

ESTIMATION OF P - V - T BEHAVIOUR OF GAS MIXTURES

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Received October 9th, 1980

A review of methods is presented which allow to determine the P - V - T behaviour of gas mixtures. This review is based on the computations performed for about 2 200 P - V - T - X data of 12 binary mixtures. The method of combination of the equation-of-state constants, the Joffe method and the modified Bartlett rule proved to be the most suitable.

Although one encounters in practice much more often with gas mixtures than with pure gases, there exist very few data on the volumetric behaviour of mixtures compared to pure substances. The greater attention should be paid to the methods for estimating the P - V - T behaviour of multicomponent systems. In this work an evaluation is carried out of seven methods: Dalton's and Amagat's laws, the Bartlett rule, the Joffe rule, a modified Bartlett rule, the combination of the equation-of-state constants and the theorem of corresponding states represented here by the Lee-Kesler equation. Further we present a brief description of the methods and the way of evaluating.

Methods of Estimating the P - V - T Behaviour of Gas Mixtures

To estimate the P - V - T behaviour of gas mixtures, the following methods¹⁻³ are used:

Dalton's law. Dalton's law pertains to the oldest attempts to describe the behaviour of mixtures. The validity of this law requires the fulfilment of the relation

$$P(T, d, x_1, x_2, \dots, x_{N-1}) = \sum_{i=1}^N P_i^0(T, x_i d) = \sum_{i=1}^N P_i^0(T, d_i), \quad (1)$$

where $P(T, d, x_1, x_2, \dots, x_{N-1})$ is the pressure of a mixture with composition x_1, x_2, \dots, x_{N-1} at a temperature T and molar density d , $P_i^0(T, x_i d)$ is the pressure of pure component i at a temperature T and molar density $d_i = x_i d$. For the compressibility factor of the mixture we get

$$z(T, d, x_1, x_2, \dots, x_{N-1}) = \sum_{i=1}^N x_i z_i^0(T, x_i d), \quad (2)$$

where z_i^0 is the compressibility factor of pure component i at a temperature T and density $d_i = x_i d$.

Amagat's law. The molar volume and the compressibility factor of the mixture which conforms to Amagat's law are given by the relations

$$V(T, P, x_1, x_2, \dots, x_{N-1}) = \sum_{i=1}^N x_i V_i^0(T, P), \quad (3)$$

$$z(T, P, x_1, x_2, \dots, x_{N-1}) = \sum_{i=1}^N x_i z_i^0(T, P), \quad (4)$$

where $V_i^0(T, P)$ and $z_i^0(T, P)$ are the molar volume and the compressibility factor, respectively, of pure component i at a temperature T and pressure P .

A great advantage of Amagat's law (unlike Dalton's law or the Bartlett rule – see below) is its easier application. Far most often one requires the knowledge of density, volume or compressibility factor of a mixture at a certain temperature and pressure. In such a case it is sufficient to find out the respective values at this temperature and pressure in tables of pure substances and to multiply them by the respective mole fractions. When applying Dalton's law or the Bartlett rule we must in such cases proceed tentatively. In this work the Newton method was applied in calculations.

*Bartlett rule*⁴. In this case we have the relation for the mixture pressure

$$P(T, d, x_1, x_2, \dots, x_{N-1}) = \sum_{i=1}^N x_i P_i^0(T, d) \quad (5)$$

and for the compressibility factor

$$z(T, d, x_1, x_2, \dots, x_{N-1}) = \sum_{i=1}^N x_i z_i^0(T, d), \quad (6)$$

where $P_i^0(T, d)$ and $z_i^0(T, d)$ are the pressure and the compressibility factor of pure component i at a temperature T and molar density d .

From the hitherto given rules or laws, the Bartlett rule is the most accurate⁵⁻⁷ except for extremely high pressures where density is comparable to the density in the liquid phase and where Amagat's law is more suitable.

