Estimation of second virial coefficients for rare gases in thermodynamic views

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ABSTRACT

Using the Gaussian 2003 software and MP_2/ 6–311 ++ G** method for He: He, Ne:Ne and MP_2/6-31G method for Ar: Ar, Kr: Kr and HF/STO-3G method for Xe: Xe, the optimized interaction energies between two like atoms of rare gases (He, Ne, Ar, Kr and Xe) as a function of the distances between the centers of two considered atoms were evaluated and the results were interpreted according to the Lennard – Jones equation . In addition, the second virial coefficient of each rare gas was calculated upon the appropriate equations of statistical thermodynamics. The resultent coefficients were comparable with those are available in the literature.

Keywords: Rare gases; Lennard – Jones potential; Virial coefficient

INTRODUCTION

The Lennard – Jones potential is one of the simple models that approximates the interaction between a pair of notral atoms or molecules [1, 13, 15, 18]. The simplified from of Lennard – Jones potential, VL – J, is as follow [1, 3, 4, 8]:

$$V_{L-J}(r) = \frac{A}{r^{12}} - \frac{B}{r^6} \qquad (1)$$

where r is the separation of the centers of two atoms or molecs and A and B are the desired constants.The plot of V(r) versus r intercepts the r axis at r = σ, where V(r) = 0 and has a minimum at r = re , where V(r) = -ε , while ε is the depth of the potential well (Fig.1)

In order to improve the equation (1), we may pay attention to the fact that at r =σ, we have V(r) = 0 and at r = re, V(r) = - ε and $(\partial V / \partial r) = 0$ at r = re [3, 4, 7].

These conditions lead to the following results [1, 13, 14]

$$A = 4\varepsilon\, \sigma^{12} \; ; \; B = 4\varepsilon\, \sigma^6 \qquad (2)$$

And

$$VL - J(r) = 4\varepsilon \left[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6 \right] \qquad (3)$$

Equation (3) is quite straight forward in application .If we take r = 2.5σ , we will obtain the value VL-J(r) = - 0.0163ε which is labeled as " truncated Lennard – Jones Potential "

$$VL\text{-}J(rc) = VL\text{-}J\,(2.5\,\sigma) \simeq -\,0.0163\epsilon \qquad (4)$$
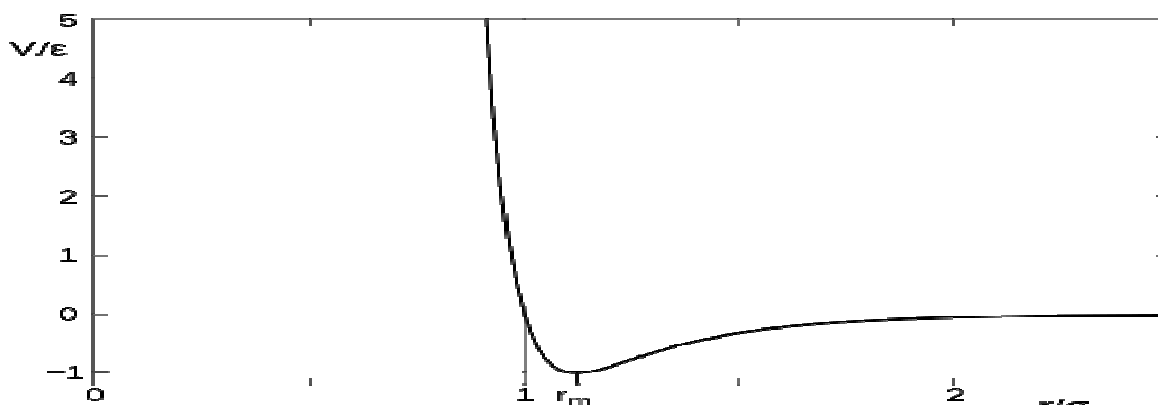
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Fig.1. A plot of potential energy, V, versus the reduced separation, r/σ, for the Lennard – Jones interactions (rm = re).

