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Estimating the Second virial Coefficients of some Real Gases NH_3: NH_3, CH_3NH_2: CH_3NH_2, $(CH_3)_2$ NH : $(CH_3)_2$ NH, (CH3)$_3$ N : $(CH_3)_3$ N, CH_3NH_2: (CH3)$_2$ NH, CH_3NH_2:, (CH_3)N and $(CH_3)_2$ NH : $(CH_3)_3$N pairs and related Thermodynamic aspects

M. Baghernejad [*]***, M. Aghaie*** [**]***, K. Zare*** [***] ***and H. Aghaie*** [***]
[*]*Ph.D. Student, Department of Chemistry, Tehran Science and Research Branch,*
Islamic Azad University, Tehran, Iran
[**] *Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran*
[***]*Department of Chemistry, Tehran Science and Research Branch, Islamic Azad University, Tehran, Iran*

(Corresponding author: Mehdi Baghernejad)
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ABSTRACT: Using the Gaussian 2003 software and MP_2/6-311++G(d,p) method for the NH_3:NH_3, CH_3NH_2: CH_3NH_2, $(CH_3)_2$ NH : $(CH_3)_2$ NH, $(CH_3)_3$ N : $(CH_3)_3$ N, CH_3NH_2: $(CH_3)_2$ NH, CH_3NH_2:, (CH_3)N and $(CH_3)_2$ NH : $(CH_3)_3$N gas pairs the optimized interaction energies between two molecules of each considered pair as a function of the distances between the centers of two considered molecules in the pair were evaluated and the results were interpreted according to the Lennard–Jones equation. In addition, the second virial coefficient of each gas pair was calculated upon the appropriate equations of statistical thermodynamics. The resultant virial 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 or unlike molecules. The simplified form of the Lennard – Jones potential, U(r), is as follow (Atkins, 1960; Baghernejad *et al.*, 2013; Menduna, Carlos, *et al* 2001), Vargas *et al.*, 2000)

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

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 $U(r) = -\varepsilon$, 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 $r = r_m$, $U(r) = -\varepsilon$ and $(\partial U/\partial r) = 0$ at $r = r_m$ (Atkins, 1960; Mac Quarrie 1976; Haar, (1971); Baghernejad, *et al.*, 2013). These conditions lead to the following equation (Atkins,1960; Aghaie, *et al.*, 2010; Haar, (1971); Baghernejad, *et al.*, 2013).

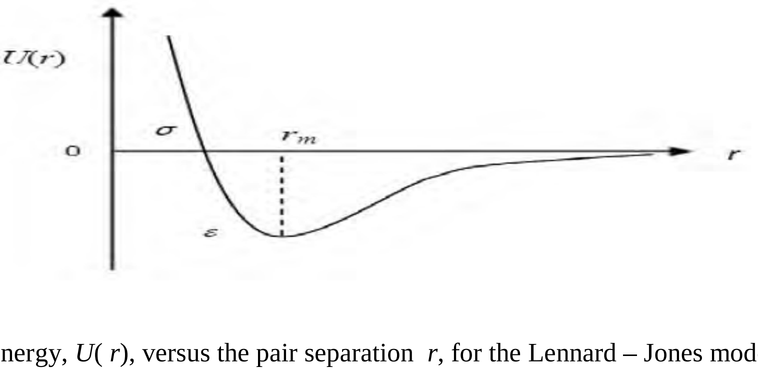

Fig.1. A plot of potential energy, $U(r)$, versus the pair separation r, for the Lennard – Jones model ($r_m = r_e$).

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

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 " ($U(r_c)$)

$$U\,(r_c) = U(r)\ (2.5\ \sigma)\ \approx\ -0.0163\varepsilon \qquad \ldots(3)$$

Equations 1-3 may be used for interpreting the interaction energy between tow molecules of a gas pair of unlike molecules (Atkins, 1960; Aghaie, *et al.*, 2010; Maity, *et al.*,1999, Baghernejad, *et al.*, 2013)

STATISTICAL VIRIAL EQUATION

State equations are very important in calculating the thermodynamic properties of pure and mixed fluids (Atkins, 1960; Aghaie, *et al.*, 2010; Maity, *et al.*1999, Baghernejad, *et al.*, 2013; Garret,1980). The results of such calculations are very helpfull in industrial processes and theoretical studies (Atkins, 1960; Aghaie, *et al.*, 2010; Maity, *et al.*1999, Baghernejad, *et al.*, 2013; Garret, 1980). We can find many state equations for pure and mixed fluids in the literature, but virial equation of state is more intrest fluids Virial equation of state can be represented as follow (Atkins, 1960; Aghaie, *et al.*, 2010; Baghernejad, *et al.*, 2013):

$$Z \;=\; \frac{PV}{nRT} = 1 + B^{'}(T\,)P \;+ C^{'}(T\,)P^{\,2} + \quad \ldots (4)$$