A drawback of all the three approximations is their limited applicability at temperatures lower than the critical temperature of substances. In such cases the knowledge is often required of the volumetric behaviour under conditions when the substance occurs already in the liquid region. A simple example can be a mixture of H_2O

($x_1 = 0.05$) and H_2 ($x_2 = 0.95$) at 100°C and pressure 2 MPa. When using Amagat's law we need to know the volumes of H_2 and H_2O in the gas state at 100°C and 2 MPa. The use of Amagat's law is in this case practically impossible (as well as that of Dalton's law or the Bartlett rule). This unpleasant property is not peculiar to further two rules which stem as well from the knowledge of the volumetric behaviour of pure components.

Joffe rule^{8,9}. The compressibility factor of mixture is given according to the Joffe rule by the relation

$$z(T, P, x_1, x_2, \dots, x_{N-1}) = \sum_{i=1}^N x_i z_i^0(T_i, P_i), \quad (7)$$

where

$$T_i = T(T_{ki}/T'_k), \quad P_i = P(P_{ki}/P'_k) \quad (8)$$

and T'_k and P'_k are the pseudocritical temperature and pseudocritical pressure of the given mixture. Eq. (7) can also be written in the form

$$z(T/T'_k, P/P'_k) = \sum_{i=1}^N x_i z_i^0(T/T'_k, P/P'_k). \quad (9)$$

It means that the compressibility factor of mixture at a pseudoreduced temperature $T_r = T/T'_k$ and a pseudoreduced pressure $P_r = P/P'_k$ is determined on the basis of the compressibility factor of pure substances at the same reduced variables.

For the mixture volume we get the relation from Eq. (7)

$$V(T, P, x_1, x_2, \dots, x_{N-1}) = (T'_k/P'_k) \sum_{i=1}^N x_i (P_{ki}/T_{ki}) V_i^0(T_i, P_i), \quad (10)$$

where T_i and P_i are determined by relations (8).

Up to now rather little is known about the use of this rule. The pseudocritical quantities needed for calculating will be discussed below.

*Modified Bartlett rule*¹⁰. The Joffe rule can be looked on as the application of the theorem of corresponding states to Amagat's law. Considering that the Bartlett rule gives better results with mixtures than Amagat's law it can be expected that also an analogous improvement of the Bartlett rule might yield the same if not better results than the Joffe rule. For this reason Malijevský and Novák¹⁰ proposed the relation for estimating the P-V-T behaviour of mixtures

$$z(T, d, x_1, x_2, \dots, x_{N-1}) = \sum_{i=1}^N x_i z_i^0(T_i, d_i), \quad (11)$$

where

$$T_i = T(T_{ki}/T'_k), \quad d_i = d(d_{ki}/d'_k) = d(V'_k/V_{ki}). \quad (12)$$

For the mixture pressure we get

$$\begin{aligned} P &= T'_k d'_k \sum_{i=1}^N x_i P_i^0(T_i, d_i) / (T_{ki} d_{ki}) = \\ &= (T'_k / V'_k) \sum_{i=1}^N x_i (V_{ki} / T_{ki}) P_i^0(T_i, d_i), \end{aligned} \quad (13)$$

where $P_i^0(T_i, d_i)$ is the pressure of pure component i at a temperature T_i and density d_i determined by relations (12).

A great advantage of the last two rules is that they are applicable even in the case when some of components is under critical temperature. It approximately holds that the mixture occurs at the saturation boundary at similar reduced variables as the pure substance. Extrapolating into heterogeneous region (as *e.g.* on using Amagat's law) is not usually necessary or is very small⁹.

A disadvantage of these two rules, however, is that they require that the P - V - T behaviour of substances should be described under reduced variables which correspond to the given mixture, which in some systems can limit their applicability. Most likely it can occur in systems containing hydrogen or organic substances with higher molecular mass. Let us assume that $T'_r = 1.05$, $P'_r = 2.0$ would hold for a mixture. If this mixture contains hydrogen then the compressibility factor of hydrogen at $T = 1.05 \times 33.2 = 34.8$ K and at pressure $P = 2.58$ MPa would be required for application of the Joffe rule. Providing that the P - V - T behaviour of hydrogen were expressed in terms of an equation of state whose constants were determined from the region 100–600 K, it would not be possible in such a case to ensure reliable results.

