Properties of Gases and Gaseous Mixtures with a Morse Potential

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(Z. Naturforschg. **19 a**, 1478—1485 [1964]; eingegangen am 4. August 1964)

Second virial coefficients, viscosity, thermal conductivity and diffusion coefficients of binary gas mixtures have been computed for the Morse potential in conjunction with a set of combination rules for the unlike interactions. These calculated values are compared with the experimental values with a view to derive inferences regarding the adequacy of the recently proposed Morse potential. On the basis of this detailed comparison of theory and experiment some specific and useful conclusions have been drawn which enable one to understand the relative footing of this potential in reference to the other two realistic potentials, viz. L-J (12-6) and exp-six.

Konowalow, Taylor, and Hirschfelder [1] have extended the scope of calculation of the various equilibrium and non-equilibrium properties of gases by introducing the Morse potential. Konowalow and Hirschfelder [2] have determined the potential parameters for a number of nonpolar gases using the second virial and crystal data. They [2] found for all the gases except Kr that this potential is as successful in correlating the second virial coefficient, $B(T)$, data as the two other realistic potentials, viz. the Lennard-Jones $(12-6)$ and the modified Buckingham exp-six. For Kr they [2] suggested a five parameter hybrid potential and the situation is not at all satisfactory in the case of exp-six potential also [3]. Saxena and Gambhir [4] gave a set of combination rules to determine the unlike interactions from like interactions. They [4] found that the second virial data of mixtures can be interpreted by this potential somewhat better than by the other two potentials. This conclusion was based on the analysis of data on four systems only. Gambhir and Saxena [5] also interpreted the Joule-Thomson data of a few nonpolar gases with reasonable success. Thus, on the whole this potential was found to be satisfactory in correlating the equilibrium properties of gases and gaseous mixtures.

Lovell and Hirschfelder [6] further extended the scope of work on Morse potential by tabulating the transport properties Chapman-Enskog collision integrals. Saxena and Bahethi [7] examined the experimental data on the three elementary transport properties and arrived at the conclusion that it is not possible to reproduce precisely these data using the potential parameters of Konowalow and Hirschfelder [2]. This conclusion was further supported by the work on He [8] and H_2 [9]. In these two latter works [8, 9] it was found that if the potential parameters are determined from viscosity then the remaining data on non-equilibrium properties can be reasonably explained. Saran [10] has recently examined the viscosity data of a number of pure gases and also arrived at the same conclusion. Thus, this overall study suggests that it is not possible to correlate all the data on equilibrium and non-equilibrium properties by the choice of a single set of potential parameters. We in this paper propose to investigate the properties of gas mixtures. Second virial data of mixtures will be interpreted with $B(T)$ parameters while the binary viscosity, η_{mix}; diffusion, D_{12}; and thermal conductivity, λ_{mix}, with η parameters.

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[2] D. D. Konowalow and J. O. Hirschfelder, Phys. Fluids **4**, 629 [1961]. See also, University of Wisconsin, Theoretical Chemistry Laboratory Report WIS-AF-17, 1960.

[3] O. P. Bahethi and S. C. Saxena, Indian J. Pure Appl. Phys., to be published. References to earlier works are given in this paper.

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1. Potential Parameters

The Morse potential is

$$\Phi(r) = \varepsilon[\exp\{-2C(r^* - r_m^*)\} - 2\exp\{-C(r^* - r_m^*)\}], \quad (1)$$

where, $\Phi(r)$ is the potential energy of two molecules separated by a distance r, ε is the depth of the potential energy minimum where $r = r_m$, $r^* = r/\sigma$, σ is a distance parameter having the physical significance that $\Phi(\sigma) = 0$, and the constant C determines the curvature of the potential at the minimum as well as the steepness of the repulsive potential. C, ε/k and σ or r_m are called the potential parameters, where k is the BOLTZMANN constant.

Combination rules to determine the potential parameters characterizing the unlike interactions from those corresponding to the like interactions were given by SAXENA and GAMBHIR [4]. However, these can also be represented by the following simpler and equivalent expressions:

$$\varepsilon_{12} = (\varepsilon_{11} \cdot \varepsilon_{22})^{1/2}, \quad (2)$$

$$C_{12} = \tfrac{1}{2}(C_{11} + C_{22}), \quad (3)$$

$$\sigma_{12} = 2C_{12}\left[\frac{C_{11}}{\sigma_{11}} + \frac{C_{22}}{\sigma_{22}}\right]^{-1}, \quad (4)$$

and

$$(r_m)_{12} = \sigma_{12}[1 + \{\ln 2/C_{12}\}]. \quad (5)$$

MORSE potential parameters for pure gases are given in Table 1. Two sets are reported, one determined from η and the other from $B(T)$. For Ne we have determined the parameters using η data and following the procedure of MASON and RICE [11]. In the case of He we show the potential parameters of two different workers. It is not possible to prefer one to the other for both the sets reproduce η data equally well on the whole. We use the parameters of BAHETHI and SAXENA [8] in our present work.

