

A New Piecewise EOS for Compressibility Factor Prediction Based on the M-factor Theory

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ABSTRACT: *In this study for the first time a new description of compressibility factor is rendered based on the virial expansion. The compressibility factor as a function of M-factor is qualitatively and quantitatively expressed. At first, we present how may the third, fourth and higher order virial coefficients be logically ignored in order to simplify the virial equation. The results show, when the compressibility factor is presented as a function of M-factor instead of pressure, an improved regression operation on experimental data is possible. Moreover, the results show the compressibility factor will not depend on kind of substance, if it is considered as a function of M-factor. Also we found that the compressibility factor can easily be estimated by a second order polynomial in respect to M-factor or in more mature form at most by a third order polynomial. The simplifying effects of M-factor to present the compressibility factor of some binary mixtures are investigated. It was found that the classical mixing rules can never be applied for predicting the compressibility factor under special conditions. Also we affirm the distinct characteristics of M-factor compared to its composer parameters, qualitatively. A quantitative study on M-factor properties, which supplies a prolegomena to a new comprehensive equation of state, was accomplished as well. We find the favorable EOS is a multi-domain function estimating experimental data with high accuracy.*

KEY WORDS: *Compressibility factor, EOS, Isotherm, M-factor, Virial coefficients.*

INTRODUCTION

From view point of engineering, calculation of compressibility factor of pure and mixture fluids is

necessary because the correct prediction of thermodynamic properties and phase equilibrium is an important step

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1021-9986/10/2/

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in the design of any industrial process. Several attempts were made in the past for this purpose and have been expressed in form of equation of state (EOS). These equations include the virial, analytical and non-analytical equations of state. The virial equation, which can be derived from molecular theory, is limited in range of applicability [1]. This limitation is due to difficult calculation of the third and higher order virial coefficients. Analytical equations of state [2,3], which are cubic or quadratic in volume, can find molar volume analytically from specified pressure and temperature and subsequently the compressibility factor can be found from $Z=Pv/RT$. These equations can predict the compressibility factor of both liquid and vapor over limited ranges of temperature and pressure for many but not all substances. Non-analytical equations are applicable over much broader of pressure and temperature than analytical equations. But usually require many parameters to be fitted on large amount of experimental data. These equations include empirical forms of original and modified *Benedict-Webb-Rabin* [4,5] as well as *Wagner* models [4,5,6], semi-theoretical models such as perturbation models [7] that include higher order polynomials in density, and chemical theory equations [8] for strongly associating species. By selecting an EOS for PVT properties, users, should first evaluate what errors they will accept for substance and condition of interest, as well as the effort it would take to obtain parameter values if those are not available in literature. On the other hand, if users choose analytical forms, which are accurate models, some times this takes much effort as implementing is more complex. Consequently, most of equations of state whether analytical or non-analytical are time consuming and complex for use. Source of this problem returns to years ago. Most of non-analytical equations of state had been derived from a regression analysis on the experimental data to obtain an appropriate model associated with its parameters. The regression procedure had been carried out while the compressibility factor was varying with pressure at any given reduced temperature. This fact that the compressibility factor may easily be expressed with simpler parameters had been neglected. So the curve fitting analysis was intricate. Fig. 1 shows that isotherms of compressibility factor in terms of pressure do not follow any special trend for appreciating aspects. This trend, as an obstacle to analysis, occurs for any substance, similarly.

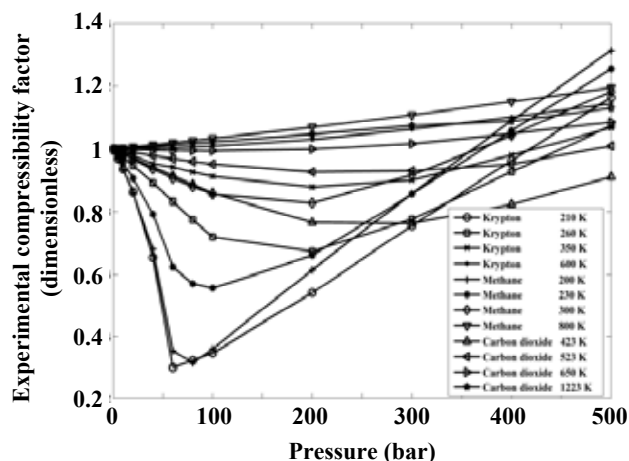


Fig. 1: Variation of the experimental compressibility factor with pressure for carbon dioxide, methane and krypton along 4 isotherms for each of them. The isotherms irregularity is often an impediment to trace the reasonable functionality of compressibility factor.

From this figure, it is clear that the compressibility factor varies with pressure, kind of substance and temperature, therefore $Z=Z(T, P, \omega)$ or in generalized form as $Z=Z(T_r, P_r, \omega)$. Thermodynamic properties of gas mixtures may readily be calculated from knowledge of mixing rules and the binary interaction parameter, k_{ij} [9,10]. For mixtures, the compressibility factor has a surplus dependency on composition mole fraction. For a n-spices mixture, the compressibility factor functionality is $Z=Z(T_m, P_m, \omega_m, x_i, x_{i+1}, \dots, x_{n-1})$.

As one can see in Fig. 1, functional relation between the compressibility factor and mentioned parameters (T, P, ω) is complicated and for mixtures more. Some people made efforts to estimate the compressibility factor via fitting operation on the experimental data involving these parameters. Their results have been represented in form of the generalized correlation equations of state such as *Lee-Kesler* [11], *Benedict-Webb-Rabin* [12], *Kedge-Trebble* [6] and etc. Unfortunately, they never tried to simplify their equations based on the simpler parameters like M-factor (BP/RT). For the first time *Mohebbi & Mohammadikhah* [13] have represented a new EOS based on the virial equation including M-factor, reduced temperature and reduced pressure, nevertheless, they never paid attention to interesting properties of M-factor. In this study, we develop the M-factor theory and investigate its properties as a semi-independent parameter. To our knowledge, to date no quantitative and

qualitative analogous study has been reported on this matter in literature.

THEORETICAL SECTION

The virial EOS was originally introduced by *Kammerligh-Onnes* as an ascending power of density to represent the compressibility factor. Later on, *Ursell & Mayer* [14] developed the statistical mechanic for the virial equation, which is formally presented as a series expansion of either the radial distribution function or the grand canonical partition function for low-density gases. The virial coefficients are related to the intermolecular potential energy so that B is linked through rigorous relations to the so-called pair potential energy function, which is responsible for many thermodynamic and transport properties of fluid [15], C is related to the energy of interaction between triples of molecules, and so forth. The *Leiden* virial equation of state gives the compressibility factor as a power series in the reciprocal molar volume:

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots \quad (1)$$

The mathematically analogous power series in pressure can be derived from Eq. (1) and is known as the *Berlin* virial EOS:

$$Z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (2)$$

Two sets of coefficients in Eq. (1) and Eq. (2) are related as below:

$$B' \approx \frac{B}{RT} \quad C' \approx \frac{C - B^2}{(RT)^2} \quad D' \approx \frac{D - 3BC + 2B^3}{(RT)^3} \quad (3)$$

$$E' \approx (RT)^4 \left(\frac{E - 5B^4 - 2C^2 - 4BD}{(RT)^4} + 10B^2C \right)$$

Because C, D, E and higher virial coefficients are responsible for molecular interactions, thus they are generically dependent on binary interactions. From Eq. (3), it is clear that whatever the molecular interactions become more intense, the second virial coefficient takes higher order of magnitude. For example, C' and D' are proportional to second and third power of B. Mathematically, there is the same term of B/RT in all of the above relations. Also, much less is known about the third and fourth virial coefficients than the second virial coefficient

though data of C for certain gases can be found in literature [16-19]. Besides, it is feasible to enter the effects of all terms in Eq. (3), except B-included, into several temperature dependent coefficients. For these reasons, in Eq. (3), when the third, fourth and higher order virial coefficients are ignored for the present, Eq. (3) diminishes to:

$$B' = \frac{B}{RT} \quad C' = \alpha(T) \left(\frac{B}{RT} \right)^2 \quad (4)$$

$$D = \beta(T) \left(\frac{B}{RT} \right)^3 \quad E' = \gamma(T) \left(\frac{B}{RT} \right)^4$$

