

## New Correlation for Second Virial Coefficients by Using Refractive Index

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Mawaheb M. Derdar<sup>1</sup>  
Najia E. Elgandouri<sup>3</sup>

Asia A. Almeshergi<sup>2</sup>  
Mohamed M. Amer<sup>4</sup>

<sup>1,2,3,4</sup>Chemical Engineering Department, Faculty of Engineering,  
University of Tripoli, Tripoli-Libya  
[m.derdar@uot.edu.ly](mailto:m.derdar@uot.edu.ly)

### Abstract

The development of a virial equation of state requires understanding numerous interaction virial coefficients. Given the relationship between these coefficients and the intermolecular potential, the corresponding states principle (CSP) can also be applied to extend its use to virial coefficients. In this study, the second virial coefficient has been developed using molar refraction. Molar refraction (R) is directly related to a substance's polarizability, which influences how molecules interact with each other. The more polarizable a molecule is, the stronger the attractive forces between them, which affects the second virial coefficient. This correlation has been theoretically sound since it is based on the molar refraction of compounds instead of depending on anacentric factor. Furthermore, this new correlation is characterized by minimum data requirement for calculation; only temperature. This correlation is agreed upon in the literature for several non-polar compounds. The new correlation provided satisfactory results for light non-polar compounds at low temperatures across all comparisons. For heavy non-polar compounds, its performance surpassed that of previous correlations based on the acentric factor. Additionally, both the new and previous correlations produced good results at high temperatures.

**Keywords:** Second virial coefficients; Thermodynamic; Refractive index; Non-polar..

## ارتباط جديد لمعاملات فيريال الثانية باستخدام معامل الانكسار

<sup>1</sup>مواهب محمد الدرار، <sup>2</sup>آسيا علي المشرقي، <sup>3</sup>نجية امحمد الغندوري، <sup>4</sup>محمد مسعود عامر  
قسم الهندسة الكيميائية، كلية الهندسة، جامعة طرابلس، طرابلس، ليبيا  
m.derdar@uot.edu.ly

### الملخص

تطوير معادلة الحالة باستخدام معادلة "فيريال" يتطلب فهم العديد من معاملات "فيريال" التفاعلية. وبالنظر إلى العلاقة بين هذه المعاملات وجهد التفاعل بين الجزيئات، يمكن أيضاً تطبيق مبدأ الحالات المقابلة (CSP) لتوسيع استخدامه ليشمل معاملات "فيريال". في هذه الدراسة، تم تطوير المعامل الثاني "فيريال" باستخدام الانكسار الجزيئي. يرتبط الانكسار الجزيئي ( $R$ ) بشكل مباشر باستقطابية المادة، التي تؤثر على كيفية تفاعل الجزيئات مع بعضها البعض. كلما زادت استقطابية الجزيء، زادت قوة قوى الجذب بين الجزيئات، مما يؤثر على المعامل الثاني "فيريال". وتعتبر هذه العلاقة نظرية سليمة لأنها تعتمد على الانكسار الجزيئي (molar refraction) للمركبات بدلاً من الاعتماد على عامل لامركزي (acentric factor). علاوة على ذلك، يتميز هذا الارتباط الجديد بمتطلبات بيانات قليلة للحساب، حيث يعتمد فقط على درجة الحرارة. وقد تم الاتفاق على هذا الارتباط في المراجع العلمية لعدة مركبات غير قطبية. وقد قدم الارتباط الجديد نتائج مرضية للمركبات غير القطبية الخفيفة عند درجات حرارة منخفضة في جميع المقارنات. أما بالنسبة للمركبات غير القطبية الثقيلة، فقد تفوق أدائه على الارتباطات السابقة التي تعتمد على العامل اللامركزي. بالإضافة إلى ذلك، قدمت كل من الارتباطات الجديدة والسابقة نتائج جيدة عند درجات الحرارة العالية.

**الكلمات المفتاحية:** معامل فيريال الثاني، الديناميكا الحرارية، معامل الانكسار، مركبات غير القطبية.

### Introduction

Accurate thermodynamic and transport property data are essential when assessing the viability of various compounds in binary and

multicomponent mixtures for industrial applications as working fluids. In particular, it is crucial to consider vapor phase non-ideality, especially under moderate pressures, when analyzing and correlating vapor-liquid equilibrium. To account for this non-ideality, a virial coefficient parameter is incorporated into the correlation. These virial coefficients play a critical role in determining several key properties, including gas density, liquid-vapor equilibrium fugacity, thermal conductivity, and viscosity. These properties are essential for calculating heat and mass flow in various industrial processes (Smith et al., 2022).

