

POTENTIAL PARAMETERS FOR LIKE AND UNLIKE INTERACTIONS ON MORSE POTENTIAL MODEL

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ABSTRACT. Viscosity data have been utilised to determine the force constants for the Morse potential model for Ar, N₂, He, CO₂ and O₂. These parameters can reproduce the experimental viscosity data more satisfactorily than the parameters determined from the second virial and crystal property data. A set of combination rules for unlike interactions has been proposed and tested in relation to the inter diffusion coefficients. The results thus obtained show a good agreement with the experimental values available in the literature.

INTRODUCTION

Of the various forms of the inter-molecular potential, the Lennard-Jones (12 : 6) model and Buckingham Exp-six model are quite realistic and are, therefore, invariably used for calculating the transport and equilibrium properties of gases. Recently, Konowalow, Taylor and Hirschfelder (1961a) have calculated the second virial coefficient for the Morse potential and these have been utilised by Konowalow and Hirschfelder (1961b) for determining the potential parameters for some non-polar molecules from the virial coefficients and crystal data. Over a wide range of temperature, the theoretical second virial coefficients determined from the Morse potential agree very well with the experimental data and are quite comparable with those obtained by using Lennard-Jones (12 : 6) and Buckingham Exp-six potential.

Morse potential is written in the form,

$$\phi(r) = c\{\exp[-2(c/\sigma)(r-r_m)] - 2\exp[-(c/\sigma)(r-r_m)]\} \quad \dots (1)$$

where $\phi(r)$ is the potential energy of the two molecules separated by a distance r , c is the maximum attraction energy at $r = r_m$, σ is the finite value of r at which $\phi(r) = 0$, and the parameter c is related to the width of the potential well. The quantity c is given by the relation

$$c = \sigma(1 + 1/c \ln 2) \quad (2)$$

Very recently, Lovell and Hirschfelder (1962) have evaluated the collision integrals for the gases obeying the Morse potential and hence the evaluation of the parameters from transport data is also possible. Usually viscosity data are used for this purpose. Very accurate data for the viscosity of Ar, N₂, He, CO₂ and O₂

are available for a wide range of temperature. We have here utilised these data to obtain the potential parameters for these substances.

A set of combination rules has been proposed to determine the unlike molecular interactions from a knowledge of the like interactions. These were so chosen as to fit in with the experimental data on the inter-diffusion coefficients of the systems He-Ar, He-N₂, CO₂-N₂ and CO₂-O₂ given by Walker and Westenberg (1958, 1959 and 1960) and by workers in this laboratory.

CALCULATIONS OF POTENTIAL PARAMETERS FROM VISCOSITY

Various methods can be employed to determine the potential parameters from the experimental viscosity data. In the present paper, we have used the ratio method. The viscosity data for Ar, N₂, He and O₂ in the temperature range 100°K-1000°K and for CO₂ in the temperature range 200°K-1000°K were utilised for this purpose.

On the Chapman-Enskog theory, the coefficient of viscosity η is given to the first approximation as (Hirschfelder *et al.*, 1954).

$$[\eta]_1 \times 10^7 = \frac{266.93 \times \sqrt{T^* \times M}}{\sigma^2 \Omega^{(2,2)*}[c, T^*]} \quad (3)$$

where T is the absolute temperature, M is the molecular weight of the substance, $\Omega^{(2,2)*}[c, T^*]$ are the collision integrals depending on c and $T^* = T/(e/k)$ as tabulated by Lovell and Hirschfelder (1962).

