An Equation of State for Gas Mixtures

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A pressure-volume-temperature equation for mixtures of two or more gases has been developed using the "reference substance" technique of comparing the properties of one substance with those of a standard substance under the same conditions.

The compressibility factor is a function of temperature and pressure, with the variation from one substance to another being determined by the forces of attraction and repulsion between molecules. Thus, if the Lennard-Jones 6-12 potential function is used to describe the molecular interaction, the change in the compressibility function reflects the different force constants, which in turn are functions of the critical constants.

A mixture of gases is assumed to have the same thermodynamic properties as some hypothetical or pseudo gas which would have the same force constants existing between each pair of molecules in the mixture. The force constants of the pseudo gas may be evaluated from pseudo critical constants, which may be evaluated from the critical constants of individual components of the mixture.

With the resultant force constants, there can be calculated the ratio of the compressibility factors of the gas mixture to those of a pure gas, nitrogen, taken as a reference substance, all values taken at the same reduced temperature and pressure. The compressibility factor of the mixture may be calculated from this ratio and the compressibility factor of the reference substance; and the PVT relations are immediately determinable.

A comprehensive survey of the literature for PVT data of gas mixtures was made. More than 1,000 experimental values of PVT data for thirty-four binary systems and four ternary systems have been studied. The proposed method showed an average deviation from experimental data, representing all published work, of 2.3%.

The chemical industry deals with an ever increasing number of chemical compounds. For these substances, the experimental evaluation of accurate pressure-volume-temperature (PVT) data and the thermodynamic properties derivable therefrom, is, in itself, a never ending task. However, most chemical processes deal with mixtures, usually multicomponent, and the evaluation of the required data becomes a much larger and more complex task, which has produced few results to date. Experimental determinations of data for all possible mixtures can never be made. It is important, therefore, to determine how relationships for pure gases may be generalized to cover the more complex case of mixture.

Numerous equations of state have been proposed for pure gases. Since almost all are empirical, or at best semi-empirical in nature, it has not been possible to make an accurate assessment of the physical meaning which is associated with the various constants of these equations, and in many cases there may be no physical meaning. This deficiency of equations of state for pure gases prevents their extension to gas mixtures. The present study was undertaken to develop an understanding and a means of expressing PVT relations for mixtures of two or more gases. The method of analysis used in this research was based on the reference substance technique of comparing the properties of one substance with those of a reference substance for which more data exists.

THEORETICAL DEVELOPMENT

Pitzer (*25*) has shown that substances which obey the corresponding state's principle are those for which: (1) quantum effects are negligible, (2) the potential energy of molecular interaction can be expressed as the sum of the energies of interaction between each two molecules, and (3) the intermolecular potential energy between any two molecules of a substance can be represented by

$$\varphi = \epsilon f\left(\frac{\sigma}{\gamma}\right) \tag{1}$$

Here the function f is the same for all the substances and the constants σ and ϵ are peculiar to each substance.

When conditions (1), (2), and (3) are satisfied for a group of substances, then the PVT behavior of each substance can be represented by (*25*, *9*, p. 245).

$$Z = \frac{PV}{RT} = f\left(\frac{kT}{\epsilon}, \frac{V}{b_0}\right) \tag{2}$$

where

$$b_o = \frac{2}{3}\pi \tilde{N} \sigma^3 \tag{3}$$

Therefore, it may be concluded that, to the extent that the molecular interactions can be represented by Equation (1), the equation of state of a material may be described by a single equation, such as Equation (2).

Nelson and Obert (*22*) have used a molecular principle of corresponding states to obtain a generalized compressibility chart for predicting the PVT behavior of pure gases in the range somewhat beyond that which can be reached by the virial coefficient calculation.

Recently, Boas (*4*) investigated the relationship between PVT data and molecular forces for pure gases. The potential energy of interaction was used, since it is more convenient than the force of interaction. The analysis is based on the use of the potential energy function in conjunction with reference substance techniques (*24*). The work described here also builds upon these two basic concepts in defining PVT relations for approach to gas mixtures.

For those substances that are mixtures, it must be an adequate approximation that the intermolecular potential energy between any two molecules can be represented by a single function as Equation (1); this leads to the view that the mixture is a pseudo pure substance—that the

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mixture is made up of a collection of pseudo molecules that are all alike insofar as the potential energy of interaction is the same between any two.

For densities up to approximately one half of that at the critical, the pressure of either a pure or mixed gas is adequately represented by the virial equation terminated after the second virial coefficient.