Accurate equilibrium thermodynamic and transport properties data are required for binary and multicomponent mixtures of compounds to determine the systems which would be most suitable as working fluids in industry units. Vapor phase nonideality should properly be taken into account in the analysis and correlation of vapor-liquid equilibrium, especially at moderate pressure (Green and Southard, 2019). To represent this non-ideality virial coefficient parameter is introduced to this correlation. The second virial coefficient accounts for non-ideal gas behavior, which is influenced by factors like molecular size and intermolecular forces.

The acentric factor  $\omega$  used in the two discussed methods (Pitzer et al, 1957 and Tsonopoulos, 1974) shows in Equation (1).

$$\omega = \log_{10} \left( \frac{P^o}{P_c} \right)_{T_R=0.7} - 1.00 \quad (1)$$

This parameter  $\omega$  obtained analytically and has no theoretical meaning. The second virial coefficient is directly related to pair of interactions between molecules, which can be expected to give a good macroscopic description of the configuration properties of fluids.

Many works have been published for predicting the second virial coefficient based on a centric factor (Vega et al. 1999, Visak et al. 2000, Tourino et al. 2005, Iuloan et al. 2006, Rathore et al. 2006, Vadamar et al. 2009, Ezhil Pavai et al. 2011, Dikio et al. 2012, Dopazo et al 2014, and Duan et al. 2021), but this work have

not been studied so far with the molar refraction. The precision in measuring refractive indices allowed for accurate calculation of virial coefficients, contributing to the understanding of molecular interactions in gases. The authors discussed experimental limitations, such as the challenges posed by adsorption and the precision of fringe measurements (Ashton and Halberstadt 1958).

Since polarizability affects how molecules attract or repel each other, using molar refraction gives a way to account for these intermolecular interactions more precisely when estimating the second virial coefficient. The second virial coefficient accounts for non-ideal gas behavior, which is influenced by factors like molecular size and intermolecular forces. Molar refraction, reflecting a molecule's ability to polarize and thus interact with others, offers a more detailed insight into these forces. Incorporating molar refraction into the estimation process helps refine the model, especially for gases or liquids where polarizability is significant.

### The Virial Equation of State

The virial equation is a power series in the reciprocal molar volume,  $1/v$  temperature (Privat et al., 2009).

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

Equation (2) provides accurate predictions for  $Z$  up to approximately half of the critical densities. In theory, the right side of Equation (2) is an infinite series. However, in practical applications, only a finite number of terms are considered.

Interestingly, when examining PVT data at low pressures, it becomes evident that truncating the series after just two terms frequently yields satisfactory outcomes. In the context of most chemical processes, where pressures typically do not exceed 15 atm, the second virial coefficient alone is often sufficient to account for vapor phase non-ideal behavior. As a result, the equation of state used is as follows (Smith et al., 2022):

Equation (2) predicts  $Z$  accurately up to one half the critical densities. In principle, the right side of Equation (2) is an infinite series. However, in practice a finite number of terms are used. In

fact, PVT data show that at low pressures truncation after two terms often provides satisfactory results. For most chemicals, applications, the pressure is under 15 atm, and hence the second virial coefficient alone can account for vapor phase nonidealities. Thus, the equation of state that will be used is

$$Z = 1 + \frac{B}{v} \quad (3)$$

The major event in the prediction of the second virial coefficient for pure compounds is represented by the Pitzer work<sup>[1]</sup>. Pitzer was able to show that an universal function of the type  $B = f(\omega, T_R)$  enables the prediction of the second virial coefficients of all nonpolar or slightly polar compounds.

$$\frac{BP_C}{RT_C} = f_{P_C}^{(o)}(T_R) + \omega f_{P_C}^{(1)}(T_R) \quad (4)$$

Where

$$f_{P_C}^{(o)}(T_R) = 0.1445 - \frac{0.33}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} \quad (5)$$

$$f_{P_C}^{(1)}(T_R) = 0.073 - \frac{0.46}{T_R} - \frac{0.5}{T_R^2} - \frac{0.097}{T_R^3} - \frac{0.0073}{T_R^8} \quad (6)$$

