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On the Compressibilities of Gas Mixtures

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In recent years many investigators[2] have made contributions to the knowledge of the compressibilities of gaseous mixtures. The aim of the present paper is to show that the generalized Beattie–Bridgeman equation of state as communicated earlier[3] or the generalized μ-charts[4] ($\mu = pV/RT$) may be used to calculate the compressibilities of mixtures of real gases, when suitable pseudo-critical temperatures and pressures are assigned to the mixtures.

For the pseudo-critical temperature, $(T_c)_m$, and pressure, $(p_c)m$, of a given gas mixture we shall take the linear molal average of the critical temperatures and the pressures of the components, respectively, as suggested by Kay[5] in his study of gaseous hydrocarbon mixtures

$$(T_c)m = x_1T_{c1} + x_2T_{c2} + \dots \quad (1)$$

$$(p_c)m = x_1p_{c1} + x_2p_{c2} + \dots \quad (2)$$

where $x_1, x_2, \cdots$, are the mole fractions of the components. We shall define the ideal critical volume $(V_{ci})m$ of the mixture as follows

$$(V_{ci})m = R(T_c)m/(p_c)m \quad (3)$$

It would be the "ideal" critical volume for one mole of the mixture at $(T_c)m$ and $(p_c)m$. With the use of these pseudo-critical quantities, the compressibility behavior of any gaseous mixture will be treated exactly in the same manner as if it were a single pure gas. The solution is easily done either graphically by means of a generalized μ-chart or analytically by means of a generalized equation of state if the point in consideration falls in the validity region of the equation of state.

The generalized Beattie–Bridgeman equation of state is

$$\pi = \frac{\theta(1-\epsilon')}{\varphi^2}[\varphi + B'] - \frac{A'}{\varphi^2} \quad (4)$$

$$A' = A_0'(1 - a'/\varphi)$$

$$B' = B_0'(1 - b'/\varphi)$$

$$\epsilon' = c'/\varphi\theta^3$$

where, for mixtures, $\pi = p/(p_c)m$, $\theta = T/(T_c)m$, $\varphi = V/(V_{ci})m$, π being the reduced pressure, θ, the reduced temperature, and φ the ideal reduced volume. The generalized constants for the mixtures will have the same numerical values as those for any real gas. They are

$A_0' = 0.4758$ $b' = 0.03833$
$a' = 0.1127$ $c' = 0.05$
$B_0' = 0.18764$

Eq. (4) is valid from the critical temperature to temperatures well above the Boyle temperature, and from low densities to about the critical density or up to $1/\varphi = 3.5$. For higher densities, the generalized μ-chart must be used. The μ-chart, however, may be used for practically all the temperature and pressure ranges.

TABLE I

COMPARISON OF THE CALCULATED PRESSURES AND THE OBSERVED PRESSURES OF THE GAS MIXTURES

Mixture	Literature	Composition, mole %	Maximum pressure, atm.	Maximum density, moles/liter	Temp. range, °C.	Number of points	Maximum deviation, %	Average deviation, %
C_2H_4–A	6	C_2H_4, 59.86	125	7.6	25	11	1.4	0.5
H_2–CO	7	H_2, 51.7	160	6.0	25	6	1.5	0.9
N_2–CH_4	2a	N_2, 56.65	90	4.4	0	5	1.2	0.9
CH_4–N–C_4H_{10}	8	CH_4, 50.436	225	5.0	100 to 300	72	8.4	2.2
CH_4–C_2H_6	9	CH_4, 50.71	238	14.1	21 to 121	140	6.3	2.2
Air	10	N_2, 78 O_2, 21 A, 1	168	8.0	−145 to 200	168	4.7	0.3

We have studied the compressibilities of six mixtures as listed in Table I. The components of some mixtures studied like the systems, argon and ethylene, hydrogen and carbon monoxide, etc., differ greatly in chemical nature as well as molecu-

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lar weights. The data cover a rather large range of the temperature and the pressure. The over-all average deviation is about 1%. The maximum deviation infrequently exceeds 6%. The method is extremely simple. Actual calculations are easy and time-saving especially by means of a generalized μ-chart.