An advantage of all the rules is that they are connected with no particular equation of state or tables. For each substance we can therefore use the optimum equation of state or tabular data.

Combination of the equation-of-state constants. At present the description of P - V - T behaviour by means of equation of state in an analytical form continues to put through more and more. If we wish to describe P - V - T behaviour and thermodynamic properties, which are connected with this P - V - T behaviour, with experimental accuracy (in the optimum case) we are forced to use more and more complicated equations because the demands on the equations of state increase all the time.

The method of combination of the equation-of-state constants stems from the assumption that the equation which describes the P - V - T behaviour of pure substances

is able to describe also the P - V - T behaviour of mixture on using a suitable choice of the concentration dependence of "constants" (henceforth we shall use the expression parameter instead of constant).

With respect to the concentration dependence of the second and third virial coefficients on composition, the relations² are used most often

$$A = \sum_{i=1}^N \sum_{j=1}^N x_i x_j A_{ij} \quad (14)$$

$$A = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k A_{ijk} \quad (15)$$

If we start from these relations, the problem is shifted to the determination of the mixed parameters A_{ij} , A_{ijj} , A_{ijk} . The parameters A_{ii} , A_{jj} , A_{iii} , ... pertain to pure substances. Unless we wish to determine these parameters on the basis of experimental data, which would require a large effort, it is necessary to estimate them on the basis of the parameters which belong to the pure substances.

The following estimates are used:

a) Arithmetic mean

$$A_{ij} = (A_{ii} + A_{jj})/2, \quad A_{ijj} = (2A_{iii} + A_{jjj})/3. \quad (16)$$

In this case Eqs (14) and (15) reduce to

$$A = \sum_{i=1}^N x_i A_{ii}, \quad A = \sum_{i=1}^N x_i A_{iii}. \quad (17)$$

b) Geometric mean (if all A_{ii} or A_{iii} are positive or negative)

$$A_{ij} = \text{sign}(A_{ii})(A_{ii}A_{jj})^{1/2}, \quad (18)$$

$$A_{ijj} = (A_{iii}^2 A_{jjj})^{1/3}. \quad (19)$$

On inserting Eqs (18) and (19) into (14) and (15) we get

$$A = \text{sign}(A_{ii}) \left[\sum_{i=1}^N x_i |A_{ii}|^{1/2} \right]^2, \quad (20)$$

$$A = \left(\sum_{i=1}^N x_i A_{iii}^{1/3} \right)^3. \quad (21)$$

c) In case of a parameter which characterizes the excluded volume of molecules, the Lorentz average is used most often

$$A_{ij}^{1/3} = (A_{ii}^{1/3} + A_{jj}^{1/3})/2, \quad (22)$$

which after inserting into Eq. (14) yields the relation

$$A = (1/8) \sum_{i=1}^N \sum_{j=1}^N x_i x_j (A_{ii}^{1/3} + A_{jj}^{1/3})^3. \quad (23)$$

d) If we wish to take into account experimental data on the given system then the arithmetic or geometric mean is altered by introducing a correction coefficient k_{ij} for some of parameters, *e.g.*³

$$A_{ij} = (1 - k_{ij})(A_{ii} + A_{jj})/2 \quad (24)$$

or

$$A_{ij} = (1 - k_{ij}) \cdot \text{sign}(A_{ii}) \cdot (A_{ii} A_{jj})^{1/2}. \quad (25)$$

The correction coefficients k_{ij} are determined on the basis of experimental data of the corresponding binary system and their absolute value does not usually exceed the value 0.1.

For every equation of state it is necessary to check what kind of concentration dependence is suitable for single parameters. For instance with the Benedict-Webb-Rubin equation we use Eq. (17) for the constant B_0 , Eq. (20) for A_0 , C_0 , γ and Eq. (21) for a , b , c , α .

With more complicated equations of state, the parameters for different substances have not a similar order of magnitude and often even the sign and therefore more complicated concentration dependences than Eq. (17) cannot be used frequently. These facts make then the obtained results worse. The greatest extension found the method of combination of the equation-of-state constants in case of two-constant equations and generalized equations. As to the more complicated equations, the method of combination of the equation-of-state constants is used in connection with the Benedict-Webb-Rubin equation.