VIRIAL EQUATION

State equations are very important in calculating the thermodynamic properties of pure fluids [1, 2, 14]. The results of such calculations are very help full in industrial processes [1, 2, 14]. We can find many state equations for pure fluid in the literature, but virial equation of state is more intrest [1, 2, 14]. Virial equation of state can be represented as follow [2, 3, 19, 20]:

$$Z = \frac{PV}{RT} = 1 + B'(T)P + C'(T)P^2 + \dots \quad (5)$$

Or

$$Z = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots \quad (6)$$

where Z is the compressibility factor of pure fluid and B'(T), C'(T), C'(T), …, B(T), C(T), … are constants for a particular fluid and only a function of temperature; P is pressure and V is molar volume of fluid .

ESTIMATION OF SECOND VIRIAL COEFFICIENT

In statistical thermodynamics, the equation relating the pressure of a nonideal fluid to its canonical partition function is [1, 10, 11, 14]:

$$P = kT \left(\frac{\ln Q}{\partial V}\right)_{T,N} \quad (7)$$

Classical partition function for a sample of a real dilute gas, containing N molecules, can be written as follow [9, 10, 14, 16, 19]:

$$Q = \frac{1}{N!} \left(\frac{2\pi mkT)^{sN/2}}{h^{sN}}\right) V^N \left(1 - \frac{N^2 \beta(T)}{V}\right) \quad (8)$$

where

$$\beta = \frac{1}{2} \int_0^\infty (1 - e^{-\frac{V(r)}{kT}}) \, dv \quad (9)$$

and V(r) is the pair potential energy as shown in equation (3). By means of equation (7) and (8), we obtain [9, 14]:

$$P = \frac{NkT}{V} \left(1 + \frac{B}{V}\right) \quad (10)$$

where

$$B = 2\pi N_A \int_0^\infty (1 - e^{-V(r)/kT}) r^2 dr$$

is the second virial coefficient of state equation of the real dilute gas (see equation 6); NA is Avogadro constant, k is Boltzmann constant, and T is temperature in Kelvin.

RESULTS AND DISCUSSION

The total electronic energies, Ee(r), of two like atoms of every rare gas (He: He, Ne: Ne, Ar: Ar, Kr: Kr, Xe: Xe) as a

function of separation, r, of two like atoms were calculated by using the Gaussian 2003 software MP2/ 6–311 ++ G** method for He: He, Ne: Ne and MP2/6-31G method for Ar: Ar ,Kr:Kr and HF/STO-3G method for Xe: Xe. Then, the interaction energies between two like atoms, Eint (r) as a function of separation, r, were evaluated by means of following equation:

$$E_{int(r)} = E_{e(r)} - E(\infty) \qquad (12)$$

where Ee(∞) refers to Ee(r) at a long separation, where the Eint(r) ≃ 0.
We assume that Eint coincides with the Lennard – Jones potential, VL-J(r) in equation (3).

The calculated values of Ee(r) and Eint(r) ≡ VL-J(r) for each of systems He: He, Ne: Ne, Ar: Ar, Kr: Kr and Xe: Xe, are gathered in tables 1, 3, 5, 7 and 9 and ploted in figure, 2-6.

In addition, the second virial coefficient for each rare gases was calculated upon equation (11) and the resultant values are given in tables 2, 4, 6, 8 and 10.

In order to calculate equation (3) and then integral (11), we desine two programs by using matlab 2012 software.

The values of $E_{int(r)}$ (table 1) were represented by an equation like eq. (3) with σ = 2.75Å and ε =31.5 k (k represents the Boltsmann constant). Then, by means of these values and equation (11), we estimate the values of B at 100 K and 600 K. The results are given in table 2, that are comparable with those can be found in the literature [2].

The procedure was repeated for Ne: Ne, Ar: Ar, Kr: Kr and Xe: Xe systems. The obtained results are given in tables 3, 5, 7, 9.