Since the third, fourth and higher order virial coefficients depend only on temperature; several coefficients are inserted behind the relations of Eq. (4) to estimate considerable effects of eliminated virial coefficients. These coefficients have only temperature dependency and would make up effects of C, D, ..., which were removed in the previous step. Substituting B', C', D', E', ... from Eq. (4) into Eq. (2) gives:

$$Z = 1 + \frac{BP}{RT} + \alpha(T) \left(\frac{BP}{RT} \right)^2 + \beta(T) \left(\frac{BP}{RT} \right)^3 + \dots \quad (5)$$

$$\gamma(T) \left(\frac{BP}{RT} \right)^4 + \dots$$

Eq. (5) may be rewritten as:

$$Z = 1 + \left(\frac{BP_c}{RT_c} \right) \frac{P_r}{T_r} + \alpha(T) \left(\frac{BP_c}{RT_c} \right)^2 \left(\frac{P_r}{T_r} \right)^2 + \dots \quad (6)$$

$$\beta(T) \left(\frac{BP_c}{RT_c} \right)^3 \left(\frac{P_r}{T_r} \right)^3 + \gamma(T) \left(\frac{BP_c}{RT_c} \right)^4 \left(\frac{P_r}{T_r} \right)^4 + \dots$$

Pitzer & Curl proposed a correlation, which expresses the quantity $\frac{BP_c}{RT_c}$ as:

$$\frac{BP_c}{RT_c} = f^{(0)} \left(\frac{T}{T_c} \right) + \omega f^{(1)} \left(\frac{T}{T_c} \right) \quad (7)$$

The function $f^{(0)}$ gives the reduced second virial coefficients for simple fluids ($\omega=0$) while $f^{(1)}$ is a correction function which, when multiplied by ω gives the effect of eccentricity on the second virial coefficient. The two functions $f^{(0)}$ and $f^{(1)}$ were determined from experimental data and modified by *Tsonopoulos* [20].

Meng et al. [21] presented a modified corresponding correlation that compares well with experimental data for the second virial coefficient for most non-polar pure compounds, since the predictions have been corrected for most physical effects such as adsorption. Detailed comparisons with the well-known *Tsonopoulos* correlation showed that this model is somewhat better than *Tsonopoulos* correlation for non-polar substances. The correlations for non-polar fluids are:

$$f^{(0)}\left(\frac{T}{T_c}\right) = 0.13356 - \frac{0.30252}{T_r} - \frac{0.15668}{T_r^2} - \frac{0.00724}{T_r^3} - \frac{0.00022}{T_r^8} \quad (8)$$

$$f^{(1)}\left(\frac{T}{T_c}\right) = 0.17404 - \frac{0.15581}{T_r} + \frac{0.38183}{T_r^2} - \frac{0.44044}{T_r^3} - \frac{0.00541}{T_r^8} \quad (9)$$

For slightly polar substances it is better to utilize *Tsonopoulos* correlation. Also for polar substances, the second virial coefficient may be calculated from *Janecek et al.* [22] or *Pires et al.* [23] correlation. For mixtures, the mixing second virial coefficient can be usually predicted with the help of mixing rules. The binary second virial coefficient, for example, is given by:

$$B_m = \sum_i \sum_j x_i x_j B_{ij} \quad (10)$$

The dimensionless form of M-factor is [13]:

$$M = \left(\frac{BP_c}{RT_c}\right) \left(\frac{P_r}{T_r}\right) = \frac{BP}{RT} \quad (11)$$

With substituting Eq. (11) into Eq. (6) we get:

$$Z = 1 + M + \alpha(T)M^2 + \beta(T)M^3 + \gamma(T)M^4 + \dots \quad (12)$$

As a consequence, this equation explains that the compressibility factor of every substance just depends on M-factor and temperature. Though M-factor is a compound parameter but can be assumed as a novel parameter with different properties than its composer parameters such as T_r or P_r . Thus the compressibility factor can be written such:

$$Z = Z(M, T_r) \quad (13)$$

In this study, it is verified that M-factor identification is different than its composer parameters. Also a simpler qualitative presentation of compressibility factor as a function of M-factor is exhibited. At the end, it is shown that M-factor can be considered as a semi independent parameter with appealing properties.

RESULTS AND DISCUSSION

Pure Fluid

At first, experimental data of air, argon, carbon dioxide, carbon monoxide, ethanol, ethylene, krypton, methane, methanol, normal hydrogen, normal heptane, neon, nitrogen, oxygen, propane, R32, R123, R124, R134a, water and xenon were assembled from certain sources [8,10,24,25]. To obtain reliable values of compressibility factor, the data were carefully investigated and doubtful data points were rejected. All the property parameters used in this study, namely, P_c , T_c and ω were from the DIPPR[®]801 data base [25]. The compressibility factor data were plotted versus M-factor as well as pressure for all fluids, repeatedly. For instance, results for Methane, carbon dioxide and krypton are shown in Figs. 2 to 7. As one can see in these figures, 12 experimental points along 7 isotherms are collected in temperature range from 200 K to 1100 K. In all of mentioned figures numerical values of the M-factor were determined using both Eq. (7) and Eq. (11), with this assumption; the obtained second virial coefficient from Eq. (11) is true. For polar and quantum gases such as neon, the appropriate correlation and experimental data for the second virial coefficient are available [8,26-32]. Also experimental second virial coefficient may directly be applied to M-factor calculation. This way is far preferable. In absence of experimental data and suitable correlations, the second virial coefficient may be predicted via statistical thermodynamics as equation in below [33]:

$$B(T) = \quad (14)$$

$$\frac{-2\pi}{\Omega} \int_0^\infty r_{ij}^2 dr_{ij} \int d\Omega_i \int d\Omega_j \exp(-V(\Omega_i, \Omega_j, r_{ij})/K_B T) - 1$$

Where $\Omega=4\pi$ for a linear molecule and $\Omega=8\pi^2$ for a non-linear one. Of course an appropriate potential model must be devoted for system description and replaced to Eq.14. The pair Figs. 2-3, 4-5 and 6-7 in comparison, for sample fluids, show that the superiority of the new presentation of compressibility factor as a function of

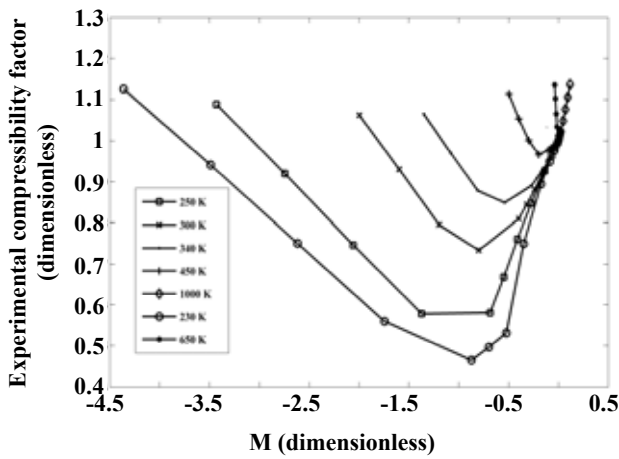


Fig. 2: Experimental compressibility factor of krypton vs. M-factor (7 isotherms).

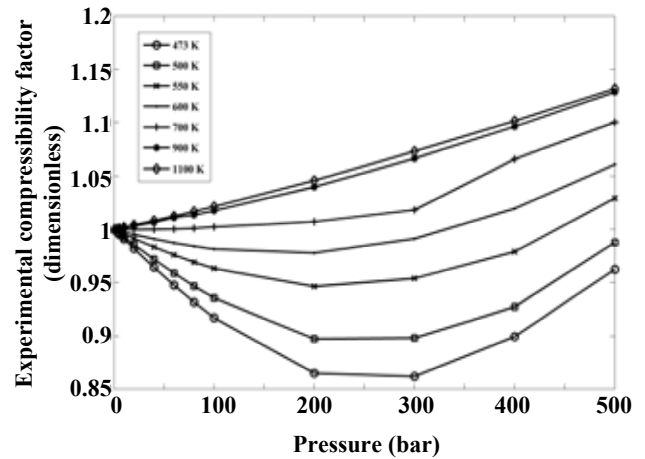


Fig. 5: Experimental compressibility factor of carbon dioxide vs. pressure (7 isotherms).

