

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 MP₂/6-311+G method for the C₂H₄:O₂, CO:Cl₂ and CO₂:CO₂ pairs and MP₂/6-311++G** method for the CO₂:H₂O pair and B3lyp/6-31G method for the O₂:O₂ pair the optimized interaction energies between two considered pair molecules of studied gases (C₂H₄:O₂, CO:Cl₂, CO₂:H₂O, O₂:O₂ and CO₂:CO₂ 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]:

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

The plot of U(r) versus r intercepts the r axis at $r = \sigma$, 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 $r = \sigma$, 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]

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

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

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

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

In order to improve the equation (1), we may pay attention to the fact that at $r = \sigma$, we have $U(r) = 0$ and at $r = r_m$, $U(r) = -\varepsilon$ 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]

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

Equation (2) is quite straightforward in application. If we take $r = 2.5\sigma$, we will obtain the value $U(r) = -0.0163 \varepsilon$ which is labeled as "truncated Lennard – Jones Potential" ($U(r_c)$)

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

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 helpful 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 interest [1, 2, 3, 10, 14, 15]. Virial equation of state can be represented as follow [2, 3, 14, 15]:

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

Or

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

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]:

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

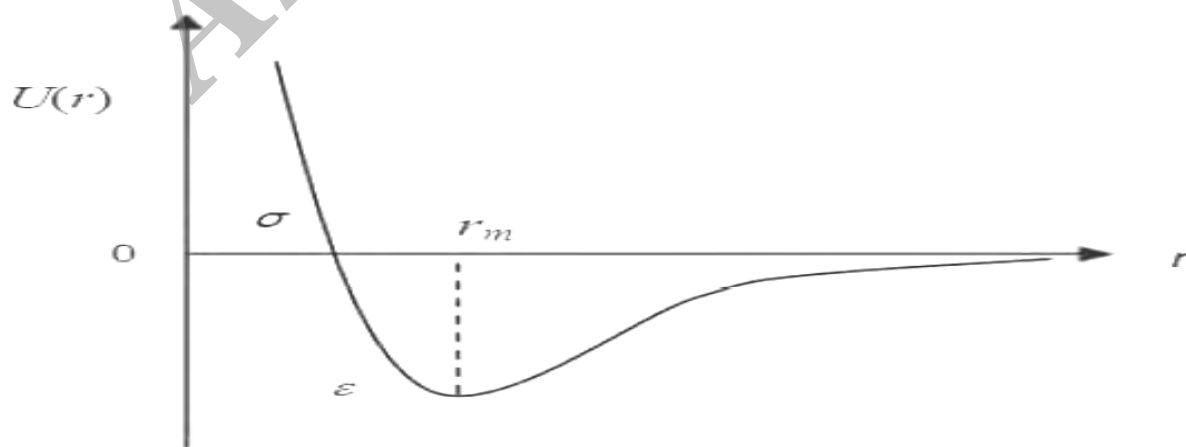


Fig.1. A plot of potential energy, $U(r)$, versus the pair separation, r , for the Lennard – Jones model ($r_m = r_c$).

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

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

where

$$\beta = \frac{1}{2} \int_0^\infty \left(1 - e^{-\frac{U(r)}{kT}} \right) dV \quad (8)$$

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]:

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

where

$$B = 2\pi N_A \int_0^\infty \left(1 - e^{-U(r)/kT} \right) r^2 dr \quad (10)$$

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 MP2/ 6-311+G method for $C_2H_4:O_2$, $CO:Cl_2$, $CO_2:CO_2$ pairs and MP2/6-31++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 $E_{int(r)} \approx 0$.

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 $CO_2:CO_2$ pairs) are gathered in tables 1, 3, 5, 7 and 9 and plotted 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.