Gas	From η			Ref.	From $B(T)$			Ref.
	C	ε/k(°K)	σ(Å)		C	ε/k(°K)	σ(Å)	
He	6.0	8.55	2.687	8	4.0	14.43	2.976	8
	6.0	11	2.622	10				
Ne	8.0	67.1	2.611	*	5.1	43.99	2.775	2
Ar	5.7	120	3.461	10	5.0	144.8	3.386	2
H_2	6.0	45.3	2.898	9	5.0	39.4	3.005	9
N_2	6.1	92	3.697	10	5.5	134.4	3.579	2
O_2	5.9	98	3.544	10	—	—	—	
CO_2	5.1	196	3.968	10	—	—	—	

* Present work.

Table 1. MORSE potential parameters for like interactions.

Gas pair	From η parameters			From $B(T)$ parameters		
	C	ε/k (°K)	σ (Å)	C	ε/k (°K)	σ (Å)
Ar – He	5.9	32.0	3.016	4.5	45.7	3.191
N_2 – He	6.1	28.0	3.116	4.8	44.0	3.298
Ar – H_2	5.9	73.7	3.148	5.0	75.5	3.184
N_2 – H_2	6.1	64.5	3.253	5.3	72.8	3.281
He – H_2	6.0	19.7	2.789	4.5	23.8	2.992
Ar – Ne	6.9	89.7	2.908	5.1	79.8	3.035
Ar – N_2	5.9	105	3.579	5.3	139.5	3.484
Ne – H_2	7.0	55.1	2.727	5.1	49.6	2.873
Ne – He	7.0	24.0	2.643	4.6	25.2	2.860
CO_2 – N_2	5.6	134.3	3.816	—	—	—
CO_2 – O_2	5.5	138.6	3.727	—	—	—
O_2 – N_2	6.0	95	3.619	—	—	—
O_2 – H_2	6.0	66.6	3.185	—	—	—
CO_2 – H_2	5.6	94.2	3.308	—	—	—
Ar – O_2	5.8	108	3.503	—	—	—
O_2 – He	6.0	28.9	3.053	—	—	—
CO_2 – He	5.6	40.9	3.155	—	—	—

Table 2. MORSE potential parameters for unlike interactions.

Potential parameters for the unlike interactions are given in Table 2 and in their evaluation we have used for pure interactions the data of Table 1 and equations (2) to (4).

2. Properties of Pure Gases

Considerable work on pure gases has already been done and it was found that the potential parameters determined from any of the equilibrium properties can only explain such properties. Similarly viscosity parameters could only reproduce the non-equilibrium properties. For this reason we evaluated the potential parameters of Ne from η. The viscosity parameters determined for O_2 and CO_2 were also subjected to this test, although SARAN [10] has already shown that η data can be adequately reproduced with the help of these parameters. In Fig. 1 are shown the λ and η data of Ne as a function of temperature and compared with the calculated values from the MORSE potential using viscosity parameters and theoretical expression as given by HIRSCHFELDER, CURTISS and BIRD [12]. The agreement between theory and experiment is good and is better than the consistency of the experimental data of different workers. Calculated and experimental [13] values of the diffusion coefficient for this gas are plotted in Fig. 2 and the agreement between the two is reasonable. Consequently it can be inferred that the parameters of Ne derived from η are capable of reproducing the other non-equilibrium properties.

[11] E. A. MASON and W. E. RICE, J. Chem. Phys. **22**, 522 [1954].
[12] J. O. HIRSCHFELDER, C. F. CURTISS, and R. B. BIRD, Molecular Theory of Gases and Liquids, Chapman & Hall Ltd., London 1954.
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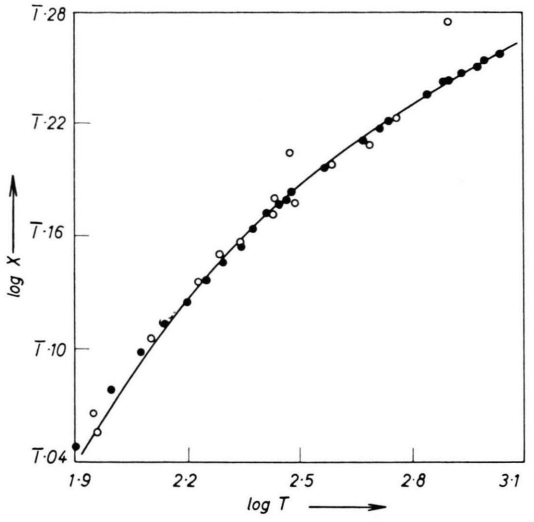

