Compressibility of Real Binary Gas Mixtures

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The P-V-T-x properties of binary gas mixtures and their dependence on reduced temperature and pressure have been reviewed in detail.

A modified form of Kay's original method for estimating P-V-T-x properties of mixtures is suggested for purposes of engineering calculations.

In correlating the P-V-T-x data of binary mixtures the gross mixture properties can scarcely be described with greater accuracy than can those of the pure components. For example Kay's (*7*) treatment of gas mixtures is limited by, among other things, the failure of reduced temperatures and reduced pressures to describe accurately the compressibility of pure components. Now that significant advances have been made by investigators such as Curl and Pitzer (*1*) and Lydersen, Greenkorn, and Hougen (*8*) in correlating the P-V-T properties of pure gases with a third parameter in addition to reduced temperature and reduced pressure, the question of a new mixture correlation arises.

In order to avoid having a mixture correlation dependent on the success of a pure component correlation, mixing effects rather than gross mixture properties have been studied. Consider the equation

$$y = Z_{\text{mix}} - \Sigma\, x_i Z_i \qquad (1)$$

The property y is an experimentally determined change in compressibility factor on mixing at constant temperature and pressure. The correlation of y is independent of any pure component study. There is a further advantage in the use of mixing effects rather than gross mixture properties. Suppose that a given experimenter introduces a systematic error in his measurements of Z_{mix} and the Z's of the pure components. While all of the gross properties are subject to this error and subsequent correlation with these gross properties are thereby more inaccurate, there is the possibility that the systematic error might cancel itself in Equation (1) and thereby preserve the accuracy of y. In this way a y measured by one investigator with methods that contain such systematic errors can be combined with pure component properties measured with greater certainty by another investigator, yielding a more accurate gross mixture property.

To correlate y a parameter X is defined by

$$X = Z'_{\text{mix}} - \Sigma\, x_i Z'_i \qquad (2)$$

where all of the gross properties here are computed from some function of reduced temperatures and pressures. The function which was finally chosen is the compressibility factor for propane. It is tabulated in the Appendix.* The Z'_i's in Equation (2) for each pure component are taken directly from this function with its own critical properties. The Z'_{mix} of Equation (2) is also taken from this function with Kay's (*7*) pseudocritical properties for the mixture:

$$P_{c\ \text{mix}} = \Sigma\, x_i P_{c_i} \qquad (3)$$

$$T_{c\ \text{mix}} = \Sigma\, x_i T_{c_i} \qquad (4)$$

A correlation was attempted with methane and ethane as reference gases instead of propane, and it was found that while ethane could be used, the most satisfactory results were obtained with propane. The functions that now appear in the literature (*2, 11*), which work so well for pure components, were not used because they can only be interpolated with difficulty and contain fewer significant figures than were necessary for the purpose of computing an X value.

EXPERIMENTAL DATA

References to all the data used in this correlation are given in Table 1.

Thus in all cases considered the same apparatus at the same site was used to measure the individual gas components and the binary mixture. However in most cases measurements were made over a number of years. The basis of selection made it impossible to use a significant body of data, even though there is no reason to believe that the unused data are not of equal quality.

A further restriction on the use of the data was the necessity that they had to be taken at the same temperature and pressure for the pure components and the binary mixture. Within the systems used there was no arbitrary selection of data; all the reported information was used.

CORRELATION

A linear relation between y and X was assumed to exist, since this was the relation indicated by graphs of all the systems for which data was available. The linear regression analysis followed the scheme outlined by Hald (*4*). A linear relation

$$Y = \bar{y} + G(X - \bar{X}) \qquad (5)$$

is sought which is an approximation of the true function $y = f(X)$. The statistics for the individual systems are given in Table 2.

System 5, hexane-toluene, consisted of a very small number of points at low pressures. Watson (*19*) who measured the data was disappointed in the accuracy he could report. However the y values which were measured are rather small and for the most part amount to about 1% of the gross properties. The propane-propene system, 6, also exhibits very small values of y obeying Amagat's law closely over wide ranges of temperature and pressure, and for this reason lends little to the correlation. System 7, propene-butane, does not obey the correlation very well, since all of the measurements were made at temperatures between the critical temperatures of the two pure components and the correlation is most erratic in the region of the critical point. At low pressures and very high pressures the system obeys Amagat's law as would be expected, and therefore lends little to the final correlation.