Or

$$Z \;= 1 + \frac{B\,(T\,)}{V_{m}} + \frac{C\,(T\,)}{V_{m}^{\;2}} + \ldots \qquad (5)$$

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 ”Q” is (Tsuchiya, *et al.*, 1996; Aghaie, *et al.*, 2010; *William et al.*,1964) :

$$\mathrm{P} \;=\; k\,T\;\left(\frac{\partial\ \ln \mathrm{Q}}{\partial\,V}\right)_{T\ ,N} \qquad \ldots (6)$$

Translational classical partition function for a sample of a real dilute gas, containing N molecules, can be written as follow(Aghaie, *et al.*, 2010; Mason, *et al.*, 1996):

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

where

$$\beta \;=\; \frac{1}{2}\int_{0}^{\infty}\left(1\;-\;e^{\;-\frac{\mathrm{U}\,(\,r\,)}{k\,T}}\right)\mathrm{d\,V} \qquad \ldots(8)$$

and U(r) is the pair potential energy as shown in equation (2). By means of equation (6) and (7), we obtain (Aghaie, *et al.*, 2010; Mac Quarrie, 1976; Ley-koo, *et al.*, 1951):

$$P \;=\; \frac{N\,k\,T}{V}\left(1 + \frac{B}{V}\right) \qquad \ldots(9)$$

Where B:

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

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 molecules of every pair : NH_3:NH_3, CH_3NH_2: CH_3NH_2 , $(CH_3)_2$ NH $(CH_3)_2$ NH, $(CH_3)_3$ N : $(CH_3)_3$ N pairs and two unlike molecules of every pair CH_3NH_2: $(CH_3)_2$ NH , CH_3NH_2: (CH_3)N and $(CH_3)_2$ NH : $(CH_3)_3$N pairs as a function of separation *r*, of two molecules were calculated by using the Gaussian 2003 software MP_2/6-311++G(d,p) method for NH_3:NH_3, CH_3NH_2: CH_3NH_2 , $(CH_3)_2$ NH $(CH_3)_2$ NH, $(CH_3)_3$ N : $(CH_3)_3$ N ,CH_3NH_2: $(CH_3)_2$ NH ,CH_3NH_2: (CH_3)N and $(CH_3)_2$ NH : $(CH_3)_3$N.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 :

$$U(\mathrm{r})\ \ \equiv E_{\,int\,(\,r\,)} = E_{e\,(\,r\,)} - \ E(\infty)\ \ldots(11)$$ where $E_{e(\infty)}$ refers to $E_{e(r)}$ at a long separation , while the $E_{int(r)}$ □ 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 (NH_3:NH_3, CH_3NH_2: CH_3NH_2, $(CH_3)_2$ NH $(CH_3)_2$ NH, $(CH_3)_3$ N : $(CH_3)_3$ N, CH_3NH_2: $(CH_3)_2$ NH, CH_3NH_2:, (CH_3)N and $(CH_3)_2$ NH : $(CH_3)_3$N pairs) are gathered in tables 1,3,5,7,9,11 and 13 and ploted in Fig. 2-8.

In addition, the second virial coefficient for each gas-pair was calculated upon equation (10) and the resultant values are given in Tables 2,4,6,8,10,12 and 14. In order to calculate equation (2) and then integral (10), we desine two programs by using matlab 2012 software.

Table1. Total electronic energies, $E_e(r)$ of two molecules of NH_3:NH_3 pair and interaction energies between them, $E_{int}(r)$, as a function of NH_3:NH_3 separation "r".

$r/\overset{0}{A}$	$E_e(r)$/hartree	$E_{int}(r)$/hartree	$E_{int}(r)$/J molecule^{-1}	$E_{int}(r)$/k
1.00	-111.3169	1.5134	6.59234E-18	4.78×10^{5}
1.34	112.0695	224.8998	9.79659E-16	7.10×10^{7}
1.68	-112.4563	0.374	1.62914E-18	1.18×10^{5}
2.02	-112.7001	0.1302	5.67149E-19	4.11×10^{4}
2.36	-112.7879	0.0424	1.84694E-19	1.34×10^{4}
2.70	-112.8175	0.0128	5.57565E-20	4.04×10^{3}
3.04	-112.8271	0.0032	1.39391E-20	1.01×10^{3}
3.38	-112.83	0.0003	1.30679E-21	94.7
3.72	-112.8308	-0.0005	-2.17799E-21	-1.58×10^{2}
4.06	-112.8309	-0.0006	-2.61359E-21	-1.89×10^{2}
4.4	-112.8307	-0.0004	-1.74239E-21	-1.26×10^{2}
4.74	-112.8306	-0.0003	-1.30679E-21	-94.7
5.08	-112.8304	-0.0001	-4.35598E-22	-31.6
5.42	-112.8303	0.0	0.0	0.00
5.76	-112.8303	0.0	0.0	0.00
6.10	-112.8303	0.0	0.0	0.00
6.44	-112.8303	0.0	0.0	0.00
6.78	-112.8303	0.0	0.0	0.00
7.12	-112.8303	0.0	0.0	0.00
7.46	-112.8303	0.0	0.0	0.00
7.80	-112.8303	0.0	0.0	0.00
8.14	-112.8303	0.0	0.0	0.00
8.48	-112.8303	0.0	0.0	0.00
8.82	-112.8303	0.0	0.0	0.00

Table 2: The results of our calculations of σ and ε for NH_3:NH_3 system.