Fig. 1. Comparison of experimental and calculated values of η and λ as a function of temperature. Here, X is $10^7\,\eta\,(266.93\,M^{1/2}\,T^{1/2})^{-1}$ or $(10^7\,\lambda\,M^{1/2}\,f_\eta^3)\cdot(1989.1\,T^{1/2}\,f_\lambda^3)^{-1}$. Experimental points: ● from η, ○ from λ, continuous curve is calculated from theory.

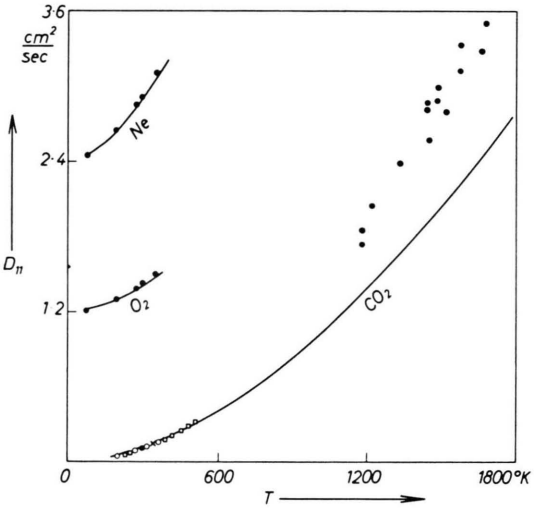

Fig. 2. Comparison of experimental and calculated D_{11} values. In the case of O_2 and Ne the curves have been displaced upwards by 1.2 and 2.4 units, respectively. Experimental data: CO_2, ○ AMDUR, IRVINE, MASON and ROSS, × WINN, ● EMBER, FERRON and WOHL, □ SCHÄFER and REINHARD; O_2 and Ne, ● WINN.

The parameters of O_2 and CO_2 determined from viscosity were subjected to a similar test. In Fig. 2 are displayed the experimental data of diffusion, D_{11}, for O_2 [13] and CO_2 [13–18] along with the computed values. The agreement in the case of O_2 is satisfactory while for CO_2 the disagreement is quite pronounced at high temperatures. We feel that this is because the rigorous CHAPMAN-ENSKOG theory does not strictly apply to this molecule which is polyatomic and nonspherical. The $B(T)$ data for these two gases [19–21] as a function of temperature are reproduced in Fig. 3 where the continuous curves represent the calculated values. Here also, as in the case of other gases, we find that the viscosity parameters fail to reproduce the $B(T)$ data.

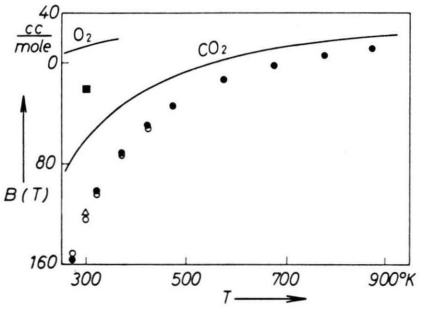

Fig. 3. Comparison of experimental and calculated $B(T)$ values. Experimental data: CO_2, ○ MICHELS and MICHELS, ● MACCORMACK and SCHNEIDER, △ EDWARDS and ROSEVEARE; O_2, ■ EDWARDS and ROSEVEARE.

3. Properties of Binary Gas Mixtures

The second virial coefficient of a binary mixture, B_{mix} is given by [12]

$$B_{\mathrm{mix}} = X_1^2\,B_{11} + 2\,X_1\,X_2\,B_{12} + X_2^2\,B_{22}\,. \quad (6)$$

Here, X_1 and X_2, and B_{11} and B_{22} are the mole fractions and second virial coefficients of the heavier and lighter components respectively, and B_{12} is the virial coefficient of a hypothetical pure gas whose molecules interact according to the potential law for (1, 2) interactions. B_{12} is given by

$$B_{12} = b_0\,B^*(C, T^*), \quad (7)$$

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[19] A. E. EDWARDS and W. E. ROSEVEARE, J. Amer. Chem. Soc. **64**, 2816 [1942].
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[21] K. E. MACCORMACK and W. G. SCHNEIDER, J. Chem. Phys. **18**, 1269 [1950].

where $$b_0 = (2/3)\,\pi N \sigma_{12}^3, \qquad (8)$$

B^* is the reduced second virial coefficient and N is the AVOGADRO number.

