

EQUILIBRIUM PROPERTIES OF GASES AND GASEOUS MIXTURES

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The scope of the Lennard-Jones type (18-6) potential recently suggested by Saxena and Joshi has been extended to include the theoretical description of one more sensitive property, *viz.* the limiting value of the pressure derivative of the specific heat at a constant temperature. Results have been applied to a few more cases of pure gases and the use of this potential to explain the behaviour of binary mixtures is also illustrated. Detailed comparison of results of theory with those of experiment for a number of properties and gas pairs as functions of temperature and composition indicates that for complicated molecules at high temperatures this potential may prove to be superior to the L-J (12-6) potential.

INTRODUCTION

The correlation of the various macroscopic properties of gases and gaseous mixtures within the framework of a rigorous kinetic theory of non-uniform gases (Chapman and Cowling 1939) on the assumption of a central force field is well known (Hirschfelder *et al.* 1954). The spherically symmetric potentials which are used mostly for describing the behaviour of gases are: the Lennard-Jones (12-6), the modified Buckingham exp-six and the Morse potentials. The first is a two-parameter potential while the other two involve three parameters. Many potentials have been suggested on the basis that the repulsive part of the potential may be much steeper than that given by the inverse twelfth power (Hamann and Lambert 1954; Pollara and Funke 1959). Saxena and Joshi (1962*a*, 1962*b*), who gave a critical account of these potentials, suggested the following Lennard-Jones type (18-6) potential:

$$\phi(r) = 4\epsilon_0[(\sigma_0/r)^{18} - (\sigma_0/r)^6]. \quad \dots \dots \dots (1)$$

Here $\phi(r)$ is the potential energy of interaction between two molecules which are separated by a distance r . Now if ϵ be the depth of the potential energy minimum and σ its position, we have

$$\epsilon = 8\epsilon_0/3\sqrt{3} \quad \text{and} \quad \sigma = (3)^{1/3}\sigma_0. \quad \dots \dots \dots (2)$$

Saxena and Joshi (1962*b*) computed the second virial coefficient, B , and the zero pressure Joule-Thomson coefficient, μ° , for a few gases composed of

non-polar quasi-spherical molecules and found that the reproduction on the basis of the potential given by Eqn. (1) was better than that given by the conventional (12-6) potential. Here we have extended this work in the following directions:

- (a) We have recalculated the values of the reduced second virial and Joule-Thomson coefficients superseding the earlier tabulations inasmuch as that results which are correct to more significant places have been reported and further they have been close-spaced, so as to facilitate accurate interpolation.
- (b) A new function has been tabulated which enables us to calculate the quantity, $\lim_{p \rightarrow 0} \left(\frac{\partial c_p}{\partial p} \right)_T$, which is the limiting value of the pressure derivative of the specific heat, C_p , when the temperature T is constant.
- (c) On the basis of these tabulations four new gases, *viz.* N_2 , CO_2 , N_2O and C_2H_4 , have been interpreted which were not considered by Saxena and Joshi (1962*b*) in their work.
- (d) Mixture data have been considered. Conventional combination rules for determining the unlike interactions from the like interactions have been exploited and light on their appropriateness has been thrown.

THEORY AND FORMULAE

As shown by Saxena and Joshi (1962*b*), B can be written for the potential of Eqn. (1) in the form

$$B = (2/3)\pi N\sigma_0^3 F(y), \quad \dots \dots \dots (3)$$

where

$$F(y) = y^{-2} \{H_{18}(y) - (1/3)H_6(y)\}, \quad \dots \dots \dots (4)$$

$$y = 2(\epsilon_0/kT)^{\frac{1}{2}}, \quad \dots \dots \dots (5)$$

and

$$H_k(y) = y^{\frac{39-K}{9}} \sum_{l=0}^{\infty} \frac{1}{l!} y^{\frac{4l}{3}} \Gamma\left(\frac{K+6l-3}{18}\right). \quad \dots \dots (6)$$

Further μ^0 is given by

$$\mu^0 = (b_0/c_p^0) [F_1(y) - F(y)]. \quad \dots \dots \dots (7)$$

Here c_p^0 is the zero-pressure molar specific heat,

$$b_0 = (2/3)\pi N\sigma_0^3, \quad \dots \dots \dots (8)$$

and

$$F_1(y) = -\frac{y}{2} \frac{dF(y)}{dy}. \quad \dots \dots \dots (9)$$

We write Eqn. (7) in the following form in terms of the isothermal Joule-Thomson coefficient, ϕ^0 , as it facilitates comparison with experiment sometimes:

$$\phi^0 = \mu^0 c_p^0 = b_0 [F_1(y) - F(y)]. \quad \dots \quad (10)$$

For a binary mixture, the second virial coefficient, B_{mix} , is given by

$$B_{\text{mix}} = (1-x)^2 B_{11} + 2x(1-x) B_{12} + x^2 B_{22}, \quad \dots \quad (11)$$

where x is the mole fraction of the component 2 whose second virial coefficient is B_{22} , B_{11} is the value of B for the pure component 1 and B_{12} is given by

$$B_{12} = (2/3)\pi N(\sigma_0)_{12}^3 F(y_{12}). \quad \dots \quad (12)$$

Here $(\sigma_0)_{12}$ is the value of σ_0 for the dissimilar molecules and y_{12} is defined as

$$y_{12} = 2[(\epsilon_0)_{12}/kT]^{1/2} \quad \dots \quad (13)$$

where $(\epsilon_0)_{12}$ is the value of ϵ_0 corresponding to the molecules of components 1 and 2.