	300K	350K	400K	450K	500K
(σ/Å) = 5.42:c*	-	-	-	-	-
(ε/k)= 189 :c	-	-	-	-	-
B/cm^{3}mol^{-1} :c	- 184	-122	-77.8	- 44.7	-19.1

* c refers to calculated .The MP2/ 6–311++G(d,p) method was used for NH3: NH3 pair.

The values of $E_{int(r)}$ wite respect two the NH_3:NH_3 pair (Table 1) were represented by an equation like eqn. (2) with σ = 5.42 Å and ε = 189 k(k represents the Boltsmann constant). Then, by means of these values and equation (10), we estimated the values of B at 300, 350, 400, 450 and 500K . that are comparable with those can be found in the literature (Atkins, 1960) The procedure was repeated for CH_3NH_2: CH_3NH_2, $(CH_3)_2$ NH : $(CH_3)_2$ NH, $(CH_3)_3$ N : $(CH_3)_3$ N, CH_3NH_2: $(CH_3)_2$ NH, CH_3NH_2:, (CH_3)N and $(CH_3)_2$ NH : $(CH_3)_3$N systems at 300, 350, 400, 450 and 500 K and the obtained results are given in Tables 3-14.

Generally, it may be concluded whatever the smaller size of gas molecules and the higher temperature, the agreement between the experimental results and the calculated values is better. (Baghernejad, *et al.*, 2013).

Table 3: Total electronic energies, $E_e(r)$ of two molecules of CH_3NH_2: CH_3NH_2 pair and interaction energies between them, $E_{int}(r)$, as a function of CH_3NH_2: CH_3NH_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
1.00	-173.3421	17.841	7.7715E-17	5.63×10^6
1.34	-186.2983	4.8848	2.12781E-17	1.54×10^6
1.68	-189.9616	1.2215	5.32083E-18	$3.86E\times10^5$
2.02	-190.7647	0.4184	1.82254E-18	1.32×10^5
2.36	-191.0344	0.1487	6.47734E-19	4.69×10^4
2.70	-191.1349	0.0482	2.09958E-19	1.52×10^4
3.04	-191.1705	0.0126	5.48853E-20	3.98×10^3
3.38	-191.1819	0.0012	5.22718E-21	3.79×10^2
3.72	-191.1849	-0.0018	-7.84076E-21	-5.68×10^2
4.06	-191.1852	-0.0021	-9.14756E-21	-6.63×10^2
4.40	-191.1848	-0.0017	-7.40517E-21	-5.37×10^2
4.74	-191.1843	-0.0012	-5.22718E-21	-3.79×10^2
5.08	-191.184	-0.0009	-3.92038E-21	-2.84×10^2
5.42	-191.1837	-0.0006	-2.61359E-21	-1.89×10^2
5.76	-191.1834	-0.0003	-1.30679E-21	-94.7
6.10	-191.1833	-0.0002	-8.71196E-22	-63.1
6.44	-191.1832	-0.0001	-4.35598E-22	-31.6
6.78	-191.1831	0.0	0.0	0.00
7.12	-191.1831	0.0	0.0	0.00
7.46	-191.1831	0.0	0.0	0.00
7.8	-191.1831	0.0	0.0	0.00
8.14	-191.1831	0.0	0.0	0.00
8.48	-191.1831	0.0	0.0	0.00
8.82	-191.1831	0.0	0.0	0.00
9.16	-191.1831	0.0	0.0	0.00
9.50	-191.1831	0.0	0.0	0.00
9.84	-191.1831	0.0	0.0	0.00

Table 4: The results of our calculations of σ and ε for CH_3NH_2: CH3NH$_2$ system.

	300K	350K	400K	450K	500K
(σ/Å) = 6.78:c*	-	-	-	-	-
(ε/k)= 663 :c	-	-	-	-	-
B/cm^{3}mol^{-1} :	-4010	-2940	-2280	-1830	-1510

* c refers to calculated .The MP2/ 6–311++G(d,p) method was used for CH_3NH_2: CH_3NH_2 pair.

Table 5: Total electronic energies, $E_e(r)$ of two molecules of $(CH_3)_2NH : (CH_3)_2NH$ pair and interaction energies between them, $E_{int}(r)$, as a function of $(CH_3)_2NH : (CH_3)_2NH$ separation "r".

