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Estimating the second virial coefficients of some real gas mixtures and related thermodynamic views

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ABSTRACT

Using the Gaussian 2003 software and MP_2 /6 – 311+ G method for the C_2H_4 : O_2, CO:Cl_2 and CO_2:CO_2 pairs and MP_2/6-311++G** method for the CO_2:H_2O pair and B3lyp/6-31G method for the O_2:O_2 pair the optimized interaction energies between two considered pair molecules of studied gases(C_2H_4:O_2, CO:Cl_2, CO_2:H_2O, O_2:O_2 and CO_2:CO_2 pairs) as a function of the distances between the centers of two considered molecules were evaluated and the results were interpreted according to the Lennard – Jones equation. In addition, the second virial coefficient of each pair gas was calculated upon the appropriate equations of statistical thermodynamics. The resultant coefficients were almost comparable with those are available in the literature.

Keywords: Interaction energy; Lennard – Jones Potential;Virial coefficient

INTRODUCTION

The Lennard – Jones Potential is one of the simple models that approximates the interaction energy between a pair of like molecules or unlike molecules [3, 4, 5, 7, 15]. The simplified form of the Lennard – Jones Potential, U(r), is as follow [3, 4, 6, 8]:

$$U(r) = \frac{A}{r^{12}} - \frac{B}{r^6} \tag{1}$$

The plot of U(r) versus r intercepts the r axis at r = σ, where U(r) = 0 and has a minimum at r = r_e, where U(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 U(r) = 0 and at r = r_m, U(r) = -ε and $(\partial U / \partial r) = 0$ at r = r_m [1, 3, 4, 5].

These conditions lead to the following equation [3, 4, 5, 6, 8]

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

Equation (2) is quite straightforward in application .If we take $r = 2.5\sigma$, we

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will obtain the value U(r) = - 0.0163 ε which is labeled as " truncated Lennard – Jones Potential " ($U(r_c)$)

$$U(r_C) = U(r)(2.5\sigma) ; -0.0163\varepsilon$$

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$$U(r_C) = U(r)(2.5\sigma); -0.0163\varepsilon \quad (3)$$

VIRIAL EQUATION

State equations are very important in calculating the thermodynamic properties of pure and mixed fluids [2, 3, 5, 8, 9, 10, 15]. The results of such calculations are very helpfull in industrial processes [2, 3, 4. 5, 8]. We can find many state equations for pure and mixed fluids in the literature, but virial equation of state is more intrest [1, 2, 3, 10, 14, 15]. Virial equation of state can be represented as follow [2, 3, 14, 15]:

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

Or

$$Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^{\;2}} + \ldots \quad (5)$$

where Z is the compressibility factor of pure or mixed fluid and B'(T), C'(T), D'(T), …, B(T), C(T), … are constants for a particular fluid and only a function of temperature; P is pressure and V_m 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 [10, 11, 12, 15]:

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \quad (6)$$

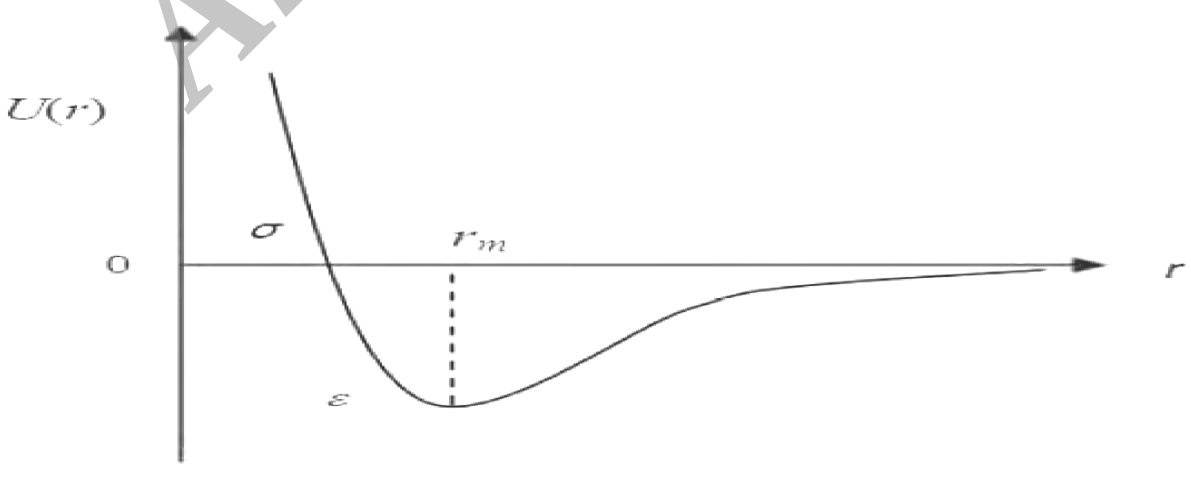

Fig.1. A plot of potential energy, U(r), versus the pair separation, r, for the Lennard – Jones model ($r_m = r_e$).

Translational classical partition function for a sample of a real dilute gas, containing N molecules, can be written as follow [10, 12, 13, 15]:

$$Q = \frac{1}{N!}\left(\frac{2\pi mkT)^{3N/2}}{h^{3N}}\right)V^{N}\left(1-\frac{N^{2}\beta(T)}{V}\right) \quad (7)$$

where

$$\beta = \frac{1}{2}\int_{0}^{\infty}(1-e^{-\frac{U(r)}{kT}})\,dV \quad (8)$$

and U(r) is the pair potential energy as shown in equation (2). By means of equation (6) and (7), we obtain [12, 13, 15]:

$$P = \frac{NkT}{V}(1+\frac{B}{V}) \quad (9)$$

where

$$B = 2\pi N_{A}\int_{0}^{\infty}(1-e^{-U(r)/kT})\,r^{2}dr \quad (10)$$

is the second virial coefficient of state equation of the real dilute gas (see equation 5); N_A is Avogadro constant, k is Boltzmann constant, and T is temperature in Kelvin.

RESULTS AND DISCUSSION

The total electronic energies, $E_{e(r)}$, of two like or unlike molecules of every pair (C_2H_4:O_2, CO:Cl_2, CO_2:H_2O, O_2:O_2 and CO_2:CO_2 pairs) as a function of separation, r, of two molecules were calculated by using the Gaussian 2003 software MP_2/ 6–311+G method for C_2H_4:O_2, CO:Cl_2, CO_2:CO_2 pairs and MP_2/6-31++G** method for CO_2:H_2O pair and B3lyp/6-31G method for O_2:O_2 pair Then, the interaction energies between two considered molecules, $E_{int(r)}$ as a function of separation, r, were evaluated by means of the following equation:

$$U(r) \equiv E_{int(r)} = E_{e(r)} - E(\infty) \quad (11)$$

where $E_{e(\infty)}$ refers to $E_{e(r)}$ at a long separation, where the $E_{int(r)} \simeq 0$.

We assume that E_{int} coincides with the Lennard – Jones potential, U(r) in equation (2).

The calculated values of $E_{e(r)}$ and $E_{int(r)} \equiv U(r)$ for each of the studied systems (C_2H_4:O_2, CO:Cl_2, CO_2: H_2O, O_2:O_2 and CO_2:CO2 pairs) are gathered in tables 1, 3, 5, 7 and 9 and ploted in figures, 2-6.

In addition, the second virial coefficient for each gas- pair was calculated upon equation (10) and the resultant values are given in tables 2, 4, 6 and 10.

In order to calculate equation (2) and then integral (10), we desine two programs by using matlab 2012 software.

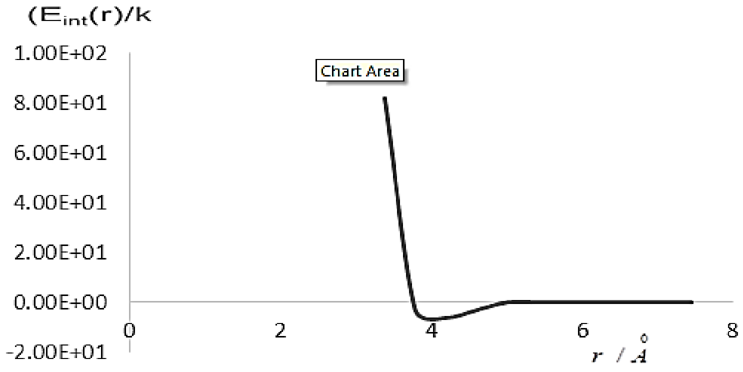

Fig. 2. Plot of " $E_{int(r)}$/k " versus separation , r , for " C_2H_4 : O_2 " system.