The virial equation of state for a mixture may be expressed as a pressure series:

$$Z_M = 1 + \bar{B}/RT\ P \tag{4}$$

In Equation (2) the parameters σ and ϵ may be written with an overbar to emphasize that, for mixtures, they are some kind of average representation of the molecular interaction. These are called pseudo force constants. Here they are used as the basis for reducing the variables. The following terminology is used:

$$\bar{B}^* = \bar{B}/\bar{b}_o \tag{5}$$

$$\bar{T}_c^* = k\bar{T}_c/\bar{\epsilon} \tag{6}$$

$$\bar{P}_c^* = (\bar{b}_o/R)(k/\bar{\epsilon})\bar{P}_c \tag{7}$$

$$\bar{T}_r = \bar{T}/\bar{T}_c \tag{8}$$

$$\bar{P}_r = \bar{P}/\bar{P}_c \tag{9}$$

Combination of Equations (4) to (9) will give the resulting expression

$$Z_M = 1 + \left(\frac{\bar{B}^*\bar{P}_c^*}{\bar{T}_c^*}\right)\left(\frac{\bar{P}_r}{\bar{T}_r}\right) \tag{10}$$

The ratio of the compressibility factor may be defined for two different substances at the same reduced temperature $\overline{Tr}$ and reduced pressure $\overline{Pr}$, as follows:

$$ZTZ = Z_M/Z_R \tag{11}$$

By substituting Equation (10) and a similar expression for a reference substance into Equation (11), one obtains

$$ZTZ = \frac{Z_M}{Z_R} = \frac{1 + \left(\frac{\bar{B}^*\bar{P}_c^*}{\bar{T}_c}\right)_M \left(\frac{\bar{P}_r}{\bar{T}_r}\right)}{1 + \left(\frac{B^*P_c^*}{T_c^*}\right)_R \left(\frac{\bar{P}_r}{\bar{T}_r}\right)} \tag{12}$$

It is clear that Equation (12) meets the requirements of Equation (2). Thus, the following expression is obtained for an equation of state for gas mixtures:

$$Z_M = (ZTZ)(Z_R) = \left[\frac{1 + \left(\frac{\bar{B}^*\bar{P}_c^*}{\bar{T}_c^*}\right)_M \left(\frac{\bar{P}_r}{\bar{T}_r}\right)}{1 + \left(\frac{B^*P_c^*}{T_c^*}\right)_R \left(\frac{\bar{P}_r}{\bar{T}_r}\right)}\right](Z_R) \tag{13}$$

ZTZ is a means of determining the deviations from the generalized compressibility chart. The generalized chart assumes that ZTZ is always equal to 1.0, because the same compressibility factor Z is read from the same values of T_r and P_r regardless of the substance.

The reference substance concept compares properties of one substance with those of a reference material for which much data exist. ZTZ as defined in Equation (12) has been related to the pseudo force constants of the substance in question. Hence, from a knowledge of the pseudo force constants, it is possible to calculate ZTZ and, subsequently, the compressibility factors for a mixture from Equation (13).

PSEUDO LENNARD-JONES FORCE CONSTANTS

Based on the virial theorem (9, p. 136), the equation of state for a gas mixture can be expressed as

$$\frac{P}{kT} = \frac{N}{V} - \frac{2\pi N(N-1)}{3kTV^2} \sum_i^c \sum_j^c y_i y_j \int_o^\infty \gamma_{ij}^3 \left(\frac{d\varphi_{ij}}{d\gamma_{ij}}\right) h\, d\gamma_{ij} \tag{14}$$

where the radial distribution function h may be expressed as

$$h = e^{-\frac{\varphi_{ij}}{kT}}(1 + f_1 + f_2 + \ldots\ldots) \tag{15}$$

Some knowledge is available regarding the second or higher terms in Equation (15). Thus, by truncating at the first term, Equation (15) becomes

$$P = \frac{NkT}{V} - \frac{2\pi N(N-1)}{3V^2} \sum_i^c \sum_j^c y_i y_j \int_o^\infty \gamma_{ij}^3 \left(\frac{d\varphi_{ij}}{d\gamma_{ij}}\right) e^{-\frac{\varphi_{ij}}{kT}} d\gamma_{ij} \tag{16}$$

If the pseudo concept is valid, the equation of state of a gas mixture, including N molecules, at temperature T, and volume V, can be expressed as

$$\bar{P} = \frac{NkT}{V} - \frac{2\pi N(N-1)}{3V^2} \int_o^\infty \bar{\gamma}^3 \left(\frac{d\bar{\varphi}}{d\bar{\gamma}}\right) e^{-\frac{\bar{\varphi}}{kT}} d\bar{\gamma} \tag{17}$$

Now let

$$P = \bar{P} \tag{18}$$

Finally, there is obtained

$$\int_o^\infty \bar{\gamma}^3 \left(\frac{d\bar{\varphi}}{d\bar{\gamma}}\right) e^{-\frac{\bar{\varphi}}{kT}} d\bar{\gamma} = \sum_i^c \sum_j^c y_i y_j \int_o^\infty \gamma_{ij}^3 \left(\frac{d\varphi_{ij}}{d\gamma_{ij}}\right) e^{-\frac{\varphi_{ij}}{kT}} d\gamma_{ij} \tag{19}$$

It is interesting to note that the Lennard-Jones 6-12 potential meets the requirement of Equation (2). In the mixtures where both materials have nonpolar molecules, or in those containing both nonpolar and polar molecules, the potential function in the Lennard-Jones form is (9, p. 223)

$$\varphi_{ij} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{\gamma_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{\gamma_{ij}}\right)^6\right] \tag{20}$$

where

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)\cdot(FLJ)^{-\frac{1}{6}} \tag{21}$$

$$\epsilon_{ij} = (\epsilon_i \cdot \epsilon_j)^{\frac{1}{2}} \cdot (FLJ)^2 \tag{22}$$

and

$$FLJ = 1 + \frac{16\,\eta_i \cdot \mu_j^2}{(\sigma_i + \sigma_j)^6 \cdot (\epsilon_i \cdot \epsilon_j)^{1/2}} \tag{23}$$