$r/\overset{0}{A}$	$E_e(r)$/hartree	$E_{int}(r)$/hartree	$E_{int}(r)$/J molecule^{-1}	$E_{int}(r)$/k
1.00	-205.154	64.3952	2.80504E-16	2.03×10^{7}
1.34	-259.4285	10.1207	4.40856E-17	3.19×10^{6}
1.68	-267.3345	2.2147	9.64719E-18	6.99×10^{5}
2.02	-268.8165	0.7327	3.19163E-18	2.31×10^{5}
2.36	-269.286	0.2632	1.14649E-18	8.31×10^{4}
2.70	-269.4623	0.0869	3.78535E-19	2.74×10^{4}
3.04	-269.5259	0.0233	1.01494E-19	7.35×10^{3}
3.38	-269.5466	0.0026	1.13255E-20	8.21×10^{2}
3.72	-269.5522	-0.003	-1.30679E-20	-9.47×10^{2}
4.06	-269.5521	-0.0029	-1.26323E-20	-9.15×10^{2}
4.40	-269.5515	-0.0023	-1.00188E-20	-7.26×10^{2}
4.74	-269.5508	-0.0016	-6.96957E-21	-5.05×10^{2}
5.08	-269.5503	-0.0011	-4.79158E-21	-3.47×10^{2}
5.42	-269.55	-0.0008	-3.48478E-21	-2.53×10^{2}
5.76	-269.5497	-0.0005	-2.17799E-21	-1.58×10^{2}
6.10	-269.5495	-0.0003	-1.30679E-21	-9.47×10^{1}
6.44	-269.5494	-0.0002	-8.71196E-22	-6.31×10^{1}
6.78	-269.5493	-0.0001	-4.35598E-22	-3.16×10^{1}
7.12	-269.5492	0.0	0.0	0.00
7.46	-269.5492	0.0	0.0	0.00
7.80	-269.5492	0.0	0.0	0.00
8.14	-269.5492	0.0	0.0	0.00
8.48	-269.5492	0.0	0.0	0.00
8.82	-269.5492	0.0	0.0	0.00
9.16	-269.5492	0.0	0.0	0.00
9.50	-269.5492	0.0	0.0	0.00
9.84	-269.5492	0.0	0.0	0.00

Table 6 : The results of our calculations of σ and ε for $(CH_3)_2NH : (CH_3)_2NH$ system.

	300K	350K	400K	450K	500K
$(\sigma/\text{Å})$ = 7.12:c*	-	-	-	-	-
$(\mathcal{E}/k)$= 947:c	-	-	-	-	-
B/cm^{3}mol^{-1} :c	-1.09×10^{4}	-7.42×10^{3}	-5.5×10^{3}	-4.3×10^{3}	-3.49×10^{3}

* c refers to calculated. The MP2/ 6–311++G(d,p) method was used for $(CH_3)_2NH : (CH_3)_2NH$ pair.

Table 7: Total electronic energies, $E_e(r)$ of two molecules of $(CH_3)_3N : (CH_3)_3N$ pair and interaction energies between them, $E_{int}(r)$,as a function of $(CH_3)_3N : (CH_3)_3N$ separation "r".

$r/\overset{0}{A}$	**$E_e(r)$/hartree**	**$E_{int}(r)$/hartree**	**$E_{int}(r)$/J molecule^{-1}**	**$E_{int}(r)$/k**
1.00	-330.2558	17.6718	7.6978E-17	5.58×10^6
1.34	-337.1758	10.7518	4.68346E-17	3.39×10^6
1.68	-344.9663	2.9613	1.28994E-17	9.35×10^5
2.02	-346.8296	1.098	4.78287E-18	3.47×10^5
2.36	-347.5007	0.4269	1.85957E-18	1.35×10^5
2.70	-347.7754	0.1522	6.6298E-19	4.80×10^4
3.04	-347.8807	0.0469	2.04295E-19	1.48×10^4
3.38	-347.9175	0.0101	4.39954E-20	3.19×10^3
3.72	-347.9289	-0.0013	-5.66277E-21	-4.10×10^2
4.06	-347.9316	-0.004	-1.74239E-20	-1.26×10^3
4.40	-347.9315	-0.0039	-1.69883E-20	-1.23×10^3
4.74	-347.9307	-0.0031	-1.35035E-20	-9.79×10^2
5.08	-347.9299	-0.0023	-1.00188E-20	-7.26×10^2
5.42	-347.9292	-0.0016	-6.96957E-21	-5.05×10^2
5.76	-347.9287	-0.0011	-4.79158E-21	-3.47×10^2
6.10	-347.9284	-0.0008	-3.48478E-21	-2.53×10^2
6.44	-347.9281	-0.0005	-2.17799E-21	-1.58×10^2
6.78	-347.928	-0.0004	-1.74239E-21	-1.26×10^2
7.12	-347.9278	-0.0002	-8.71196E-22	-6.31×10^1
7.46	-347.9277	-0.0001	-4.35598E-22	-3.16×10^1
7.80	-347.9277	-0.0001	-4.35598E-22	-3.16×10^1
8.14	-347.9276	0.0	0.0	0.00
8.48	-347.9276	0.0	0.0	0.00
8.82	-347.9276	0.0	0.0	0.00
9.16	-347.9276	0.0	0.0	0.00
9.50	-347.9276	0.0	0.0	0.00
9.84	-347.9276	0.0	0.0	0.00
10.18	-347.9276	0.0	0.0	0.00
10.52	-347.9276	0.0	0.0	0.00