Similarly, for the zero-pressure isothermal Joule-Thomson coefficient of a binary mixture, ϕ_{mix}^0 , we have

$$\phi_{\text{mix}}^0 = (1-x)^2 \phi_{11}^0 + 2x(1-x) \phi_{12}^0 + x^2 \phi_{22}^0, \quad \dots \quad (14)$$

where

$$\phi_{12}^0 = (b_0)_{12} [F_1(y_{12}) - F(y_{12})], \quad \dots \quad (15)$$

$$(b_0)_{12} = (2/3)\pi N(\sigma_0)_{12}^3. \quad \dots \quad (16)$$

and ϕ_{11}^0 and ϕ_{22}^0 are the values of ϕ^0 for the pure components 1 and 2 respectively.

The second derivative of $F(y)$, $F_1(y)$ and $\lim_{p \rightarrow 0} \left(\frac{\partial c_p}{\partial p} \right)_T$ are connected by the relation

$$\lim_{p \rightarrow 0} \left(\frac{\partial c_p}{\partial p} \right)_T = -0.02421 (b_0/T) F_2(y). \quad \dots \quad (17)$$

Here,

$$F_2(y) = -\frac{3}{4} F_1(y) + \frac{y^2}{4} \frac{d^2 F(y)}{dy^2}, \quad \dots \quad (18)$$

and c_p and p are in cal/mole-deg and in atmospheres respectively.

The computed values of $F(y)$, $F_1(y)$ and $F_2(y)$ are given in Table I.

POTENTIAL PARAMETERS FOR LIKE AND UNLIKE INTERACTIONS

The two potential parameters for pure gases, *viz.* ϵ_0 and σ_0 , were determined by Saxena and Joshi (1962b) for seven non-polar gases on the basis of B data as a function of temperature. They employed either the familiar graphical method of translation along two axes or a numerical method. Here, we have utilized the latter method and evaluated the two parameters for the

TABLE I
F functions for evaluating B , μ^0 and $\lim_{p \rightarrow 0} \left(\frac{\partial c_p}{\partial p} \right)_T$

y	$F(y)$	$F_1(y)$	$F_2(y)$
0.04	0.381652	—	—
0.08	0.472476	—0.0703449	—
0.12	0.529375	—0.0700815	+0.0667633
0.16	0.568381	—0.0648403	+0.0502712
0.20	0.595391	—0.0553398	+0.0268806
0.24	0.613318	—0.0420661	—0.0030169
0.28	0.623847	—0.0252785	—0.0393236
0.32	0.628042	—0.0051880	—0.0817153
0.36	0.626624	0.0182239	—0.130911
0.40	0.620081	0.0448683	—0.186071
0.44	0.608779	0.0747119	—0.247749
0.48	0.592985	0.107822	—0.316539
0.52	0.572886	0.144347	—0.392858
0.56	0.548611	0.184278	—0.475925
0.60	0.520261	0.227716	—0.567248
0.64	0.487896	0.274933	—0.667779
0.68	0.451540	0.325883	—0.775767
0.72	0.411209	0.380954	—0.895513
0.76	0.366877	0.440265	—1.02374
0.80	0.318518	0.503739	—1.16174
0.84	0.266093	0.572204	—1.31730
0.88	0.209507	0.645585	—1.48001
0.92	0.148691	0.723981	—1.65665
0.96	0.0835566	0.807998	—1.85210
1.00	0.0139761	0.898218	—2.06398
1.04	—0.0601899	0.994529	—2.29217
1.06	—0.0990317	1.04484	—2.40427
1.08	—0.139068	1.09784	—2.55202
1.10	—0.180342	1.15164	—2.65559
1.12	—0.222848	1.20811	—2.82091
1.14	—0.266637	1.26639	—2.94712
1.16	—0.311716	1.32590	—3.08061
1.18	—0.358096	1.38790	—3.25422
1.20	—0.405822	1.45230	—3.41805
1.22	—0.454925	1.51895	—3.58457
1.24	—0.505432	1.58764	—3.75465
1.26	—0.557369	1.65913	—3.94755
1.28	—0.610775	1.73236	—4.12413
1.30	—0.665674	1.80975	—4.36334
1.32	—0.722128	1.88804	—4.50857
1.34	—0.780128	1.96974	—4.76938
1.36	—0.839743	2.05499	—5.00260
1.38	—0.901017	2.14308	—5.21325
1.40	—0.963970	2.23224	—5.41749
1.42	—1.02814	2.32644	—5.77628
1.44	—1.09508	2.42739	—6.07973
1.46	—1.16341	2.52571	—6.31908
1.48	—1.23353	2.62878	—6.60245
1.50	—1.30559	2.74300	—7.04184