Values of B_{12} for a number of binary systems at temperatures where experimental data are available were computed according to equations (7) and (8) and tabulations of KONOWALOW et al. [1]. These calculated values along with the experimental values [19, 22–25] are shown in Table 3. The agreement between the two sets of values is quite satisfactory in all cases except Ar – He where the discrepancies are systematic and slightly more than can be explained on the basis of uncertainties in the experiments.

Gas pair	Temp. °K	B_{12}, cc/mole		Dev. cc/mole
		Exptl.	Calc.	
N_2-H_2	298	14.1	12.8	− 1.3
N_2-He	298	12.5	16.4	+ 3.9
	448	22.92	19.43	− 3.49
	523	22.41	19.58	− 2.83
	598	21.73	19.73	− 2.00
	673	21.20	19.88	− 1.32
	748	20.33	20.03	− 0.30
$He-H_2$	298.2	15.60	13.34	− 2.26
	323.2	15.66	13.43	− 2.23
	348.2	15.24	13.52	− 1.72
	373.5	15.61	13.60	− 2.01
	398.4	14.39	13.69	− 0.70
	423.3	15.81	13.78	− 2.03
	448.2	14.55	13.87	− 0.68
Ne – He	273.2	13.49	11.94	− 1.55
	373.2	13.94	12.20	− 1.74
	473.2	13.18	12.47	− 0.71
	573.2	12.79	12.47	− 0.32
	673.2	11.72	12.35	+ 0.63
$Ar-H_2$	298.2	7.93	8.73	+ 0.80
	322.2	9.30	10.22	+ 0.92
	348.2	10.98	11.57	+ 0.59
	373.2	12.53	12.64	+ 0.11
	398.2	13.78	13.43	− 0.35
	423.2	14.88	14.19	− 0.69
	447.2	15.82	14.91	− 0.91
Ar – He	298.2	18.38	12.37	− 6.01
	323.2	18.78	13.24	− 5.54
	348.2	19.28	14.06	− 5.22
	373.2	19.68	14.66	− 5.02
	398.2	20.22	15.07	− 5.15
	423.2	20.60	15.42	− 5.18
	447.2	20.86	15.79	− 5.07

Table 3. Comparison of experimental and calculated B_{12} (cc/mole).

Binary viscosity data, η_{mix}, are specially useful for testing the potential as well as the combination rules because of the high accuracy associated with these data. Experimental data on ten binary systems at several temperatures and in each case as a function of composition were considered. All these data [26, 27] along with the calculated values according to the theoretical expression given by HIRSCHFELDER et al. [12] are listed in Table 4. The agreement between theory and experiment on the whole seems quite satisfactory if due consideration is given to the accuracy of the data, and to the complexity of the molecules involved to which the theory does not strictly apply.