Rewriting Equation (5) in a more simple form one gets

$$Y = A + GX \qquad (6)$$

where A is easily recognized as $\bar{y} - G\bar{X}$. One has for the first four systems

Methane-ethane:

TABLE 1

More volatile component, 1	Less volatile component, 2	Mixture	Apparatus
Methane (*11*)	Ethane (*13*)	(*16*)	(*17*)
Ethane (*13*)	Propene (*3*)	(*10*)	(*17*)
Argon (*9*)	Ethylene (*9*)	(*9*)	(*9*)
Oxygen (*9*)	Ethylene (*9*)	(*9*)	(*9*)
n-Hexane (*19*)	Toluene (*19*)	(*19*)	(*19*)
Propane (*4*)	Propene (*3*)	(*15*)	(*17*)
Propene (*3*)	1-Butene (*12*)	(*2*)	(*17*)

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[*] The Appendix for this work, which contains the reference tables, can be obtained by writing to the Department of Chemical Engineering, Carnegie Institute of Technology, Pittsburgh 13, Pennsylvania.

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TABLE 2

No.	System	$\overline{y}$	$s_{\bar{y}}$	G	s_G	$\overline{X}$	Deviation of Y	n
1.	Methane-ethane	+0.004986	0.00087	0.80705	0.020	+0.035739	0.016	319
2.	Ethane-propene	—0.012656	0.00052	0.90611	0.019	—0.0065537	0.010	394
3.	Argon-ethylene	+0.077017	0.00120	0.82278	0.022	+0.084997	0.012	100
4.	Oxygen-ethylene	+0.091944	0.00170	0.86006	0.037	+0.096081	0.013	60
5.	*n*-hexane-toluene	+0.01012	0.00251	1.79484	0.702	+0.003961	0.014	30
6.	Propene-propane	—0.00001	0.00185	0.017738	0.109	+0.000892	0.037	400
7	Propene-1-butene	—0.022782	0.00525	0.22586	0.037	—0.041487	0.076	207

$$Y = -0.02386 + 0.80705X \quad (7)$$

Ethane-propene:

$$Y = -0.00672 + 0.90611X \quad (8)$$

Argon-ethene:

$$Y = 0.00807 + 0.82278X \quad (9)$$

Oxygen-ethene:

$$Y = 0.00931 + 0.86006X \quad (10)$$

CONCLUSIONS

For the correlation to be completely successful the A term of Equation (6) must be zero because Y must approach zero as the composition of either component approaches zero and as the system pressure approaches zero. This suggests that the A term, and perhaps G as well, depends on composition and pressure. The pressure effect, particularly at low pressure, could not be found since all of the reported data were measured at reduced pressures greater than 0.3. A composition effect was not sought, since the over-all correlation would not be improved with this added embellishment. The individual system correlations could be greatly enhanced by a substitution of a term Bx_1x_2 for A and a low pressure correction term, but there are much better ways of describing y for individual systems.

What is learned from the four correlations given in Equations (7) to (10) is that the mixing effect is not a simple function of the physical properties of the pure components. Changing the reference gas of the correlation will change all the Equations (7) to (10) in the same direction and does not tend to bring them together. As a matter of fact A tends away from zero if ethane and methane are chosen as reference gases. A third parameter involving other physical properties of the pure components does not improve the situation either. From the point of view of the physical properties of the pure components methane stands in the same relationship to ethane that oxygen and argon stand with respect to ethylene. Any change in one system brought about by such a third parameter affects the other systems in the same way and therefore does not bring the individual correlations together.

There is a question as to the reliability of the experimental y values. For instance Sage, Webster, and Lacey (*18*) first reported ethane data in 1937. The mixture, methane-ethane, was reported in 1939 by Sage and Lacey (*16*). Then in 1943 Olds, Reamer, Sage, and Lacey (*11*) remeasured ethane and obtained results which differed from the first measurements in 1937 by as much as 0.0214 in compressibility factor. Since this is the order of magnitude of y values, the difference in the compressibility of ethane seriously affects the correlation presented here. If the older, less reliable data were used, the first term in Equation (7) would be increased making the correlation far more satisfactory, and perhaps the older data should be employed. It was pointed out in the introduction that systematic errors could be cancelled if they appear in both the pure component and mixture measurements. It could very well be that the errors present in the first ethane measurements are also present in the mixture measurements, and Equation (7) reflects these errors.

In spite of the extreme care to use only data measured at the same site with the same apparatus for any one system, large uncertainties are present in these correlations.

It is not suggested however that the A values are in fact zero. A nonzero A value arises from the fact that X sometimes becomes zero at higher pressures for compositions other than zero, and y is not exactly zero at this same point.