In the calculation the critical constants for ethane and normal butane are those recently determined by Beattie and co-workers.[11] For hydrogen, the pseudo-critical temperature and pressure as defined by Newton[12] are used. The calculations have been checked in a greater part by employing two methods of calculation, firstly by means of a large plot of the μ-chart and secondly by means of the generalized Beattie–Bridgeman equation of state, the agreement of the results from these two methods being excellent.

The method is of general application. The validity of the correlation as pointed out elsewhere[13] is not affected by the inconstancy of the critical ratios, RT_c/p_cV_c. Thus, the generalized equation of state either in the graphical form like the μ-chart or in some analytical expression like the generalized Beattie–Bridgeman equation of state is applicable to all real gases and their mixtures.

Discussion

1. There is some similarity between the present method of the employment of the pseudo-critical quantities and the usual method of the combination of the equation of state constants. Consider the constant B_0 of the Beattie–Bridgeman equation of state. Our present method is that the generalized constant A'_0 for one mole of any mixture will be numerically the same as that of one mole of any pure gas. The relation between the generalized constant B'_0 and the original Beattie–Bridgeman B_0 has been shown when applied to a mixture as follows

$$B'_0 = (B_0)m\Big/\frac{R(T_c)m}{(p_c)m} \tag{4a}$$

or

$$(B_0)m = B'_0\,\frac{R(T_c)m}{(p_c)m} \tag{5}$$

We shall introduce a simplifying assumption for the purpose of the present reasoning, only as

$$\frac{R(T_c)m}{(p_c)m} = x_1\frac{RT_{c1}}{p_{c1}} + x_2\frac{RT_{c2}}{p_{c2}} + \cdots \tag{6}$$

where $(T_c)m$ and $(p_c)m$ are defined according to Eqs. (1) and (2). We have shown[3] that

$$B'_0 = B_{01}\Big/\frac{RT_{c1}}{p_{c1}} = B_{02}\Big/\frac{RT_{c2}}{p_{c2}} = \cdots \tag{7}$$

Combining Eqs. (6) and (7) into Eq. (5), we get

$$(B_0)m = x_1B_{01} + x_2B_{02} + \cdots$$

which is the identical result of the usual method of the combination of equation of state constants. Similar reasoning may be applied to the constants a and b. For the constants A_0 and c, the expressions become more involved. Further simplifying assumptions will have to be introduced and will not be discussed here.

2. In the original communication of Kay, it is remarked that for mixtures whose constituents differ greatly in molecular weight as well as chemical nature, values of the pseudo-critical temperature and pressure calculated in this manner (Eqs. (1) and (2)) are likely to be in error by an amount greater than that allowable in most engineering calculations. Our present study well removes these qualifying conditions and therefore greatly extends the use of the method.

3. For air, the pseudo-critical temperature and pressure calculated by the present method are $-140.8°$ and 37.1 atm. which are in excellent agreement with the observed values of Kuenen[14] and Clark, namely, $t_c = -140.7°$ and $p_c = 37.2$ atm., the latter being also the accepted[15] values of t_c and p_c for air at present.

4. It is suggested that other derived thermodynamic properties of gaseous mixtures under high pressures may be successfully treated in a similar manner.

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Summary

1. The generalized Beattie–Bridgeman equation of state as well as the generalized compressibility–factor charts may be applied to calculate the compressibilities of gaseous mixtures with the pseudo-critical temperature and pressure defined as the linear molal average of the critical temperatures and pressures of the components as suggested by Kay. The over-all average deviation of the six mixtures studied is about 1%.

2. It is pointed out that the present method is general in application, independent of the nature of the gaseous components. It is shown that a similarity exists between the present method and the usual method of the combination of the equation of state constants.

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