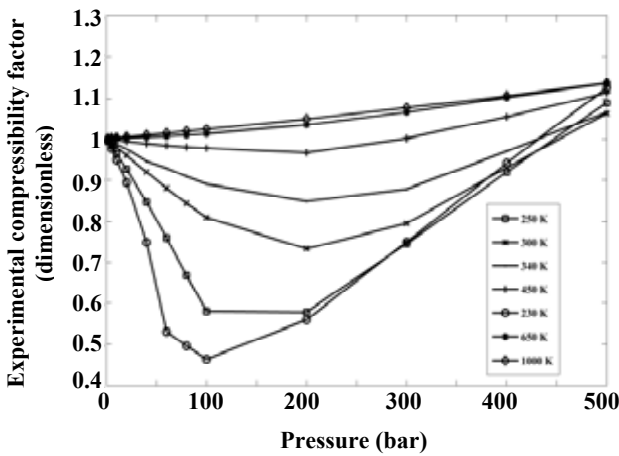


Fig. 3: Experimental compressibility factor of krypton vs. pressure (7 isotherms).

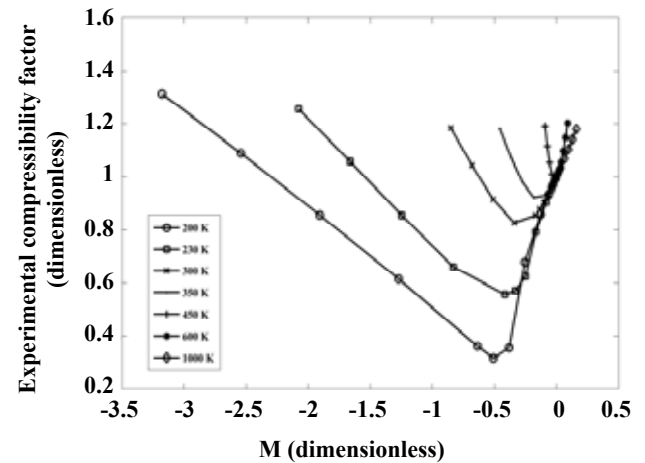


Fig. 6: Experimental compressibility factor of methane vs. M-factor (7 isotherms).

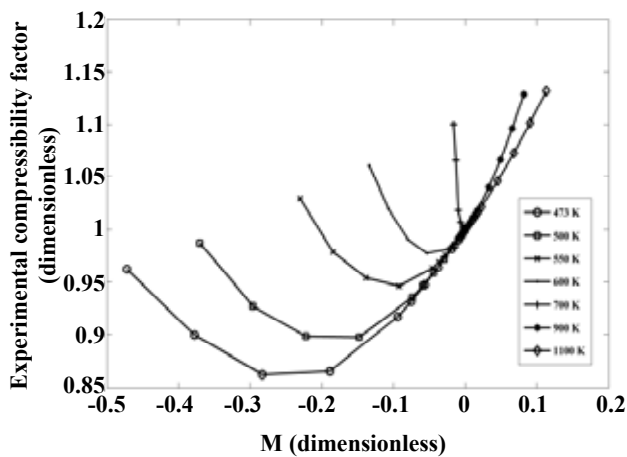


Fig. 4: Experimental compressibility factor of carbon dioxide vs. M-factor (7 isotherms).

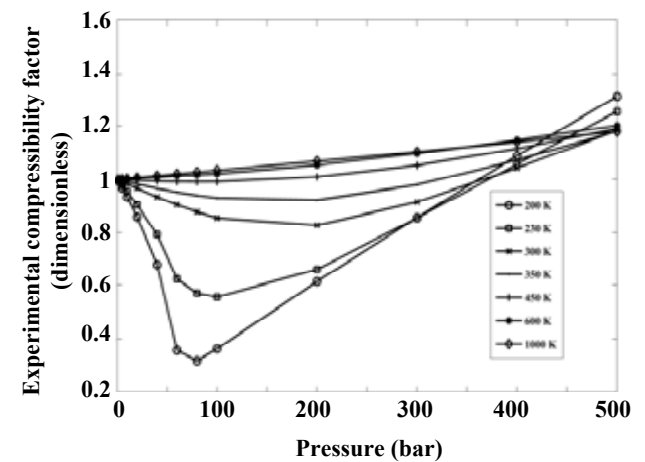


Fig. 7: Experimental compressibility factor of methane vs. pressure (7 isotherms).

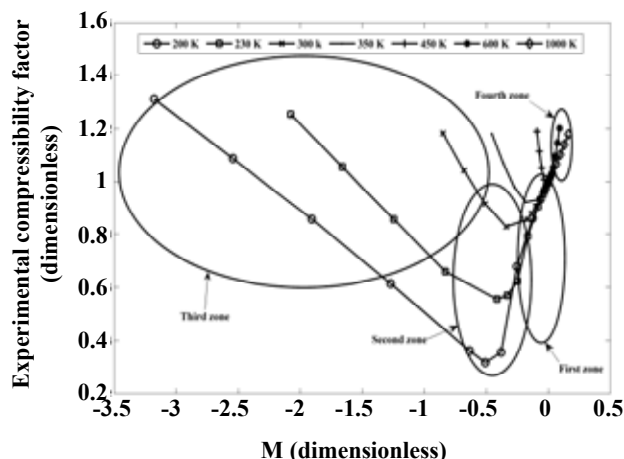


Fig. 8: Experimental compressibility factor of methane vs. M -factor along instances of temperatures (four zones are illustrated, the first, second, third and fourth are linear, parabolic, linear and semi-linear, respectively).

M -factor is evident. These figures are showing the new curves of compressibility factor versus M -factor are simpler for analyzing than previous curves of compressibility factor versus pressure. In addition, these new curves illustrate four supposable zones, where the compressibility factor isotherms have different basic treatment justifiable by molecular theory, as shown in Fig 8. In the first zone, related to low pressure as well as low negative M value, the isotherms of compressibility factor are exactly linear, following constant unit slope for all substances. This is a very nice rediscovery of the two term virial expansion theory in which only the binary interactions exist. Although at low pressures the isotherms of compressibility factor versus pressure are linear, the isotherms slope changes with temperature and kind of fluid, erratically (see Fig. 1). The second zone, which is related to moderate pressure, the isotherms of compressibility factor versus M -factor can be approximately estimated applying a second order polynomial in terms of M -factor. We called this zone as transition zone because it is like a bridge between the first and third zones. The binary and triple interactions together are efficient in this region but the relevant apart contributions for each are unknown. Since the M -factor technique beforehand removed the triple interactions in becoming way (Eq. (12)), the overall interactions in this region may come from the binary form. In the third zone, where pressure is high, the compressibility factor isotherms versus M -factor treat linearly analogous to the first zone nonetheless the slope varies with temperature

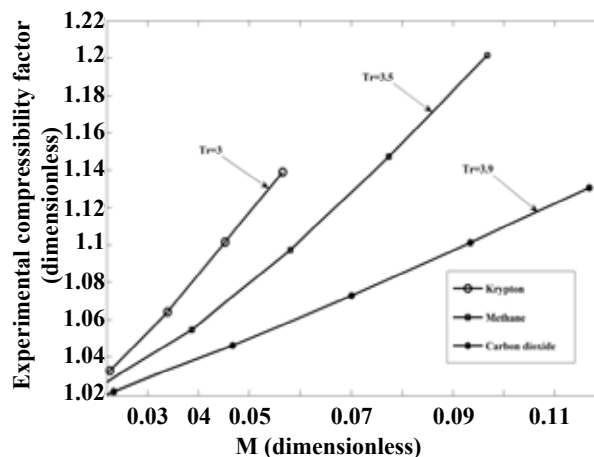


Fig. 9: A schematic diagram from fourth zone (high temperature supercritical zone for krypton, methane and carbon dioxide).

whereas remains unchanged with kind of fluid. We think when the gas is under high pressures, because of vigorous molecule repulsions, unlike the molecule attraction that can be ternary or more, the whole authority of a molecule is spent to repulse another one, selectively. Therefore, under high pressures perforce the binary interactions are dominant.

In general, it seems that in all zones, perhaps, the interaction of pairs of molecules should be significant. Therefore, this idea may be developed to make a comprehensive semi-theoretical equation of state. Just a linear equation of state is with good consistency required for the first and third zones and a parabolic equation for the second zone providing that the compressibility factor is represented in terms of M -factor. This fact is completely according to what Eq. (12) dictates after truncating to three terms. Then it is essential to modify the coefficients of Eq. (12) as a function of temperature. In the following, new curves of compressibility factor were plotted for high temperature supercritical systems. All supercritical data in this study were taken from Refs [24,34,35]. When these data were used, an interesting distribution was observed as one can see in Fig. (9). Each isotherm in the vicinity of high temperature supercritical region is almost linear for which the slope changes with respect to temperature. At critical point, the M -factor value is achieved as -0.33 for all substances which means that the degree of freedom at critical point decreases from two, former value, to one. In the fourth zone, where M values are positive, an increase in temperature leads to approaching

Table 1: Calculated reduced Boyle temperature from this work compared to Refs [36,37].