Table 8: The results of our calculations of σ and ε for $(CH_3)_3N : (CH_3)_3N$ system.

	300K	**350K**	**400K**	**450K**	**500K**
$(\sigma/\AA)$ = 8.14:c*	-	-	-	-	-
(ε/k)= 1260:c	-	-	-	-	-
B/cm^{3}mol^{-1} :	-4.3×10^4	-2.62×10^4	-1.81×10^4	-4.80×10^4	-1.06×10^4

* c refers to calculated .The MP2/ 6–311++G(d,p) method was used for $(CH_3)_3N : (CH_3)_3N$ pair.

Table 9: Total electronic energies, $E_e(r)$ of two molecules $CH_3NH_2:(CH_3)_2NH$ pair and interaction energies between them, $E_{int}(r)$, as a function of $CH_3NH_2:(CH_3)_2NH$ separation "r".

$r/\overset{0}{A}$	$E_e(r)$/hartree	$E_{int}(r)$/hartree	$E_{int}(r)$/J molecule^{-1}	$E_{int}(r)$/k
1.00	-228.5095	1.3311	5.79824E-18	4.2×10^5
1.34	-228.9509	0.8897	3.87552E-18	2.81×10^5
1.68	-229.2816	0.559	2.43499E-18	$1.76E\times10^5$
2.02	-229.6488	0.1918	8.35477E-19	6.05×10^4
2.36	-229.7794	0.0612	2.66586E-19	1.93×10^4
2.7	-229.822	0.0186	8.10212E-20	5.87×10^3
3.04	-229.8356	0.005	2.17799E-20	1.58×10^3
3.38	-229.8396	0.001	4.35598E-21	3.16×10^2
3.72	-229.8469	-0.0063	-2.74427E-20	-1.99×10^3
4.06	-229.8408	-0.0002	-8.71196E-22	-63.1
4.4	-229.8407	-0.0001	-4.35598E-22	-63.1
4.74	-229.8406	0.0	0.0	0.00
5.08	-229.8406	0.0	0.0	0.00
5.42	-229.8406	0.0	0.0	0.00
5.76	-229.8406	0.0	0.0	0.00
6.1	-229.8406	0.0	0.0	0.00
6.44	-229.8406	0.0	0.0	0.00
6.78	-229.8406	0.0	0.0	0.00
7.12	-229.8406	0.0	0.0	0.00
7.46	-229.8406	0.0	0.0	0.00
7.8	-229.8406	0.0	0.0	0.00
8.14	-229.8406	0.0	0.0	0.00

Table 10. The results of our calculations of σ and ε for $CH_3NH_2:(CH_3)_2NH$ system.

	300K	350K	400K	450K	500K
(σ/Å) = 4.74:c*	-	-	-	-	-
(ε/k)= 1990:c	-	-	-	-	-
B/cm^{3}mol^{-1} :	-6.07×10^4	-2.65×10^4	-1.45×10^4	-9.09×10^3	-6.29×10^3

* c refers to calculated. The MP_2/ 6–311++G(d,p) method was used for CH_3NH_2: $(CH3)_2NH$ pair.

Table 11: Total electronic energies, $E_e(r)$ of two molecules of CH_3NH_2: $(CH_3)_3N$ pair and interaction energies between them, $E_{int}(r)$ as a function of CH_3NH_2: $(CH_3)_3N$ separation “r”