The values of $E_{int(r)}$ (table 3) were represented by an equation like eq. (3) with σ = 2.84 Å and ε =31.6k. Then, by means of these values and equation (11), we estimate the values of B at 100 K and 600 K. The results are given in table 4, that are comparable with those can be found in the literature [2].

Table 1. Total electronic energies, Ee(r), of two atoms of He and interaction energies between them, Eint(r), as a function of He: He separation "r"

| $r / \overset{0}{A}$	$E_e(r)$/hartree	$E_{int}(r)$/hartree	$E_{int}(r)$/k	$E_{int}(r)$/J molecule^{-1}
0.50	-4.7176	1.0517	332000	4.58E-18
0.875	-5.5211	0.2482	78300	1.08E-18
1.25	-5.7148	0.0545	17200	2.37E-19
1.625	-5.7581	0.0112	3530	4.88E-20
2.00	-5.7672	0.0021	663	9.15E-21
2.375	-5.769	0.0003	94.6	1.31E-21
2.75	-5.7693	0.0	0.0	0.0
3.125	-5.7694	-0.0000.1	-31.5	-4.36E-22
3.50	-5.7694	-0.00001	-31.5	-4.36E-22
3.875	-5.7693	0.0	0.0	0.0
4.25	-5.7693	0.0	0.0	0.0
4.625	-5.7693	0.0	0.0	0.0
5.00	-5.7693	0.0	0.0	0.0
5.375	-5.7693	0.0	0.0	0.0
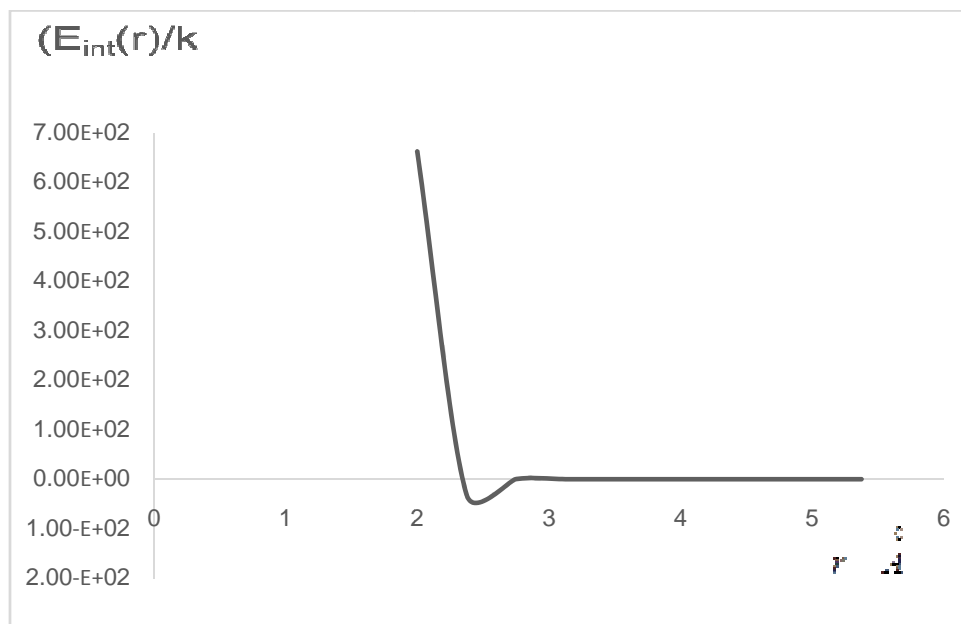
Fig. 2. Plot of " $E_{int(r)}/k$ " versus separation , r , for " He : He " system .
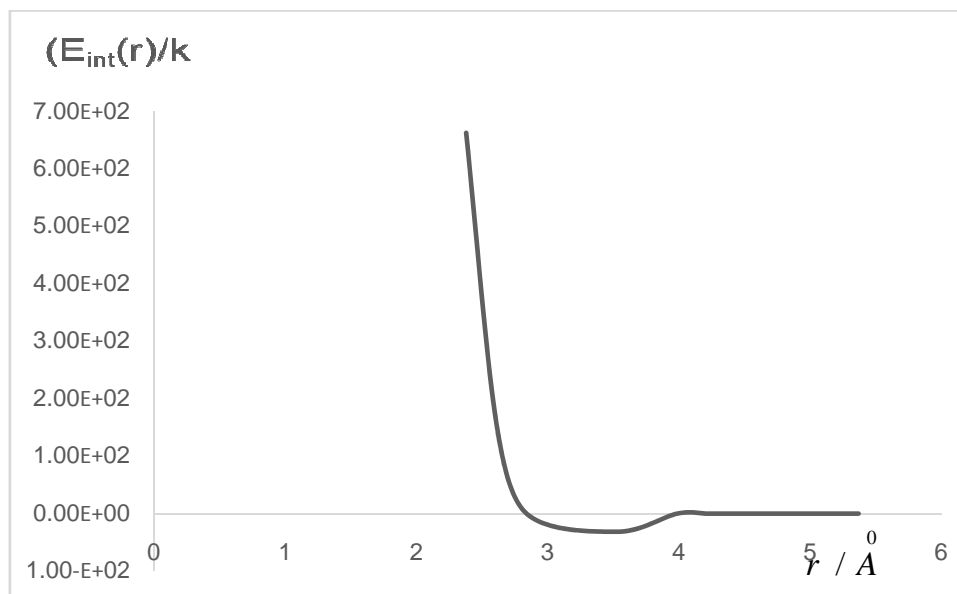
Table 2. Comparing the results of our calculations of σ and ε for He : He system with the literary values [2]