If the intermolecular potential of the pseudo gas is assumed to be made up of molecules that are hypothetically identical, an equation results of the same form as Equation (20):

$$\bar{\varphi} = 4\bar{\epsilon}\left[\left(\frac{\bar{\sigma}}{\bar{\gamma}}\right)^{12} - \left(\frac{\bar{\sigma}}{\bar{\gamma}}\right)^{6}\right] \qquad (24)$$

Substitution of Equations (20) and (24) into Equation (19) gives

$$a_1 T^{-\frac{1}{4}}\left[\bar{\sigma}^3\,\bar{\epsilon}^{\frac{1}{4}} - \sum_i^c \sum_j^c y_i y_j\, \sigma_{ij}^3\, \epsilon_{ij}^{\frac{1}{4}}\right] +$$

$$b_1 T^{-\frac{3}{4}}\left[\bar{\sigma}^3\,\bar{\epsilon}^{\frac{3}{4}} - \sum_i^c \sum_j^c y_i y_j\, \sigma_{ij}^3\, \epsilon_{ij}^{\frac{3}{4}}\right] + \ldots\ldots +$$

$$b_n T^{-\left(\frac{2n+1}{4}\right)}\left[\bar{\sigma}^3\,\bar{\epsilon}^{\left(\frac{2n+1}{4}\right)} - \sum_i^c \sum_j^c y_i y_j\, \sigma_{ij}^3\, \epsilon_{ij}^{\left(\frac{2n+1}{4}\right)}\right]$$

$$= 0 \qquad (25)$$

It follows that all terms in the brackets in Equation (25) must be equal to zero. Since this gives an infinite number of equations and only two variables $\bar{\epsilon}$ and $\bar{\sigma}$, there is obviously no single set of values for $\bar{\epsilon}$ and $\bar{\sigma}$. In other words, there are no rigorous pseudo Lennard-Jones force constants for a multicomponent system. However, the series in Equation (25) may be replaced with an approximate equation containing a term considering the molecules as hard spheres and a single one of the remaining terms which could for intermolecular forces, as shown in Equation (26).

$$a\left[\bar{\sigma}^3 - \sum_i^c \sum_j^c y_i y_j\, \sigma_{ij}^3\right] +$$

$$bT^{-q}\left[\bar{\sigma}^3\,\bar{\epsilon}^{q} - \sum_i^c \sum_j^c y_i y_j\, \sigma_{ij}^3\, \epsilon_{ij}^{q}\right] = 0 \qquad (26)$$

This may be written

$$\bar{\sigma} = \left[\sum_i^c \sum_j^c y_i\, y_j\, \sigma_{ij}^3\right]^{\frac{1}{3}} \qquad (27)$$

$$\bar{\epsilon} = \left(\frac{\sum_i^c \sum_i^c y_i y_j\, \sigma_{ij}^3\, \epsilon_{ij}^{q}}{\bar{\sigma}^3}\right)^{\frac{1}{q}} \qquad (28)$$

However, the results shown in Equations (27) and (28) are identical to those found by Leland and Muller (*16*). Leland and Muller empirically correlated the values of q as a function of $\left[T \sum_i^c y_i (P_c)_i / P \sum_j^c y_i (T_c)_i\right]$. All of the empirically evaluated q values fall in the range of 2.20 to 1.00.

In the present work, the values of q were determined by using Equations (13), (27), and (28) to predict compressibility factors which have also been measured experimentally. Twenty one points of experimental PVT data at saturated conditions have been studied. These include values for methane-propane, methane–*n*-butane, and methane–*n*-pentane. Nitrogen was taken as the reference substance. It was found that these q values could be correlated against $\left[T \sum_i^c y_i (P_c)_i / P \sum_j^c y_i (T_c)_i\right]$.

As shown in Figure 1, the evaluated q values are all in the range of 0.15 to 1.62. Using the method described by King (*14*), one finds the equation which accurately fits the curve in Figure 1 to be

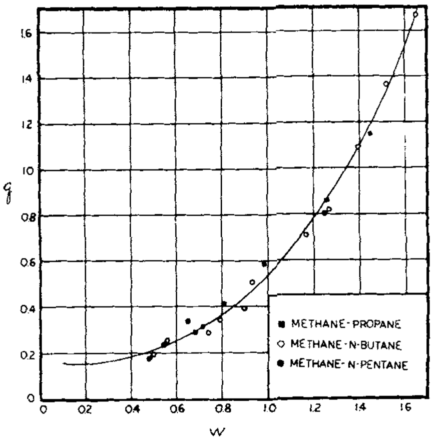

Fig. 1. q vs. W.

$$q = 1.62, \text{ if } W \geqq 1.64 \qquad (29)$$

$$q = 0.15, \text{ if } W \leqq 0.20 \qquad (30)$$

$$q = 0.15 + 0.025\,(W - 0.2) + 0.563\,(W - 0.2)^2 - 0.089\,(W - 0.2)^3 + 0.124\,(W - 0.2)^4, \text{ if } 0.20 \leqq W \leqq 1.64. \qquad (31)$$

where

$$W = T \sum_i^c y_i (P_c)_i / P \sum_j^c y_i (T_c)_i \qquad (32)$$

On the basis of the good correlation of the three binary mixtures in Figure 1, it is surmised that Equations (29) to (32) can be applied to any binary or multicomponent system for the prediction of compressibility factors.