TABLE I—concl.
 Functions for evaluating B , μ^0 and $\lim_{p \rightarrow 0} \left(\frac{\partial c_p}{\partial p} \right)_T$

y	$F(y)$	$F_1(y)$	$F_2(y)$
1.52	— 1.37971	2.85031	— 7.40622
1.54	— 1.45575	2.97066	— 7.72929
1.56	— 1.53397	3.09058	— 7.99497
1.58	— 1.61429	3.21602	— 8.29429
1.60	— 1.69683	3.34683	— 8.68425
1.62	— 1.78166	3.48339	— 9.10017
1.64	— 1.86885	3.62283	— 9.45744
1.66	— 1.95844	3.77062	— 10.0104
1.68	— 2.05055	3.92031	— 10.3405
1.70	— 2.14520	4.07993	— 11.0194
1.72	— 2.24255	4.24546	— 11.3790
1.74	— 2.34261	4.40775	— 11.7049
1.76	— 2.44539	4.59074	— 12.3690
1.78	— 2.55124	4.77685	— 13.1060
1.80	— 2.66010	4.96845	— 13.6694
1.82	— 2.77203	5.15940	— 14.1672
1.84	— 2.88709	5.37750	— 15.5392
1.86	— 3.00564	5.58221	— 16.1877
1.88	— 3.12754	5.81605	— 16.6544
1.90	— 3.25302	6.04773	— 17.3915
1.92	— 3.38219	6.29148	— 18.2673
1.94	— 3.51519	6.54405	— 19.0701
1.96	— 3.65213	6.81150	— 20.1354
1.98	— 3.79319	7.08296	— 20.7971
2.00	— 3.93842	7.37116	— 22.1818
2.02	— 4.08809	7.67356	— 23.2203
2.04	— 4.24235	7.98532	— 24.2330
2.06	— 4.40133	8.31364	— 25.6168
2.08	— 4.56526	8.65605	— 26.7745
2.10	— 4.73429	9.00957	— 27.9640
2.12	— 4.90857	9.38188	— 29.5059
2.14	— 5.08834	9.76290	— 30.8352
2.16	— 5.27379	10.1831	— 32.2130
2.18	— 5.46539	10.6047	— 33.7780
2.20	— 5.66304	11.0413	— 35.7531
2.22	— 5.86704	11.5070	— 38.0009
2.26	— 6.29541	12.4976	— 41.8104
2.30	— 6.75276	13.5948	— 46.5461
2.34	— 7.24172	14.7819	— 51.0709
2.38	— 7.76454	16.0885	— 56.9605
2.42	— 8.32447	17.5363	— 63.4522
2.46	— 8.92499	19.1216	— 70.2352
2.50	— 9.56951	20.8751	— 78.2584
2.54	—10.2621	22.7879	— 86.5902
2.58	—11.0068	24.9163	— 97.2811
2.62	—11.8091	27.2799	—108.581
2.66	—12.6745	29.8859	—120.809
2.70	—13.6087	32.7566	—134.879
2.74	—14.6183	35.9639	—151.877
2.78	—15.7114	39.5316	—170.061

gases N_2 , N_2O , CO_2 and C_2H_4 . All these values, along with the ones earlier reported by Saxena and Joshi (1962*b*) and those relevant for our work, are listed in Tables II and III.

It is now common to use a set of relations for determining the potential

TABLE II
Values of ϵ/k for the modified Lennard-Jones (18-6) potential
(ϵ/k values expressed in $^{\circ}K$)

	Neopentane	Sulphur hexafluoride	Ethylene	Ethane	Methane	Carbon dioxide	Nitrous oxide	Nitrogen
Neopentane ..	337	--	--	--	259	--	--	--
Sulphur hexafluoride ..		243	--	--	220	--	--	--
Ethylene ..			271	--	--	262	269	--
Ethane ..				291	241	272	--	193
Methane ..					199	224	--	--
Carbon dioxide ..						253	260	180
Nitrous oxide ..							267	184
Nitrogen ..								127

TABLE VI

Comparison of the experimental and calculated (18-6) and (12-6) *B* values
(*B* values expressed in cc/mole.)