The values of $E_{int(r)}$ (table 1) were represented by an equation like eq. (2) with σ = 5.006Å and ε = 63.1 k (k represents the Boltzmann constant). Then, by means of these values and equation (10), we estimated the values of B at 100, 273, 373 and 600 K. The results are given in table.

The procedure was repeated for CO:Cl_2, CO_2:H_2O ,O_2:O_2 and CO_2:CO_2 systems. The obtained results are given in tables 3-10.

Table1. Total electronic energies, $E_e(r)$,of two molecules (C_2H_4 : O_2 pair) and interaction energies between them, $E_{int}(r)$,as a function of C_2H_4 : O_2 separation "r"

r / $\overset{0}{A}$	**E_e(r)/hartree**	**E_{int}(r)/hartree**	**E_{int}(r)/ J molecule^{-1}**	**E_{int}(r)/k**
1.74537	-228.70699	0.13754	5.99121E-19	4.34E+04
2.16	-228.81168	0.03285	1.43094E-19	1.04E+04
2.56	-228.84452	1E-05	4.35598E-23	3.15E+00
2.969753	-228.84301	0.00152	6.62109E-21	4.80E+02
3.377068	-228.84427	0.00026	1.13255E-21	8.20E+01
3.784383	-228.84454	-1E-05	-4.356E-23	-3.15E+00
4.191698	-228.84455	-2E-05	-8.712E-23	-6.31E+00
4.599013	-228.84454	-1E-05	-4.356E-23	-3.15E+00
5.006328	-228.84453	0.0	0.0	0.0
5.413643	-228.84453	0.0	0.0	0.0
5.820958	-228.84453	0.0	0.0	0.0
6.228273	-228.84453	0.0	0.0	0.0
6.635588	-228.84453	0.0	0.0	0.0
7.042903	-228.84453	0.0	0.0	0.0
7.450218	-228.84453	0.0	0.0	0.0

Table 2. Results of our calculations of σ and ε for **C_2H_4 : O_2** system

	100K	**273K**	**373K**	**600K**
(σ/Å) = 5.006: c*	-	-	-	-
(ε /k)= 6.31: c	-	-	-	-
B/cm^{3}mol^{-1} : c	-170.3058	25.5312	49.6367	70.9123

* c to calculated .The **MP_2/ 6–311+G** method was used for **C_2H_4 : O_2** pair.

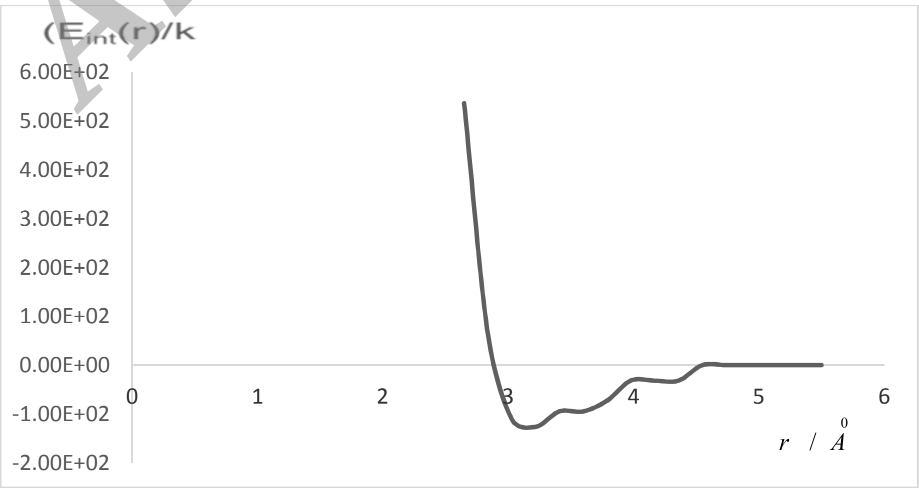

Fig.3. Plot of" E_{int}(r)/k " versus separation, r,for "CO:Cl_2" system.