CALCULATING PROCEDURES

Through this work, the required computations were done on the IBM-650 computer for the earlier part and on the IBM-7040 for the latter. The calculations were carried out in the following sequence:

1. The value of q was evaluated at any given temperature, pressure, and composition with Equations (29) to (32).
2. The pseudo force constants were predicted using q from Equations (21), (22), (23), (27), and (28).
3. The pseudo critical constants were evaluated from the pseudo force constants obtained from (2), and the pseudo reduced temperatures and pressures immediately found from the pseudo critical constants.

For determining the pseudo criticals for a mixture, the following relations may be used (*33*):

$$\bar{T}_c = \left(\frac{1}{0.77}\right)\left(\frac{\bar{\epsilon}}{k}\right) \qquad (33)$$

$$\bar{V}_c = \left(\frac{1}{0.5805}\right)(\bar{\sigma}^3) \qquad (34)$$

However, it is more convenient to change the variables of pseudo critical volume to a pseudo critical pressure by defining a pseudo critical compressibility factor for the mixture

$$\bar{Z}_c = \sum_i^c y_i\, Z_{ci} \qquad (35)$$

4. The ratio of the compressibility factor of the gas mixture to the compressibility factor of the reference substance is a known function of the pseudo force constants, as shown in Equation (12), and is calculated therefrom.

For the reference substance, as well as a nonpolar mixture, the Lennard-Jones potential function was used. The second virial coefficients of a mixture $\overline{B^*}$ can be expressed as

$$\overline{B}^* = \sum_{j=0}^{\infty} \frac{-2^{j+\frac{1}{2}}}{4j!} \Gamma\left(\frac{2j-1}{4}\right) \left(\frac{kT}{\overline{\epsilon}}\right)^{-\frac{2j+1}{4}} \tag{36}$$

For a polar mixture, or a mixture containing one or more polar components, the Stockmayer potential function (*37*) is assumed. The $\overline{\epsilon}$ and $\overline{\sigma}$ used to evaluate the reduced molecular quantities would be the ones corresponding to the Stockmayer potential. An additional parameter $\overline{\mu}$, the pseudo dipole moment, is needed to evaluate the pseudo reduced second virial coefficient for a mixture.

$$\overline{B}^* = f(\overline{T}^*, \overline{\mu}^*) \tag{37}$$

where

$$\overline{\mu}^* = \frac{\overline{\mu}}{\sqrt{\overline{\epsilon} \cdot \overline{\sigma}^3}} \tag{38}$$

and

$$\overline{\mu} = \left(\frac{\sum_i^c \sum_j^c y_i\, y_j\, \sigma_{ij}^{-3}\, \epsilon_{ij}\, \mu_{ij}^4}{\overline{\epsilon}\, \overline{\sigma}^{-3}}\right)^{\frac{1}{4}} \tag{39}$$

Equation (39) is an approximation obtained by substituting the Stockmayer potential function into Equation (19).

5. The compressibility factor of the reference substance is determined at the reduced temperatures and pressures corresponding to the pseudo values of (3). In this work, the reference substance is always nitrogen. The compressibility factors for nitrogen at various temperatures and pressures have been predicted by the following equation:

$$Z = \frac{PV}{RT} = 1 + \alpha P + \beta P^2 + \gamma P^3 \tag{40}$$

where the coefficients α, β, and γ were tabulated in U.S. National Bureau of Standards Circular 564.

6. The compressibility factor of the gas mixture may now be calculated from the ratio of 4 and the compressibility factor of the reference substance of 5.

7. The volume of the gas mixture at the given temperature, pressure, and composition may be determined from the compressibility factor of 6.

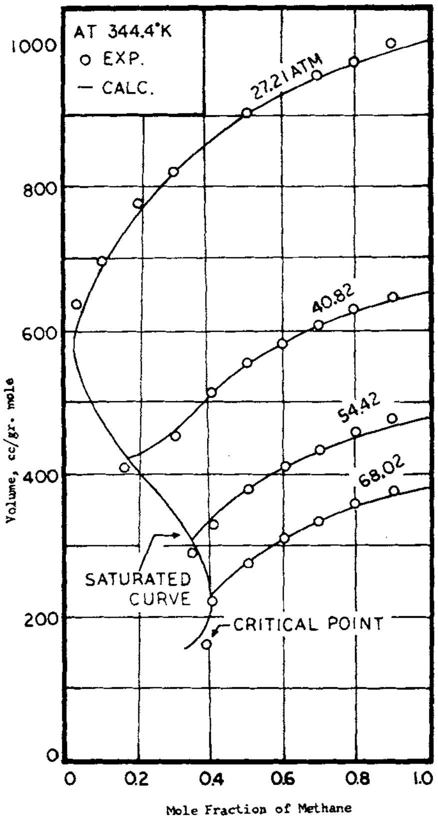

Fig. 2. Molal volume of the mixture of methane and propane by the proposed method.

