garner and McCoubrey (*2*) have reported measurements on n-C_6F_{14}.

APPARATUS

A recent review (*3*) describes numerous types of compressibility apparatus and discusses the limitations and accuracy of each apparatus. The apparatus selected for this work was based upon the designs of Kay and Rambosek (*4*) and Connolly and Kandalic (*5*). This design was adopted because with the proper auxiliary equipment a high degree of accuracy could be attained with only a small amount of sample.

The measurements were made by confining the sample in a calibrated glass piezometer over mercury, maintaining a constant temperature around the piezometer by boiling liquid at constant pressure in a vapor jacket, and then measuring the pressure exerted by the sample with a manometer or dead weight pressure gauge. The compressibility data were obtained as isotherms, and the virial coefficients could be calculated directly.

The apparatus is shown schematically in Figure 1. The main components are a glass piezometer (a), vapor jacket (b), mercury reservoir (c), mercury-oil interface detector (d), dead weight gauge (e), and manometer (f). Auxiliary apparatus included a compressed gas source, vacuum system, manostat, thermocouples, potentiometer, mercury level indicator, magnetic stirring device, and cathetometer.

The piezometer was constructed of 3 mm. I.D. precision bore borosilicate glass capillary tubing of 3 mm. wall thickness. It was 70 cm. in length and was connected to a ¼ in. stainless steel tubing system by a compression block (g). Gasketing between the piezometer and compression block was accomplished by the use of viton 0 rings.

The piezometer was surrounded by a vapor jacket (b) which could be sealed to the compression block (g) with 0 ring gaskets. The vapor jacket was 20 mm. I.D. glass tubing, surrounded with an evacuated jacket. The interior of the vacuum jacket was silvered except for a 1 cm. strip along the length of the jacket for observation of the piezometer. The vapor jacket could be removed without disturbing the piezometer connection. A boiling flask (h) was attached to the vapor jacket. A ground glass joint (i) at the top of the vapor jacket allowed for the connection of a condenser, thermocouples, and pressure control line. The pressure control line was connected through a Cartesian manostat to a vacuum system.

The mercury reservoir was constructed of stainless steel and had a volume of approximately 1 liter and could be opened to the piezometer. It was connected so that either vacuum or pressure could be exerted on the surface of the mercury in the reservoir.

The mercury-oil interface detector was a stainless steel cylinder and had a volume of approximately 1 liter and a cross-sectional area of 75 sq. cm. Three tungsten wires were inserted in the detector, each one connected in series with an indicating lamp. The middle detector was used as the reference to which the interface was adjusted for all measurements. The other two indicators served as safety devices. The interface detector was connected to the deadweight tester directly and could be opened to the piezometer.

The deadweight tester (e) was a commercial type. It was designed for a pressure range of 5 to 500 lb./sq.in. gauge and contained weights so that determinations could be made at 5 lb./sq. in. intervals.

The two open end manometer tubes (f) could be connected to the piezometer. One manometer was constructed of

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