The values of $E_{int(r)}$ (table 3) were represented by an equation like eq. (2) with σ = 4.55 Å and ε =126k. Then, by means of these values and equation (10), we estimate the values of B at 100, 273, 373 and 600 K. The results are given in table 4.

Table3. Total electronic energies, $E_e(r)$,of two molecules (CO : Cl_2 pair) and interaction energies between them, $E_{int}(r)$,as a function of CO:Cl_2 separation "r"

$r/\overset{0}{A}$	**$E_e(r)$/hartree**	**$E_{int}(r)$/hartree**	**$E_{int}(r)$/ J molecule^{-1}**	**$E_{int}(r)$/k**
1.700000007	-1033.6507	0.1081	4.71E-19	3.41E+04
1.890000007	-1033.7007	0.0581	2.53E-19	1.83E+04
2.080000007	-1033.73	0.0288	1.25E-19	9.09E+03
2.270000007	-1033.7457	0.0131	5.71E-20	4.13E+03
2.460000007	-1033.7535	0.0053	2.31E-20	1.67E+03
2.650000007	-1033.7571	0.0017	7.41E-21	5.36E+02
2.840000007	-1033.7586	0.0002	8.71E-22	6.31E+01
3.030000007	-1033.75915	-0.00035	-1.52E-21	-1.10E+02
3.220000007	-1033.7592	-0.0004	-1.74E-21	-1.26E+02
3.410000007	-1033.7591	-0.0003	-1.31E-21	-9.46E+01
3.600000007	-1033.7591	-0.0003	-1.31E-21	-9.46E+01
3.790000007	-1033.75903	-0.00023	-1.00E-21	-7.26E+01
3.980000007	-1033.7589	-1E-04	-4.36E-22	-3.15E+01
4.170000007	-1033.7589	-1E-04	-4.36E-22	-3.15E+01
4.360000007	-1033.7589	-1E-04	-4.36E-22	-3.15E+01
4.550000007	-1033.7588	0.0	0.0	0.0
4.740000007	-1033.7588	0.0	0.0	0.0
4.930000007	-1033.7588	0.0	0.0	0.0
5.120000007	-1033.7588	0.0	0.0	0.0
5.310000007	-1033.7588	0.0	0.0	0.0
5.500000007	-1033.7588	0.0	0.0	0.0

Table 4 . Results of our calculations of σ and ε for CO: Cl_2 system

	100K	**273K**	**373K**	**600K**
(σ/**Å**) = 4.55: c*	-	-	-	-
(ε/k) = 126:c	-	-	-	-
B/cm^{3}mol^{-1} : c	- 426.960	- 73.096	- 28.468	12.7031

*c to calculated. The **MP_2/ 6–311+G** method was used for CO: Cl_2 pair.

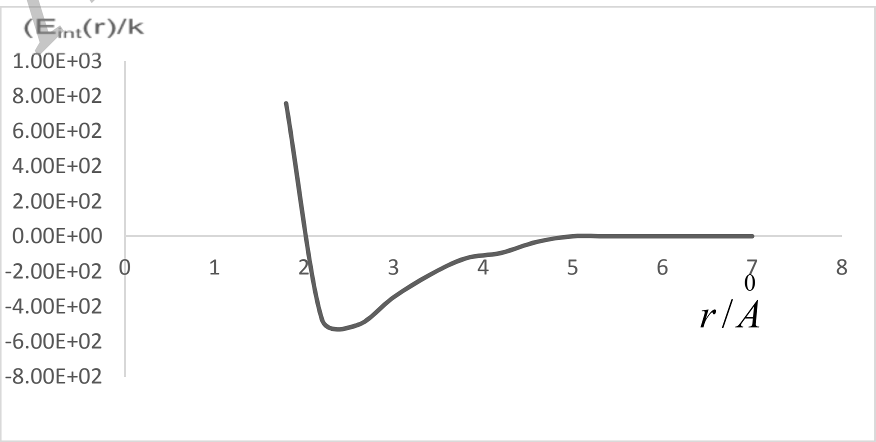

Fig.4. Plot of" $E_{int}(r)$/k " versus separation, r,for "**CO_2 : H_2O** " system.