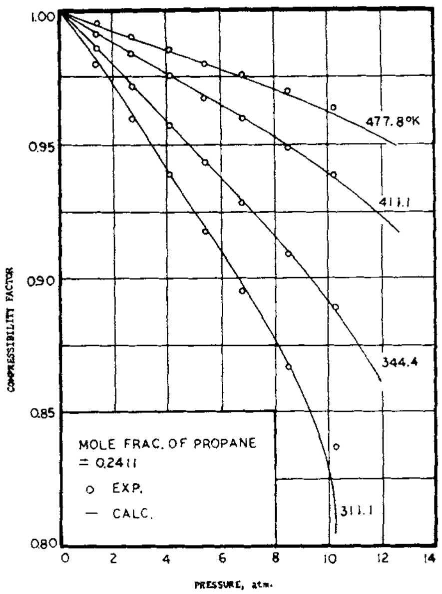

Fig. 3. Compressibility factor of the mixture of propane and propene by the proposed method.

COMPARISON OF EQUATION WITH EXPERIMENTAL DATA

A comprehensive survey of the literature for experimental data of PVT relations of gas mixtures was made. The search revealed data on thirty-four binary systems and

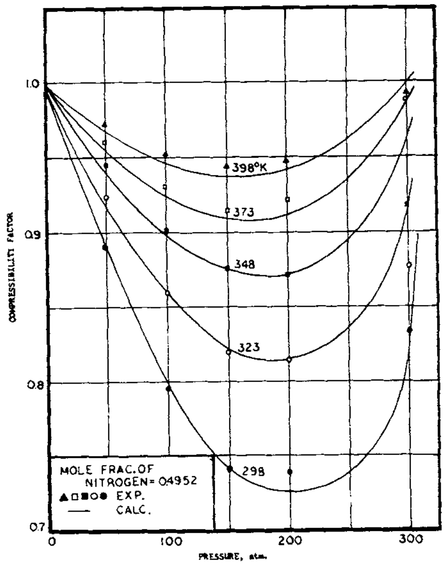

Fig. 4. Compressibility factor of the mixture of nitrogen and carbon dioxide by the proposed method.

Table 1. Comparison of the Results Calculated by the Proposed Method with the Experimental Data. Summary