RECOMMENDED EQUATION FOR ENGINEERING ESTIMATION

Although based on very meager data it is seen that the equation

$$Y = 0.85\,X \qquad (11)$$

is more or less a mean of the four Equations (7) to (10) particularly in light of the uncertainty associated with the system methane-ethane which is discussed above. The root mean square deviation from this equation is as large as 10% in Z_{mix} in the region of the critical where Z_{mix} is small. At other temperatures and pressure where Z_{mix} is larger the relative deviation from Equation (11) is much smaller or about 3%. A review made by Chao and Tang (5) of forty different systems and 1,100 mixtures indicates root mean square deviations of 9% when Kay's mixture rules were used for the gross property along with a third parameter, the molal average of the compressibility factor at the critical point.

If precise experimental P-V-T data are available for the pure components, then Equation (11) gives a good estimate of the P-V-T-x properties of the mixtures. In the absence of experimental information the excellent correlations of Curl and Pitzer (*1*) or Lydersen, Greenkorn, and Hougen (*8*) may be used for the pure components properties. Reference tables* list the compressibility factor at a sufficient number of intervals of T_R and P_R so that interpolation is easily accomplished.

THERMODYNAMIC PROPERTIES

Once the P-V-T-x properties of a mixture have been estimated, corresponding thermodynamic properties can also be calculated. Also listed in the reference tables are enthalpy and entropy functions.

Define

$$X_H = \left(\frac{H-H^\circ}{T}\right)'_{\text{mix}} - \sum x_i \left(\frac{H-H^\circ}{T}\right)'_i \qquad (12)$$

$$X_S = (S_R - S_I)'_{\text{mix}} - \sum x_i (S_R - S_I)'_i \qquad (13)$$

where all of the terms in the right-hand sides of Equations (12) and (13) are taken from the reference tables with critical properties for the pure components and pseudocritical properties, Equations (3) and (4), for the mixtures. The best estimate of the heat of mixing for the system Y_H is $0.85\ T\ X_H$, and the best estimate for the excess entropy of mixing Y_S is $0.85\ X_S$. The excess free energy of mixing Y_F is given by $0.85\ \text{T}\ (X_H - X_S)$.

The enthalpy, entropy, and free energy of a mixture are given by

$$H_{\text{mix}} = \Sigma\ x_i\ H_i + 0.85\,T\,X_H \quad (14)$$

$$S_{\text{mix}} = \Sigma\ x_i\ S_i - R\,\Sigma\,x_i\ \ln\ x_i + 0.85\ X_S \quad (15)$$

$$F_{\text{mix}} = \Sigma\,x_i\ F_i + RT\,\Sigma\,x_i\ \ln\ x_i + 0.85\,T(X_H - X_S) \quad (16)$$

The quantities H_i, S_i, and F_i can be taken from precise thermodynamic tabulations for the pure components or estimated from the correlations of Curl and Pitzer (*1*) or Lydersen, Greenkorn, and Hougen (*8*). It should be noted that $F_R - F_I$ is also $RT \ln f/p$. The fugacity functions f/p is usually tabulated in the literature.

It has been noted by Joffe (*6*) that if Kay's mixture rules are valid, one can compute the fugacity of a component in a mixture with the equation

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* See footnote on page 343.

$$\ln \frac{f_i}{Px_i} = (\ln f/p)'_{\mathrm{mix}} + \left(\frac{H-H^\circ}{T}\right)'_{\mathrm{mix}} \frac{T_{c_i} - T_{c_{\mathrm{mix}}}}{RT_{c_{\mathrm{mix}}}} - (Z'_{\mathrm{mix}} - 1)\, \frac{P_{c_i} - P_{c_{\mathrm{mix}}}}{P_{c_{\mathrm{mix}}}} \quad (17)$$

Since

$$\ln f/p = \frac{F_R - F_I}{RT} = \frac{H - H^\circ}{RT} - \frac{(S_R - S_I)}{R} \quad (18)$$

then

$$\ln \frac{\overline{f_i}}{Px_i} = \left(\frac{H-H^\circ}{T}\right)'_{\mathrm{mix}} \frac{T_{c_i}}{RT_{c_{\mathrm{mix}}}} - \left(\frac{S_R - S_I}{T}\right)'_{\mathrm{mix}} - (Z'_{\mathrm{mix}} - 1)\, \frac{P_{c_i} - P_{c_{\mathrm{mix}}}}{P_{c_{\mathrm{mix}}}} \quad (19)$$