The values of $E_{int(r)}$ (table 5) were represented by an equation like eq. (2) with σ = 5.0 Å and ε = 505k. Then, by means of these values and equation (10), we estimate the values of B at 100, 273, 373 and 600 K. The results are given in table 6.

Table5. Total electronic energies, $E_e(r)$,of two molecules (CO_2 : H_2O pair) and interaction energies between them, $E_{int}(r)$,as a function of CO_2 : H_2O separation "r"

$r/\overset{0}{A}$	**$E_e(r)$/hartree**	**$E_{int}(r)$/hartree**	**$E_{int}(r)$/ J molecule^{-1}**	**$E_{int}(r)$/k**
1.0	-263.551	0.1361	5.93E-19	4.30E+04
1.4	-263.662	0.0251	1.09E-19	7.92E+03
1.8	-263.6847	0.0024	1.05E-20	7.58E+02
2.2	-263.6886	-0.0015	-6.53E-21	-4.73E+02
2.6	-263.6887	-0.0016	-6.97E-21	-5.05E+02
3.0	-263.6882	-0.0011	-4.79E-21	-3.47E+02
3.4	-263.6878	-0.0007	-3.05E-21	-2.21E+02
3.8	-263.6875	-0.0004	-1.74E-21	-1.26E+02
4.2	-263.6874	-0.0003	-1.31E-21	-9.47E+01
4.6	-263.6872	-0.0001	-4.36E-22	-3.16E+01
5.0	-263.6871	0.0	0.0	0.0
5.4	-263.6871	0.0	0.0	0.0
5.8	-263.6871	0.0	0.0	0.0
6.2	-263.6871	0.0	0.0	0.0
6.6	-263.6871	0.0	0.0	0.0
7.0	-263.6871	0.0	0.0	0.0

Table6. Results of our calculations of σ and ε for **CO_2: H_2O** system

	100K	**273K**	**373K**	**600K**
(σ/**Å**) = 5.0 : c*	-	-	-	-
(ε/k) = 505:c	-	-	-	-
B/cm^3 mol^{-1} :c	-18200	-1190	- 679	-279

*c to calculated .The **MP$_2$/6-311++G**** method was used for **CO_2: H_2O pair**.

Table7. Total electronic energies, $E_e(r)$,of two molecules (O_2: O_2 pair) and interaction energies between them, $E_{int}(r)$,as a function of O_2: O_2 separation "r"

$r/\overset{0}{A}$	**$E_e(r)$/hartree**	**$E_{int}(r)$/hartree**	**$E_{int}(r)$/J molecule^{-1}**	**$E_{int}(r)$/k**
0.82	-300.4774	0.0141	6.14193E-20	4.45E+03
1.22	-300.4567	0.0348	1.51588E-19	1.10E+04
1.62	-300.4526	0.0389	1.69448E-19	1.23E+04
2.02	-300.4471	0.0444	1.93406E-19	1.40E+04
2.42	-300.4439	0.0476	2.07345E-19	1.50E+04
2.82	-300.4418	0.0497	2.16492E-19	1.57E+04
3.22	-300.4402	0.0513	2.23462E-19	1.62E+04
3.62	-300.4919	-0.0004	-1.7424E-21	-1.26E+02
4.02	-300.4915	0.0	0.0	0.0
4.42	-300.4915	0.0	0.0	0.0
4.82	-300.4915	0.0	0.0	0.0
5.22	-300.4915	0.0	0.0	0.0
5.62	-300.4915	0.0	0.0	0.0
6.02	-300.4915	0.0	0.0	0.0
6.42	-300.4915	0.0	0.0	0.0

The values of $E_{int(r)}$ (table 7) were represented by an equation like eq. (2) with σ = 4.02Å and ε =126k. Then, by means of these values and equation (10), we estimate the values of B at 100, 273, 373 and 600 K. The results are given in table 8, that are comparable with those can be found in the literature [2].