Fluid	Reported reduced Boyle temperature[36,37]	Observed from present work	%RE
Argon	2.720	2.660	2.21
Nitrogen	2.590	2.600	0.39
Ammonia	2.50	-	-
Methane	2.675	2.640	1.33
Carbon Dioxide	2.349	2.360	0.44
Hydrogen	3.310	2.993	9.58
Helium	4.345	-	-
Krypton	2.746	2.660	3.13
Neon	2.747	2.660	3.17
Oxygen	2.622	2.620	0.07
Xenon	2.650	2.650	0.02

the isotherms to straight lines having unit slope while the isotherms shift to a vertical position with temperature decrease. At Boyle temperature, the isotherms altogether become a vertical line, exactly.

It was found that M values are negative in the first, second and third zones and are positive in the fourth. In the high temperature supercritical region, which is a subset of fourth zone, the M -factor values are essentially positive and very small. Since all of the T_c , P_c , R , P_r and T_r are positive, the sign of M indeed signifies on the sign of the second virial coefficient. For all fluids, the positive values of M refer to $T > T_{Boyle}$, which is the temperature where the second virial coefficient changes its sign. The temperature where the M -factor changes its sign is also obtained to be $T_r=2.6$ for most of fluids except carbon dioxide and normal hydrogen with $T_r=2.3$ and $T_r=2.99$, respectively. The obtained Boyle temperature values are listed in Table 1, where there is good agreement with reported data [36,37]. The maximum relative error is less than 10% corresponded to normal hydrogen. The second virial coefficient evaluation from Eqs. (7-9) probably has caused these deviances.

Surprisingly, when the compressibility factor of different fluids at the same reduced temperature was used as the y-coordinate and the M -factor as the x-coordinate, an interesting distribution was observed as it can be seen in Figs.10 (a), 11 (a) and 12 (a) showing that at any given reduced temperature the compressibility factor is independent

of kind of fluid, i.e $Z=Z(M)_{T_r-known}$. As a merit, there is a single uniform compressibility factor curve for sample fluids at any reduced temperature. Already, M -factor parameter for more simplification of regression procedure successfully incorporated the eccentricity effect into itself as Eqs. (7) and (11) show. Oddly enough, the compressibility factor plots versus pressure, shown in Figs.10 (b), 11 (b) and 12 (b), are dispersed due to the effect of eccentricity. Preliminary compressibility factor calculation in suggested way will practically be better although this particular result has been recognized for many years (e.g. three-parameter corresponding-state theory). Despite of *Pitzer and Brewer's* hard work to tabulate the compressibility factor in terms of these three parameters, the original three parameter *Pitzer's* correlation is inadequate for calculations performed in the critical region and for liquid in low temperatures [38]. Consequently, M -factor identification as a semi-independent parameter can be verified from its simplifying effects whether for critical region or for liquid in low temperatures as we demonstrated (see Fig.10).

Once more, we found that compressibility factor treatment can be represented by a third order polynomial with respect to M -factor with high precision in the first and second zones together (neighbour zones), as long as they are combined to fabricate a unified zone, and in the fourth zone. Accordingly, the favorable EOS must certainly be recognized as a multi-domain function, one is

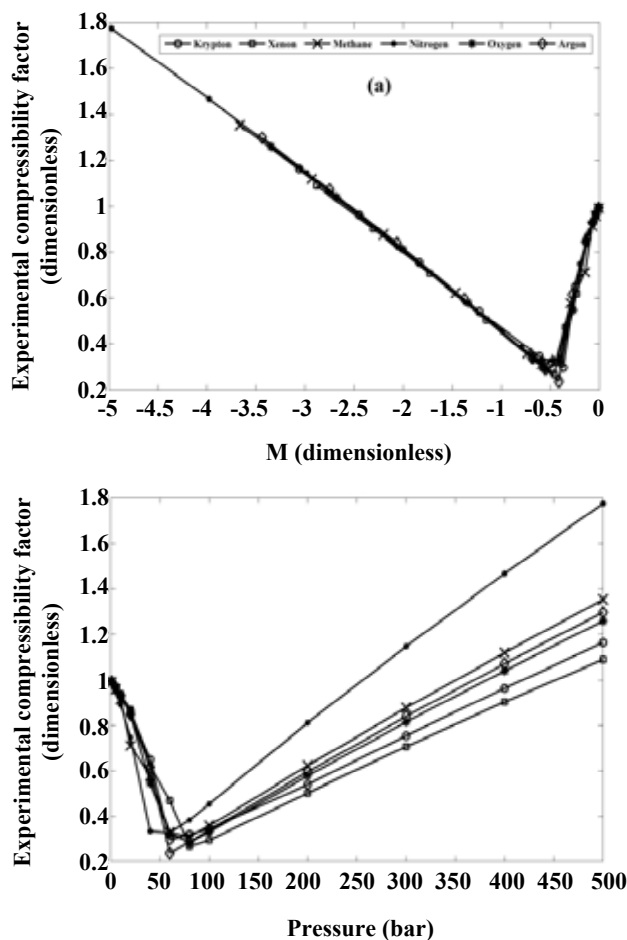


Fig. 10: Experimental compressibility factor vs. (a) M-factor and (b) pressure at critical temperature for krypton, xenon, methane, nitrogen, oxygen and argon.

responsible for the linear parts (third and high temperature supercritical zones) and other for the bent parts (first and second zones together and fourth zone), discretely. Fig.13 shows the compressibility factor treatment qualitatively within separation zones.

Among the many forms of Eq. (12) tested for predicting the compressibility factor, we found a modified form of Eq.12 with at most four parameters nicely fitted the experimental data in the bend part. However, the three order polynomial, capable of explaining the compressibility factor, was superior to flexible fit of isotherm data than two order one, although its physical meaning is arguable. Now, we propose the modified correlation of Eq. (12) as follows:

$$Z = a(T_r) + b(T_r)M \quad \text{for linear part} \quad (15)$$

$$Z = 1 + \alpha(T_r)M + \beta(T_r)M^2 + \gamma(T_r)M^3 \quad \text{for bend part}$$

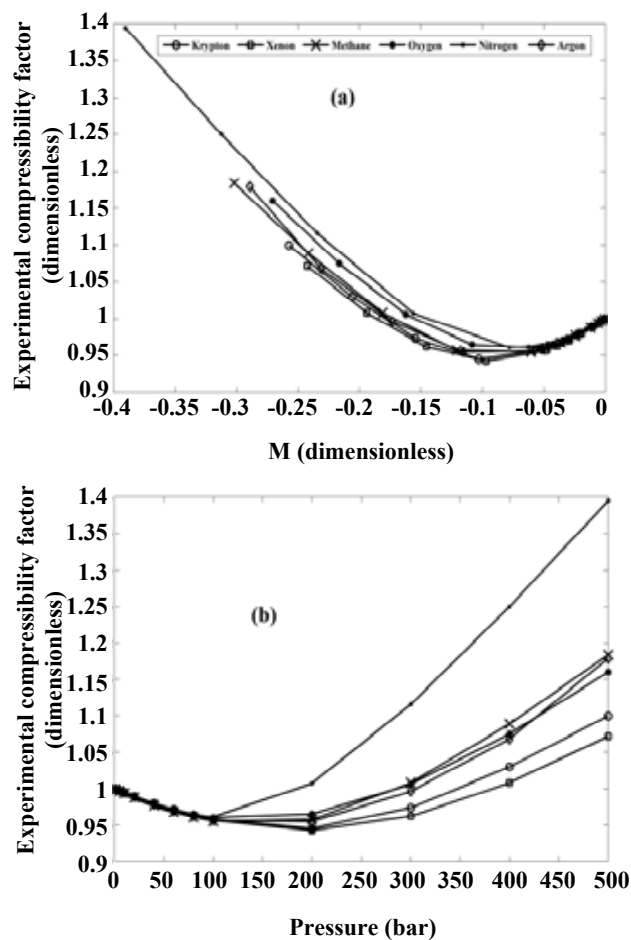


Fig. 11: Experimental compressibility factor vs. (a) M-factor and (b) pressure at $T=2T_c$ for krypton, xenon, methane, nitrogen, oxygen and argon.