	System	Ref.	No. of expt. pt.	T, °K.	P, atm.	Y_1*	Absolute deviation, % Maximum	Absolute deviation, % Average
(1)	Methane-ethane	*36*	52	294.4 to 394.4	1.36 to 136.1	0.3191 to 0.9	3.847	1.293
(2)	Methane-carbon dioxide	*26*	42	311.11 to 511.1	13.6 to 544.2	0.406 to 0.8469	5.622	2.230
(3)	Methane-hydrogen sulfide	*29*	39	277.7 to 344.4	13.1 to 102.0	0.1 to 0.9	5.459	1.365
(4)	Methane-propane	*28*	63	344.4 to 511.1	13.6 to 102.0	0.1 to 0.9	8.052	1.095
(5)	Methane-*n*-butane	*35*	24	294.4 to 377.8	3.03 to 102.0	0.2868 to 0.8	6.458	3.773
(6)	Methane-isobutane	*23*	48	411.1 to 511.1	13.6 to 136.1	0.16 to 0.7101	7.394	1.816
(7)	Methane-pentane	*34*	28	411.1 to 511.1	13.6 to 102.0	0.1 to 0.9	6.506	1.313
(8)	Methane-isopentane	*1*	26	411.1 to 477.7	13.6 to 102.0	0.4976	8.492	4.430
(9)	Methane-nitrogen	*3*	24	101.9 to 373.0	2.6 to 600	0.1577 to 0.7121	9.145	5.274
(10)	Ethane-carbon dioxide	*27*	21	411.1	13.6 to 68.0	0.1 to 0.9	4.976	2.509
(11)	Ethane-propene	*19*	22	377.8 to 477.8	13.6 to 102.0	0.4958	5.981	2.620
(12)	Ethane-benzene	*13*	20	381.6 to 513.4	20.4 to 81.6	0.3922 to 0.8523	8.730	3.191
(13)	Ethane-*n*-heptane	*10*	12	422.9 to 485.1	20.4 to 81.6	0.5871 to 0.7709	8.534	3.445
(14)	Ethane-nitrogen	*28*	28	444.4	13.6 to 170.0	0.2 to 0.8	5.776	1.946
(15)	Propane-carbon dioxide	*30*	24	444.1	13.6 to 54.4	0.1 to 0.9	5.178	2.658
(16)	Propane-propene	*31*	56	311.1 to 477.8	1.361 to 10.2	0.2411 to 0.7589	3.996	0.604
(17)	Propane-isopentane	*39*	35	373 to 573	5 to 70	0.899	6.786	1.871
(18)	Propane-benzene	*6*	12	411.1 to 444.4	13.6 to 54.4	0.8827	4.390	1.642
(19)	Propane-nitrogen	*43*	19	422.2	6.272 to 415.7	0.319 to 0.834	5.641	1.124
(20)	Propene-l-butene	*7*	11	311.1 to 377.8	5.44 to 40.82	0.083 to 0.938	9.028	4.181
(21)	*n*-Butane-*n*-heptane	*11*	11	408.8 to 496.1	5.44 to 35.37	0.4249 to 0.801	5.832	1.483
(22)	*n*-Butane-*n*-nitrogen	*42*	27	427.8	13.6 to 204.1	0.1 to 0.9	5.459	1.909
(23)	*n*-Pentane-hydrogen sulfide	*32*	8	444.4	13.6 to 54.4	0.2 to 0.3	8.282	2.549
(24)	Toluene-*n*-hexane	*41*	12	498.2 to 558.2	13.4 to 36.1	0.3 to 0.634	7.151	3.804
(25)	Ethylene-*n*-heptane	*12*	12	369.6 to 510.4	10.2 to 54.4	0.2857	6.354	2.397
(26)	Ethylene-argon	*18*	26	298	30 to 120	0.2474 to 0.7073	9.482	3.340
(27)	Ethylene-oxygen	*18*	12	298	30 to 120	0.2527 to 0.5984	7.324	3.386
(28)	Argon-helium	*38*	18	298	10 to 120	0.1643 to 0.8352	6.386	1.496
(29)	Argon-hydrogen	*38*	28	298	10 to 120	0.1647 to 0.8352	1.914	0.659
(30)	Nitrogen-carbon dioxide	*15*	25	298 to 398	50 to 300	0.4952	5.325	1.135
(31)	Oxygen-argon	*18*	7	298	30 to 120	0.5001	3.043	1.811
(32)	Hydrogen-helium	*5*	9	298	10 to 50	0.2601 to 0.736	6.454	3.399
(33)	Nitrogen-hydrogen	*40*	14	273	100 to 400	0.115 to 0.863	6.151	3.071
(34)	Nitrogen-ethylene	*8*	18	323.07	1.2 to 314.5	0.198 to 0.796	4.643	1.592
(35)	Methane-*n*-butane-decane	*30*	83	311.1 to 511.1	27.2 to 187.1	Y_1 = 0.8423 to 0.9279 Y_2 = 0.0603 to 0.1318	6.721	1.837
(36)	Hydrogen-nitrogen-methane	*2*	38	373 to 473	100 to 600	Y_1 = 0.198 to 0.5266 Y_2 = 0.2618 to 0.555	8.988	2.643
(37)	Hydrogen-nitrogen-carbon dioxide	*15*	60	323.2 to 473.2	50 to 500	Y_1 = 0.271 to 0.544 Y_2 = 0.235 to 0.547	8.894	4.780
(38)	Hydrogen-nitrogen-ammonia	*20, 21*	63	323 to 423	1 to 220	Y_1 = 0.5856 to 0.6650 Y_2 = 0.1960 to 0.2640	7.997	2.833
Total			1,077			Total average	6.564	2.281

* Y_1 = mole fraction of the first component.

four ternary systems. No data for mixtures with more components were found. More than 1,000 experimental values of compressibility factors of gas mixtures were so obtained for thirty-four binary systems and four ternary systems. This equation of state was developed for the use of an IBM-650 and also IBM-7040 digital computer. The values of pressure, temperature, and composition at the conditions of each experimental point were fed into the program, and the compressibility factor was determined. This was compared with the experimental data. The average deviation of the calculated compressibility factor, compared with the experimental compressibility factor, was 2.281%. This is probably within the range of the experimental error for the original determinations of the compressibility factors. Some of these results are illustrated in Figures 2 to 4. A summary appears in Table 1.

Figures 5 to 7 compare the compressibility factors of different mixtures by three methods: the Proposed method, Equation (13); published generalized table [Lydersen, Greenkorn, and Hougen (*17*)] in which pseudo critical temperature and pressures are usually determined from

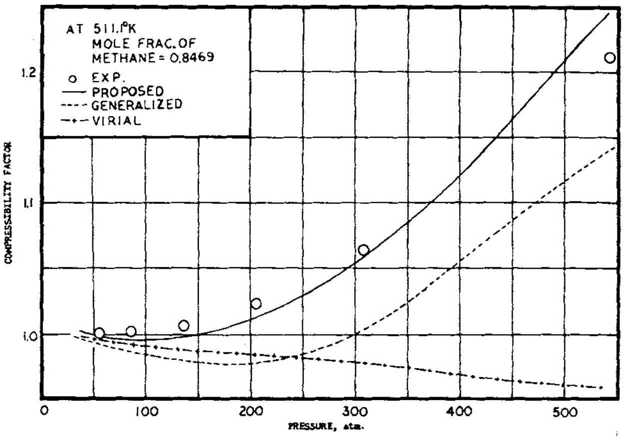

Fig. 5. Compressibility factor of the mixture of methane and carbon dioxide by different methods.