$r/\overset{0}{A}$	**$E_e(r)$/hartree**	**$E_{int}(r)$/hartree**	**$E_{int}(r)$/J $molecule^{-1}$**	**$E_{int}(r)$/k**
1.00	-251.3644	17.4259	7.59069E-17	5.50×10^{6}
1.34	-262.7544	6.0359	2.62923E-17	1.91×10^{6}
1.68	-262.2086	6.5817	2.86698E-17	2.08×10^{6}
2.02	-266.3065	2.4838	1.08194E-17	7.84×10^{5}
2.36	-268.2104	0.5799	2.52603E-18	1.83×10^{5}
2.70	-268.6223	0.168	7.31805E-19	5.30×10^{4}
3.04	-268.7436	0.0467	2.03424E-19	1.47×10^{4}
3.38	-268.7777	0.0126	5.48853E-20	3.98×10^{3}
3.72	-268.78858	0.00172	7.49229E-21	5.43×10^{2}
4.06	-268.7913	-0.001	-4.35598E-21	-3.16×10^{2}
4.40	-268.7915	-0.0012	-5.22718E-21	-3.79×10^{2}
4.74	-268.7912	-0.0009	-3.92038E-21	-2.84×10^{2}
5.08	-268.7908	-0.0005	-2.17799E-21	-1.58×10^{2}
5.42	-268.7906	-0.0003	-1.30679E-21	-94.7
5.76	-268.7904	-1E-04	-4.35598E-22	-31.6
6.10	-268.7903	0.0	0.0	0.0
6.44	-268.7903	0.0	0.0	0.0
6.78	-268.7903	0.0	0.0	0.0
7.12	-268.7903	0.0	0.0	0.0
7.46	-268.7903	0.0	0.0	0.0
7.80	-268.7903	0.0	0.0	0.0
8.14	-268.7903	0.0	0.0	0.0

Table 12 . The results of our calculations of σ and ε for CH_3NH_2: $(CH_3)_3N$ system.

	300K	**350K**	**400K**	**450K**	**500K**
(σ/Å) = 6.1: c*	-	-	-	-	-
($\mathcal{E}$/k)= 379:c	-	-	-	-	-
B/cm^3mol^{-1} :	-1.01×10^{3}	-7.53×10^{2}	-5.80×10^{2}	-4.55×10^{2}	-3.60×10^{2}

* c refers to calculated .The MP2/ 6–311++G(d,p) method was used for CH_3NH_2 : $(CH3)_3N$ pair.

Table 13. Total electronic energies, $E_e(r)$ of two molecules of $(CH_3)_2$ NH : $(CH_3)_3$ N pair and interaction energies between them, $E_{int}(r)$ as a function of $CH_3)_2$ NH : $(CH_3)_3$ N separation “r”.

$r/\overset{0}{A}$	$E_e(r)$/hartree	$E_{int}(r)$/hartree	$E_{int}(r)$/J molecule^{-1}	$E_{int}(r)$/k
1.00	-305.7342	2.2436	9.77308E-18	7.08×10^5
1.34	-306.4113	1.5665	6.82364E-18	4.94×10^5
1.68	-306.5768	1.401	6.10273E-18	4.42×10^5
2.02	-306.854	1.1238	4.89525E-18	3.55×10^5
2.36	-307.5517	0.4261	1.85608E-18	1.34×10^5
2.70	-307.8106	0.1672	7.2832E-19	5.28×10^4
3.04	-307.9164	0.0614	2.67457E-19	1.94×10^4
3.38	-307.9605	0.0173	7.53585E-20	5.46×10^3
3.72	-307.9748	0.003	1.30679E-20	9.47×10^2
4.06	-307.979	-0.0012	-5.22718E-21	-3.79×10^2
4.40	-307.9798	-0.002	-8.71196E-21	-6.31×10^2
4.74	-307.9795	-0.0017	-7.40517E-21	-5.37×10^2
5.08	-307.9791	-0.0013	-5.66277E-21	-4.10×10^2
5.42	-307.9787	-0.0009	-3.92038E-21	-2.84×10^2
5.76	-307.9784	-0.0006	-2.61359E-21	-1.89×10^2
6.1	-307.9782	-0.0004	-1.74239E-21	-1.26×10^2
6.44	-307.978	-0.0002	-8.71196E-22	-63.1
6.78	-307.9779	-0.0001	-4.35598E-22	-31.6
7.12	-307.9778	0.0	0.0	0.00
7.46	-307.9778	0.0	0.0	0.00
7.8	-307.9778	0.0	0.0	0.00
8.14	-307.9778	0.0	0.0	0.00

Table 14 : The results of our calculations of σ and ε for $CH_3)_2$ NH : $(CH_3)_3$ N system.

	300K	350K	400K	450K	500K
$(\sigma/\text{Å})$ = 7.12:c*	-	-	-	-	-
(ε/k)= 379:c	-	-	-	-	-
B/cm^{3}mol^{-1} :	-1.65×10^3	-1.24×10^3	-9.7×10^2	-7.71×10^2	-6.2×10^2

* c refers to calculated. The MP2/ 6–311++G(d,p) method was used for $(CH_3)_2$NH: $(CH_3)_3$N pair.