Tsonopoulos<sup>[2]</sup> improved Pitzer-Curl for larger temperature range for zero acentric factor of nonpolar component to overcome temperature range higher than  $T_R > 0.8$ .

$$f_{P_C}^{(o)}(T_R) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} - \frac{0.000607}{T_R^8} \quad (7)$$

$$f_{P_C}^{(1)}(T_R) = 0.0637 - \frac{0.331}{T_R^2} - \frac{0.423}{T_R^3} - \frac{0.008}{T_R^8} \quad (8)$$

### New Correlation

The previous method for predicting the second virial coefficient was designed for nonpolar gases and demanded an extensive dataset of PVT (pressure-volume-temperature) information. It also had limitations in terms of its applicability to a wide temperature range and numerous chemical components. To address these shortcomings, a new approach is necessary.

It has become apparent that a desirable alternative should possess specific characteristics and merits as a second parameter. This novel parameter should be linked to electrostatic properties and molecular structure, considering polarity aspects. Moreover, it should be easily accessible or measurable, relying only on temperature and without the need for extensive PVT data. Furthermore, it should be theoretically sound and not directly associated with critical properties, especially critical volume. To address these criteria, attention has been directed towards molecular refraction, which is a function of molecular weight.

The estimated new second virial coefficient is contingent on the interaction parameter between molecules rather than the acentric factor. Theoretically, this new correlation is grounded in molecular reactivity. For non-polar gases, the representation of the second virial coefficient is as follows:

The previous correlation for second virial coefficient prediction is build up for nonpolar gases and requires a large PVT data. Also, it covers small temperature ranges for large number of components. To overcome these disadvantages; new correlation is required. It was seemed that a property with the following requirements is desirable and should be explored further, as a new second parameter. The new parameter should be related to the electrostatic properties and to the molecular structure taking into account polarity characteristics.

The developed parameter should be readily available or easily measurable with minimum amount of data; only temperature, and do not require PVT data. Farther more this parameter has theoretical sound and not directly related to critical properties especially critical volume. To overcome all these estimation studies was focused about molecular refraction which is function of molecular weight.

The estimated new second virial coefficient depends on interaction parameter between molecules instead of acentric factor. Theoretically the new correlation is based on molecular reactivity. For non-polar gases, the second virial coefficient will be represented as:

$$B = f(T_r, R_m) \quad (9)$$

Where  $R_m$  the molar refraction is having the dimensions of volume  $T_r$  is reduced temperature. This parameter has theoretical sound; it is related to electrostatic properties and to molecular structure. Physically the molar refraction is defined by:

$$R_m = R_s . M \quad (10)$$

Where M is molecular weight and  $R_s$  is the specific refraction of pure component  $R_s$  is given by the formula

$$R_s = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{\rho} \quad (11)$$

Where n is the refractive index, and  $\rho$ , the density

Equation (4) can be writing as function of reduced temperature:

$$\frac{BP_C}{RT_C} = f_{PC}^{(0)}(T_R) + R_m f_{PC}^{(1)}(T_R) \quad (12)$$

Several attempts were made numerically using different technique to establish  $f_{PC}^{(0)}$ ,  $f_{PC}^{(1)}$  as function reduced temperature. Finally, the best representation to literatures is found to be

$$f_{PC}^{(0)}(T_R) = 0.046038 - \frac{0.08085}{T_R} - \frac{0.361147}{T_R^2} + \frac{0.066414}{T_R^3} \quad (13)$$

$$f_{PC}^{(1)}(T_R) = 0.025906 - \frac{0.078856}{T_R} + \frac{0.085391}{T_R^2} - \frac{0.0331499}{T_R^3} + \frac{0.0001087}{T_R^8} \quad (14)$$

The new correlation can be applied to different pure non-polar gases. It was found in great agreement with experimental data in literature by Dymond and Smith, (1980) and the new correlation satisfies all the qualities of good parameters as:

1. It has theoretical meaning since it considers the molecule selectivity and structure.
2. No PVT data is required to obtain the parameters.

3. It can be obtained from minimum data; it is a function of temperature only.

Non-polar compounds are characterized by zero dipole moment ( $\mu$ ) which expresses the effect of electrostatic forces between molecules. To examine this new correlation; the second virial coefficient of several hydrocarbons (methane, propane, n-hexane, sulphur hexafluoride, n-octane, and n-heptane) also some gases (oxygen, nitrogen, and argon) were estimated and compared with experimental data and with previous correlations each compound for large temperature range. The final results of these computations and experimental data are tabulated in Table (1). It can be shown that the difference between the new correlation and Pitzer & Tsonopoulos is very small.