Theorem of corresponding states. According to the theorem of corresponding states it is possible to express the compressibility factor for all substances as a function of dimensionless quantities $T_r = T/T_k$, $P_r = P/P_k$ and, if need be, z_k or ω and so like. In case of mixtures we usually have recourse to the so-called one-liquid approximation according to which the mixture is replaced by a hypothetical pure substance which the parameters T'_k , P'_k and, if need be, z'_k or ω' pertain to and which are designed as pseudocritical.

The greatest extension found the tables of compressibility factor prepared by Lydersen and coworkers¹¹ and by Pitzer and coworkers¹². Their drawback is that they cannot be used directly in connection with a computer. This disadvantage has been removed by Lee and Kesler¹³ who have recently proposed a generalized equation of state which can be considered to be an analytical transcription of the Pitzer tables.

When applying not only these generalized methods but also the rules which have been proposed by Joffe⁸ and Malijevský and Novák¹⁰, it is necessary to have a method for determining the pseudocritical quantities. We shall present here only three prescriptions which will be applied below.

According to Kay¹⁴ the pseudocritical quantities are determined by the relations

$$T'_k = \sum_{i=1}^N x_i T_{ki}, \quad P'_k = \sum_{i=1}^N x_i P_{ki}, \quad (26)$$

$$V'_k = \sum_{i=1}^N x_i V_{ki}, \quad \omega'_k = \sum_{i=1}^N x_i \omega_i,$$

TABLE I
Basic data on systems tested

System	Ref.	Number of points	Range of t , °C	Range of P , MPa	Range of z
Ethylene-carbon dioxide	21	202	40-100	0.5-50	0.6 - 1.1
Nitrogen-n-butane	22	221	155-205	2.7-68	0.3 - 1.8
Hydrogen sulphide-nitrogen	23	90	20-100	≤ 24	0.9 - 1.1
Methane-ethane	24	208	70-120	≤ 21	0.5 - 1.0
Methane-propane	24	200	35-340	≤ 70	0.5 - 1.0
Methane-n-butane	24	240	35-340	≤ 70	0.15-2.3
Methane-n-pentane	24	218	35-340	≤ 35	0.15-1.4
Methane-n-decane	24	225	35-340	≤ 70	0.15-4.6
Propene-1-butene	25	200	5-130	≤ 7	0.6 - 1.0
Hydrogen-methane	26	153	25- 80	≤ 9	0.9 - 1.1
Hydrogen-ethane	26	154	25- 80	≤ 9	0.9 - 1.1
Hydrogen-propane	26	72	25- 80	≤ 4.9	0.9 - 1.1

TABLE II
Obtained mean deviations in compressibility factor

Equation	Dalton (2)	Amagat (4)	Bartlett (6)	Joffe rule (9) + Eq. (26)	Eq. (27) ^a	Modified Bartlett rule (11) + Eq. (26)	Eq. (27) ^a	Combin. of const.	Lee- Kesler
	Ethylene-carbon dioxide								
BWR	0.0583	0.0099	0.0087		0.0055 (0.97)	0.0053 (0.97)		0.0045	0.0078
Starling		0.0125	0.0122		0.0061 (0.97)	0.0059 (0.97)			
Bender			0.0082	0.0056	0.0056 (0.97)	0.0056 (0.94)			
Bender						0.0052 (0.97)			
	Nitrogen-n-butane								
BWR		0.0860	0.1035	0.0290	0.0162 (1.13)	0.0335	0.0152 (1.13)	0.0198	0.0234
Bender					0.0102 (1.10)		0.0189 (1.10)		
	Nitrogen-hydrogen sulphide								
BWR		0.0669	0.0409		0.0131 (0.93)		0.0129 (0.93)	0.0142	0.0102
	Methane-ethane								
BWR			0.0125	0.0128	0.0094 (1.03)		0.0090 (1.03)	0.0099	0.0126
Starling	0.0624	0.0326	0.0126		0.0094 (1.03)	0.0127			
	Methane-propane								
BWR		0.0488	0.0478	0.0157	0.0070 (1.07)	0.0175	0.0076 (1.07)	0.0097	0.0081
Starling		0.0442	0.0397		0.0095 (1.07)		0.0092 (1.07)		
Bender		0.0430	0.0397		0.0063 (1.07)		0.0059 (1.07)		
CH ₄ (BWR)- propane (Bender)			0.0474		0.0070 (1.07)		0.0075 (1.07)		
	Methane-n-butane								
BWR	0.12	0.088	0.117	0.0228	0.0151 (1.11)	0.0269	0.0156 (1.11)	0.0166	0.0200
Starling		0.0746	0.1017		0.0179 (1.11)		0.0152 (1.11)		
Bender					0.0191 (1.11)		0.0154 (1.11)		
Bender					0.0093 (1.06)		0.0099 (1.06)		
Bender					0.0090 (1.04)		0.0110 (1.04)		