Let η_1 and η_2 be the viscosity coefficients at temperatures T_1 and T_2 respectively. Then

$$\left[\frac{\eta_2}{\eta_1} \right] = \left[\frac{T_2}{T_1} \right]^{\frac{1}{2}} \frac{\Omega_1^{(2,2)*}[c, T_1^*]}{\Omega_2^{(2,2)*}[c, T_2^*]} \quad (4)$$

By knowing experimentally the quantities η_1 and η_2 , values of c and c/k can be so adjusted that the right hand side of eqn. (4) becomes equal to the experimental $[\eta_2/\eta_1]$. A particular value of $[\eta_2/\eta_1]$ was chosen and for various values of c , values of c/k were found satisfying the eqn. (4). Thus for one particular value of $[\eta_2/\eta_1]$ we found corresponding values of c and c/k . The values of c were plotted against c/k for various values of $[\eta_2/\eta_1]$ and from the intersection of the curves c and c/k were found. The values of σ was then calculated using eqn. (3) at two or three temperatures and mean taken. Eqn. (2) now determines the value of r_m . The values of the force constants thus obtained are shown in the Table I. For the sake of comparison the values obtained by Konowalow and Hirschfelder (1961b) from virial and crystal data are also included in the table.

It is seen from the table, that the potential parameters determined from viscosity and those from the virial and crystal data are mutually not quite con-

sistent. This type of discrepancy between the potential parameters determined from the non-equilibrium and the equilibrium properties of fluids has been observed in the case of other potential models as well.

TABLE I
Values of the force constants on Morse potential model

Substance	From viscosity				From Virial and crystal data			
	c	$\epsilon/k^\circ K$	$\sigma \text{ \AA}$	$r_m \text{ \AA}$	c	$\epsilon/k^\circ K$	$\sigma \text{ \AA}$	$r_m \text{ \AA}$
Ar	5.7	120	3.461	3.882	5.0	144.8	3.386	3.855
N ₂	6.1	92	3.697	4.117	5.5	134.4	3.679	4.030
He	6.0	11	2.622	2.925	—	—	—	—
CO ₂	5.1	196	3.968	4.507	—	—	—	—
O ₂	5.9	98	3.544	3.957	—	—	—	—

COMPARISON WITH EXPERIMENT

In order to test the reliability of the force constants thus determined, it is necessary to see how far they reproduce the experimental data over a wide range of temperature.

TABLE II
Experimental and calculated viscosity coefficients for Ar, N₂, He, CO₂ and O₂ at different temperatures

Substance	$T^\circ K$	$\eta \times 10^7$ g/cm sec expt	$\eta \times 10^7$ g/cm sec. calculated with force constants from	
			Viscosity	Virial and crystal property data
Ar	100	839 ^a	841	769
	120	993 ^a	1003	921
	140	1146 ^a	1157	1077
	160	1298 ^a	1308	1226
	180	1447 ^a	1457	1377
	200	1594 ^a	1602	1527
	220	1739 ^a	1743	1671
	240	1878 ^a	1878	1813
	260	2014 ^a	2000	1952
	280	2145 ^a	2125	2083

TABLE II—(contd)

Substance	T °K	$\eta \times 10^7$ g/cm. sec expt	$\eta \times 10^7$ g/cm. sec. calculated with force constants from	
			Viscosity	Virial and crystal property data
Ar	300	2270 ^a	2254	2200
	800	4621 ^b	4617	4761
	1000	5302 ^b	5380	5593
N ₂	100	698 ^c	705	620
	120	826 ^c	832	737
	140	948 ^c	955	858
	160	1068 ^c	1072	972
	180	1183 ^c	1186	1084
	200	1295 ^c	1290	1194
	220	1403 ^c	1391	1304
	240	1505 ^c	1493	1410
	260	1603 ^c	1588	1510
	280	1696 ^c	1681	1606
	300	1786 ^c	1769	1698
	800	3493 ^b	3504	3563
1000	4011 ^b	4064	4158	
Po	100	947 ^a	941	—
	120	1068 ^a	1062	—
	140	1182 ^a	1178	—
	160	1290 ^a	1288	—
	180	1395 ^a	1393	—
	200	1496 ^a	1495	—
	220	1595 ^a	1594	—
	240	1692 ^a	1688	—
	260	1789 ^a	1783	—
	280	1888 ^a	1875	—
	300	1987 ^a	1963	—
	800	3840 ^d	3861	—
1000	4455 ^d	4521	—	

TABLE II (contd.)