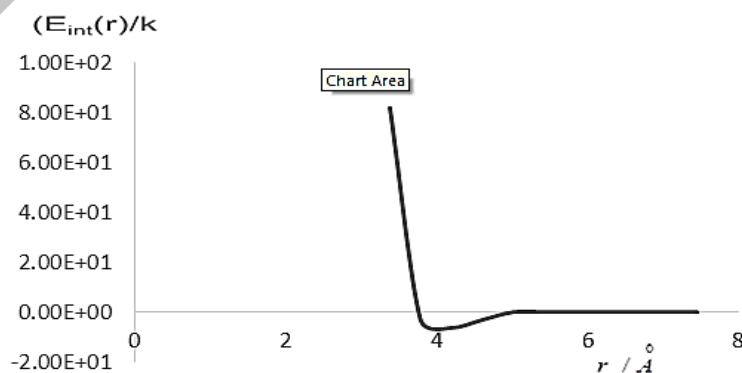


Fig. 2. Plot of " $E_{int(r)}/k$ " versus separation, r , for " $C_2H_4 : O_2$ " system.

The values of $E_{\text{int}(r)}$ (table 1) were represented by an equation like eq. (2) with $\sigma = 5.006 \text{ \AA}$ and $\varepsilon = 63.1 \text{ k}$ (k represents the Boltsmann 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 $\text{CO}:\text{Cl}_2$, $\text{CO}_2:\text{H}_2\text{O}$, $\text{O}_2:\text{O}_2$ and $\text{CO}_2:\text{CO}_2$ systems. The obtained results are given in tables 3-10.

Table1.Total electronic energies, $E_e(r)$, of two molecules ($\text{C}_2\text{H}_4 : \text{O}_2$ pair) and interaction energies between them, $E_{\text{int}}(r)$, as a function of $\text{C}_2\text{H}_4 : \text{O}_2$ separation “r”

$r / \text{\AA}$	$E_e(r)/\text{hartree}$	$E_{\text{int}}(r)/\text{hartree}$	$E_{\text{int}}(r)/\text{J molecule}^{-1}$	$E_{\text{int}}(r)/\text{k}$
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 $\text{C}_2\text{H}_4 : \text{O}_2$ system

	100K	273K	373K	600K
$(\sigma/\text{\AA}) = 5.006: \text{c}^*$	-	-	-	-
$(\varepsilon/\text{k}) = 6.31: \text{c}$	-	-	-	-
$B/\text{cm}^3\text{mol}^{-1}: \text{c}$	-170.3058	25.5312	49.6367	70.9123

* c to calculated .The $\text{MP}_2/6-311+\text{G}$ method was used for $\text{C}_2\text{H}_4 : \text{O}_2$ pair.

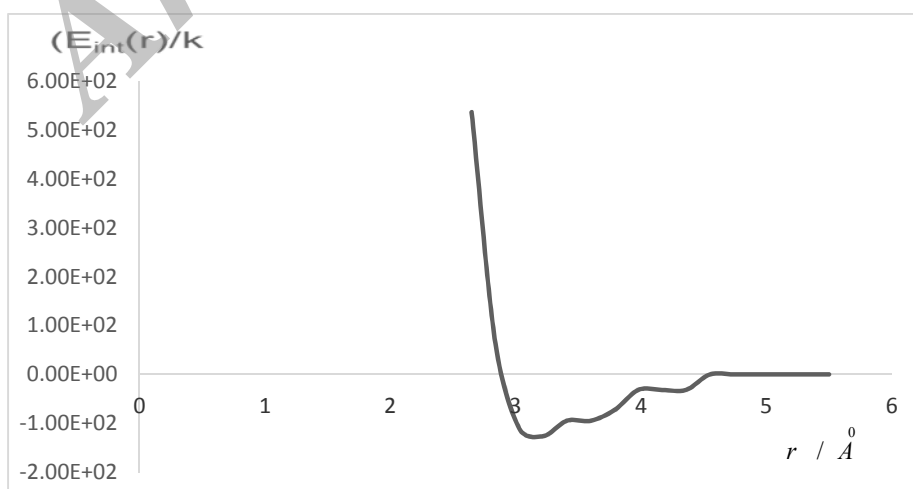


Fig.3. Plot of “ $E_{\text{int}}(r)/\text{k}$ ” versus separation, r, for “ $\text{CO}:\text{Cl}_2$ ” system.