Gas pair	X_1	$10^7\,\eta_{mix}$		Gas pair	X_1	$10^7\,\eta_{mix}$	
		Exptl.	Calc.			Exptl.	Calc.
Ar – He				O_2-N_2			
291 °K	0.000	1940	1930	300 °K	0.0000	1781	1778
	0.061	2050	2090		0.2178	1843	1832
	0.299	2270	2320		0.4107	1894	1881
	0.520	2290	2330		0.7592	1995	1973
	0.645	2270	2300		1.0000	2057	2038
	0.782	2250	2260	550 °K	0.0000	2727	2736
	0.914	2220	2220		0.2178	2840	2821
	1.000	2200	2200		0.4107	2932	2900
373 °K	0.0000	2320	2286		0.7592	3109	3052
	0.5094	2750	2795		1.0000	3220	3163
	0.6180	2745	2779	CO_2-H_2			
	1.0000	2684	2678	300 °K	0.0000	891	902
523 °K	0.0000	2903	2888		0.2150	1370	1422
	0.6180	3488	3551		0.5871	1506	1541
	1.0000	3448	3448		0.8007	1501	1527
$Ar-H_2$					1.0000	1493	1502
293 °K	0.0000	875	887	550 °K	0.0000	1341	1355
	0.3485	1857	1870		0.2150	2173	2254
	0.5543	2056	2061		0.5871	2506	2545
	0.7058	2140	2138		0.8007	2542	2557
	1.0000	2211	2214		1.0000	2556	2541
523 °K	0.0000	1296	1310	N_2-H_2			
	0.3485	2826	2853	292 °K	0.0000	882	885
	0.5543	3164	3174		0.2500	1396	1413
	0.7058	3310	3308		0.5000	1609	1617
	1.0000	3448	3448		0.7500	1700	1704
					1.0000	1746	1740
O_2-H_2							
300 °K	0.0000	889	902	$He-H_2$			
	0.2192	1494	1531	293 °K	0.0000	875	887
	0.3970	1784	1772		0.3082	1166	1186
	0.6055	1925	1922		0.3931	1252	1272
	0.8165	2019	2001		0.4480	1317	1328
	1.0000	2057	2038		1.0000	1974	1938
550 °K	0.0000	1381	1355	523 °K	0.000	1296	1310
	0.2192	2288	2337		0.3082	1732	1753
	0.3970	2733	2720		0.3931	1852	1882
	0.6055	2978	2965		0.4480	1939	1967
	0.8165	3147	3098		1.0000	2903	2888
	1.0000	3220	3163	Ne – He			
Ar – Ne				291 °K	0.000	1920	1930
291 °K	0.000	3070	3090		0.250	2440	2340
	0.221	2850	2920		0.565	2810	2720
	0.436	2670	2720		0.783	2990	2930
	0.638	2470	2530		1.000	3080	3090
	0.803	2360	2380	523 °K	0.000	2853	2895
	1.000	2200	2200		0.2379	3555	3506
523 °K	0.000	3460	3439		0.7341	4310	4375
	0.7420	3658	3741		1.0000	4501	4542
	0.6091	3793	3901	$Ne-H_2$			
	0.2680	4150	4298	523 °K	0.0000	1296	1309
	1.0000	4501	4542		0.2285	2476	2488
$Ne-H_2$					0.5391	3540	3626
293 °K	0.0000	875	887		0.7480	4054	4102
	0.2285	1684	1693		1.0000	4501	4542
	0.5391	2427	2423				
	0.7480	2782	2794				
	1.0000	3092	3110				

Table 4. Comparison of experimental and theoretical η_{mix} (g/cm-sec).

[22] R. J. WITONSKY and J. G. MILLER, J. Amer. Chem. Soc. **85**, 282 [1963].
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[25] C. W. GIBBY, C. C. TANNER, and I. MASSON, Proc. Roy. Soc., Lond. A **122**, 283 [1929].
[26] E. THORNTON and W. A. D. BAKER, Proc. Phys. Soc., Lond. **80**, 1171 [1962].
[27] J. O. HIRSCHFELDER, R. B. BIRD, and E. L. SPOTZ, Chem. Rev. **44**, 205 [1949].

The theory of thermal conductivity is understood accurately only when the molecules involved are monatomic [28]. We therefore consider only three systems, which permute out of the gases of Table 1, for which experimental data are available. Computed as well as the experimental values [26, 29, 30] are recorded in Table 5. Here again the experiments are in good agreement with the predictions of theory if one keeps in mind the enhanced uncertainty associated with these measurements.

Gas pair	X_1	$10^5\,\lambda_{mix}$		Gas pair	X_1	$10^5\,\lambda_{mix}$	
		Exptl.	Calc.			Exptl.	Calc.
Ar – He				Ar – Ne			
311 °K	1.0	4.38	4.33	793 °K	1.000	9.14	8.62
	0.9	5.58	5.64		0.842	10.3	9.66
	0.7	8.61	8.89		0.642	12.7	11.3
	0.5	12.88	13.37		0.423	15.8	14.4
	0.3	19.36	19.81		0.237	18.6	17.1
	0.1	30.09	29.35		0.000	23.6	21.9
	0.0	37.53	37.68	Ne – He			
793 °K	1.000	9.14	8.64	291 °K	1.000	11.6	11.5
	0.710	17.9	17.0		0.783	15.3	14.9
	0.541	26.0	23.2		0.565	19.9	18.1
	0.276	42.2	39.1		0.250	28.4	26.2
	0.106	59.0	56.9		0.000	35.6	36.0
	0.000	73.6	72.2	793 °K	1.000	23.6	21.9
Ar – Ne					0.755	31.7	28.3
291 °K	1.000	4.16	4.11		0.382	47.4	44.7
	0.803	5.20	5.14		0.130	65.8	67.1
	0.638	6.20	6.16		0.119	65.8	68.2
	0.436	7.60	7.53		0.000	73.6	72.1
	0.221	9.30	9.25				
	0.000	11.6	11.5				

Table 5. Comparison of experimental and theoretical λ_{mix} (cal/cm-sec-deg).

