CODEN: IAASCA   ORIGINAL ARTICLE

Numerical Evaluation of Second Virial Coefficient and Boyle's Temperature for Argon

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ABSTRACT
An approach for the measurement of second virial coefficients for Argon is described. The results of second virial coefficient for two potentials (Lennard Jones and Yukawa) are tabulated over wide range of temperature. The Lennard Jones is well fit potential compared to Yukawa potential for second virial coefficient. There is a large discrepancy at higher temperatures (T > 373.15(K)), the second virial coefficients B (T) is positive. At low temperatures (T≤ 373.15(K)), the virial coefficients B (T) is negative, there is a good agreement between experimental and calculated results. The temperature at which B (T) tends to zero is known as the Boyle's temperature T_B (Peter Atkins and Julio De Paula, 2010). For the second virial coefficient of Argon, we obtain the Boyle's temperature (Artit Hutem and Sutee Boonchui, May. 2012) as follow: TB ≈ 403.7612(K), B (T) ≈ 0.000147931(cm3/mol) for L-J (6-12). Similarly, as follow: T_B ≈ 389.611(K), B (T) ≈ 0.000101461(cm³/mol) for Yukawa potential.
Keywords. *The Second virial coefficient; Lennard-Jones potential; Argon; Boyle's temperature*

INTRODUCTION

The virial coefficients provide valuable information about the intermolecular forces. Using different type of potential, the virial coefficients for several materials have been calculated over a wide range of temperature [1]. All of the potential functions previously described are applicable only to non polar molecules. We now briefly consider molecules that have a permanent dipole moment; for such molecule Stockmayer proposed a potential that adds to the Lennard-Jones (L-J) formula for non polar forces an additional term for the potential energy due to dipole-dipole interactions. For polar molecules, the potential energy is a function not only of intermolecular separation but also of relative orientation.
Rowlinson [2] demonstrated the successful correlation of second virial coefficient of polar gases with the potential . Sexana and Joshi [3] extended the model by using 18-6-3 and 28-7-3 power of the reciprocal of the intermolecular separation. If two molecules have very high kinetic energy, they may be able to interpenetrate to separations smaller than the collision diameter σ. For many gases, second virial coefficient, as well as other thermodynamic and transport properties, has been interpreted and correlated successfully with the Lennard-Jones potential. R Khordad et.al. [4] found that temperature-dependent width of the attractive well is fairly correct especially at moderate and high temperatures.
The purpose of this paper is to present theoretical estimates values of effective temperature-dependent potential, second virial coefficient, for Argon (Ar) which helps to obtain the Boyle's temperature. This is used to calculate the temperature-dependence of second virial coefficient for Argon which compares well with the experimental results.

BRIEF DESCRIPTION OF THE THEORETICAL BACKGROUND: SECOND VIRIAL COEFFICIENT

One important relation is the virial equation of state, which is generally expressed as
$$P= \rho RT [1+B (T) \rho +C (T) \rho^2 +D (T) \rho^3 +\ldots\ldots\ldots] \qquad (1)$$
Where P, R, T, and ρ are pressure, gas constant, temperature, and density [5], and coefficients B (T), C (T)....in the expression (1) are called the second and third etc. virial coefficients [6].
The Lennard- Jonnes model is most commonly used with index of attraction equal to 6 and the index of repulsion equal to 12. For specific case of L-J (6-12) model the intermolecular potential energy and the corresponding intermolecular force are giver by
$$V(r) = 4\varepsilon[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}] \qquad (2)$$

$$F(r) = -dV(r)/dr \tag{3}$$

From equation (2) and (3), we get

$$F(r) = 24\varepsilon/\sigma[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}] \tag{4}$$

In the above equations, r is the intermolecular separation, σ is the value of r for which the Lennard-Jones (L-J) (12-6) potential V(r) = 0, ε is the maximum energy of attraction (or depth of the potential wall) which occurs at r = $2^{1/6}$ σ [7]. Where $\varepsilon\ and\ \sigma$ is the parameter of the L-J potential, the first part $\left(\frac{\sigma}{r}\right)^{12}$ of the equation (2), describes the repulsive forces between particles while the latter part of the equation, $\left(\frac{\sigma}{r}\right)^{6}$ denotes attraction. A simple expression for the second virial coefficient has been given by [8,9].