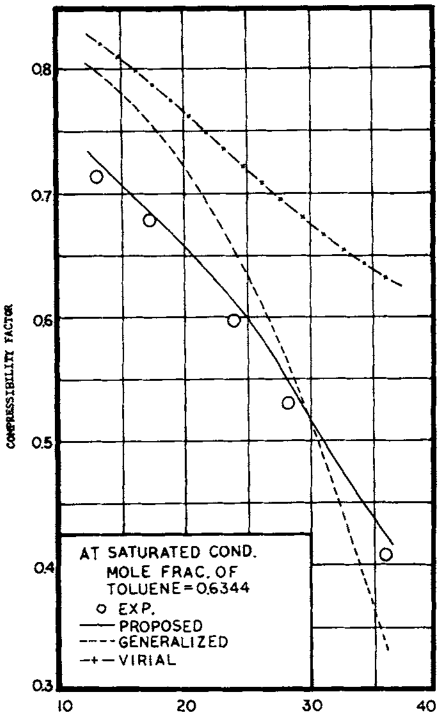

Fig. 6. Compressibility factor of the mixture of toluene and *n*-hexane by different methods.

Kay's rule; virial equation, terminated at the second virial coefficient, which was determined from the pseudo conditions derived in this research, Equation (10).

It is not surprising to find that the compressibility factor determined from the generalized table does not compare well with the experimental data for a mixture containing polar or high molecular weight components, which cannot be expected to follow Kay's rule for calculating the pseudo critical conditions. Kay's rule was based on PVT correlations with lighter hydrocarbons, and there is no physical significance in this rule.

The compressibility factors calculated by the virial equation come out poorly at higher pressures compared with the experimental because it was terminated at the second virial coefficient. Thus, it is concluded that a larger number of virial coefficients are required at high densities.

The proposed equation of state gives results which compare very well with the experimental data in every case. It might be of interest to note that there is no limitation of temperatures and pressures covered by the proposed equation of state, as in the case of the use of the virial equation, although both of the proposed equations of state and virial equations consider the second virial coefficients only. This is also one of the advantages of the reference substance technique. Table 2 shows the comparison of the results obtained by these three methods for seven representative systems.

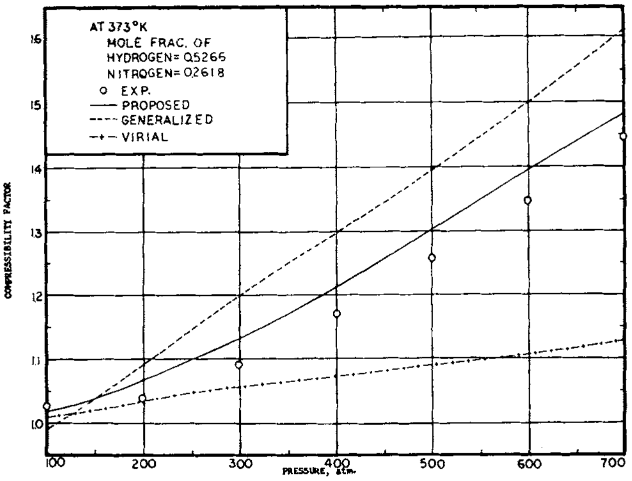

Fig. 7. Compressibility factor of the mixture of hydrogen, nitrogen, and methane by different methods.

RESULTS AND CONCLUSIONS

An equation of state for gas mixtures has been developed in terms of compressibility factors and based on the reference substance relation and the forces of attraction of the molecules in the mixture. From the compressibility factor, the relations of PVT are immediately determinable. Only the critical constants of the individual components are necessary to calculate the compressibility factors of the gas mixtures. No other experimental data are required. This equation holds for a mixture of nonpolar components and polar components, or nonpolar and polar components.

Heretofore, the forces of attraction or repulsion between molecules, the Lennard-Jones force constants have been considered only for a simple case where all molecules are alike; that is, for pure gases. A theoretical approach was developed for presenting these constants representing the force of interaction for the unlike molecules present in a gas mixture. An additional parameter, dipole moment, is needed for a polar mixture.

A mixture of gases may be assumed to have the same thermodynamic properties as some hypothetical or pseudo gas of only one component. Thus, the force constants between the molecules of this pseudo pure gas mixture may

TABLE 2. COMPARISON OF THE RESULTS OBTAINED BY DIFFERENT METHODS

				Absolute deviation, %					
				This work		Generalized table		Virial equation	
System	Temp., °K.	Pressure, atm.	Composition	Max.	Aver.	Max.	Aver.	Max.	Aver.
Methane-carbon dioxide	511.11	54.42 to 544.22	Methane = 0.8469	3.619	1.353	6.640	3.449	20.957	6.187
Methane-isopentane	477.7	27.21 to 88.43	Methane = 0.4976	3.838	1.247	6.465	5.597	30.122	12.144
Ethylene-argon	298	30 to 100	Ethylene = 0.5986	4.987	2.632	6.990	3.273	25.732	14.210
Propane-benzene	411.1	13.61 to 54.44	Propane = 0.8827	2.428	1.051	16.955	5.046	39.211	8.548
n-Butane-nitrogen	427.7	40.83	*n*-Butane = 0.1-0.9	2.273	1.415	11.667	4.600	10.000	6.758
Toluene-*n*-hexane	Saturated conditions		Toluene = 0.6344	5.348	3.549	16.461	10.030	55.282	28.061
Hydrogen-nitrogen-methane	373	100 to 700	Hydrogen = 0.5266 Nitrogen = 0.2611	4.033	3.103	11.973	8.949	22.082	9.466

be regarded as equal to the force constants of the gas mixture in question.