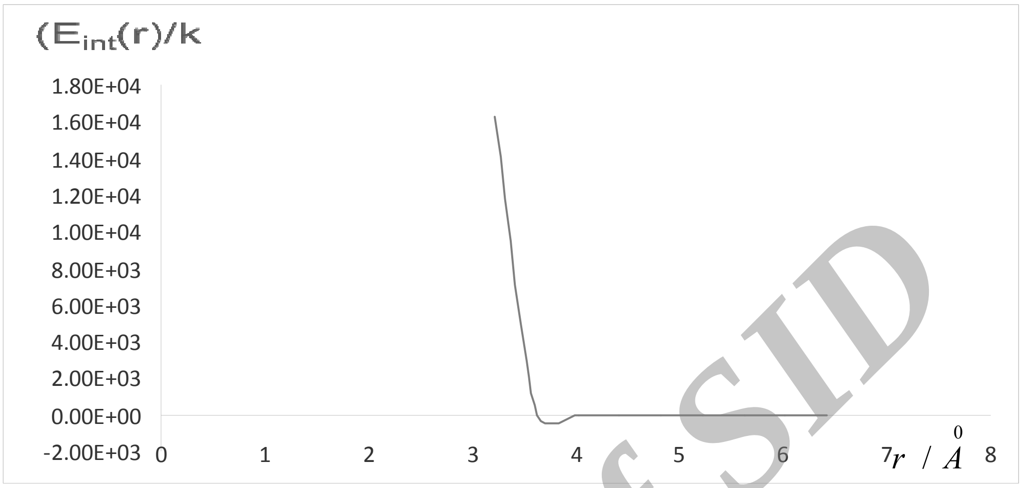

Fig.5. Plot of" Eint(r)/k " versus separation , r,for "$\mathbf{O_2 : O_2}$" system.

Table 8. Comparing the results of our calculations of σ and ε for $\mathbf{O_2 : O_2}$ system with the literary values [2]

	100K	**273K**	**373K**	**600K**
(σ/Å) = 3.43:l*	-	-	-	-
(σ/Å) = 4.02: c*	-	-	-	-
(ε/k)= 113 :l	-	-	-	-
($\mathcal{E}$/k)= 126:c	-	-	-	-
B/cm^3mol^{-1} :	-197.5	-22	-3.7	13
B/cm^{3}mol^{-1} : c	-310.7367	- 41.8416	-11.0601	17.3367

* l refers to literary and c to calculated . The **B3lyp/6-31G** method was used for $\mathbf{O_2 : O_2}$ **pair**.

Table 9. Total electronic energies, E_e(r) ,of two molecules (C$\mathbf{O_2}$**: C** $\mathbf{O_2}$ **pair)** and interaction energies between them, E_{int}(r),as a function of C$\mathbf{O_2}$ **:C** $\mathbf{O_2}$ separation "r"

$r\ /\ \overset{0}{A}$	**E_e(r)/hartree**	**E_{int}(r)/hartree**	**E_{int}(r)/ J molecule^{-1}**	**E_{int}(r)/k**
1.5	-375.5791	0.1859	8.09777E-19	5.87E+04
1.68	-375.6661	0.0989	4.30806E-19	3.12E+04
1.86	-375.7158	0.0492	2.14314E-19	1.55E+04
2.22	-375.7549	0.0101	4.39954E-20	3.19E+03
2.58	-375.7637	0.0013	5.66277E-21	4.10E+02
2.76	-375.7649	1E-04	4.35598E-22	3.16E+01
2.94	-375.7654	-0.0004	-1.7424E-21	-1.26E+02
3.3	-375.7655	-0.0005	-2.178E-21	-1.58E+02
3.48	-375.76552	-0.00052	-2.2651E-21	-1.64E+02
3.66	-375.7654	-0.0004	-1.7424E-21	-1.26E+02
3.84	-375.7653	-0.0003	-1.3068E-21	-9.47E+01
4.02	-375.765	0.0	0.0	0.0
4.2	-375.765	0.0	0.0	0.0
4.38	-375.765	0.0	0.0	0.0
4.56	-375.765	0.0	0.0	0.0
4.74	-375.765	0.0	0.0	0.0
4.92	-375.765	0.0	0.0	0.0
5.1	-375.765	0.0	0.0	0.0
5.28	-375.765	0.0	0.0	0.0
5.46	-375.765	0.0	0.0	0.0