Gas	T °K	Exp.	Calc.				Ref.
			(18-6)	Dev.	(12-6)	Dev.	
CO ₂	273	-145.0	-146.9	-1.9	-128.7	+16.3	<i>a</i>
	323	-102.6	-102.7	-0.1	-92.43	+10.17	
	373	-71.85	-72.73	-0.88	-67.28	+4.57	
	423	-50.59	-51.03	-0.44	-49.19	+1.40	
	473	-34.08	-34.61	-0.53	-35.29	-1.21	
	573	-13.58	-11.58	+2.00	-15.78	-2.20	
	673	-1.58	+3.11	+4.69	-2.83	-1.25	
	773	+6.05	+13.25	+7.20	+6.43	+0.38	
873	+12.11	+21.64	+9.53	+13.20	+1.09		
N ₂ O	273	-160.92	-158.69	+2.23	-158.92	+2.00	<i>b</i>
	298	-133.18	-132.99	+0.19	-133.57	-0.39	
	323	-111.51	-112.09	-0.58	-112.75	-1.24	
	348	-94.30	-94.67	-0.37	-92.04	+2.26	
	373	-80.21	-80.73	-0.52	-80.77	-0.56	
	398	-68.40	-68.49	-0.09	-68.56	-0.16	
	423	-58.30	-58.01	+0.29	-57.49	+0.81	
C ₂ H ₄	273	-168.69	-167.78	+0.91	-167.17	+1.52	<i>c</i>
	298	-140.98	-140.21	+0.77	-140.89	+0.09	
	323	-118.69	-118.31	+0.38	-119.31	-0.62	
	348	-100.01	-100.71	-0.70	-101.45	-0.44	
	373	-85.55	-85.55	0.00	-86.29	-0.74	
	398	-72.90	-72.84	+0.06	-73.40	-0.50	
N ₂	273	-10.462	-10.105	+0.357	-10.110	+0.352	<i>d, e</i>
	298	-4.684	-4.739	-0.055	-4.707	-0.023	
	323	-0.241	-0.285	-0.044	-0.287	-0.046	
	373	+6.027	+6.280	+0.253	+6.550	+0.523	
	423	+11.515	+11.504	-0.011	+11.545	+0.030	
	473	+15.369	+15.586	+0.217	+15.384	+0.015	
	573	+20.365	+21.010	+0.645	+21.238	+0.873	
	673	+23.460	+24.721	+1.261	+24.211	+0.751	

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CALCULATION OF B , ϕ° AND $\lim_{p \rightarrow 0} \left(\frac{\partial c_p}{\partial p} \right)_T$ FOR PURE GASES

It was shown by Saxena and Joshi (1962*b*) that the second virial data as a function of temperature could be adequately correlated on the basis of the (18-6) potential. We investigate this prospect by considering the gases CO_2 , N_2O , C_2H_4 and N_2 in this section. Computed values of B according to Eqns. (3) to (6) in conjunction with the tabulated values of $F(y)$ as given in Table I at the temperatures where experimental data are available are recorded in Table VI. This table also lists the calculated values for the L-J (12-6) potential. The gas CO_2 , for which extensive data are available, presented some difficulties of interpretation on the basis of these two central force-field models. This is due to the high sensitivity of B to the shapes of the molecules; and CO_2 is known for its non-spherical nature (Saxena, Saksena and Gambhir 1964). We have, however, confined to data below 500°K ; for the other data of this pure gas or of its combinations with other gases are in this range only; and this may be of some help in assessing the potential though the parameters may not have the correct weighted values embracing the whole range. Of course, a look at the reproduced values of B for this gas at high temperatures does confirm the view and shows the over-all deficiency of this potential for this gas. It seems that only a theory in which the non-spherical nature of this molecule is taken into account can be expected to represent successfully the behaviour of this gas. The reproduction of the values of B for the other three gases and at all the temperatures is satisfactory and the two potentials seem almost equally good.

The calculated values of the isothermal Joule-Thomson coefficient for all these gases as a function of temperature, along with the experimental values, are given in Table VII for both the potentials. Theoretically speaking, ϕ° is a more appropriate property for assessing the suitability of the potential energy function; for, it involves the first derivative of $F(y)$ also. In practice, lack of sufficient elaborate data limits the scope of such a possibility. For CO_2 the listings of Table VII indicate a better reproduction of ϕ° in agreement with the experimental values; but this is obviously due to the reason pointed out in the previous paragraph. As in the case of B , here also, we find comparable success for the two potentials. The rather large discrepancy found in the case of N_2 at high temperature end is again somewhat unexpected; specially, as B is accounted with a much better accuracy.

A still more sensitive property for assessing a potential is the limiting value of the pressure to derivative of the specific heat at constant temperature. This is because its magnitude is related to the curvature of the B versus T graph. Unfortunately, data are available for only N_2 and CO_2 and these are quoted in Table VIII. For N_2 we find that better agreement is obtained for the

(12-6) potential at low temperatures and for the (18-6) potential at high temperatures. This feature of the (18-6) potential is not substantiated by the data of Table VII and we, therefore, feel that still all the evidence available support the superiority of (18-6) potential for N_2 gas at high temperature end. This conclusion is interesting in view of the simple linear nature of this diatomic molecule.