Rearranging in unified form results in:

$$Z = f^1(T_r) + f^2(T_r)M + f^3(T_r)M^2 + f^4(T_r)M^3 \quad (16)$$

Detailed studies on the fitting operation reconsidering Eq.16 were carried out and primary results revealed that:

(i) For $T_r \geq 5$ the linear part solely exists and a R-square greater than 0.9977 for fitting is possible and the proper EOS should be $Z=1+M$. We declare that in this region absolutely the second virial coefficient is dominant.

(ii) For $2.25 < T_r < 5$ the bend part exists and a mean R-square of 0.99997 calculated along 28 isotherms is possible and the proper EOS should be $Z = 1 + f^2(T_r)M + f^3(T_r)M^2 + f^4(T_r)M^3$.

(iii) For $1.1 < T_r \leq 2.25$ the bend part exists and a mean R-square of 0.9962 calculated along 14 isotherms is possible and the proper EOS should be $Z = 1 + 1.3M + f^3(T_r)M^2 + f^4(T_r)M^3$.

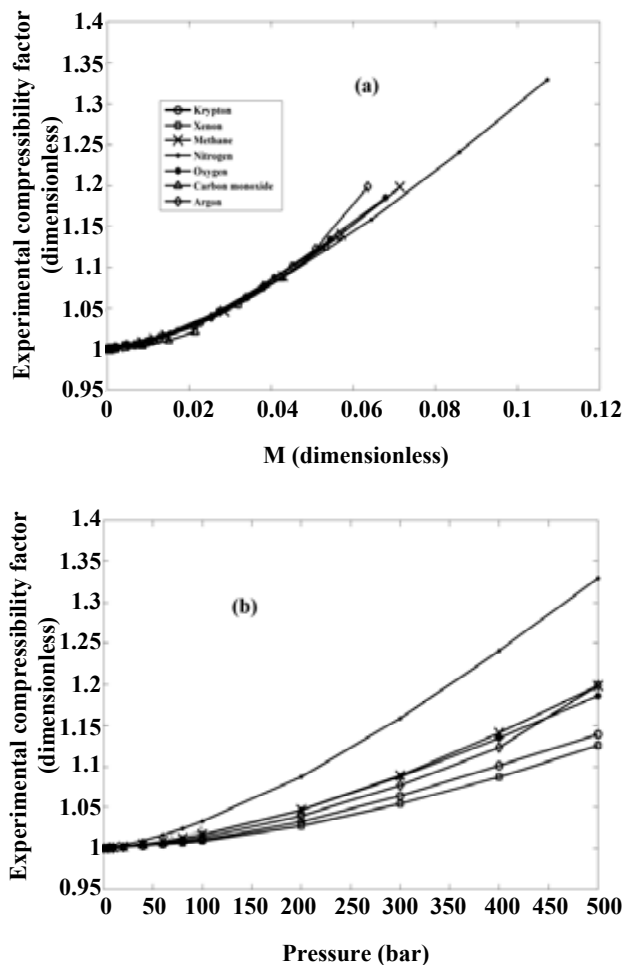


Fig. 12: Experimental compressibility factor vs. (a) M-factor and (b) pressure at $T=3T_c$ for krypton, xenon, methane, nitrogen, oxygen and argon.

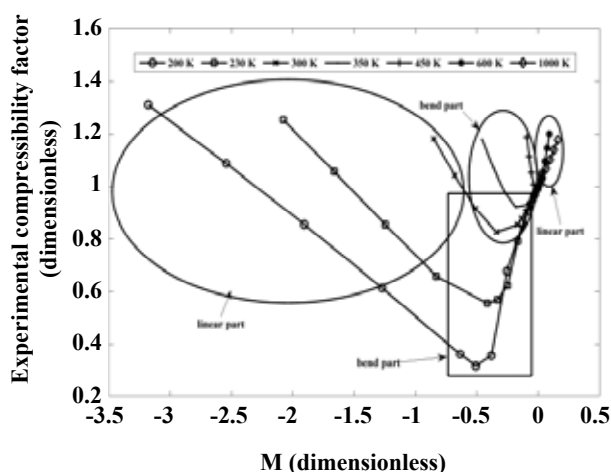


Fig. 13: Experimental compressibility factor of methane vs. M-factor along instances of temperatures. The figure is showing that desired EOS must be a piecewise function.

(iv) For $T_r \leq 1.1$ the bend part still are observed and a mean R-square of 0.9997 calculated along 7 isotherms is possible. The bend part extent dwindles with temperature decrease. The proper EOS for bend part should be $Z = 1 + M + f^3(T_r)M^2 + f^4(T_r)M^3$. At $T_r = 1.1$ the concavity of the curve, representative of the bend part, changes its sign so that the concavity transforms to the convexity, which predicts the saturated line. Also the bend and linear part are successive as the linear part with $Z = f^1(T_r) + f^2(T_r)M$ is preceded by the bend part.

The desired EOS was correlated on experimental data, after an onerous regression operation to find the temperature dependent coefficients (times correction functions). We named this new EOS as "Mohammadikhah, Mohebbi, Abolghasemi" EOS or "MMA" EOS. The coefficients of the EOS, altogether, were determined by a nonlinear least-square fitting routine of the Trust-Region, performed by MATLAB CF TOOLBOX software environment. The coefficients $f^1(T_r)$, $f^2(T_r)$, $f^3(T_r)$ and $f^4(T_r)$ were obtained with R-square higher than 0.99. The appropriate correlations are according to Tables 2&3:

A comparison of three equations of state, namely, MMA (present work), *Lee, Kesler, Plocker* [39] and *Peng-Rabinson* [40], for predicting the compressibility factor of oxygen, krypton, methane, xenon, nitrogen and carbon monoxide was accomplished as one can see the results in Table 4. The average absolute relative deviation (AARD) is calculated for 12 data points by the following equation:

$$\%AARD = \frac{1}{N} \sum_{i=1}^N \left(\left| \frac{Z_{\text{exp}} - Z_{\text{calc}}}{Z_{\text{exp}}} \right| \right) \times 100 \quad (17)$$

It can be seen that the present equation with no adjustable parameters, in comparison to conventional EOS like the *Peng-Rabinson* has more accuracy even occasionally to *Lee-Kesler-Plocker* correlation, which has 12 adjustable parameters for kind of fluid.

According to table 4 the present equation describes the compressibility factor of simple pure fluids very well. At reduced temperatures less than 0.8; this equation does not have enough accuracy as the *Lee-Kesler-Plocker* and *Peng-Rabinson* also do not. It should be kept in mind that the deviation obtained from present EOS could have decreased if the experimental second virial coefficients had directly been inserted into M-factor calculation.

Table 2: The coefficients of Eq. (16).

Domain of reduced temperature	Domain of M	f ¹	f ²
$T_r \geq 5$	-	1	1
$2.25 < T_r < 5$	-	1	$\frac{-7.57T_r + 20.8}{T_r^3 - 9.019T_r^2 + 18.39T_r - 4.21}$
$1.1 < T_r \leq 2.25$	$M \geq \frac{0.04545T_r^2 - 0.2746T_r + 0.2509}{T_r^3 - 3.269T_r^2 + 3.817T_r - 1.578}$	1	1.3
	$M < \frac{0.04545T_r^2 - 0.2746T_r + 0.2509}{T_r^3 - 3.269T_r^2 + 3.817T_r - 1.578}$	$\frac{0.6592T_r^2 - 0.7257T_r + 0.208}{T_r^2 - 2.4T_r + 2.607}$	$\frac{729.5T_r^2 - 2499T_r + 821.8}{T_r^2 - 1836T_r + 4545}$
$T_r < 1$	$M \geq -0.39312T_r^3 + 0.0252T_r^2 - 0.001235$	1	1
	$M < -0.39312T_r^3 + 0.0252T_r^2 - 0.001235$	$(\frac{0.6592T_r^2 - 0.7257T_r + 0.208}{T_r^2 - 2.4T_r + 2.607}) \times 0.95$	$(\frac{729.5T_r^2 - 2499T_r + 821.8}{T_r^2 - 1836T_r + 4545}) \times 0.95$

Table 3: The coefficients of Eq. (16).¹

Domain of reduced temperature	Domain of M	f ³	f ⁴
$T_r \geq 5$	-	0	0
$2.25 < T_r < 5$	-	$\frac{5.796}{T_r^2 - 5.247T_r + 6.88275} \times n$	$\frac{6.973 \cdot \frac{10.73}{ T_r - 2.625 } - \frac{11.99}{(T_r - 2.625)^2}}{(\frac{6.776}{ T_r - 2.625 })^3 - \frac{0.0004369}{(T_r - 2.625)^4}} \times i$
$1.1 < T_r \leq 2.25$	$M \geq \frac{0.04545T_r^2 - 0.2746T_r + 0.2509}{T_r^3 - 3.269T_r^2 + 3.817T_r - 1.578}$	$\frac{1.88T_r - 2.148}{T_r^3 - 6.059T_r^2 + 11.59T_r - 6.725}$	0
	$M < \frac{0.04545T_r^2 - 0.2746T_r + 0.2509}{T_r^3 - 3.269T_r^2 + 3.817T_r - 1.578}$	0	0
$T_r < 1$	$M \geq -0.39312T_r^3 + 0.0252T_r^2 - 0.001235$	$75.36T_r^2 - 157.7T_r + 82.86$	$\left \frac{0.05038T_r + 0.0001896}{T_r^3 - 2.508T_r^2 + 2.098T_r - 0.5845} \right $
	$M < -0.39312T_r^3 + 0.0252T_r^2 - 0.001235$	0	0

¹ The correction factors *i* and *n* are defined as 1.4 and 1 for $T_r > 2.625$ else are 0.5 and 0.15, respectively.