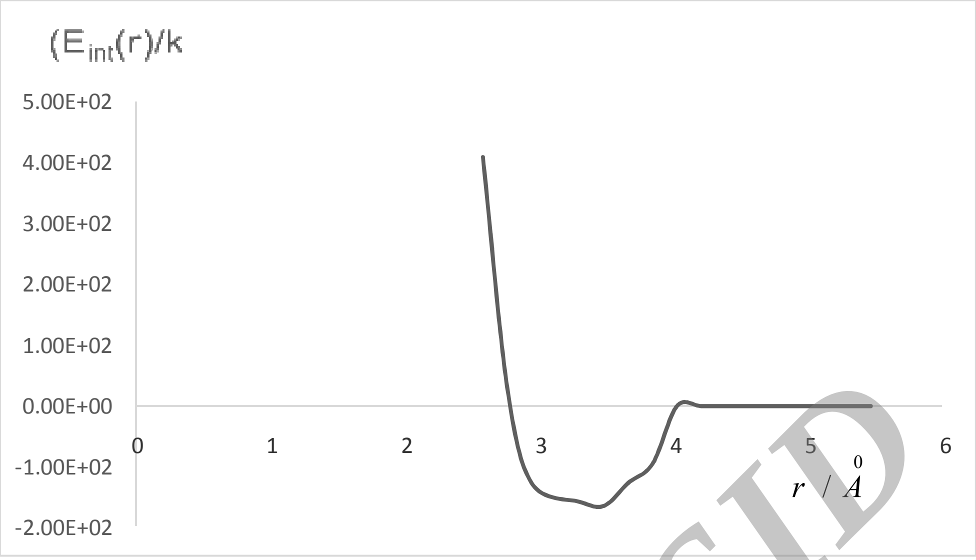

Fig.6. Plot of" Eint(r)/k " versus separation, r, for "CO_2 :C O_2" system.

Table 10. Comparing the results of our calculations of σ and ε for CO_2 :C O_2 system with the literary values [2]

	100K	**273K**	**373K**	**600K**
(σ/Å) = 4.0:l*	-	-	-	-
(σ/Å) = 4.02: c*	-	-	-	-
(ε/k)= 190 :l	-	-	-	-
($\mathcal{E}$/k)= 164:c	-	-	-	-
B/cm^3mol^{-1} : l	-	-149.7	-72.2	-72.2
B/cm^3mol^{-1} : c	-503.3045	-89.3495	-45.7714	-5.8103

* l refers to literary and c to calculated. The MP_2/6-31+G method was used for CO_2 : C O_2 pair.

The values of $E_{int(r)}$ (table 9) were represented by an equation like eq. (2) with σ = 4.02Å and ε =164k. Then, by means of these values and equation (10), we estimate the values of B for CO_2: C O_2 pair at 100, 273, 373 and 600 K. The results are given in table 10, that are comparable with those can be found in the literature [2].

CONCLUSION

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

The plot of interaction energies versus the separations of two considered molecules has a well while a depth of -ε The trend of ε for studied gas-pairs is as follow:

$$\sigma_{C2H4:O2} > \sigma_{CO2:\ H2O} > \sigma_{CO:Cl2} > \sigma_{O2:O2} \cong \sigma_{CO2:CO2}$$

Similarly :

$$\varepsilon_{CO2:H2O} > \varepsilon_{CO2:CO2} > \varepsilon_{O2:O2} \cong \varepsilon_{CO:Cl2} > \varepsilon_{C2H4:O2}$$

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

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

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