**TABLE1. Comparison between new correlation, Pitzer and Tsonopoulos correlations.**

Substance	$\mu$	$R_m$	$\omega$	BR Exp.	BR Pitzer	BR Tsonp.	BR New Corr	RE%	Range Temp., K
Methane	0.0	6.82	0.008	-0.3445	-0.3416	-0.34744	-0.34402	0.15	110-600
Ethane	0.0	11.4	0.098	-0.3474	-0.3562	-0.35415	-0.3494	0.57	200-600
n-Butane	0.0	20.7	0.193	-0.5952	-0.5823	-0.56247	-0.5705	4.15	250-560
Ethylene	0.0	11	0.085	-0.2732	-0.2761	-0.27534	-0.2733	0.03	240-450
Propylene	0.4	15.5	0.148	-0.3625	-0.3674	-0.36154	-0.35925	0.92	280-500
Acetylene	0.0	9.43	0.184	-0.9896	-0.7012	-0.6769	-0.6218	37.16	200-273
Propane	0.0	16.0	0.152	-0.45607	-0.4647	-0.4551	-0.4533	0.59	240-550
Hydrogen	0.0	2.2	-0.22	-0.3795	-0.1182	-0.3760	-0.42113	10.9	14-400
Nitrogen	0.0	4.64	0.04	-0.2696	-0.2764	-0.27982	-0.2683	0.48	75-700
Carbon dioxide	0.0	6.84	0.228	-0.12606	-0.1164	-0.12448	-0.12253	2.8	220-1100
Argon	0.0	4.2	-0.004	-0.3239	-0.3137	-0.3273	-0.3159	2.45	81-1000
Neon	0.0	0.99	0.0	-0.00985	-0.0303	0.000814	0.00081	208.2	60-600
Krypton	0.0	6.25	-0.002	-0.4784	-0.4549	-0.47582	-0.4667	2.44	110-700
Oxygen	0.0	3.87	0.021	-0.3488	-0.3503	-0.3557	-0.3444	1.26	90-400
1-Butane	0.3	18.4	0.187	-0.5894	-0.5925	-0.5722	-0.5683	3.59	243-420
Isopentane	0.0	25.4	0.227	-0.7134	-0.6161	-0.5907	-0.6065	14.98	280-450
Cyclopropane	0.0	13.8	0.264	-1.6301	-0.6446	-0.6136	-0.5675	65.18	298-322
Isobutene	0.1	20.6	0.176	-0.4478	-0.4277	-0.4174	-0.4215	5.87	273-511
Neopentane	0.0	25.2	0.197	-0.47506	-0.5515	-0.5332	-0.5542	16.68	300-550
Benzene	0.0	26.3	0.212	-0.8990	-0.9250	-0.8714	-0.9233	2.7	290-600
n-Octane	0.0	39.1	0.394	-0.9665	-0.9762	-0.8990	-0.9543	1.27	373-414
n-Heptane	0.0	34.5	0.251	-0.7221	-0.6752	-0.6396	-0.7043	2.46	300-700
n-Hexane	0.0	29.9	0.296	-0.8461	-0.8679	-0.8116	-0.8437	0.28	300-450
Sulfur hexafluoride	0.0	16.4	0.286	-0.3714	-0.4224	-0.4070	-0.3876	0.97	200-525
Propyne	0.7	14.0	0.218	-0.3373	-0.3431	-0.3351	-0.3307	1.93	348-473
Cyclohexane	0.3	27.7	0.213	-0.8723	-0.9053	-0.8585	-0.9315	6.78	300-560
Hydrogen sulphide	0.9	9.25	0.100	-0.2418	-0.2538	-0.2533	0.2534	4.82	373-493
Nitrous oxide	0.2	6.38	0.16	-0.3759	-0.3791	-0.3720	-0.3580	4.77	240-400



$$RE\% = \frac{BR_{Exp.} - BR_{Theo.}}{BR_{Exp.}} \times 100$$

The difference between the new correlation and Pitzer & Tsonopoulos for methane and propane is shown in Figures (1,2).