The values of $E_{\text{int}(r)}$ (table 3) were represented by an equation like eq. (2) with $\sigma = 4.55 \text{ \AA}$ and $\varepsilon = 126\text{k}$. 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 : Cl₂ pair) and interaction energies between them, $E_{\text{int}}(r)$, as a function of CO:Cl₂ separation “r”

$r / \text{\AA}$	$E_e(r)/\text{hartree}$	$E_{\text{int}}(r)/\text{hartree}$	$E_{\text{int}}(r)/ \text{J molecule}^{-1}$	$E_{\text{int}}(r)/\text{k}$
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: Cl₂ system

	100K	273K	373K	600K
$(\sigma/\text{\AA}) = 4.55; c^*$	-	-	-	-
$(\varepsilon/\text{k}) = 126;c$	-	-	-	-
$B/\text{cm}^3 \text{mol}^{-1}; c$	- 426.960	- 73.096	- 28.468	12.7031

*c to calculated. The MP₂/ 6-311+G method was used for CO: Cl₂ pair.

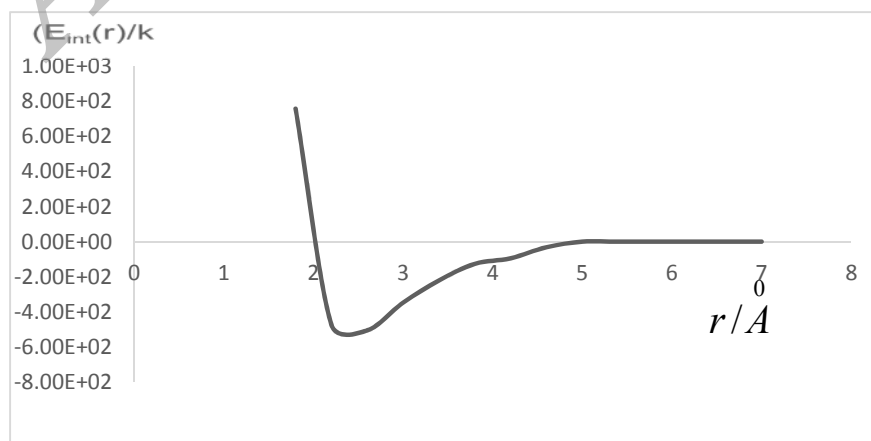


Fig.4. Plot of $E_{\text{int}}(r)/\text{k}$ “ versus separation, r, for “CO₂ : H₂O ” system.

The values of $E_{\text{int}(r)}$ (table 5) were represented by an equation like eq. (2) with $\sigma = 5.0 \text{ \AA}$ and $\varepsilon = 505\text{k}$. 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 ($\text{CO}_2 : \text{H}_2\text{O}$ pair) and interaction energies between them, $E_{\text{int}}(r)$, as a function of $\text{CO}_2 : \text{H}_2\text{O}$ separation “r”

$r/\text{\AA}$	$E_e(r)/\text{hartree}$	$E_{\text{int}}(r)/\text{hartree}$	$E_{\text{int}}(r)/\text{J molecule}^{-1}$	$E_{\text{int}}(r)/\text{k}$
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 $\text{CO}_2 : \text{H}_2\text{O}$ system

	100K	273K	373K	600K
$(\sigma/\text{\AA}) = 5.0 : \text{c}^*$	-	-	-	-
$(\varepsilon/\text{k}) = 505 : \text{c}$	-	-	-	-
$\text{B}/\text{cm}^3 \text{ mol}^{-1} : \text{c}$	-18200	-1190	-679	-279

*c to calculated .The $\text{MP}_2/6\text{-}311++\text{G}^{**}$ method was used for $\text{CO}_2 : \text{H}_2\text{O}$ pair.

Table7. Total electronic energies, $E_e(r)$, of two molecules ($\text{O}_2 : \text{O}_2$ pair) and interaction energies between them, $E_{\text{int}}(r)$, as a function of $\text{O}_2 : \text{O}_2$ separation “r”

$r/\text{\AA}$	$E_e(r)/\text{hartree}$	$E_{\text{int}}(r)/\text{hartree}$	$E_{\text{int}}(r)/\text{J molecule}^{-1}$	$E_{\text{int}}(r)/\text{k}$
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 $E_{\text{int}(r)}$ (table 7) were represented by an equation like eq. (2) with $\sigma = 4.02\text{\AA}$ and $\varepsilon = 126\text{k}$. 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].