Binary diffusion data are specially suited for testing the reliability and appropriateness of potential energy functions due to their enhanced sensitivity to the law of molecular interactions, though the reduced accuracy of the diffusion data sometimes presents a serious handicap. For theoretical calculation we have used the first approximation expression given by HIRSCHFELDER et al. [12]. In Fig. 4 we compare the experimental data [31, 32] on five systems as a function of temperature with the calculated values. Similar comparisons for $N_2 - He$ and $O_2 - H_2$ systems [31, 33] are given in Fig. 5. In Fig. 6 we discuss the result on $O_2 - CO_2$ and $N_2 - CO_2$ [33], and in Fig. 7 on $Ar - He$ [34–37] and $Ar - H_2$ [31, 36, 38]. Lastly in Fig. 8

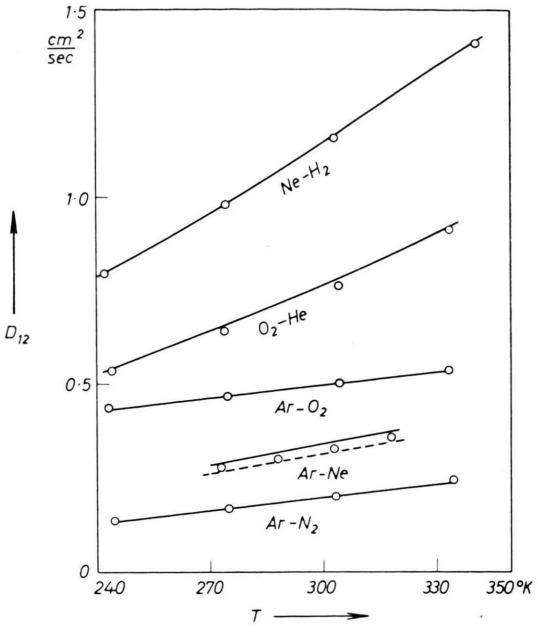

Fig. 4. Comparison of experimental and calculated D_{12} values. In the case of $Ar - O_2$ the ordinates have been displaced by +0.3 units.

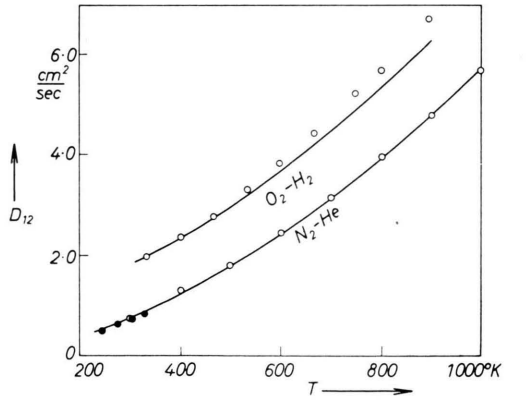

Fig. 5. Comparison of experimental and calculated D_{12} values. The curve for $O_2 - H_2$ has been displaced upward by 1.0 unit. Experimental points: ● PAUL and SRIVASTAVA, ○ WALKER and WESTENBERG.

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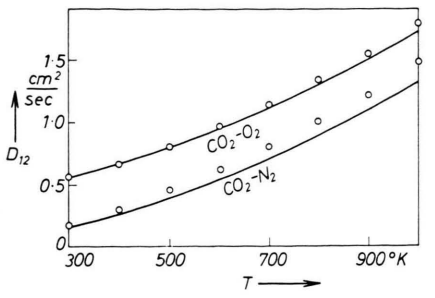

Fig. 6. Comparison of experimental and calculated D_{12} values. The D_{12} values for CO_2-O_2 have been increased by 0.4 units.

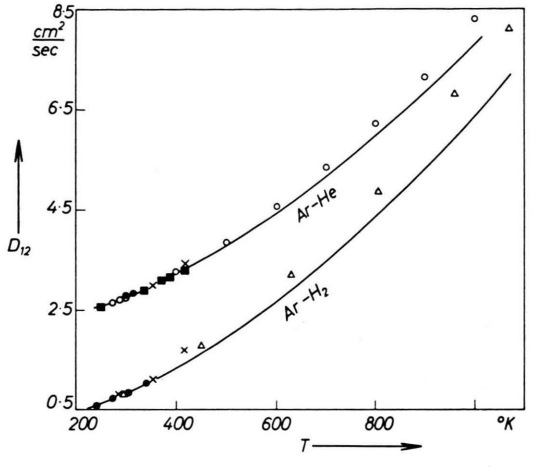

Fig. 7. Comparison of experimental and calculated D_{12} values. The ordinates of Ar—He system have been displaced by +2.0 units. Experimental points: Ar—He, ● Srivastava, × Strehlow, ○ Walker and Westenberg, ■ Saxena and Mason; Ar—H_2, ● Paul and Srivastava, × Strehlow, △ Westenberg and Frazier.