$$B(T) = 2\pi N_{A} 10^{-24} \int_{0}^{\infty} r^{2}\left(1 - exp\left(-\frac{V(r)}{kT}\right)\right)dr. \tag{5}$$

Where $N_{A} = 6.02 \times 10^{23}$, k=Boltzman's Constant and T= Temperature in Kelvin.
We obtain the numerical values of second virial coefficient for Argon as displayed in table1.
Since the coefficient of viscosity is not particularly sensitive to long range forces [10] such as those associated with permanent dipole-dipole and dipole-quadrupole interactions. Therefore, we take the numerical values for Argon from [11], which are in the form of L-J potential, i.e. $\frac{\varepsilon}{k} = 118.13\ (K), \sigma = 3.499(A^{0})$. The special potential given by Lennard-Jonnes (6-12) potential, F. Mandl. Statistical Physics [12] has been used in calculation B (T) in Mathematica program Hutem and Boonchui [8].

	Calculate Values B (T)		Experimental Values B (T)	
T (K)	For L-J	For Yukawa Pot	**C.A. Hwang**[a]	**E.Whalley**[b]
273.15	-22.28	-12.86	-22.41	-22.10
323.15	-11.31	-6.03	-11.20	-11.17
373.15	-3.63	-1.26	-4.34	- 4.14
423.15	1.99	2.23	1.01	1.46
473.15	6.28	4.90	5.28	4.99
573.15	12.33	8.66	10.77	10.77
673.15	16.33	11.14	15.74	15.74
773.15	19.14	12.88	17.76	17.76
873.15	21.19	14.15	19.48	19.48

Table-1: Comparison of calculated and experimental values of B (T) with temperature in (K)
[a] **C.A. Hwang and G.A. Mansoori, [11]**
[b]**E.Whalley and W.G.Schneider [13]**

RESULTS AND DISCUSSION

The variation of second virial coefficients B (T) [7] with temperature is shown in figure 3. C.A. Hwang's and E. Whalley experimental values are also shown in this figure. Second virial coefficient, B(T) shows qualitative agreement with the experimental value. Calculated values are compared with the experimental data in table 1.
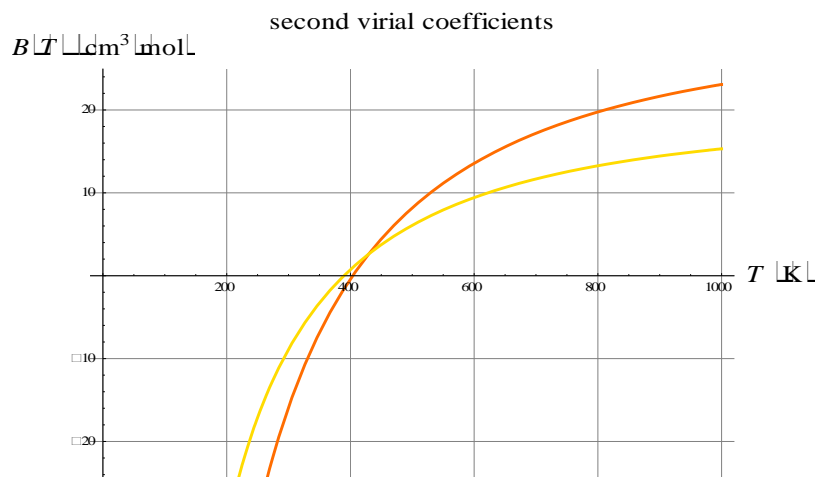
Figure 1. Temperature-dependence second virial coefficient B (T) for Ar. Calculated curve (red) for Ar (L-J, (6-12) parameters $\frac{\varepsilon}{k} = 118.13\ (K), \sigma = 3.499\ (A^0)$) and similarly yellow curve for Ar (Y-P parameters $\frac{\varepsilon}{k} = 113.99\ (K)\ and\ \sigma = 3.033(A^0)$ [14].
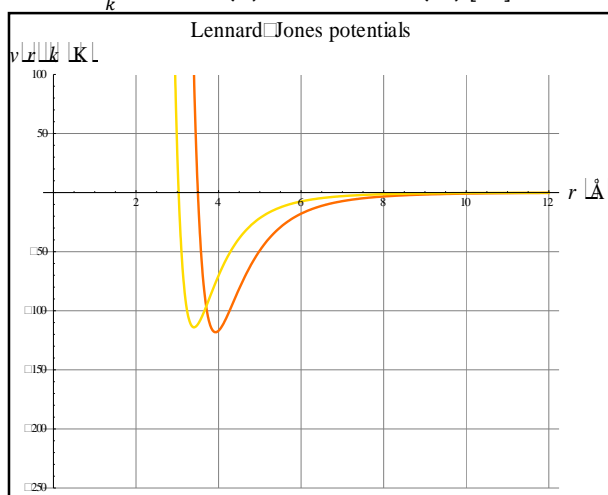