Some interesting conclusions are possible on the basis of the listings of Table VIII for CO_2 gas also. The strange situation encountered while discussing the results of Table VI gets somewhat clarified when we see that there is a much better fit for the (18-6) potential than for the (12-6) potential. In spite of the failure of both the potentials to account for the B behaviour of

TABLE VII
Comparison of the experimental and calculated (18-6) and (12-6) ϕ° values
(ϕ° values expressed in cc/mole.)

Gas	T °K	Exp.	Calc.				Ref.
			(18-6)	% dev.	(12-6)	% dev.	
CO_2	.. 273	467	447	- 4.3	372	-20.4	a
	298	390	382	- 2.1	323	-17.2	
	318	345	343	- 0.6	291	-15.7	
N_2O	.. 273	489	473	- 3.3	464	- 5.1	a
	288	437	434	- 0.7	425	- 2.7	
	298	407	407	0.0	403	- 1.0	
	308	380	384	+ 1.1	382	+ 0.5	
	318	362	363	+ 0.3	362	0.0	
C_2H_4	.. 273	496	496	0.0	484	- 2.6	a
	288	440	456	+ 3.6	445	+ 1.1	
	298	418	428	+ 2.4	421	+ 0.7	
	313	395	393	- 0.5	389	- 1.5	
	318	376	382	+ 1.6	380	+ 1.1	
N_2	.. 173	179	174	- 2.8	168	- 6.1	b
	223	109	111	+ 1.8	109	0.0	
	273	73.2	75.8	+ 3.6	74.8	+ 2.2	b
	298	62.0	63.4	+ 2.3	62.6	+ 1.0	a
	318	53.5	54.5	+ 1.9	54.3	+ 1.5	a
	323	51.3	52.6	+ 2.5	52.4	+ 2.1	b
	373	36.0	37.9	+ 5.3	36.7	+ 1.9	b
	423	24.3	27.6	+13.6	25.3	+ 4.1	b
	473	15.7	19.4	+23.6	16.3	+ 3.8	b
	573	3.93	4.68	+19.5	3.76	- 4.3	b

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TABLE VIII

Comparison of the experimental and calculated (18-6) and (12-6) values of $\lim_{p \rightarrow 0} \left(\frac{\partial c_p}{\partial p} \right)_T$

$\left(\lim_{p \rightarrow 0} \left(\frac{\partial c_p}{\partial p} \right)_T \right)$ values expressed in cal/mole. deg. atm.)

Gas	T °K	Exp.	Calc.				Ref.
			(18-6)	dev.	(12-6)	dev.	
N ₂	223	0.0176	0.0226	+0.0050	0.0211	+0.0035	b
	273	0.0129	0.0137	+0.0008	0.0132	+0.0003	
	323	0.00672	0.00928	+0.00256	0.00896	+0.00224	
	373	0.00480	0.00663	+0.00183	0.00647	+0.00167	
	423	0.00208	0.00500	+0.00292	0.00487	+0.00279	
	473	0.00175	0.00387	+0.00212	0.00429	+0.00254	
	573	0.00327	0.00251	-0.00076	0.00246	-0.00081	
CO ₂	273	0.080	0.068	-0.012	0.053	-0.027	a
	323	0.057	0.043	-0.014	0.034	-0.023	
	373	0.040	0.029	-0.011	0.024	-0.016	
	423	0.024	0.021	-0.003	0.018	-0.006	
	473	0.017	0.016	-0.001	0.014	-0.003	
	573	0.010	0.010	0.0	0.0087	-0.0013	
	673	0.0070	0.0070	0.0	0.0060	-0.0010	
	773	0.0050	0.0051	+0.0001	0.0044	-0.0006	
	873	0.0036	0.0039	+0.0003	0.0033	-0.0003	

a. McCormack, K. E., and Schneider, W. G. (1950). Thermodynamic properties of gaseous CO₂ at temperatures 0°-600° C and pressures up to 50 atmospheres. *J. chem. Phys.*, **18**, 1269.

b. Roebuck, J. R., and Osterberg, H. (1935). The Joule-Thomson effect in nitrogen. *Phys. Rev.*, **48**, 450.

CO₂ gas over the whole temperature range, the (18-6) potential is relatively superior for high temperatures. This belief mainly stems from the findings of Table VIII and to some extent from those of Table VII. This conclusion may be regarded as the main motivation of this paper, *viz.* the better suitability of the (18-6) potential for calculating the properties of complicated molecules at high temperatures. Douslin and Waddington (1955) were the first to suggest the use of the quantity $\lim_{p \rightarrow 0} \left(\frac{\partial c_p}{\partial p} \right)_T$, for determining the potential parameters. As the accuracy with which this quantity can usually be known is likely to be relatively small we have utilized it only for comparison with the calculated values. The values of c_p as a function of pressure were used to generate this quantity by a graphical method.