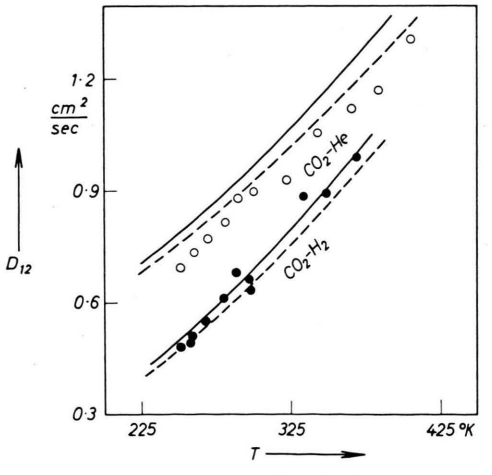

Fig. 8. Comparison of experimental and calculated D_{12} values. In the case of CO_2—He the curve has been shifted upwards by 0.3 units.

we consider H_2-CO_2 and $He-CO_2$ systems. The experimental points of Saxena and Mason [37] only are shown for the data of other workers, as shown by these authors, are in essential agreement with each other. The agreement between the calculated and experimental values is good in all cases except in O_2-H_2, N_2-CO_2, Ar – He, and Ar – H_2 systems at high temperatures, and CO_2 – He even at ordinary temperatures.

4. Discussions

In all cases where pure gases are involved we find that the viscosity parameters reproduce all the non-equilibrium properties, and virial parameters all the equilibrium properties well within the uncertainty of the experimental data. However, any attempt to describe one class of properties with the help of the parameters determined from a property of the other class fails miserably. This is a notable weak point of the Morse potential. It is relevant to mention here that the other realistic intermolecular potentials on which calculations have been performed earlier are better in this respect. The exp-six potential has shown to be for all the pure gases of Table 1, except CO_2 for which no interpretation by this potential has been done so far, a much better potential than the Morse in as much as a choice of a single set of parameters has proved reasonable and could correlate the data on both sets of properties. The Lennard-Jones (12 – 6) potential has in certain cases [12] shown superiority for two sets of parameters, one set for each class of properties, but if an attempt is made to describe all the gas properties by the choice of a single set the discrepancies are not as notable as in the case of Morse potential.

On this background what is left to be known for the complete and final assessment of this potential is its capacity to explain the properties of gas mixtures. Obviously, in this endeavour one is dictated to use the pure parameters of the same class of which the mixture properties are being considered. A detailed study of this type has been presented in section 3. In the case of equilibrium properties we consider only second virial data. A critical examination of the results indicated that Morse potential is just allright except for Ar – He system. Mason [39] found a comparable agreement for his exp-six potential. In

[39] E. A. Mason, J. Chem. Phys. **23**, 49 [1955].

the case of Ar – He system he found a somewhat better agreement than obtained here with the MORSE potential. The failure of the MORSE potential for this system is worth noting in view of the fact that these molecules accord to the requirement of CHAPMAN-ENSKOG theory very well.

Amongst the non-equilibrium properties we have considered η_{mix} and D_{12} data in detail to throw some light on the appropriateness of the MORSE potential. Except for the three systems, $H_2 - CO_2$, Ar – Ne and Ne – He, in all cases the η_{mix} calculated values for MORSE potential agree well with the experimental values. The agreement is as good as obtained with the other two realistic potentials and is also within the limits of experimental uncertainties. In the case of $H_2 - CO_2$ MORSE calculated values differ on the average about 2.3% from the experimental values. The only other calculations available for comparison are on L – J (12 – 6) potential [27]. The latter values are also equally bad at higher temperatures though these are slightly superior at low temperatures. For Ar – Ne system we get a discrepancy of about 2.2% on the average. A relatively better reproduction is obtained by both (12 – 6) and exp-six potentials [27, 39]. The situation in the Ne – He is same as in the case of $H_2 - CO_2$ both for MORSE and (12 – 6) potentials while no appreciable improvement is obtained even by exp-six potential. Thus, on the whole we can infer that the over-all success achieved by the MORSE potential is comparable to that of the exp-six and (12 – 6) potentials.