The terms in Equation (19) can be computed from the reference tables. Since

$$\ln \frac{\overline{f_i}}{Px_i} - \ln \frac{f_i}{P} = \ln \gamma_i = \frac{\tilde{y}_F}{RT} = \frac{0.85}{RT}\, \tilde{X}_F \quad (20)$$

But in accordance with Equation (19)

$$\frac{\tilde{X}_F}{RT} = \left(\frac{H-H^\circ}{T}\right)'_{\mathrm{mix}} \frac{T_{c_i}}{RT_{c_{\mathrm{mix}}}} - \left(\frac{S_R - S_I}{R}\right)'_{\mathrm{mix}} - (Z'_{\mathrm{mix}} - 1)\, \frac{P_{c_i} - P_{c_{\mathrm{mix}}}}{P_{c_{\mathrm{mix}}}} - \left(\ln \frac{f_i}{P}\right)' \quad (21)$$

where all the terms of (21) are taken from the reference tables. Substituting (21) into (20) one obtains

$$\ln \frac{\overline{f_i}}{Px_i} - \ln \frac{f_i}{P} = 0.85 \left[\left(\frac{H-H^\circ}{T}\right)'_{\mathrm{mix}} \frac{T_{c_i}}{RT_{c_{\mathrm{mix}}}} - \left(\frac{S_R - S_I}{R}\right)_{\mathrm{mix}} - (Z'_{\mathrm{mix}} - 1) \frac{P_{c_i} - P_{c_{\mathrm{mix}}}}{P_{c_{\mathrm{mix}}}} - \left(\ln \frac{f_i}{P}\right)' \right] \quad (22)$$

Rewriting and noting Equation (18) one gets

$$\ln \frac{\overline{f_i}}{Px_i} = \ln \frac{f_i}{P} + 0.85 \left[\left(\frac{H-H^\circ}{T}\right)_{\mathrm{mix}} \frac{T_{c_i}}{RT_{c_{\mathrm{mix}}}} - \frac{(S_R - S_I)'_{\mathrm{mix}}}{R} - (Z'_{\mathrm{mix}} - 1)\, \frac{P_{c_i} - P_{c_{\mathrm{mix}}}}{P_{c_{\mathrm{mix}}}} - \left(\frac{H-H^\circ}{RT}\right)_i + \left(\frac{S_R - S_I}{R}\right)'_i \right] \quad (23)$$

In the right-hand side of Equation (23) the first term is the natural logarithm of the fugacity coefficient of the pure component *i* taken from a reliable thermodynamic compilation. The remainder of the terms in the brackets are taken from the reference tables, the first three coefficients taken for the mixture and the last two for the pure component *i*.

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NOTATION

A = parameter in equation $Y = A + GX$

G = parameter in equation $Y = A + GX$

$F_R - F_I$ = free energy of the real gas less free energy of the gas in the ideal state at the same temperature and pressure

f = fugacity of pure component

$\overline{f}$ = fugacity of component in a mixture

$H - H^\circ$ = enthalpy of the real gas at system pressure less the enthalpy as pressure approaches zero at the same temperature

P = system pressure

$P_{c_{\mathrm{mix}}}$ = pseudocritical pressure of the mixture, $\Sigma x_i\, P_{c_i}$

P_{c_i} = critical pressure of the *i*th component

P_R = reduced pressure, P/P_c

R = gas constant

$S_R - S_I$ = entropy of the real gas less entropy of the ideal gas at the same temperature and pressure

T = absolute temperature of the system

$T_{c_{\mathrm{mix}}}$ = pseudocritical temperature of the mixture, $\Sigma x_i\, T_{c_i}$

T_{c_i} = critical temperature of the *i* th component

T_R = reduced temperature, T/T_c

X = $Z'_{\mathrm{mix}} - \Sigma x_i Z'_i$ (based on reduced correlations)

X_H = enthalpy change on mixing

X_F = excess free energy change on mixing

X_S = excess entropy change on mixing

$\tilde{X}_F$ = partial molal excess free energy of mixing calculated from reference table

$\overline{X}$ = mean value of x

x_i = mole fraction of the *i*th component

Y = predicted value for y as a function of X

$\tilde{y}_F$ = partial molal excess free energy of mixing

y = $Z_{\mathrm{mix}} = \Sigma x_i Z_i$ (based on experimental data)

$\overline{y}$ = mean value for y

Z = compressibility factor, PV/RT

Z_i = compressibility factor of the *i* th component at the same temperature and pressure for which Z_{mix} is given

Superscript

= quantity taken from the reference tables in the Appendix

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