However, the critical constants for a gas are related to the force constants. Thus, the pseudo critical constants of a gas mixture may be evaluated. These pseudo critical constants are based on the effective total energy of interaction of molecules in this consideration. An empirical approach such as the well-known Kay's rule has always heretofore been used for determining the pseudo critical constants of a gas mixture.

The compressibility factors were evaluated for all of thirty-four binary systems for which experimental data are available at 1,077 sets of conditions. The average percentage deviation was 2.281%, and the maximum was 6.564%, although most of the calculated values are within 3% of the experimental.

For the four ternary systems for which data are reported, 244 sets of conditions were evaluated; and the average deviation was 2.943%, the maximum was 7.938%, and most of the calculated values were within 4%.

Inasmuch as the mixtures often encountered in industry are multicomponent rather than binary, the extension of prediction methods to such mixtures is of considerable practical interest. Fortunately, theoretical considerations indicate that only binary molecular interaction need be considered in multicomponent mixtures, since only rarely does the higher order interaction occur on a statistical basis. Thus a knowledge of the binary interactions should be adequate for the prediction of multicomponent behavior. Hence, it should be possible to evaluate compressibility factors for multicomponent systems by these methods. The lack of experimental data on systems with more than two components does not prevent the use of this equation with any number of components, but, of course, experimental confirmation would be desirable. In the absence of experimental data, the equation may be used, if necessary, and with reasonable expectation of close approximation to actual values.

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NOTATION

a = constant
b_o = molecular volume
b = constant
B = second virial coefficient
B^* = reduced second virial coefficient ($= B/b_o$)
c = number of components
FLJ = induction parameter
f = function
h = radial distribution function
k = Boltzmann's constant, erg/(molecule)(°K.) ($= 1.3805 \times 10^{-16}$)
N = Avogadro's number, molecules/g.-mole, ($= 6.023 \times 10^{23}$)
N = number of molecules
P = pressure
P_r = reduced pressure ($= P/P_c$)
P^* = reduced pressure $\left(= \left(\frac{b_o}{R}\right)\left(\frac{k}{\epsilon}\right)P\right)$
q = parameter as defined by Equation (31)
R = gas constant
r = distance between molecules
T = absolute temperature
T_r = reduced temperature ($= T/T_c$)
T^* = reduced temperature ($= kT/\epsilon$)
V = volume
V_r = reduced volume ($= V/V_c$)
V^* = reduced volume ($= V_c/b_o$)
W = function as defined by Equation (32)
y = mole fraction
Z = compressibility factor
ZTZ = ratio of the compressibility factor of a mixture to that of a reference substance at the same reduced temperature and pressure

Greek Letters

α, β, γ = constants
ϵ = Lennard-Jones force constants, ergs/molecule
σ = Lennard-Jones force constant, Å.
μ = dipole moment
η = polarizability, cc.
φ = intermolecular potential energy
Γ = gamma function

Superscript

$-$ = pseudo property of a mixture

Subscripts

c = critical property
i, j = components i, j
M = property of a mixture
R = property of a reference substance

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Ion Exchange Equilibria under Pressure

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Previous work on the ionization equilibria of weak acids and bases at high pressures suggested that compression should favor the transfer of protons from a weakly acidic resin to a weakly basic one in a mixed bed system, and that the resulting increase of ionization should extract cations and anions from the surrounding solution. In agreement with this idea it has now been observed that the equilibrium concentration of a solution of sodium chloride around a mixture of De-Acidite M and Zeo-Karb 226 resins is almost halved when the pressure is raised from 1 to 3,000 atm. The change is completely reversible.

The measurements indicate that the proton transfer process involves a contraction of about 15 cc. mole^{-1}, which is remarkably close to the analogous contraction [15 to 18 cc. mole^{-1}] that occurs when a proton is transferred from a free carboxylic acid to an amine in solution.

Many measurements have been made of the influence of pressure on ionic equilibria in homogeneous solutions, and the general pattern of behavior is now quite clear (*1* to *3*). Without exception, weak electrolytes tend to become stronger when the pressure is raised, and ion pairs tend to dissociate. Qualitatively, and to some degree, quantitatively, the effects can be understood in terms of the classical macroscopic theory of electrostriction (*1*, *2*).

On the other hand very little work has been done on heterogeneous systems of the kind that are involved in ion exchange processes between solutions and resins. The only published experimental results in this field are some that Horne et al. (*4*) obtained for the equilibrium between potassium and strontium ions and hydrogen ions in a sulfonic acid resin at pressures up to 6,600 atm. The changes, under pressure, were rather small.