The comparison of diffusion data with theory leads to very notable discrepancies. The discrepancy observed in Ar – He system is particularly puzzling in view of the simple nature of these molecules. Another interesting point to note in this connection is that SARAN's work [10] also exhibits similar discrepancies though he has used different potential parameters for He and a different set of combination rules. We feel that this disagreement essentially results from the empirical nature of the potential function and not because of the combination rules. Of course, as with other potentials [34] if the MORSE potential parameters are determined from diffusion data alone one could have reproduced the data better. It is hard to understand the lack of agreement in the case of $N_2 - CO_2$ specially when $O_2 - CO_2$ and N_2 – He systems behave well in the same temperature range. The discrepancies observed in the cases of Ar – H_2 and $O_2 - H_2$ are also appreciable, but the failure in this case in our opinion is due to the inability of the potential to represent the force field of H_2. Thus, on the whole we find that systems involving polyatomic molecules are not well represented by this potential and the source of discrepancy stems from this choice and not from the combination rules. He – CO_2 system also exhibits a pronounced and systematic discrepancy. The agreement can be improved by chosing a different value of ε_{12}/k but it should not prompt one to conclude that the fault lies with the combination rules. The nonspherical nature of CO_2 will itself limit the applicability of MORSE potential. What one actually looks for in applying the theory and these potentials to such system is actually the degree of reliance that can be associated with representing the behaviour of nonspherical molecules.

SARAN [10] has calculated D_{12} values for all the systems of Figs. 5 – 7 and a few of Fig. 4. In all cases his calculated values differ only by 1 to 2 percent from our values and are in a direction to further increase the disagreement between theory and experiment. For Ar – Ne, $H_2 - CO_2$ and He – CO_2 the D_{12} values obtained using SARAN's parameters are appreciably different from ours and these are shown by dashed curves in Figs. 4 and 8. For Ar – Ne system nothing definite can be said for our values are higher and SARAN's values equally low. For $H_2 - CO_2$ our values are better while for He – CO_2 SARAN's values are preferable. Thus, on the whole we feel that the two sets of combination rules yield almost in all cases approximately identical results and the present work does not permit one to prefer one set to the other. Similar detailed calculations are not available for the other two potentials. WALKER et al. [40] have fitted all the diffusion data [33, 34, 38] and derived the exp-six and L – J parameters. When these are compared with the exp-six and L – J parameters derived from the pure parameters determined from viscosity in conjunction with the conventional combination rules very pronounced differences are observed. This analysis consequently suggests that these two potentials also are similar to the MORSE potential and will lead to similar discrepancies if direct calculations were performed. A limited number of such calculations are available [34, 38] to lend support to this view.

[40] R. E. WALKER, L. MONCHICK, A. A. WESTENBERG, and S. FAVIN, Physical Chemistry in Aerodynamics and Space Flight, Pergamon Press, London 1961, p. 221.

From Table 5 we find that MORSE potential succeeds well in reproducing the λ_{mix} data. The interesting point to note is that even Ar – Ne and Ne – He systems, where somewhat inferior agreement between theory and experiment was found in the case of η_{mix}, behave satisfactorily here. This suggests, when we recall that η_{mix} and λ_{mix} are about equally sensitive to the law of intermolecular potential, that these few discrepancies observed in η_{mix} are not important and one cannot assess the success of MORSE potential on these differences. SAXENA and GANDHI [41] have reported λ_{mix} values for these systems with exp-six potential. They found discrepancies of a similar type. Limited calculations available for L – J potential [26] are inferior to either of these two potentials.

5. Conclusions

In view of the detailed comparison of theory and experiment presented in section 3 and discussions on different systems and properties in section 4 we are in a position to infer the following conclusions:

(1) One serious drawback of the MORSE potential is its incapacity to represent equilibrium and non-equilibrium properties by the choice of a single set of parameters.

(2) The potential parameters determined from one property do however, succeed in correlating the data of the various properties of that class to which it belongs. The accuracy obtained in this correlation is good and competes very well with that obtained in the cases of L – J (12 – 6) and exp-six potentials.

(3) These parameters can also correlate the binary mixture properties of that very class with reasonable success and this confirms the adequacy of the existing set of combination rules to determine the unlike interactions from like interactions.

(4) Thus, on the whole MORSE potential seems somewhat inferior to the modified exp-six potential which has a better competance to correlate the experimental data on the various equilibrium and non-equilibrium properties by the choice of a single set of potential parameters.

(5) This work suggests that there is no need to test this potential on the basis of a more sensitive property like thermal diffusion, which offers a much more crucial and sensitive test for the adequacy of a molecular potential.

Acknowledgments

We are thankful to the Department of Atomic Energy, Bombay, and to the Council of Scientific and Industrial Research, New Delhi, for financial support and the award of scholarships to two of us (O. P. B. and R. S. G.).

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