	100K	273K	373K	600K
$(\sigma/\text{Å}) = 2.58 : l^*$	-	-	-	-
$(\sigma/\text{Å}) = 2.75: c^*$	-	-	-	-
$(\varepsilon/k)= 10.22 : l$	-	-	-	-
$(\varepsilon/k)= 31.5 : c$	-	-	-	-
$B/cm^3mol^{-1} : l$	11.4	12.0	11.3	10.4
$B/cm^3mol^{-1} : c$	-2.2233	10.7675	12.1861	13.1638

* l refers to literary and c to calculated . * The $MP_2/$ 6–311 ++ G** method was used for He:He .

Table 3. Total electronic energies, $E_e(r)$,of two atoms of Ne and interaction energies between them, $E_{int}(r)$,as a function of Ne: Ne separation "r"

$r/\overset{0}{A}$	$E_e(r)/\text{hartree}$	$E_{int}(r)/\text{hartree}$	$E_{int}(r)/k$	$E_{int}(r)/\text{J molecule}^{-1}$
2.38	-257.4762	0.0021	663	9.14756E-21
2.61	-257.4778	0.0005	158	2.17799E-21
2.84	-257.4783	0.0	0.0	0.0
3.53	-257.4784	-0.0001	-31.6	-4.356E-22
3.99	-257.4783	0.0	0.0	0.0
4.22	-257.4783	0.0	0.0	0.0
4.45	-257.4783	0.0	0.0	0.0
4.68	-257.4783	0.0	0.0	0.0
4.91	-257.4783	0.0	0.0	0.0
5.14	-257.4783	0.0	0.0	0.0
5.37	-257.4783	0.0	0.0	0.0

Fig. 3. Plot of" Eint(r)/k " versus separation , r, for "Ne: Ne" system.

Table 4 .Comparing the results of our calculations of σ and ε for Ne: Ne system with the literary values [2]

	100K	273K	373K	600K
$(\sigma/Å) = 2.79 : l*$	-	-	-	-
$(\sigma/Å) = 2.84 : c*$	-	-	-	-
$(\varepsilon/k)= 35.7 : l$	-	-	-	-
$(\varepsilon/k)= 31.6$ c	-	-	-	-
B/cm^3 mol^{-1} : l	- 4.8	10.4	12.3	13.8
B/cm^3 mol^{-1} : c	-2.4721	11.8977	13.4688	14.5541

* l refers to literary and c to calculated . The MP$_2$/ 6–311 ++ G** method was used for Ne: Ne System.