Substance	T °K	$\eta \times 10^7$ g/cm sec expt.	$\eta \times 10^7$ g/cm sec. calculated with force constants from	
			Viscosity	Viral and crystal property data
CO ₂	200	1015 ^c	1015	—
	220	1112 ^c	1111	—
	240	1209 ^c	1212	—
	260	1303 ^c	1307	—
	280	1400 ^c	1405	—
	300	1495 ^c	1499	—
	800	3391 ^b	3383	—
	1000	3935 ^b	3986	—
O ₂	100	768 ^c	794	—
	120	917 ^c	940	—
	140	1061 ^c	1080	—
	160	1202 ^c	1216	—
	180	1341 ^c	1348	—
	200	1476 ^c	1473	—
	220	1604 ^c	1587	—
	240	1728 ^c	1707	—
	260	1845 ^c	1817	—
	280	1958 ^c	1943	—
300	2071 ^c	2031	—	
800	4115 ^e	4059	—	
1000	4720 ^e	4717	—	

a = Johnston, H. L. and Gully, E. R., (1942)
b = Vasileso, V (1945)
c = Johnston, H. L., and McCloskey, K. E. (1940)
d = Trantz, M., and Zink, R., (1930)
e = Values obtained in from the interpolation of available high temperature viscosity data.

Viscosity

Experimental and calculated viscosity coefficients in the wide range of temperature for Ar, N₂, He, CO₂ and O₂ are given in the Table II. The

calculated values of the viscosity coefficients for Ar and N₂ using the force constants from virial and crystal data are also given in the table for comparison. It can be seen from the table that the experimental viscosity data are much better reproducible with the force constants determined in this paper than with those from virial and crystal property data.

COMBINATION RULES FOR UNLIKE MOLECULAR INTERACTION

The properties of gas mixtures are dependent on the forces between unlike molecules. In principle, these forces can be determined from the accurate experimental data on the transport and equilibrium properties of mixtures. In the absence of accurate experimental data it would be very helpful to be able to predict the interaction for unlike molecules from the known interaction for like molecules. In this way the properties of gas mixtures could be calculated from the data on the pure components. Combination rules for the Morse potential model can be obtained by writing the eqn. (1) in the form

$$\phi(r) = Ae^{-2br} - Be^{-br} \quad \dots (5)$$

Following Zener (1931), we get the parameter b for unlike interaction, as

$$b_{12} = \frac{1}{2}(b_1 + b_2) \quad \dots (6)$$

which, when expressed in terms of the constants of the Morse potential, gives

$$\frac{c_{12}}{\sigma_{12}} = \frac{1}{2} \left[\frac{c_1}{\sigma_1} + \frac{c_2}{\sigma_2} \right] \quad \dots (7)$$

Following the suggestion of Srivastava and Srivastava (1958), the combination rule for the parameter c is taken as

$$c_{12} = [c_1 \times c_2]^{\frac{1}{2}} \quad \dots (8)$$

The usual combination rule for σ , which is exactly valid for the rigid sphere, is given by

$$\sigma_{12} = \frac{1}{2}[\sigma_1 + \sigma_2] \quad \dots (9)$$

The value of c_{12} is fixed by eqs. (7) and (9). The fourth parameter r_m of the Morse potential for the unlike interaction is then

$$(r_m)_{12} = \sigma_{12} \left[1 + \frac{1}{c_{12}} \ln 2 \right] \quad \dots (10)$$

However, it was found that the agreement with the calculated values of the inter-diffusion coefficient from the prescribed combination rules [Eqs. (7)-(10)] and the

experimental values was not satisfactory. Consequently, we have tried the geometric mean rule for σ_{12} , i.e.

$$\sigma_{12} = [\sigma_1 \times \sigma_2]^{\frac{1}{2}} \quad \dots (11)$$

The agreement between the calculated and the experimental values of the inter-diffusion coefficients improve by using the geometric mean rule for σ_{12} . Consequently, we suggest, eqs. (7), (8), (10) and (11) as the combination rules for unlike interactions on the Morse potential. The unlike interaction parameters for the gas pairs He-Ar, He-N₂, CO₂-N₂ and CO₂-O₂ determined by using the like interaction parameters of Table I and the combination rules are given in Table III.