In the vicinity of critical temperature the present equation calculates the compressibility factor very well whereas the most of common equations of state are unable. In Table 5, the experimental critical compressibility factors of some pure fluids are compared to those calculated by the common equations of state and the present equation, where the given relative error for models shows another advantage of the present work. Since at critical point

the M value is constantly in accordance with -0.33, therefore the calculated critical compressibility factor from present work has been found to be 0.283 for all fluids but it is strictly dependent on the second virial coefficient. We used the Meng's equation [21] for M-factor calculation. If we had taken the experimental second virial coefficient into account, the relative error for the present work would surely have been far fewer.

Table 4: Evaluation of compressibility factor obtained from different methods based on %AARD in pressure range from 0 to 600 bar.

Fluid	T_r	%AARD of MMA (present work)	%AARD of Lee-Kesler-Plocker[39]	%AARD of Peng-Rabinson[40]
Oxygen	0.7	21.830	18.710	17.590
	0.8	6.790	5.630	7.210
	0.95	5.410	7.220	9.260
	1	4.330	5.020	8.070
	1.3	1.320	0.520	3.690
	2	0.520	0.220	1.920
	3	0.730	0.122	1.270
	3.5	0.100	0.128	1.250
	4	0.096	0.103	0.960
	5	0.240	0.061	0.790
	5.5	0.168	0.081	0.750
Krypton	0.8	24.640	21.690	26.480
	0.95	6.800	4.340	2.060
	1	4.500	4.540	8.410
	1.3	1.370	1.305	2.284
	2	0.200	0.630	1.281
	3	0.265	0.440	0.746
	3.5	0.361	0.549	0.445
	4	0.352	0.443	0.420
Methane	0.8	2.500	5.370	5.540
	0.95	11.250	13.085	14.190
	1	5.460	6.020	8.550
	1.3	0.080	0.851	2.900
	2	0.894	0.529	1.659
	3	0.910	0.282	1.129
	3.5	0.095	0.183	1.095
	4	0.182	0.136	1.152
	5	0.400	0.290	1.211
Xenon	0.7	7.98	26.35	9.472
	0.8	13.9	8.45	13.18
	0.95	4.47	6.46	10.25
	1	4.320	6.03	8.74
	1.3	1.069	1.243	2.241
	2	0.206	0.858	0.888
	3	0.104	0.528	0.587
Nitrogen	0.7	8.322	0.33	0.71
	0.8	3.13	6.051	6.796
	0.95	3.99	1.181	1.83
	1	3.14	4.8	8.961
	1.3	1.086	0.626	3.834
	2	0.882	0.138	2.422
	3	0.497	0.283	1.590
	3.5	0.208	0.311	1.442
	4	0.108	0.309	0.317
Carbon Monoxide	2.3	0.331	0.101	0.153
	3	0.408	0.410	0.315
	4	0.0898	0.121	0.212

Table 5: The relative error¹ of the critical compressibility factor calculated by equations of state for sample fluids.

Fluid	Experimental value	%RE of MMA (present work)	Predicted value by MMA (present work)	%RE of SRK[41]	Predicted value by SRK[41]	%RE of Peng-Rabinson	Predicted value by Peng-Rabinson[40]	%RE of Lee-Kesler-Plocker	Predicted value by Lee-Kesler-Plocker[39]	%RE of MM [13]	Predicted value by MM [13]
Argon	0.291	2.75	0.283	15.59	0.336	7.192	0.311	0.309	0.2901	0.0787	0.2908
Krypton	0.288	1.73	0.283	8.983	0.313	0.277	0.287	0.729	0.2901	0.962	0.2908
Methane	0.286	1.05	0.283	42.21	0.407	32.374	0.379	3.383	0.296	1.610	0.2906
Nitrogen	0.289	2.07	0.283	4.533	0.302	4.225	0.277	6.492	0.3077	0.435	0.2903
Carbon Dioxide	0.274	3.28	0.283	30.047	0.356	20.24	0.329	43.874	0.394	5.030	0.2880
Oxygen	0.288	1.73	0.283	32.17	0.381	22.322	0.352	4.28	0.300	0.868	0.2905
Xenon	0.286	1.05	0.283	2.126	0.292	6.528	0.267	1.433	0.2901	1.668	0.2908
Air	0.289	2.07	0.283	8.052	0.312	0.297	0.288	6.009	0.306	0.449	0.2903
Carbon Monoxide	0.299	5.35	0.283	1.749	0.294	10.1	0.269	4.485	0.312	2.968	0.290

¹ The relative error is calculated from $\%RE = \text{abs}(Z_c, \text{exp} - Z_c, \text{calc}) / Z_c, \text{exp} \times 100$

However, at the critical point again the MMA equation is more successful in compressibility factor predicting than most typical EOSs. Although the MM equation is better but unfortunately its applicability is limited in specified pressure-temperature range [13]. We applied the MMA equation to predict the compressibility factor of propane and normal heptane at critical temperature. There was an excellent agreement between values estimated by MMA equation and experimental results for propane, as one can see in Fig.14. An average of second virial coefficients obtained from Meng's equation [21] and McGlashan's equation [42] was used for M-factor calculation.

For normal heptane, the MMA equation showed an AARD of 21.48%, whereas for Lee-Kesler equation it was 23.91%. For quantum gases such as helium, hydrogen and neon our equation does not give satisfactory prediction unless some assumptions are made upon B, which has different behavior with regard to other fluids, and asterisk reduced units are considered as demonstrated in Ref [8]. Even the use of experimental B for helium is not responsible for a good agreement, so, the use of asterisk reduced unit is a must. However, the present equation can be applied for quantum gases accurately, taking into account for asterisk reduced units. Detailed analysis of quantum gases is under progress concurrent with this work and would separately be reported in due time.

Mixture

The experimental compressibility factor data for some binary mixtures such as N₂-O₂, NO₂-R41, H₂O-CH₄, N₂-butane, N₂-ethylene, N₂-CH₄ and acetonitrile-butane were collected [19,24,43,44,45,46]. The second virial coefficient in this case can also be estimated from mixing rules which are defined by the following equations:

$$T_{cij} = (T_{ci} T_{cj})^{1/2} (1 - K_{ij}) \quad (18)$$

$$P_{cij} = \frac{4T_{cij}(P_{ci}v_{ci}/T_{ci} + P_{cj}v_{cj}/T_{cj})}{(v_{ci}^{1/3} + v_{cj}^{1/3})^3} \quad (19)$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad (20)$$

Where v_{ci} and v_{cj} are the critical volumes of component i and j. Binary interaction parameter K_{ij} has been reported for many fluids by Meng *et al.* [1]. Compressibility factor curves versus M-factor as well as pressure for binary samples were provided, for instance, results for two binaries are depicted in Figs.15 and 16. It was found that if binary interaction parameter is less than 0.033, the similar curve would be for both pure and mixture fluids at any given composition of mixture components. This fact means that for $K_{ij} \leq 0.033$, the mixing rules are useless.