Table 5. Total electronic energies, Ee(r), of two atoms of Ar and interaction energies between them, Eint (r), as a function of Ar: Ar separation"r"

$r/Å$	$E_e(r)$/hartree	$E_{int}(r)$/hartree	$E_{int}(r)$/k	$E_{int}(r)$/J molecule^{-1}
2.50	-1049.1447	0.0304	9590	1.32E-19
2.875	-1049.1697	0.0054	1700	2.35E-20
3.25	-1049.1755	-0.0004	-126	-1.74E-21
3.625	-1049.1751	0.0	0.0	0.0
4.00	-1049.1751	0.0	0.0	0.0
4.375	-1049.1751	0.0	0.0	0.0
4.75	-1049.1751	0.0	0.0	0.0
5.125	-1049.1751	0.0	0.0	0.0
5.50	-1049.1751	0.0	0.0	0.0

The values of $E_{int(r)}$ (table 5) were represented by an equation like eq. (3) with σ = 4.375 Å and ε =94.6k. Then, by means of these values and equation (11), we estimate the values of B at 100 K and 600 K. The results are given in table 6, that are comparable with those can be found in the literature [2].
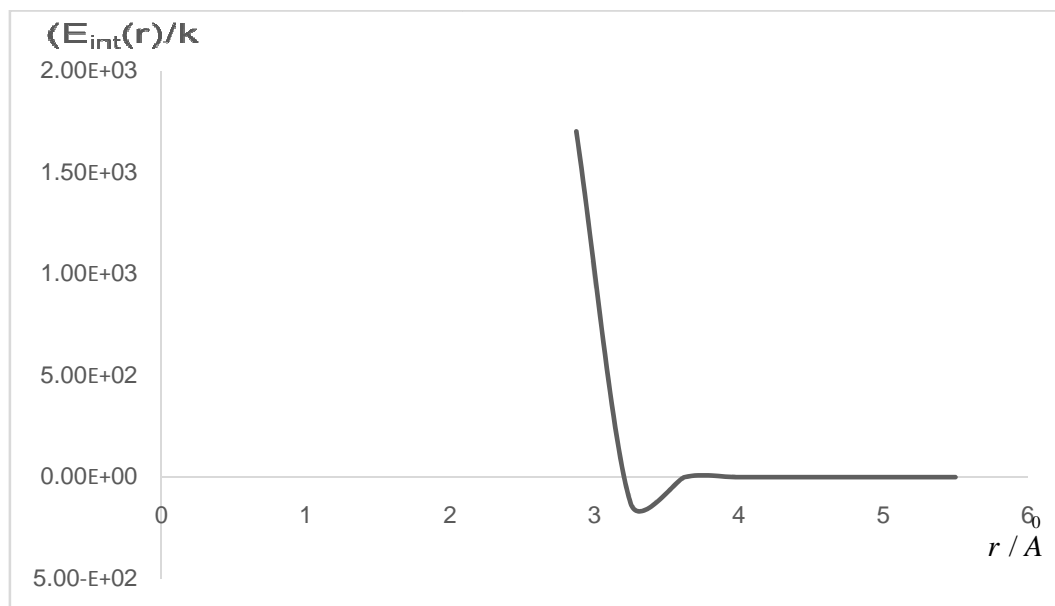
Fig. 4. Plot of" $E_{int}(r)/k$ " versus separation , r,for "Ar : Ar" system.