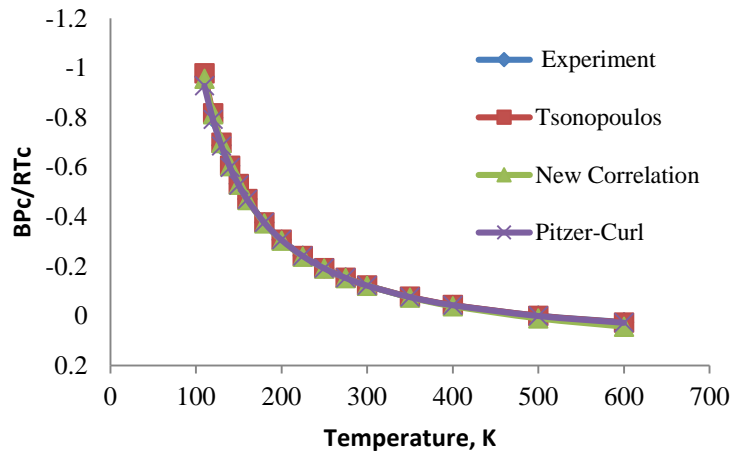


Figure1. Second virial coefficient of methane versus temperature

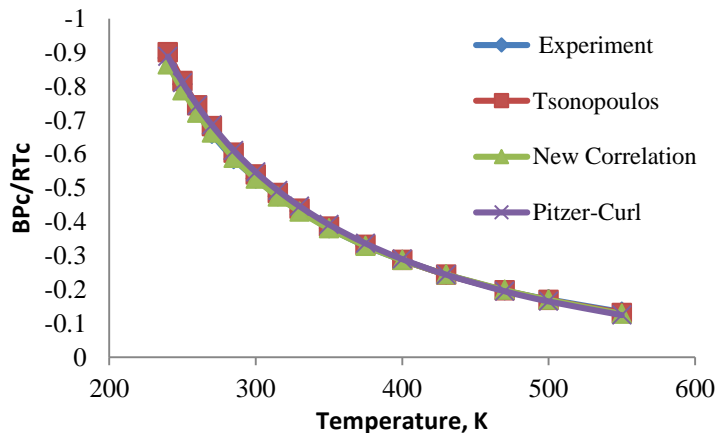


Figure 2. Second virial coefficient of propane versus temperature

The figures demonstrate that the correlations show good agreement for light hydrocarbons. However, at lower temperatures, the virial coefficient slightly deviates from the experimental data reported by Dymond et al. (2002) when compared to the new correlation. At higher temperatures, though, there is a strong agreement between the correlations, particularly for higher hydrocarbons, as illustrated in Figures (3-6).

