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Second Virial Coefficients of Noble Gases

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Abstract: ***A new three- parameter modified Berthelot equation of state has been developed and employed to calculate the second virial coefficients of neon, argon, krypton, xenon and radon. It is established that neon, argon, krypton, xenon and radon obey the single parameter law of corresponding states. It is established that the new parameter introduced in the attractive term of the equation of state is a thermodynamic similarity parameter.***

Keywords: Equation of state, Law of corresponding states, Noble gases, Second virial coefficients

1. Introduction

The noble gases have very low melting and boiling points. They are nonreactive. The noble gases have high ionisation energies and negligible electronegativities. Hence, the study of the thermodynamic properties of noble gases is scientific significance. Moreover, the noble gases have numerous technological applications. They are used as ambient media in laser ablation of materials, in the production of nanoparticles and nanostructures. Noble gases geochemistry is applied in petroleum and natural gas industry. These facts underscore [1-14] the scientific and the technological significance of study of noble gases.

One of the fundamental tasks of thermodynamics and statistical physics is to find the equation of state of matter. An equation of state is a mathematical expression that describes a system at thermodynamic equilibrium. Having accurate equations of state for the substances used in industry is important in the design of several industrial plants and for precise calculations describing a variety of thermodynamic phenomena. The benefit of using a theoretical equation for correlation is limited because they are considerably more complicated than cubic equations of state. The value in using a theoretical equation is their improved ability to predict phase equilibria rather than merely correlate data. Numerous equations of state have been proposed. These include such well-known forms as Trebble -Bishnoi - Salim equation of state [15], Redlich - Kwong - Soave equation of state [16], Peng Robinson equation of state [17], Patel - Teja equation of state [18], ε∗ - Modified Lacombe –Sanchez equation of state [19], Lawel - Lake - Silberberg equations of state [20], Schmidt - Wenzel equation of state [21], Elliott - Suresh - Donohue equation of state [22], Yu - Lu equation of state [23], Virial equation of state [24], Dieterici - type equation of state [25] and Cubic equation of state [26].

Many modifications of the known equations of state have been proposed [27-30] to improve the accuracy. These modifications result in the generalization of the known equations of state. There is a need for the generalized equations of state with numerical stability and ability to describe the thermodynamic properties of wide range of technically important substances used in industries. A comprehensive review on the generalization of equation of state can be found in the monograph of Brusilovsky [31]. To improve accuracy of an equation of state usually its attractive term and/or the repulsive term is modified [32-44]. In some cases, the equation-of-state parameters' dependence on temperature is assumed.

In recent years, an increased theoretical and technological interest has stimulated extensive research on the noble gases. Often, the applications of noble gases require the knowledge of their high-temperature properties. However, the accuracy in the experimental studies on the high-temperature properties of the noble gases is poor due to severe experimental difficulties. Hence arises the necessity for theoretical studies on the high-temperature properties of the noble gases.

The present work, on the basis of a generalized Berthelot equation, deals with a study of the high-temperature properties of noble gases. The second virial coefficients characteristic of pair-wise intermolecular interaction have been determined for neon, argon, krypton, xenon and radon.

2. Generalized Berthelot equation of state

The known two – parameter Berthelot equation of state does not lend itself to precise description of the thermodynamic properties of liquids and gases. Hence, in this work, an improvement of this equation is proposed by introducing a third parameter m in the attractive term. Such a generalized Berthelot equation of state for one mole of substance has the form:

$$P = \frac{RT}{V-b} - \frac{a}{T^m V^2} \tag{1}$$

Application of the critical-point conditions to the equation of state given by Eq. (1) produces two equations in V_c and T_c. Eliminating T_c between them gives the critical volume as

$$V_c = 3b \tag{2}$$

Back substitution in the equations then gives the critical temperature as

$$T_c = \left(\frac{8a}{27Rb}\right)^{\frac{1}{m+1}} \tag{3}$$

Finally, substitution of V_c and T_c in Eq. (1) gives the critical pressure as

$$P_c = \left(\frac{aR^m}{27 \times 8^m \times b^{m+2}} \right)^{\frac{1}{m+1}} \qquad (4)$$

The generalized Berthelot equation of state then gives the critical compressibility factor as

$$Z_c \equiv \frac{P_c V_c}{RT_c} = \frac{3}{8} \qquad (5)$$

Considering Eqs. (2)-(5), we may write the generalized Berthelot equation in the reduced form as

$$P^* = \frac{8T^*}{3V^* - 1} - \frac{3}{T^{*m} V^{*2}} \qquad (6)$$

Where,

$P^* = P/P_c$, $V^* = V/V_c$, $T^* = T/T_c$

The reduced equation of state given by Eq. (6) represents the single-parameter law of corresponding states with the thermodynamic parameter *m*. That is, substances obeying the generalized Berthelot equation of state, with the same value of parameter *m*, are thermodynamically similar. As seen from Eqs. (2)-(5) the critical pressure and critical temperature depend on the similarity parameter *m*. But, the critical volume and critical compressibility factor do not depend on the parameter *m*.

3. Determination of Equation of-State-Parameters

The parameters *a,b* and *m* of the generalized Berthelot equation of state are determined through experimental data on critical parameters [47-49] for neon, argon, krypton, xenon and radon. In these calculations, Eqs. (2)-(5) are employed. The obtained values of the parameters *a*, *b* and *m* are presented in Table 1. As seen, for the values of the thermodynamic similarity parameter *m* for neon, argon, krypton, xenon and radon only slightly differ. Thus, the parameter *m* can be considered to be a measure of intermolecular forces.