	Methane-n-pentane				
BWR	0.132	0.0265	0.0160	0.0204	0.0144
Starling		0.155	0.0265 (1.15)	0.0291 (1.15)	0.0427
Bender			0.0320 (1.15)	0.0304 (1.15)	
Bender			0.0324 (1.15)	0.0305 (1.15)	
			0.0150 (1.05)	0.0133 (1.05)	
	Methane-n-decane				
BWR			0.0514 (1.30)	0.0903 (1.30)	0.0579
BWR			0.0234 (1.15)	0.0486 (1.15)	
BWR			0.0207 (1.10)	0.0553 (1.13)	
CH ₄ (Starling)- n-decane (BWR)			0.0558 (1.30)	0.0504 (1.30)	
	Propene-1-butene				
BWR			0.0481 (1.01)	0.0436 (1.01)	0.0429
	Hydrogen-methane				
BWR	0.0078	0.0115	0.0021 (1.00)	0.0021 (1.00)	0.0030
	Hydrogen-ethane				
BWR	0.0055	0.0291	0.0023 (1.08)	0.0033 (1.00)	0.0085
BWR				0.0020 (1.08)	
	Hydrogen-propane				
BWR	0.0014	0.0107	0.0022 (1.00)	0.0022 (1.00)	0.0011

^a The values of K_{ij} used in Eq. (28) are given in parentheses.

Barner and Quinlan have proposed the relations¹⁵

$$\begin{aligned}
 T'_k &= \sum_{i=1}^N \sum_{j=1}^N x_i x_j T_{kij}, \\
 T_{kij} &= (1/2)(T_{ki} + T_{kj}) K_{ij}, \quad K_{ii} = K_{jj} = 1.0, \\
 V'_k &= (1/8) \sum_{i=1}^N \sum_{j=1}^N x_i x_j (V_{ki}^{1/3} + V_{kj}^{1/3})^3, \\
 \omega' &= \sum_{i=1}^N x_i \omega_i, \quad z'_k = 0.291 - 0.08\omega', \\
 P'_k &= z'_k R T'_k / V'_k.
 \end{aligned} \tag{27}$$

The values of parameters K_{ij} have been determined on the basis of experimental data for more than 100 binary systems and the authors give graphs as well from which it is possible to read these values in some cases.

Lee and Kesler¹³ applying their equation to mixtures use the following relations

$$\begin{aligned}
 z_{ki} &= 0.2905 - 0.085\omega_i, \quad V_{ki} = z_{ki} R T_{ki} / P_{ki}, \\
 V'_k &= (1/8) \sum_{i=1}^N \sum_{j=1}^N x_i x_j (V_{ki}^{1/3} + V_{kj}^{1/3})^3, \\
 \omega' &= \sum_{i=1}^N x_i \omega_i, \\
 T'_k &= (8V'_k)^{-1} \sum_{i=1}^N \sum_{j=1}^N x_i x_j (T_{ki} T_{kj})^{1/2} (V_{ki}^{1/3} + V_{kj}^{1/3})^3, \\
 P'_k &= (0.2905 - 0.085\omega') R T'_k / V'_k.
 \end{aligned} \tag{28}$$

Testing and Evaluating the Methods Given

To be able to carry out the testing computations by means of a computer it was assumed that the P - V - T behaviour of pure substances is described with sufficient accuracy by an equation of state. In testing we used the Benedict-Webb-Rubin (BWR)^{16,17} equation, the Starling^{18,19} and the Bender²⁰ equations. On computing, the deviation in the compressibility factor for the given temperature, pressure and composition of mixture was always evaluated. Consequently the per cent deviation would correspond to the per cent error in volume.