CALCULATION OF B_{12} AND $\phi_{\text{MIX}}^{\circ}$ FOR BINARY GAS MIXTURES

The knowledge of the final results of statistical mechanics coupled with those of the potential field of pure gases has now become quite dependable

TABLE IX
Comparison of the experimental and calculated B_{12} values for binary mixtures
(B_{12} values expressed in cc/mole.)

Gas pair	T °K	Exp.	Calc.				Ref.
			(18-6)	Dev.	(12-6)	Dev.	
CH ₄ -C ₂ H ₆	.. 273.2	-111.9	-110.6	+ 1.3	- 96.2	+15.7	a
	298.2	- 92.0	- 91.7	+ 0.3	- 80.7	+11.3	
	323.2	- 75.6	- 76.6	- 1.0	- 67.9	+ 7.7	
CH ₄ -CO ₂	.. 310.9	- 63.6	- 67.4	- 3.8	- 64.0	- 0.4	b
	344.2	- 48.2	- 51.9	- 3.7	- 50.0	- 1.8	
	377.5	- 36.6	- 39.8	- 3.2	- 38.9	- 2.3	
	410.9	- 27.4	- 29.8	- 2.4	- 29.8	- 2.4	
	444.2	- 19.8	- 22.0	- 2.2	- 22.4	- 2.6	
	477.5	- 13.6	- 14.8	- 1.2	- 16.0	- 2.4	
	510.8	- 8.4	- 8.5	- 0.1	- 10.6	- 2.2	
CH ₄ -C ₅ H ₁₂	.. 303.2	-165	-220	-55	-224	-59	c
	323.2	-138	-196	-58	-195	-57	
	333.2	-132	-177	-45	-182	-50	
	343.2	-118	-167	-49	-170	-52	
	353.2	-113	-156	-43	-158	-45	
	363.2	-106	-146	-40	-148	-42	
	383.2	- 93	-127	-34	-129	-36	
	403.2	- 78	-112	-34	-112	-34	
CH ₄ -SF ₆	.. 313.2	- 85	-108	-23	-107	-22	c
	333.2	- 68	- 91	-23	- 92	-24	
	353.2	- 57	- 78	-21	- 79	-22	
	373.2	- 45	- 66	-21	- 67	-22	
	393.2	- 33	- 55	-22	- 57	-24	
C ₂ H ₆ -CO ₂	.. 310.9	-103.0	-135.9	-32.9	-113.2	-10.2	b
	344.2	- 87.5	-109.3	-21.8	- 92.4	- 4.9	
	377.5	- 73.3	- 88.1	-14.8	- 76.0	- 2.7	
	410.9	- 60.4	- 70.8	-10.4	- 62.7	- 2.3	
	444.2	- 48.2	- 58.8	-10.6	- 51.7	- 3.5	
	477.5	- 37.0	- 45.4	- 8.4	- 42.6	- 5.6	
	510.8	- 26.0	- 35.4	- 9.4	- 34.8	- 8.8	
C ₂ H ₆ -N ₂	.. 277.6	- 65.4	- 61.7	+ 3.7	- 55.4	+10.0	
	310.9	- 38.6	- 45.6	- 7.0	- 41.8	- 3.2	
	377.5	- 20.1	- 22.8	- 2.7	- 22.6	- 2.5	
	444.3	- 3.8	- 7.9	- 4.1	- 9.9	- 6.1	
	510.9	+ 5.9	+ 2.5	- 3.4	- 8.9	-13.0	
CO ₂ -N ₂	.. 298.2	- 44.1	- 39.8	+ 4.3	- 38.8	+ 5.3	a
	323.2	- 33.6	- 31.2	+ 2.4	- 30.3	+ 3.3	
	348.2	- 27.4	- 23.5	+ 3.9	- 23.3	+ 4.1	
	373.2	- 21.5	- 16.9	+ 4.6	- 17.3	+ 4.2	
	398.2	- 17.7	- 11.3	+ 6.4	- 12.1	+ 5.6	

a. Gunn, R. D. (1958). M.S. Thesis, University of California, Berkeley.

b. Zaalishvili, Sh. D. (1956). Second virial coefficients for gas solutions. *Zh. fiz. Khim.*, 30, 1891.

c. Hamann, S. D., Lambert, J. A., and Thomas, P. B. (1955). The second virial coefficients of some gas mixtures. *Aust. J. Chem.*, 8, 149.

for purposes of calculating mixture properties. This approach is made a bit more empirical because, for achieving our aim mentioned above, we need the knowledge of the empirical formulae (very often called combination rules) connecting the nature of unlike molecular interactions with associated like interactions. Such rules relevant for the (18-6) potential have already been given. It has been a good practice to check the success of the whole procedure on the basis of available data before pushing the procedure for purposes of predictions purely. This is the aim of this section. We consider the binary virial and zero-pressure isothermal Joule-Thomson data for gas mixtures which permute from the seven pure gases earlier considered by Saxena and Joshi (1962*b*) and the four here, and for which experimental data are available.