Table 6. Comparing the results of our calculations of σ and ε for Ar: Ar system with the literary values [2]

	100K	**273K**	**373K**	**600K**
$(\sigma/\text{Å}) = 3.499 : l*$	-	-	-	-
$(\sigma/\text{Å}) = 3.625 : c*$	-	-	-	-
$(\varepsilon/k) = 118.13 : l$	-	-	-	-
$(\varepsilon/k) = 126 : c$	-	-	-	-
$B/\text{cm}^3 \text{ mol}^{-1} : l$	-187	-21.7	- 4.2	12
$B/\text{cm}^3 \text{ mol}^{-1} : c$	-225.0083	-30.8373	-8.266	12.5566

* l refers to literary and c to calculated . The MP_2/ 6–31G method was used for Ar: Ar.

Table 7. Total electronic energies, $E_e(r)$, of two atoms of Kr and interaction energies between them, $E_{int}(r)$, as a function of Kr: Kr separation "r"

$r / \overset{0}{A}$	$E_e(r)/\text{hartree}$	$E_{int}(r)/\text{hartree}$	$E_{int}(r)/k$	$E_{int}(r)/\text{J molecule}^{-1}$
3.00	-5498.4073	0.0125	3940	5.44E-20
3.375	-5498.418	0.0018	568	7.84E-21
3.75	-5498.4202	-0.0004	-126	-1.74E-21
4.125	-5498.4198	0.0	0.0	0.0
4.50	-5498.4198	0.0	0.0	0.0
4.875	-5498.4198	0.0	0.0	0.0
5.25	-5498.4198	0.0	0.0	0.0
5.625	-5498.4198	0.0	0.0	0.0

The values of $E_{int(r)}$ (table 7) were represented by an equation like eq. (3) with $\sigma = 4.125$Å and $\varepsilon = 126$k. Then, by means of these values and equation (11), we estimate the values of B at 100 K and 600 K. The results are given in table 8, that are

comparable with those can be found in the literature [2].

The values of $E_{int(r)}$ (table 9) were represented by an equation like eq. (3) with $\sigma = 4.50$Å and $\varepsilon = 221$k. Then, by means of these values and equation (11), we estimate the values of B at 100 K and 600 K. The results are given in table 10, that are comparable with those can be found in the literature [2].
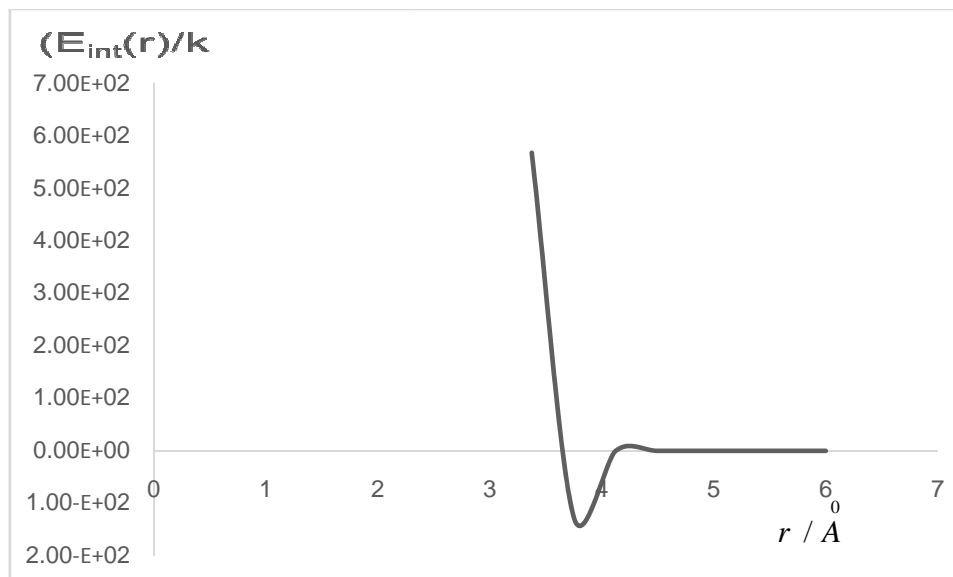

