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CALCULATION of FUGACITY COEFFICIENT using SECOND VIRIAL COEFFICIENT with STOCKMAYER POTENTIAL

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Abstract – In this work, proposed analytical formulae for calculating second virial coefficient using Stockmayer potential which are selected according to the structural properties of molecules, allow to calculate of many thermodynamic properties of polar real gases. Using this analytical formulae, fugacity coefficient of gases H_2O has been calculated in wide temperature ranges using the second virial coefficient. The calculation results were compared with the literature and the results were found to be consistent.

Keywords – Second Virial Coefficient, Stockmayer Potential, Fugacity Coefficient

INTRODUCTION

As it well known, the fugacity coefficient has been widely examined in phase and chemical reaction equilibrium works involving gases at high pressures [1-4]. The fugacity coefficient is the ratio of fugacity to pressure, and it is equal to one for ideal gases [2-4]. Fugacity coefficient is important many industries and engineering field. It is widely used, especially in the petroleum industry and engineering science. To investigate the fugacity of real gases, many experimental and theoretical methods have been suggested by researchers [4]. In addition, the fugacity coefficient of real gases can be accurately determined using the second virial coefficient at low density considering Stockmayer potential for polar molecules [4-5]. For calculate the fugacity coefficient of polar molecules according to the second virial coefficient, the selection of the intermolecular interaction potential is very important [5-6] Therefore, Stockmayer potential can be preferred to calculate the fugacity coefficient of polar molecules with second virial coefficient [5-6]. However, accurate and precise determining the fugacity coefficient of all gases is still one of the problems in chemical thermodynamics.

In this study, analytical method has been presented for the fugacity coefficient using the second virial coefficient for polar molecules. The resulting analytical method allows the fugacity coefficient of the polar real gases to be calculated accurately and precisely.

MATERIALS AND METHODS

Second virial coefficient

The second virial coefficient can be defined following as [4]:

$$B(T) = 2\pi N_A \int (1 - Exp[u(r_{12})/k_B T])$$
(1)

where N_A is Avogadro constant, $u(r_{12})$ is intermolecular interaction potential, k_B is Boltzmann constant, and T is temperature.

To obtained formula for the second virial coefficient with Stockmayer potential, Eq. (3) used in the following form:

$$B(T) = -\frac{N_A}{4}\int_0^\infty\int_0^{2\pi}\int_0^\pi\int_0^\pi \left(e^{-\frac{4\varepsilon}{kT}\left(\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right) + \frac{\mu^2}{kTr^3}(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi)} - 1 \right) r^2 \sin\theta_1 \sin\theta_2 dr d\theta_1 d\theta_2 d\phi.$$
(2)

The making the following substitute $T^* = \varepsilon / k_B T$ $x = r/\sigma$, and $t = 8^{-1/2}\mu^2/\varepsilon\sigma^3$, the second virial coefficient of Eq. (2) as following form:

$$B^*(T^*) = -\frac{3N_A}{8\pi}\int_0^\infty\int_0^{2\pi}\int_0^\pi\int_0^\pi \left(e^{-\frac{4}{T^*}(x^{-12} - x^{-6}) + \frac{t\sqrt{8}}{T^* x^3}(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi)} - \right.$$
(3)

Here, $B^*(T^*) = B(T) / (2\pi N_A \sigma^3/3)$, we obtained the following form second virial coefficient [7]:

$$B^*(T^*) = -3\lim_{N\to\infty}\sum_{n=0}^{N}\frac{1}{n!}\left(\frac{t\sqrt{8}}{T}\right)^n \sum_{i=0}^{n} F_i(n)\frac{2^{n-i}}{8\pi} I_{n-i,i+1}\ I_{n-i,i+1} I_i\ I$$
(4)

$$I_{jl} = \begin{cases} \frac{2}{j+1} & l=1,\ j=0,1,2,... \\ 0 & l=1,\quad j=1,3,5,... \\ \pi & j=0,\quad l=0 \\ \frac{1}{2}\Gamma\left(\frac{l+1}{2}\right)\left(\frac{2^{1+l+j}\pi^{3/2}\sec\left(\frac{l\pi}{2}+j\pi\right)}{\Gamma\left(\frac{1}{2}(1-l-j)\right)\Gamma\left(\frac{1}{2}-\frac{j}{2}\right)\Gamma(1+l+j)} + \frac{\Gamma\left(\frac{1+j}{2}\right)\left((-1)^j - \cos\left(\frac{l\pi}{2}\right)\sec\left(\frac{l\pi}{2}+j\pi\right)\right)}{\Gamma\left(\frac{1}{2}(2+l+j)\right)} \right) & j=0,2,4,...\ \ l=0,2,4... \\ 0 & \text{other cases} \end{cases}$$

$$I_i = \frac{(\ 1 + (-1)^i \sqrt{\pi}\ \Gamma\left(\frac{1+i}{2}\right)\ )}{\Gamma\left(\frac{2+i}{2}\right)}.$$