In Table IX are given the computed values of B_{12} for seven binary mixtures as a function of temperature for both the potentials. The experimental values as well as the deviations of the calculated values from the observed ones are also reported. For the systems $\text{CH}_4\text{-C}_2\text{H}_6$, $\text{CH}_4\text{-CO}_2$, $\text{C}_2\text{H}_6\text{-N}_2$ and $\text{CO}_2\text{-N}_2$ the agreement obtained on the basis of both the potentials is satisfactory though a slight preference for the (18-6) potential is exhibited. For the three remaining systems we find a much poorer reproduction and in at least two systems both the potentials fail. We will defer from deriving any inference regarding the unsuitability of the combination rules, for the mixture data do not refer to sufficiently high temperature range. Obviously, when more elaborate data on different properties become available one may re-examine this question or even alternatively directly determine the unlike interactions from mixture properties.

Computed values of ϕ_{mix}° for five mixtures are given in Table X as a function of temperature and composition. On the basis of comparison with experimental values one finds that the (18-6) potential is superior for all the systems except $\text{C}_2\text{H}_6\text{-CH}_4$. The percentage average absolute deviations are 1.5 and 2.5 for the (18-6) and (12-6) potentials respectively. The reason for the failure of this potential to yield adequate results of ϕ_{mix}° for $\text{CH}_4\text{-C}_2\text{H}_6$ system is not very obvious. This becomes still more puzzling when one recalls the good agreement for B_{12} . The relatively better agreement obtained for the (12-6) potential is of little consequence for it fails to correlate the B_{12} values. Thus, more experimental data of sufficient accuracy seem to be entirely necessary to resolve this discrepancy.

DISCUSSION

The degree of agreement obtained between the experimental and the theoretical values of the different properties has already been discussed at length above. Here we put forth a few arguments for why a spherically symmetric potential is to be used for explaining the properties of non-spherical molecules. Rigorously speaking, such an approach at the very outset is open

TABLE X

Comparison of the experimental and calculated (18-6) and (12-6) $\phi_{\text{mix}}^{\circ}$ values
 ($\phi_{\text{mix}}^{\circ}$ values are expressed in cc/mole, and x is the mole fraction of the first member of the gas pair)

Gas pair	T °K	x	Exp.	Calc.				Ref.
				(18-6)	% Dev.	(12-6)	% Dev.	
CO ₂ -N ₂ O ..	273	0.256	484	476	-1.7	461	-4.7	α
		0.494	480	467	-2.3	449	-6.5	
		0.630	476	465	-2.3	447	-6.1	
		0.711	475	466	-1.9	450	-5.3	
	298	0.229	400	402	+0.5	394	-1.5	
		0.448	396	398	+0.5	388	-2.0	
		0.573	403	396	-1.7	385	-4.5	
		0.624	395	395	0.0	385	-2.5	
		0.691	393	394	+0.3	385	-2.0	
	318	0.250	354	357	+0.8	349	-1.4	
		0.397	354	355	+0.3	344	-2.8	
		0.410	350	355	+1.3	344	-1.7	
		0.532	351	353	+0.6	341	-2.9	
		0.751	346	349	+0.9	340	-1.7	
	CO ₂ -C ₂ H ₄ ..	273	0.457	479	478	-0.2	456	
0.555			490	475	-3.1	453	-7.6	
0.616			474	473	-0.2	453	-4.4	
0.679			470	472	+0.4	453	-3.6	
298		0.171	416	413	-0.7	404	-2.9	
		0.387	401	416	+3.7	400	-0.2	
		0.454	397	405	+2.0	389	-2.0	
		0.643	405	400	-1.3	385	-2.0	
		0.725	393	409	+4.1	395	-4.9	
318		0.226	369	369	0.0	360	-2.4	
		0.363	356	365	+2.5	353	-0.8	
		0.424	357	363	+1.7	350	-2.0	
		0.707	350	354	+1.1	343	-2.0	
		0.805	337	358	+6.2	350	+3.9	
C ₂ H ₄ -N ₂ O		273	0.284	497	488	-1.8	486	-2.2
	0.481		520	489	-6.0	486	-6.5	
	0.708		500	491	-1.8	488	-2.4	
	298	0.203	413	411	-0.5	410	-0.7	
		0.428	410	414	+1.0	414	+1.0	
		0.522	420	415	-1.2	415	-1.2	
		0.605	419	433	+3.3	432	+3.1	
		0.724	429	417	-2.8	416	-3.0	
	318	0.179	358	366	+2.2	366	+2.2	
		0.288	363	368	+1.4	368	+1.4	
		0.541	371	372	+0.3	372	+0.3	
		0.672	372	373	+0.3	374	+0.5	

TABLE X—concl'd.