Figure 2. Red line indicated for L-J, (6-12) potential and similarly yellow line for Yukawa potential at specified potential parameters **[15].** The deeper the well depth (ε), the stronger the interaction between two particles. When the bonding potential energy is equal to zero, the distance of separation, r, will be equal to σ.
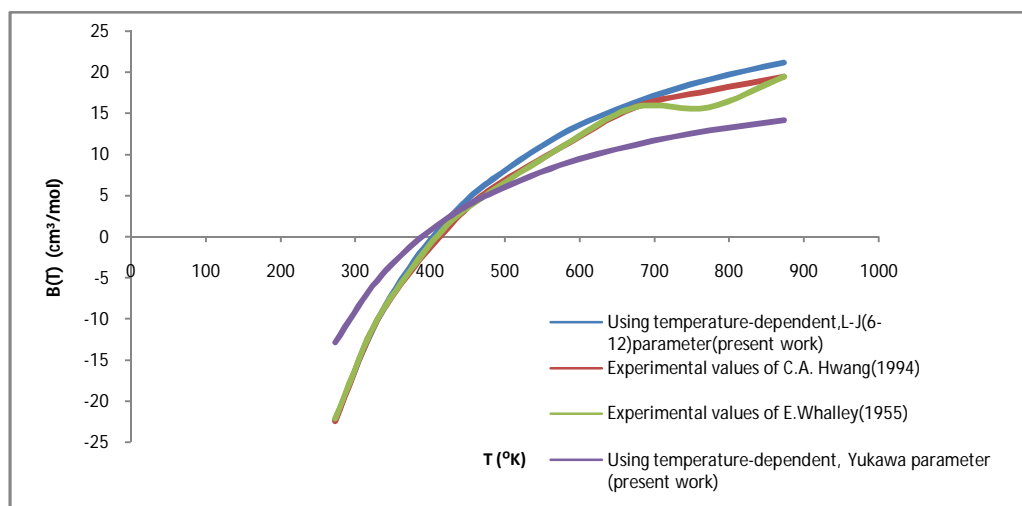

Figure3. Temperature dependence variation of the second virial coefficient for Argon

It is evident from the table 1 that the calculated values of second virial coefficient has some differences from the experimental results [11, 13] for Argon at Yukawa potential parameters i.e. $\frac{\varepsilon}{k} = 113.99\ (K)\ and\ \sigma = 3.033(A^0)$. When we used the L-J potential parameters i.e. $\frac{\varepsilon}{k} = 118.13\ (K), \sigma = 3.499(A^0)$, than the calculated values of second virial coefficient for Ar shows good results in between the temperature 273.15 to 473.15 (K) [8]. We found well suitable results of second virial coefficient for Lennard Jones potential with the experimental results [11]. Also while, at low temperatures (T≤ 373.15(K)), the virial coefficients B (T) is negative, there is a good agreement between experimental and calculated results. There is a large discrepancy at higher temperatures (T >373.15 (K)), the second virial coefficients B (T) is positive, and where the repulsive part of the interaction potential for molecule is dominates. The temperature at which B (T) tends to zero is called the Boyle's temperature T_B [16]. For Argon, the second virial coefficient, we obtain the Boyle's temperature as follow: $T_B \approx 403.7612(K)$, B (T) $\approx 0.0000147931(cm^3/mol)$. Similarly, for Yukawa potential parameter $\frac{\varepsilon}{k} = 113.99\ (K),\ \sigma = 3.033(A^0)$, the second virial coefficient, we obtain the Boyle's temperature as follow: $T_B \approx 389.611(K)$, B (T) $\approx 0.000101461(cm^3/mol)$ shown in fig.1. However, this is not equal to zero.

ACKNOWLEDGEMENTS

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