Therefore, under special conditions, compressibility factor of binary mixtures is not dependent on component

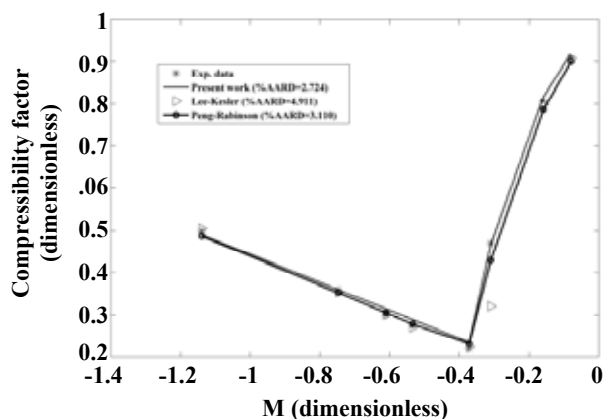


Fig. 14: Compressibility factor of propane estimated by MMA, Lee-Kesler[11] and Peng-Rabinson[40] equations in comparison to the experimental data [8] at critical temperature. The $-230 \text{ cm}^3/\text{mol}$ was inserted as the second virial coefficient into M-factor calculation.

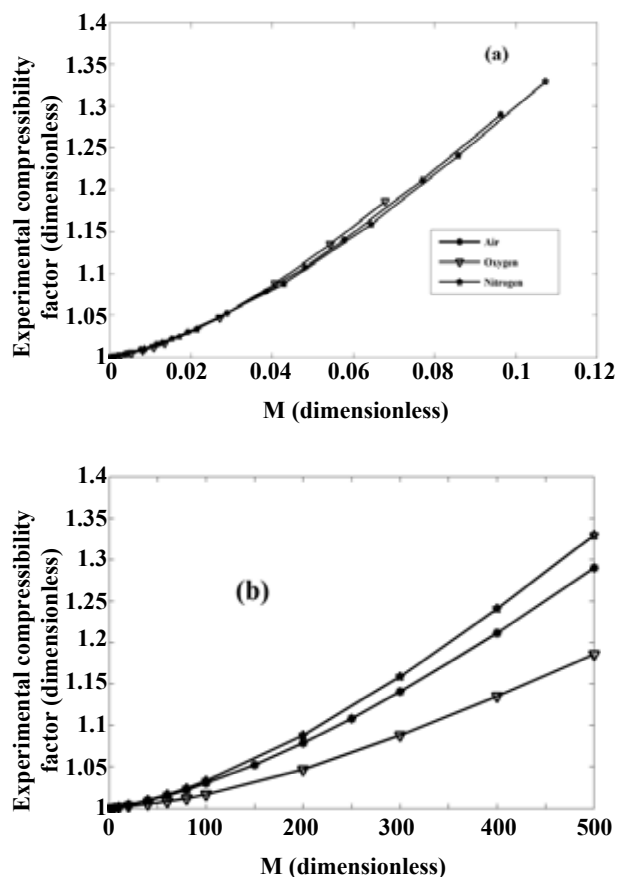


Fig. 15: Experimental compressibility factor of $\text{N}_2\text{-O}_2$ mixture vs. (a) M-factor and (b) pressure with three different compositions as pure nitrogen, pure oxygen and 21% N_2 -0.79% O_2 (Air).

mole fractions as long as it is presented with M-factor. For binary mixtures with $K_{ij} \leq 0.033$, it is adequate to conduct the compressibility factor calculation with only one component which has the greater mole fraction. We guess the trifling diversions of uniform favorable trajectory in Fig.16 (a) are due to uncertainty of experimental assessment. The M-factor can be really assumed as an intensive thermodynamic property, not an artificial property, due to its useful applications. In this work, we illustrated the astonishing properties of M-factor for both pure and binary mixture fluids and proved its different characterization. In order to evaluate the validity of present work for binary mixtures, several attempts were established, for instance, results for $\text{NO}_2\text{-R41}$ (fluoromethane) mixture compared to the experimental data are shown in Fig. 17. The pure experimental second virial coefficients in $T=283.52 \text{ K}$ and $T=345.25 \text{ K}$ were introduced to M-factor calculation [19]. These values are related to component which has the greater mole fraction. As one can see in this figure, the MMA equation in practical concepts, based on what M-factor theory dictated, quashes the authenticity of cross second virial coefficient or classical mixing rules providing that the binary interactions are $K_{ij} \leq 0.033$, since by using mixing rules the deviation from experimental data do not show salient differences. From this way the predicted values of compressibility factor of binary mixtures by MMA equation compare the experimental data with negligible average error. However, it is worth nothing that the realistic possibility of calculation of compressibility factor of multi-component mixtures could be in similar way (binary) mentioned by M-factor theory if just this property, the binary interaction, is taken into account as a criterion.

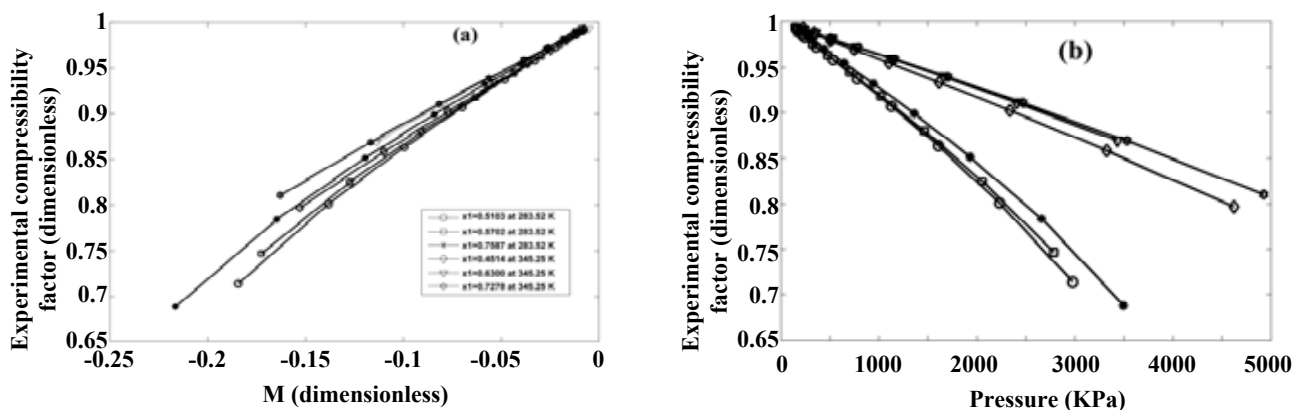
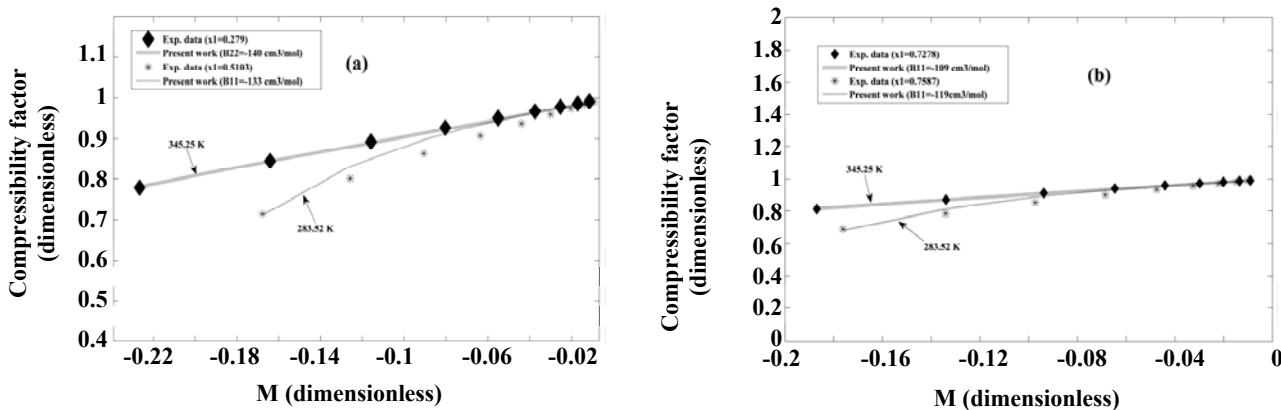
Although the MMA equation is a multi-domain function and it seems a massive outward appearance equation but for a specified T_r and M (in needed case not ever), the equation diminishes to a simple practical form.

Second virial coefficient

The present work has a strong basis as virial expansion while the most sophisticated models don't have such basis. The present EOS involves the meaningful physical parameters (B and M), thus for these reasons at least, it deserves to be known better. The model is of great interest both as an EOS to predict thermodynamic properties as long as the B is known and conversely

Table 6: The second virial coefficient obtained from different models for Nitrogen.