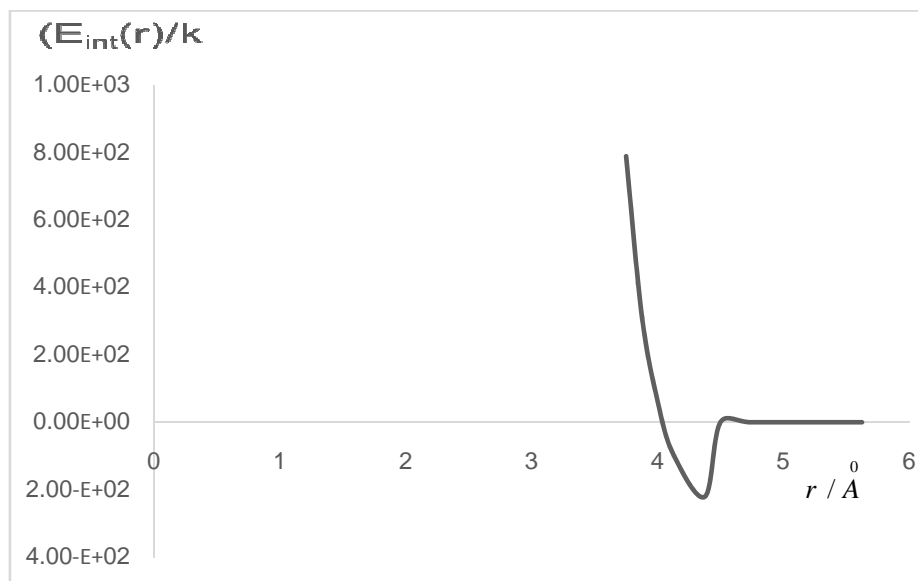**Fig. 5.** Plot of" Eint(r)/k " versus separation , r, for "Kr : Kr" system.

Table 8. Comparing the results of our calculations of σ and ε for Kr: Kr system with the literary values [2]

	100K	273K	373K	600K
$(\sigma/\text{Å}) = 3.846$:l*	-	-	-	-
$(\sigma/\text{Å}) = 4.125$: c*	-	-	-	-
$(\varepsilon/\text{k}) = 162.74$:l	-	-	-	-
$(\varepsilon/\text{k}) = 126$: c	-	-	-	-
B/cm^3 mol^{-1} : l	- 83.0	- 28.7	- 4.2	2.0
B/cm^3 mol^{-1} : c	-335.6761	- 45.1586	- 11.902	18.778

* l refers to literary and c to calculated. * The MP$_2$ /6-31G method was used for Kr: Kr.

Table 9. Total electronic energies, Ee(r), of two atoms of Xe and interaction energies between them, E_{int}(r), as a function of Xe: Xe separation "r"

$r / \overset{0}{A}$	E_e(r)/hartree	E_{int}(r)/hartree	E_{int}(r)/k	E_{int}(r)/J molecule^{-1}
3.75	-14324.205	0.0025	789	1.09E-20
3.875	-14324.2065	0.001	315	4.36E-21
4.00	-14324.2073	0.0002	63.1	8.71E-22
4.125	-14324.2078	-0.0003	-94.6	-1.31E-21
4.375	-14324.2082	-0.0007	-221	-3.05E-21
4.50	-14324.2075	0.0	0.0	0.0
4.75	-14324.2075	0.0	0.0	0.0
5.50	-14324.2075	0.0	0.0	0.0
5.625	-14324.2075	0.0	0.0	0.0

Fig. 6. Plot of" Eint(r)/k " versus separation , r, for "Xe: Xe" system.