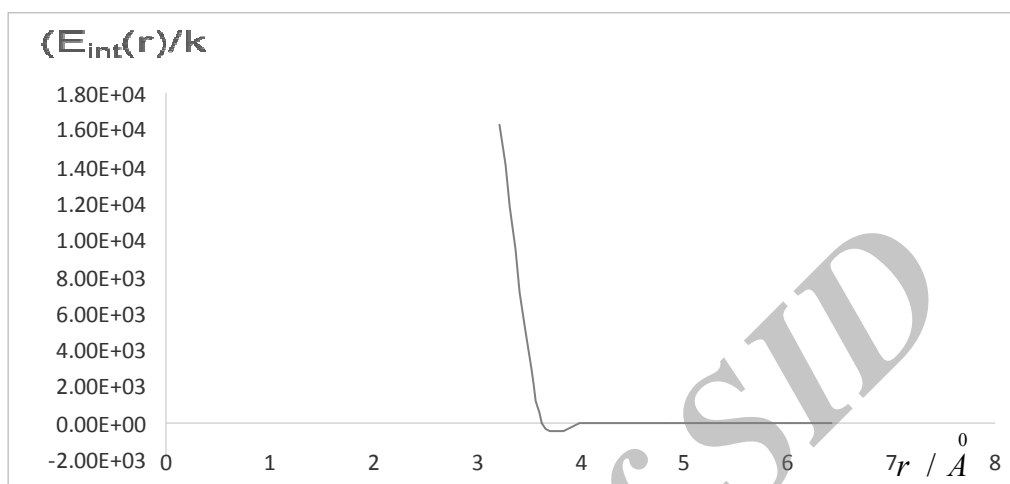


Fig.5. Plot of $E_{\text{int}(r)/k}$ versus separation r , for " $\text{O}_2 : \text{O}_2$ " system.

Table 8. Comparing the results of our calculations of σ and ε for $\text{O}_2 : \text{O}_2$ system with the literary values [2]

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

* l refers to literary and c to calculated. The B3lyp/6-31G method was used for $\text{O}_2 : \text{O}_2$ pair.

Table 9. Total electronic energies, $E_e(r)$, of two molecules ($\text{CO}_2 : \text{C O}_2$ pair) and interaction energies between them, $E_{\text{int}(r)}$, as a function of $\text{CO}_2 : \text{C O}_2$ separation " r "

$r / \text{\AA}$	$E_e(r)/\text{hartree}$	$E_{\text{int}(r)/\text{hartree}}$	$E_{\text{int}(r)/\text{J molecule}^{-1}}$	$E_{\text{int}(r)/k}$
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 " $E_{int}(r)/k$ " 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
$(\sigma/\text{\AA}) = 4.0:l^*$	-	-	-	-
$(\sigma/\text{\AA}) = 4.02:c^*$	-	-	-	-
$(\varepsilon/k) = 190:l$	-	-	-	-
$(\varepsilon/k) = 164:c$	-	-	-	-
$B/cm^3 mol^{-1}:l$	-	-149.7	-72.2	-72.2
$B/cm^3 mol^{-1}:c$	-503.3045	-89.3495	-45.7714	-5.8103

* l refers to literary and c to calculated. The MP₂/6-31+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 $\sigma = 4.02\text{\AA}$ and $\varepsilon = 164k$. 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 molecules. 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 $-\varepsilon$. The trend of ε for studied gas-pairs is as follow:

$$\sigma_{C_2H_4:O_2} > \sigma_{CO_2:H_2O} > \sigma_{CO:Cl_2} > \sigma_{O_2:O_2} \cong \sigma_{CO_2:CO_2}$$

Similarly :

$$\varepsilon_{CO_2:H_2O} > \varepsilon_{CO_2:CO_2} > \varepsilon_{O_2:O_2} \cong \varepsilon_{CO:Cl_2} > \varepsilon_{C_2H_4:O_2}$$

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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