Fluid	T(K)	B[20](cm ³ mol ⁻¹)	B[21](cm ³ mol ⁻¹)	B _{exp} [32](cm ³ mol ⁻¹)	B(cm ³ mol ⁻¹) Present work
Nitrogen	80	-256.94	-250.17	-243.9 ± 0.5	-247
	90	-202	-198.85	-195 ± 0.4	-195
	100	-164.36	-162.47	-159.8 ± 0.3	-160
	150	-73.09	-72.32	-71.5 ± 0.4	-74
	200	-36.59	-36.14	-35.6 ± 0.1	-38
	273.15	-10.86	-10.82	-10.3 ± 1	-11.7
	300	-5.02	-5.1	-4.5 ± 0.1	-5
	423.15	11.28	10.77	11.4 ± 1	11.2
Krypton	174.40	-150.29	-148.42	151.7 ± 2	-152
	204.45	-111.55	-110.34	-113.2 ± 2	-115.7
	223.15	-94.14	-93.16	-93.1 ± 0.1	-100
	273.15	-61.83	-61.30	-61.5 ± 0.1	-61.5
	323.15	-41.39	-41.21	-41.7 ± 0.1	-41.1
	423.15	-17.15	-17.53	-17.5 ± 1	-15
	673.15	8.89	7.62	7.2 ± 0.6	7.9
	873.15	18.11	16.42	17.2 ± 0.4	16.6

Fig. 16: Experimental compressibility factor of R41-N₂O mixture vs. (a) M-factor and (b) pressure at 283.52 K and 345.55 K for 6 different mole fractions of N₂O as 0.451, 0.5103, 0.5702, 0.63, 0.7278 and 0.7587.Fig. 17: Predicted compressibility factor of R41 (2)-N₂O (1) mixture for four different mole fractions of N₂O by MMA equation compared to the experimental data. The %AARD related to the thin and thick dash lines are (a) 1.734 and 0.293, (b) 1.87 and 0.157, respectively.

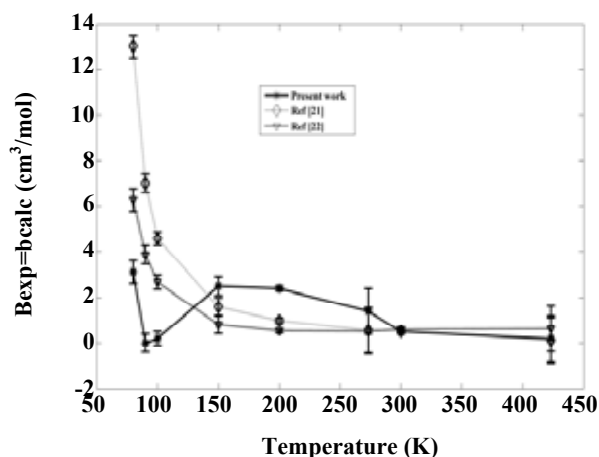


Fig. 18: The deviation of the calculated second virial coefficients by different models from the experimental values. The error bars are showing the experimental errors.

as a possible model to obtain B in the presence of valid experimental compressibility factor. Having experimental compressibility factor, the model gives the second virial coefficient via fitting on experimental data. The second virial coefficients for nitrogen and krypton obtained with a criterion of AARD less than 2%, from MMA equation and some of the current models are listed in Table 6, where there is a tolerable agreement between present work and experimental data.

For nitrogen more details manifesting the second virial coefficient can be found elsewhere [47, 48]. This table shows that the MMA equation can successfully predict the second virial coefficient; therefore, this fact can be a good evidence to justify the accuracy of the M-factor theory and subsequently the MMA equation derivation. Eventually, we supply the supplementary figure from the data in Table 6 for nitrogen to better understanding. Fig. 18 shows the present equation satisfies the experimental data well and sometimes this recipe for the second virial coefficient results in better values than those acquired from Refs[20, 21] so that for nitrogen, the figure shows low deviances from zero level. Regrettably, this trend is not noticed for krypton and the above mentioned models were superior to correlate the data.

CONCLUSIONS

A new qualitative analysis of compressibility factor based on the M-factor theory is applied for some samples of fluid. In the first step, the M-factor theory is aptly developed by adopting the separation of C , D , ...

contributions in several temperature dependent coefficients. The modified M-factor theory was successful in simplifying virial equation. Using M-factor as x-coordinate instead of pressure, the modified model was also brilliant in presenting the compressibility factor, qualitatively. For all fluids, the compressibility factor functionality from M-factor was much simpler than the compressibility factor functionality from the pressure. This is due to more different M-factor identification in comparison to its composer parameters. It is found that the compressibility factor may easily be predicted from a third order polynomial in terms of M-factor without any substance dependency. Also the M-factor theory applications for binary mixtures are revealed; the mixing rules can be never applied for compressibility factor calculation if $K_{ij} \leq 0.033$. For binary mixtures, only compressibility factor calculation of the highest component mole fraction is recommended because the obtained pure compressibility factor value from this way is somewhat equal with the true compressibility factor value of mixture. The quantitative studies to find a new comprehensive EOS are carried out and the results show the proper equation has to be a multi-domain function. Resulting EOS was tested for compressibility factor prediction of pure fluids. There was a good consistency between predicted values and the experimental data. The present EOS was often better than the *Peng-Rabinson* EOS even better than the *Lee-Kesler-plocker* correlation in some of reduced temperatures. Also the present EOS predicted the critical compressibility factor of sample fluids better than the available typical equations of state. The obtained critical compressibility factor by MMA equation was very close to real experimental data. The claims of the present work and the validity of what M-factor theory says were proved for several pure and binary mixture fluids well. The MMA correlation provided reliable results for fluids which are non-polar or only slightly polar; for these, an error of no more than 2 percent for each data point, except for one data point in range of $T_r < 0.9$, was indicated while the correspondent error by *Peng-Rabinson* was 5-8 percent. For Hydrocarbons the model was superior to *Lee-Kesler* correlation in compressibility factor prediction so that the AARD was decreased 5-10% by using the MMA correlation. When the model is applied to highly polar gases or to associate, larger error can be expected. It is suggested that the p

resent EOS to be proper for non-polar and slightly polar-simple fluids with a good precision as Table.4 and 5 showed. To be applicable over a much broader range of fluids, more attention must be paid to the respective characteristics of fluid and other effective conditions, so, certainly this would take much effort. The MMA equation may be applied for simple, non-polar, slightly polar and light hydrocarbon fluids with a high confidence level until it is developed for heavy hydrocarbons and etc. The model for the second virial coefficient proposed by the MMA correlation had acceptable agreement compared to other current models. Further studies on predicting the second thermodynamics properties such as enthalpy and entropy are under way and will be referred in the future.

Acknowledgement

We would like to thank to Dr. H. Hashemipour, from the Chemical Engineering Department, Faculty of Engineering, Shahid Bahonar University of Kerman, Iran, for helpful discussions.

Nomenclature

B_{ij}	Cross second virial coefficient
$f^1(T_r)$, $f^2(T_r)$, $f^3(T_r)$ and $f^4(T_r)$	Coefficients of Eq.(16)
K_B	Boltzmann factor
K_{ij}	Binary interaction parameter
N	Number of experimental data
P_c	Critical pressure
$P_{c\ i\ or\ j}$	Critical pressure of component i or j
P_{cij}	Mixed critical pressure of components i and j
P_r	Reduced pressure
P_{rm}	Reduced pressure of mixture
r_{ij}	Separation space between molecules i and j
R	Universal Constant of gases
%RE	Relative error percent
T_c	Critical temperature
$T_{c\ i\ or\ j}$	Critical temperature of component i or j
T_{cij}	Mixed critical temperature of components i and j
T_r	Reduced temperature
T_{rm}	Reduced temperature of mixture
$x_{i\ or\ j}$	Mole fraction of component i or j
V	Potential model
$A(T_r)$, $b(T_r)$, $\alpha(T)$, $\beta(T)$ and $\gamma(T)$	Coefficients of Eq.(12) and Eq.(15)
$\Omega_{i\ or\ j}$	Orientation of molecule i or j
$v_{ci\ or\ j}$	Critical molar volume of component i

$\omega_{i\ or\ j}$	Acentric factor of component of i or j
ω_{ij}	Mixed acentric factor of components i and j
ω_m	Acentric factor of mixture
Z_{exp}	Experimental compressibility factor
Z_{calc}	Calculated compressibility factor
$Z_{c,exp}$	Critical experimental compressibility factor
$Z_{c,calc}$	Critical calculated compressibility factor

Received : Oct. 28, 2008 ; Accepted : Dec. 28, 2009

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