Table 10. Comparing the results of our calculations of σ and ε for Xe: Xe system with the literary values [2]

	100K	273K	373K	600K
$(\sigma/\text{Å}) = 4.1$:l*	-	-	-	-
$(\sigma/\text{Å}) = 4.50$: c*	-	-	-	-
$(\varepsilon/ k) = 222.32$:l	-	-	-	-
$(\varepsilon/ k) = 221$: c	-	-	-	-
B/cm^3 mol^{-1} : l	-	- 153.8	- 81.7	- 19.6
B/cm^3 mol^{-1} : c	- 1222.6	- 200.636	- 108.3699	- 25.5479

* The HF/STO-3G method was used for Xe: Xe.

CONCLUSION

The results of this study show that interaction energy between two like atoms of a given rare gas is almost insignificant (except in very short separations) and is a function of the separation of two atoms. The interaction energies at very short separation are highly positive that indicates the high repulsion between two considered atoms. In opposite, the interaction energies are some what negative at desired separations that indicates the small attraction between two considered atoms.

The plot of interaction energies versus the separations of two like atoms has a well wilh a depth of $-\varepsilon$. The trend of ε for studied gasses is as follow:

$$\sigma_{\text{Xe-Xe}} > \sigma_{\text{Kr-Kr}} > \sigma_{\text{Ar-Ar}} > \sigma_{\text{Ne-Ne}} > \sigma_{\text{He-He}}$$

Similarly:

$$\varepsilon_{\text{Xe-Xe}} > \varepsilon_{\text{Kr-Kr}} \cong \varepsilon_{\text{Ar-Ar}} > \varepsilon_{\text{Ne-Ne}} > \varepsilon_{\text{He – He}}$$

In addition, the second virial coefficient of each rare gas is temperature depedent and increases with temperature increasing.

Generally it has been observed whatever the smaller size of atomic gasses and the higher temperature, the agreement between experimental results and calculations is better.

REFERENCE

[1] P. Vargas, E. Monuz, Second virial coefficient for the Lenard jones potential, 2000.

[2] P. W. Atkins, Physical chemistry, forth edition (1990) 934, 961.

[3] R. Ramezani. A. Jahanmiri, Optimazaition of Lenard jones parameters,shiraz university.

[4] Carlos Menduna, Crlos Vega, (2001), The second virial coefficient of quadroupolar two center Lenard jones model, chemical physics,pp. 1289-1296.

[5] E. A. Mason, T. H. Sporling" The virial equation of state"in the international encyclopedia of physical chemistry and chemical physics,Elmsford,N.Y.Pargaman press,inc.1969.

[6] H. Gay. David, R. Beck. Donald, Obtaining accurate pressur second virial cofficients for methane from an ab initio pair potential, chemical physics, 1991, 9106-9114.

[7] Ovidio Ivanciuc,internet Electronic Journal, p. 179-194, marc 2003.

[8] D. vander waals, Z, phys. chem, 1894, 13, 657.

[9] M. C. Mac Quarrie, stastical thermodynamic, Harper & Row, NewYork, 1976.

[10] R. P. Feynman, stastical thermodynamic, a set of lecture, enjamin, New York, 1972.

[11] S. M, stastical Mechanics, Word scientific, Singapour, 1985.

[12] C. V. Heer, stastical Mechanics, kenetic theory and stochastic procecess, New York, 1972.

A. J. M. Garret, J. Phys. A (1980).

[13] M. Aghaie; H. Aghaie. An Introduction to statistical thermodynamics, nafis edition, (2006), 94, 151.

[14] N. Levin, Quantum Cemistry, 5th ed, Prentice Hall, New York, 2000.

[15] E. Ley-koo, M. D Lano, J. Chem. Phys, 19 (1951) 1320.

[16] Laidler Keith. Chemical. Kinetics. Third Edition. 1987.

[17] Michael. J. Pilling, Paul W. Seakins. Reaction Kinetics. 1995.

[18] H .Dymond,and E. B. smith, the virial coefficient of gases,corendon press, Oxford, 1969

[19] J. A. Beatei, The computation of the thermodynamic properties of real gases and mixtuerd of real gasses, Chemical Review, 1949, 41-141.