Comparison of the experimental and calculated (18-6) and (12-6) $\phi_{\text{mix}}^{\circ}$ values
 ($\phi_{\text{mix}}^{\circ}$ values are expressed in cc/mole. and x is the mole. fraction of the first member of the gas pair)

Gas pair	T ° K	x	Exp.	Calc.				Ref.
				(18-6)	% Dev.	(12-6)	% Dev.	
C ₂ H ₆ -CH ₄ ..	294.3	0.25	211	224	+6.0	207	-2.2	b
		0.50	292	307	+5.1	284	-2.8	
		0.75	384	395	+2.8	377	-1.7	
	311.0	0.25	187	204	+9.2	188	+1.2	
		0.50	257	282	+9.4	260	+1.1	
		0.75	342	363	+6.2	345	+1.5	
	327.6	0.25	170	186	+9.6	172	+1.2	
		0.50	234	258	+10.1	239	+2.0	
		0.75	311	333	+7.1	319	+2.5	
	344.3	0.25	156	170	+8.8	157	+0.6	
		0.50	215	236	+9.7	220	+2.3	
		0.75	285	306	+7.2	294	+3.2	
	361.1	0.25	142	156	+9.8	145	+2.1	
		0.50	198	216	+9.1	201	+1.5	
		0.75	262	280	+6.9	268	+2.3	
	377.6	0.25	131	143	+9.2	133	+1.6	
		0.50	182	198	+8.8	183	+0.6	
		0.75	241	252	+4.6	242	+0.4	
N ₂ -N ₂ O ..	298	0.222	314	308	-1.9	308	-1.9	a
		0.450	220	219	-0.5	220	0.0	
		0.678	148	144	-2.7	145	-2.0	
		0.753	125	123	-1.6	123	-1.6	
	318	0.186	286	287	+0.3	287	+0.3	
		0.254	260	262	+0.8	262	+0.8	
		0.417	203	205	+1.0	206	+1.5	
		0.583	153	154	+0.7	155	+1.3	
		0.640	141	138	-2.2	138	-2.2	
		0.747	109	110	+0.9	110	+0.9	

a Charnley, A., Rowlinson, J. S., Sutton, J. R., and Townley, J. R. (1955). The isothermal Joule-Thomson coefficient of some binary gas mixtures. *Proc. R. Soc., A* **230**, 354.

b Budenholzer, R. A., Sage, B. H., and Lacey, W. N. (1939). Phase equilibria in hydrocarbon systems. *Ind. Enging. Chem. ind. (int.) Edn.*, **31**, 1288.

to objection and one should rely only on the kinetic theory of non-spherical polyatomic molecules. But the developments in this direction are very slow due to the complications involved; and further, as the geometry of the molecule gets involved, any detailed calculations will have to be separately performed

for the individual cases. This is one reason, though a weak one, for employing a spherically symmetric potential. However, the approach of calculating the second virial coefficient on the basis of a spherical potential and then of improving it by treating the corrections as perturbations has proved more popular and successful. Thus, Pople (1954), Buckingham (1955), Buckingham and Pople (1955), and Castle, Jansen and Dawson (1956) worked on the simple Lennard-Jones (12-6) potential. In many of the cases considered by them, the corrections amounted to a couple of per cent. Now the reason for the corrections to be small can be appreciated when we note that a non-spherical molecule whilst rotating about its centre of mass sweeps out a spherical cavity which is not easily accessible to another interacting molecule. Outside this sphere and at distances large in comparison to the molecular dimensions, the force field may be regarded as reasonably spherically symmetric, having a magnitude equal to the averaged value for all orientations. This view which was advanced by Bird, Spatz and Hirschfelder (1950) was soon after put to test by Hamann and Pearse (1952). These latter workers investigated a few ellipsoidal molecules and found that the collision diameters which were determined on the assumption of a spherically symmetric force field agreed remarkably with the lengths of the major axes of the ellipsoidal molecules.

Saxena and Joshi (1962*a*, *b*) gave various arguments in favour of using a steeper potential to represent the behaviour of polyatomic molecules. They also suggested the use of the (18-6) potential instead of the (12-6) potential for polyatomic molecules. The magnitude of the correction for second virial coefficient of non-polar non-spherical molecules has not yet been calculated for this case though the expression for the same has been given by Saksena and Saxena (1965*a*). These authors (1965*b*) have also shown that the equilibrium separation distances are better predicted by the (18-6) potential for polyatomic molecules than by the (12-6) potential. Dymond, Rigby and Smith (1964) who recently showed by considering the data of B that the index of r in the repulsive part of the general Lennard-Jones potential should lie between 16 and 20 have also preferred 18. They have considered the data of the third virial coefficient also. Guided by some considerations such as these we have employed the (18-6) potential for interpreting the behaviour of polyatomic molecules.

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