$$I_1\left(4/T^*\right) = -\frac{n}{12}\lim_{N'\to\infty}\sum_{k=0}^{N'}\frac{\left(4/T^*\right)^k}{k!}\begin{cases}\lim_{M\to\infty}\sum_{m=0}^{M}\frac{1}{\left(4/T^*\right)}\left(\frac{(-1)^m}{m+1}-\frac{(-1)^m}{m+1}\right)+E_1\left(4/T^*\right) & k=0, n=1\\ \frac{1}{\left(4/T^*\right)^{\frac{n}{4}+\frac{k}{2}-\frac{1}{4}}}\Gamma\left(\frac{n}{4}+\frac{k}{2}-\frac{1}{4}\right) & \text{other cases}\end{cases}$$

$$I_2\left(4/T^*\right) = \frac{\left(4/T^*\right)}{3}\lim_{N'\to\infty}\sum_{k=0}^{N'}\frac{\left(4/T^*\right)^k}{k!}\frac{1}{\left(4/T^*\right)^{\frac{n}{4}+\frac{k}{2}+\frac{3}{4}}}\Gamma\left(\frac{n}{4}+\frac{k}{2}+\frac{3}{4}\right)$$

$$I_3\left(4/T^*\right) = -\frac{\left(4/T^*\right)}{6}\lim_{N'\to\infty}\sum_{k=0}^{N'}\frac{\left(4/T^*\right)^k}{k!}\frac{1}{\left(4/T^*\right)^{\frac{n}{4}+\frac{k}{2}+\frac{1}{4}}}\Gamma\left(\frac{n}{4}+\frac{k}{2}+\frac{1}{4}\right).$$

Fugacity coefficient

The fugacity coefficient can be expressed in terms of second virial coefficient following forms [5]:

$$\boldsymbol{\phi = ln\left(\frac{f}{P}\right) = B(T)\frac{P}{RT} - \frac{B(T)^2}{2}\left(\frac{P}{RT}\right)^2} \qquad (5)$$

Here, f is fugacity factor, P is pressure, R is universal gas constant, T is temperature and *B(T)* is second virial coefficient. By substituting Eq. (4) into Eq. (5), we obtained analytical formula to calculate the fugacity coefficient with the second virial coefficient for polar real gases.

Table 1. The compared with fugacity coefficient of H_2O with other method

$P(atm)$	$T(K)$	f/P	f/P [8]	f/P Experimental [8]	$P(atm)$	$T(K)$	f/P	f/P [8]	f/P Experimental [8]
98.6923	723.15	0.925799	0.873	-	592.154	723.15	0.629653	0.489	-
	773.15	0.940973	0.902	0.935		773.15	0.694166	0584	0.596
	873.15	0.961543	0.943	0.961		873.15	0.790335	0.727	0.747
	973.15	0.974296	0.972	-		973.15	0.855352	0.833	-
	1073.15	0.982612	0.989	0.986		1073.15	0.900103	0.911	0.899
	1173.15	0.98825	0.994	-		1173.15	0.93154	0.953	-
	1273.15	0.992192	0.992	-		1273.15	0.954055	0.978	-
197.385	723.15	0.857105	0.763	-	789.539	723.15	0.539679	0.411	-
	773.15	0.88543	0.817	-		773.15	0.614636	0.502	0.508
	873.15	0.924564	0.894	0.913		873.15	0.730715	0.668	0.684
	973.15	0.949252	0.940	-		973.15	0.811945	0.794	-
	1073.15	0.965526	0.970	-		1073.15	0.869073	0.882	0.884
	1173.15	0.976638	0.987	-		1173.15	0.909777	0.943	-
	1273.15	0.984444	0.990	-		1273.15	0.939213	0.974	-
394.769	723.15	0.734628	0.599	-	986.923	723.15	0.462561	0.353	-
	773.15	0.783987	0.679	0.714		773.15	0.544217	0.449	0.459
	873.15	0.854819	0.800	0.824		873.15	0.675593	0.620	0.634
	973.15	0.90108	0.884	-		973.15	0.77074	0.758	-
	1073.15	0.932241	0.937	0.937		1073.15	0.839113	0.859	0.853
	1173.15	0.953823	0.968	-		1173.15	0.888524	0.928	-
	1273.15	0.96913	0.981	-		1273.15	0.924603	0.973	-

NUMERICAL RESULTS and DISCUSSION

An analytical method for the fugacity coefficient by using the second virial coefficient with the Stockmayer potential of polar real gases is presented in this paper. The analytical method proposed for calculating the fugacity coefficient of gases is exactly general and free of any limitation on its applications. The fugacity coefficient of the gas H_2O was calculated using Mathematica 7.0 software to show that the results of the calculation are accurate and precise. The calculated results were compared with literature data. As can be seen from Table 1, the analytical formula for wide ranges of temperature and pressure gives values very close to the literature data [61]. When the fugacity and pressure are equal to each other, the fugacity coefficient becomes equal to one and the polar gas shows the ideal behavior. As shown in Table 1, the fugacity of the H_2O is approximately equal to the pressure at some temperature values.

CONCLUSION

The accurateness and definiteness, of the obtained analytical formula, are confident and can be proposed for the assessment of the fugacity coefficients of polar real gases. As the pressure approaches zero, the gas shows behaviors such as the ideal gas. Here, the fugacity coefficient equals the pressure value.

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