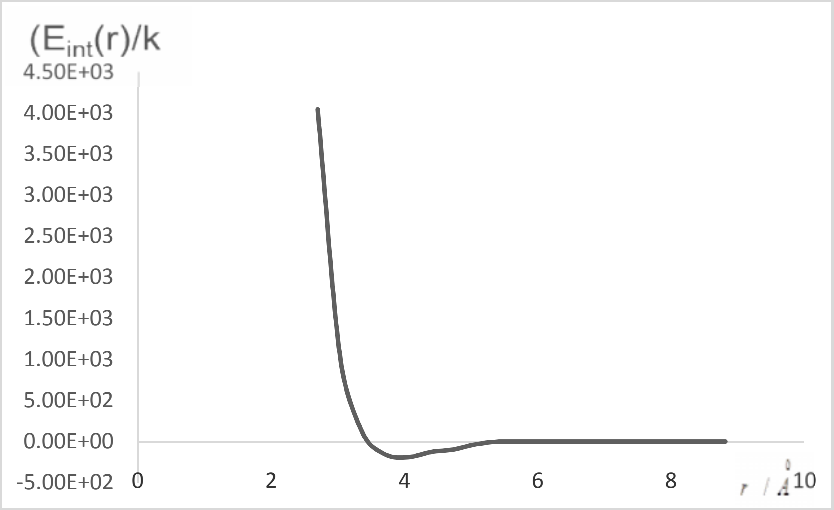

Fig. 2. Plot of" Eint(r)/k " versus separation r, for "NH_3: NH_3" system.

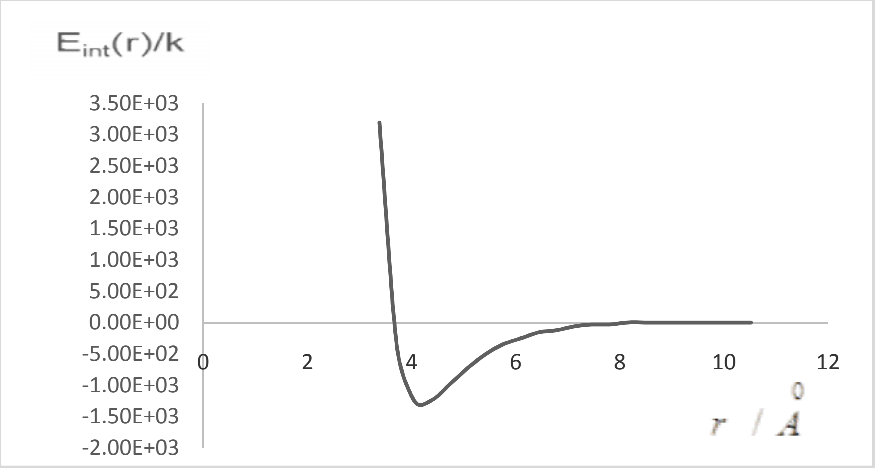

Fig. 3. Plot of" $E_{int}(r)/k$ " versus separation r, for "CH_3NH_2: CH_3NH_2 " system.

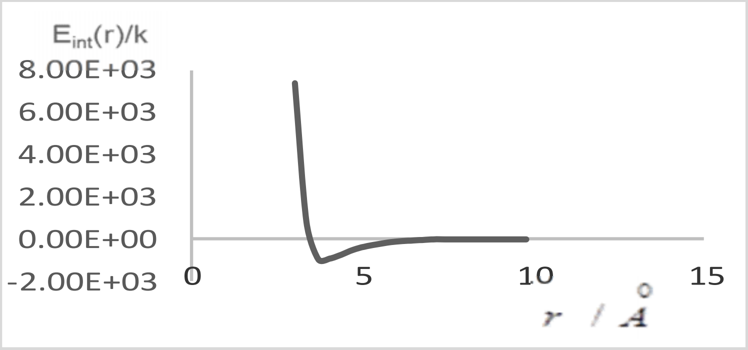

Fig. 4. Plot of" $E_{int}(r)/k$ " versus separation r, for "$(CH_3)_2NH$: $(CH_3)_2NH$ " system.

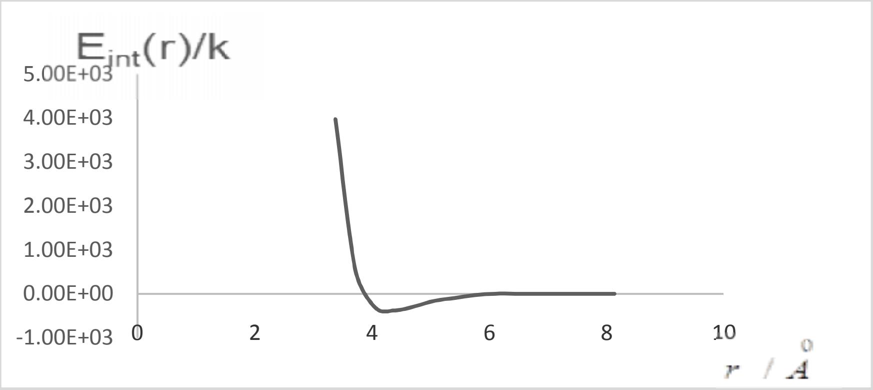

Fig. 5. Plot of" Eint(r)/k " versus separation r, for "$(CH_3)_3$ N : $(CH3)_3$ N " system.