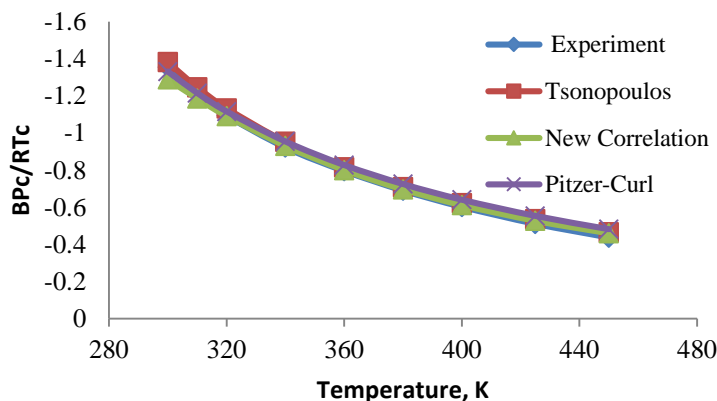


Figure 3. Second virial coefficient of n-hexane versus temperature

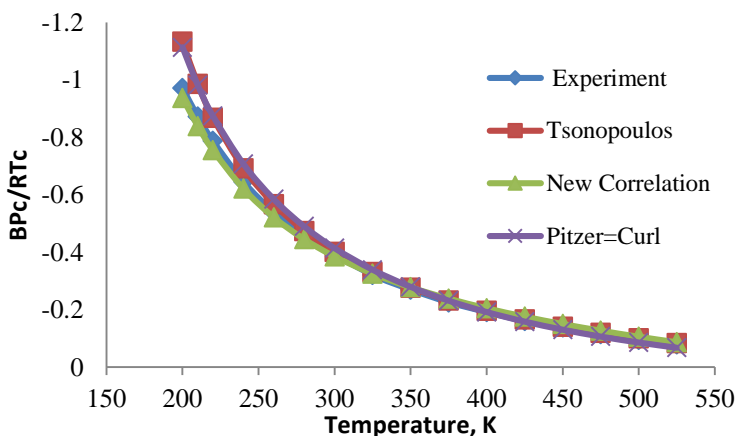


Figure 4. Second virial coefficient of sulfur hexafluoride versus temperature

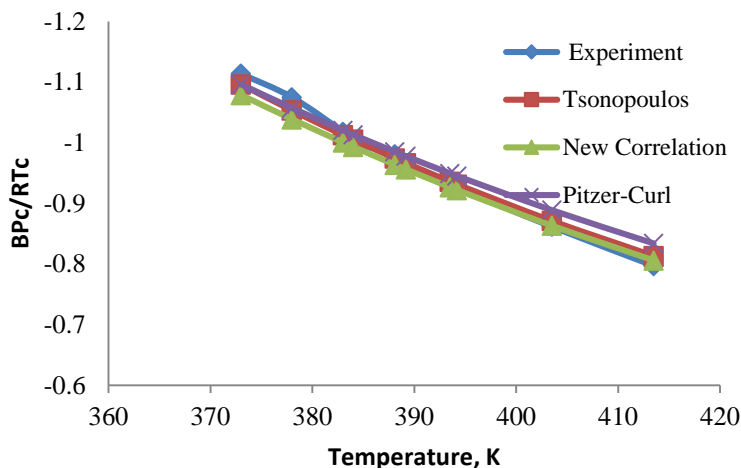


Figure (5) Second virial coefficient of n-octane versus temperature

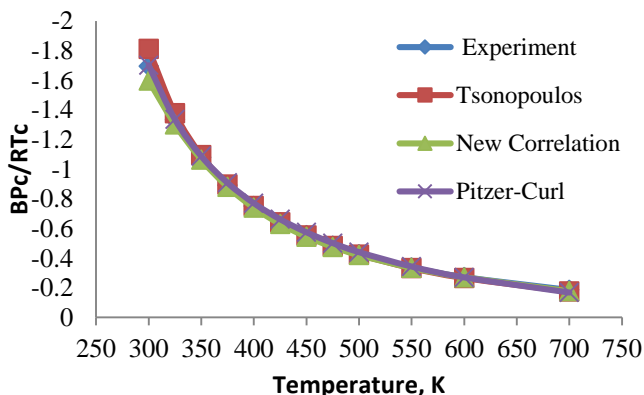


Figure 6. Second virial coefficient of n-heptane versus temperature

From the previous, it has seemed that a property with the following requirements is desirable and should be explored further as a new second the parameter should be related to the electrostatic properties and to the molecular structure to take for polar characteristics can be estimated that at high reduced temperature, the old correlations deviate and best fit is by the new correlations. It should be mentioned that even though the correlation is close to experimental

data, the new correlation is superior to experimental data. The good agreement for both previous correlations is that because Pitzer correlation is based on non-polar compounds.

### Conclusion

By incorporating molar refraction, which accounts for polarizability and intermolecular forces, the estimation of the second virial coefficient becomes more accurate. This allows for a better understanding of real gas behavior, especially when interactions between molecules deviate from ideal gas assumptions. The results shown herein indicate that the use of molar refraction instead of acentric factor in second virial coefficient calculation shows more precise results than the other available methods. The new correlation can be used in predicting various components with a wide range of temperatures, and no need for PVT data calculations. The new correlation provided satisfactory results for light non-polar compounds at low temperatures across all comparisons. For heavy non-polar compounds, its performance surpassed that of previous correlations based on the centric factor. Additionally, both the new and previous correlations produced good results at high temperatures.

### Nomenclature

B	= Second virial coefficient
C	= Third virial coefficient
N	= Refractive index
M	= Molecular weight
P	= Pressure
P <sub>C</sub>	= Critical pressure
P <sup>0</sup>	= Vapor pressure of pure component
T	= Temperature
T <sub>C</sub>	= Critical temperature
T <sub>R</sub>	= Reduce temperature
R	= Gas constant
R <sub>S</sub>	= Specific refraction
R <sub>m</sub>	= Molar refraction
V	= Molar volume

Z	= Compressibility factor
$\omega$	= Centric factor
$\rho$	= Density
$\mu$	= Dipole moment

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