The basic data on the systems with which the above-mentioned rules and laws were tested are given in Table I. The results of computations are given in Table II.

The following conclusions can be drawn on the basis of the results given in Table II: Dalton's law yields the absolutely worst results. An exception are the systems containing hydrogen, where on the contrary Dalton's law has given comparatively good results. Considering that the second virial coefficients of hydrocarbon and hydrogen have opposite signs, it is possible to expect those results.

Amagat's law and the Bartlett rule can be placed into the second group. In some cases, similar results were also obtained by means of the theorem of corresponding states represented by the Lee-Kesler equation or by both further rules (the Joffe⁸ and the modified Bartlett rule¹⁰) on using the Kay pseudocritical quantities.

To the third group pertain the Joffe rule, the modified Bartlett rule, the method of combination of the equation-of-state constants and in some cases also the procedure by Lee and Kesler. The method of combination of the equation-of-state constants has yielded very good results in the methane-n-pentane system and in the systems containing hydrogen (Table II). The Joffe rule has probably certain advantages when describing the systems with unequally large molecules (methane-n-pentane, methane-n-decane) where it has given the best results.

The good results obtained with the Joffe and modified Bartlett rules depend among others on pseudocritical quantities used. On applying the Kay relations, the error was about twice compared to that on using the relations of Barner-Quinlan. An exception is the methane-n-pentane system. When using the Barner-Quinlan relations, the sensitivity to the parameter K_{ij} was tested as well. It has proved that better results can be attained with a value closer to unity⁵. However, this problem was not investigated in detail.

A surprise were the results obtained on using more complicated equations. This is especially evident in the ethylene-carbon dioxide system (Table II), where all three equations could be used. Application of the Bender equation did not bring a marked improvement in comparison with the BWR equation. Similar results were obtained with the nitrogen-n-butane and methane-n-butane systems. Better results with the Bender equation were attained in the methane-propane system. It is to be expected, however, that the advantage of more complicated equations of state will appear when calculating other thermodynamic quantities such as enthalpy, heat capacity, and so like. It is namely well-known that small deviations in the volumetric behaviour description lead to relatively high deviations in these quantities.

An attempt was also made to mix the equations of state (for the methane-propane system) when each of the substances was described by different equation on applying the empirical rules. The results did not differ too much from the use of either the BWR or the Bender equation even if the Bender equation used for both the substances is somewhat more suitable. The reason can be seen in the fact that both equations are approximately equally good for the given system.

The constants of the equations of state used were taken from the literature. In case of the BWR equation, the parameters of the authors of the equation¹⁷ were mostly

used, for N_2 , CO_2 , H_2S , n-decane the parameters of Bishnoi and Robinson²⁷, for 1-butene the parameters of Kaufman²⁸ were employed and the parameters of H_2 were determined on the basis of generalized relations by Sua and Viswanath²⁹. For the Starling equation, only the parameters of the authors of the equation^{18,19}, were used. In case of the Bender equation, the author parameters for ethylene³⁰ were used; the Henricks and coworkers ones³¹ were used for N_2 , CO_2 , CH_4 and for propane and n-butane those of Teja and Singh³².

LIST OF SYMBOLS

A	constant (parameter) of equation of state
$d = 1/V$	molar density
i, j	(subscript) component
k	(subscript) property at the critical point, component
k_{ij}, K_{ij}	interaction parameter between components i and j
N	number of components
P	pressure
R	gas constant
T	absolute temperature
V	molar volume
x	mole fraction
$z = PV/RT$	compressibility factor
ω	acentric factor
$^{\circ}$	(superscript) property of pure component
$'$	(superscript) pseudocritical quantity

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Translated by J. Iinek.