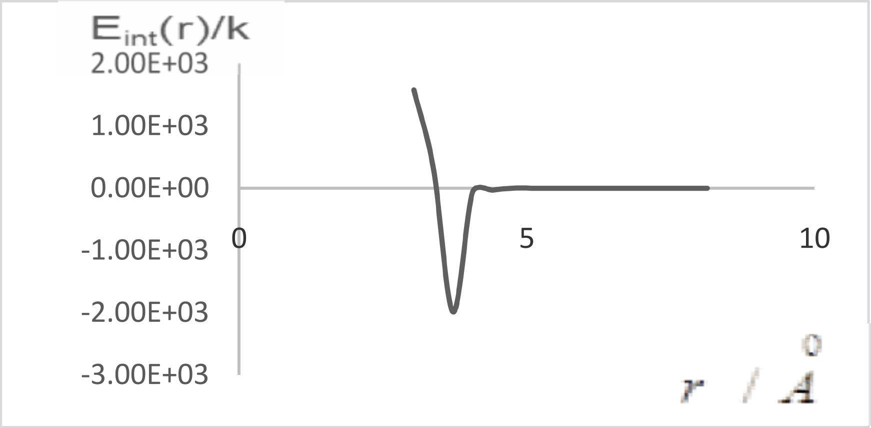

Fig. 6. Plot of" Eint(r)/k " versus separation r, for "$CH3NH_2$: $(CH3)_2$ NH" system.

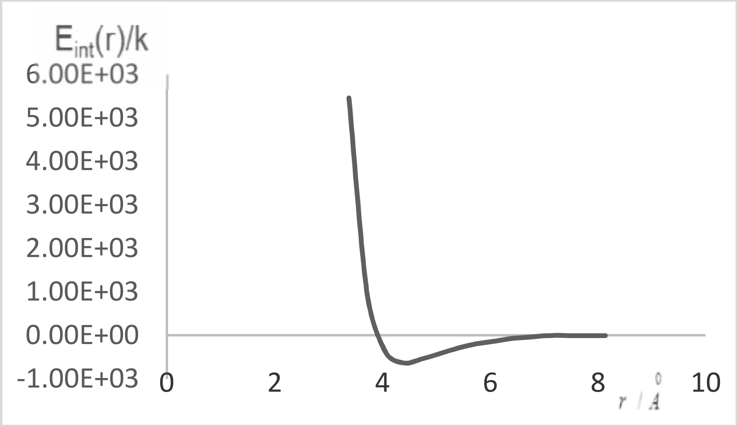

Fig. 7. Plot of" Eint(r)/k " versus separation, r, for "$CH3NH_2$: $(CH3)_3$ N" system.

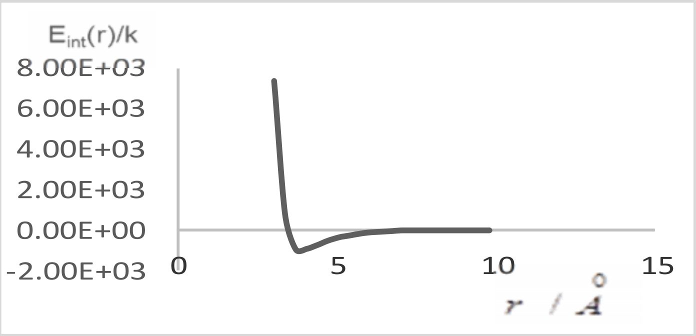

Fig. 8. Plot of" $E_{int}(r)/k$ " versus separation , r, for "$(CH3)_2$ NH :$(CH3)_3$ N" system.

CONCLUSION

The results of this study showed that the interaction energy between two like or unlike molecules of a given gas-pair is almost insignificant (except in fairly 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 the interaction energies versus the separations of two considered molecules has a well with a depth of - ε. The trend of ε for studied gas-pairs is as follow:

$\sigma\ (CH_3)_3N : (CH_3)_3N > \sigma\ (CH_3)_2NH : (CH_3)_3N = \sigma\ (CH_3)_2NH : (CH_3)_2NH > \sigma\ CH_3NH_2 : CH_3NH_2 > \sigma\ CH_3NH_2 : (CH_3)_3N > \sigma\ NH_3 : NH_3 > \sigma\ CH_3NH_2 : (CH_3)_2NH$

Similarly :

$\varepsilon\ CH_3NH_2 : (CH3)_2NH > \varepsilon\ (CH_3)_3N : (CH_3)_3N > \varepsilon\ CH_3)_2NH : (CH_3)_2NH > \varepsilon\ CH_3NH_2 : CH_3NH_2 > \varepsilon\ (CH_3)_2NH : (CH_3)_3N = \varepsilon\ CH_3NH_2 : (CH_3)_3N > \varepsilon\ NH_3 : NH_3$

The intraction energies of each studied gas pair, U(r), can be represented by an equation like that of Lennard jones equation.

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

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