In fact, the parameter *a,b* and *m* of the generalized Berthelot equation of state can be determined by several ways. Various characteristic parameters of substances can be used to determine the values of the parameters *a,b* and *m*. The choice of the critical –point parameters to determine the values of *a,b* and *m* is justified by the requirement of calculating the second virial coefficients at high temperatures.

4. Second Virial Coefficients by Generalized Berthelot Equation of State

According to statistical mechanics approach, the compressibility factor may expressed in terms of a series in $1/V$ to get the virial equation of state as

$$Z \equiv \frac{PV}{RT} = 1 + \frac{B_2}{V} + \frac{B_3}{V^2} + ... \qquad (6)$$

Where B_2 - second virial coefficient, B_3 - third virial coefficient and so on.

For a given substance, the virial coefficients depend only on temperature. In fact, the second virial coefficient is a measure of pair-wise intermolecular interaction. And , the third virial coefficient is a measure of intermolecular interaction between three molecules. Hence, the knowledge of virial coefficients will enable one to determine the intermolecular potential of substances. In general, reliable data on the virial coefficients of substances are scarce.

Usually, the second virial coefficients of substances are determined from the equilibrium *PVT* properties.

The second virial coefficient is given by

$$B_2 = \left(\frac{\partial Z}{\partial \rho} \right)_T \qquad (\text{at } \rho = 0) \qquad (7)$$

Where $\rho \equiv 1/V$ is the molar density. For fluids obeying the generalized Berthelot equation of state given by Eq. (1), the compressibility factor is

$$Z = \frac{1}{1 - \frac{b}{V}} - \frac{a}{RVT^{m+1}} \qquad (8)$$

Eq. (8) gives

$$\left(\frac{\partial Z}{\partial \rho} \right)_T = \frac{b}{(1 - b\rho)^2} - \frac{a}{RT^{m+1}} \qquad (9)$$

From Eqs. (7) and (9) we get the second virial coefficient as

$$B_2 = b - \frac{a}{RT^{m+1}} \qquad (10)$$

As seen, at high temperatures, the second virial coefficient approaches a constant value equal to that of *b*. At lower temperatures, $a/(RT^{m+1})$ dominates over *b* and for small *T* values *B* reaches negative values.

The second virial coefficient has the dimensions of volume. Hence, it may be reduced through the critical volume as

$$B_2^* = \frac{B_2}{V_c} \qquad (11)$$

Substituting Eqs. (2) and (10) into Eq. (11),we get

$$B_2^* = \frac{1}{3} - \frac{a}{8T^{*m+1}} \qquad (12)$$

5. Second Virial Coefficients of Noble gases

For neon, argon, krypton, xenon and radon, the second virial coefficients, at different temperatures, are determined by Eq. (12) with the values the parameters *a* and *m* presented in Table 1. The obtained values of the second virial coefficients, for neon, argon, krypton, xenon and radon are presented in Tables 2-6. Our calculations show that neon, argon, krypton, xenon and radon manifest similar pattern of temperature-dependence of the second virial coefficients.

Table 1: Equation-of-state parameters

Substance	*a* NKm^{4}K^m /mol^2	*b* 10^{-5}m^3/mol	*m*
Neon	0.122	1.390	0.515
Argon	1.881	2.497	0.574
Krypton	4.028	3.040	0.583
Xenon	9.111	3.933	0.591
Radon	14.012	4.667	0.564

Table 2: Second Virial Coefficients of Neon

T^*	B_2^*
0.1	-36.492
0.2	-12.552
0.3	-6.637
0.4	-4176
0.5	-2.882
0.6	-2.106
0.7	-1.598
0.8	-1.244
0.9	-0.986
1	-0.792

Table 3: Second Virial Coefficients of Argon

T^*	B_2^*
0.1	-41.849
0.2	-13.835
0.3	-7.152
0.4	-4.426
0.5	-3.016
5.6	-2.181
0.7	-1.639
0.8	-1.265
0.9	-0.995
1	-0.792

Table 4: Second Virial Coefficients of Krypton

T^*	B_2^*
0.1	-42.737
0.2	-14.042
0.3	-7.232
0.4	-4.464
0.5	-3.037
0.6	-2.192
0.7	-1.645
0.8	-1.268
0.9	-0.996
1	-0.792

Table 5: Second Virial Coefficients of Xenon

T^*	B_2^*
0.1	-43.526
0.2	-14.228
0.3	-7.304
0.4	-4.501
0.5	-3.056
0.6	-2.202
0.7	-1.651
0.8	-1.271
0.9	-0.997
1	-0.792

Table 6: Second Virial Coefficients of Radon

T^*	B_2^*
0.1	-40.891
0.2	-13.609
0.3	-7.063
0.4	-4.382
0.5	-2.993
0.6	-2.168
0.7	-1.632
0.8	-1.262
0.9	-0.993
1	-0.792

6. Results and Discussion

The new generalized Bertholet equation of state has been applied to calculate the second virial coefficients of neon, argon, krypton, xenon and radon. The performance of the generalized Berthelot equation of state in evaluating the second virial coefficients of neon, argon, krypton, xenon and radon has been demonstrated. The parameters in the generalized Berthelot equation of state are expressed in terms of the critical pressure, the critical volume and critical temperature.

7. Conclusion

A new generalized Berthelot equation is proposed by introducing a third parameter in the attractive term of the Berthelot equation. A single-parameter law of corresponding states based on the generalized Berthelot equation of state has been established. It is established that the introduced parameter *m* is a thermodynamic similarity parameter of substances. The virial form of the generalized Berthelot equation of state has been studied. The second virial coefficients of neon, argon, krypton, xenon and radon have been determined using the generalized Berthelot equation of state.

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