The combination rules for the gas pairs shown in Table III have been tested by comparing with the experimental values of the interdiffusion coefficients. To the first approximation, the inter-diffusion coefficient D_{12} is given as (Hirschfelder *et al*, 1951).

$$[D_{12}]_1 = \frac{0.002628 \sqrt{T^3 (\bar{M}_1 + \bar{M}_2) / 2 \bar{M}_1 \bar{M}_2}}{p \sigma_{12}^2 \Omega_{12}^{(1,1)*} [c_{12} T_{12}^*]} \quad (12)$$

where p is the pressure in atmosphere, M_1 and M_2 are molecular weights of species 1 and 2, T is the absolute temperature, σ_{12} is the collision diameter, $\Omega_{12}^{(1,1)*}$ [c_{12}, T_{12}^*] is the collision integral and T_{12}^* is the reduced temperature equal to kT/ϵ_{12} .

TABLE III

Unlike force constants on Morse potential model.

Gas pairs	c_{12}	$r_{12}, \text{\AA}^\circ K$	$\sigma_1, \text{\AA}$	$(\sigma_{12})_{12}, \text{\AA}$
He—Ar	5.9	36.3	3.012	3.366
He—N ₂	6.1	31.8	3.113	3.467
CO ₂ —N ₂	5.6	134.3	3.830	4.304
CO ₂ —O ₂	5.5	138.6	3.750	4.223

The experimental and the calculated values of \bar{D}_{12} over extensive range of temperatures are shown in Table IV. It may be seen that except for the measurements of Srivastava (1959) on the He-Ar system, the agreement between the experimental and the calculated values of D_{12} is only fair. A large part of the discrepancy may be attributed to the uncertainties in the experimental method of Walker and Westenberg (1958, 1959 and 1960). Consequently, till better data are available to provide a more definite answer, the combination rules for the Morse potential as suggested in this paper may be used for calculating unlike interactions.

TABLE IV

Experimental and calculated values of inter-diffusion coefficient for the systems He-Ar, He-N₂, CO₂-N₂ and CO₂-O₂ at 1 atm.

Systems	T °K	D_{12} cm ² /sec expt.	D_{12} cm ² /sec calculated using the combination rules proposed
He—Ar	273	0.640 ^a	0.640
	288	0.701 ^a	0.702
	300	0.726 ^b	0.752
	303	0.760 ^a	0.765
	318	0.825 ^a	0.830
	400	1.247 ^b	1.224
	500	1.831 ^b	1.786
	600	2.557 ^b	2.432
	700	3.347 ^b	3.158
	800	4.202 ^b	3.956
	900	5.149 ^b	4.837
1000	6.310 ^b	5.782	
He—N ₂	243.2	0.477 ^c	0.510
	275.0	0.596 ^d	0.629
	300.0	0.739 ^d	0.728
	303.55	0.719 ^c	0.743
	332.5	0.811 ^c	0.866
	400	1.218 ^d	1.183
	500	1.782 ^d	1.724
	600	2.434 ^d	2.344
	700	3.144 ^d	3.038
	800	3.940 ^d	3.849
	900	4.752 ^d	4.650
1000	5.652 ^d	5.560	
CO ₂ —N ₂	300	0.171 ^d	0.157
	400	0.300 ^d	0.264
	500	0.445 ^d	0.392
	600	0.610 ^d	0.539
	700	0.798 ^d	0.704
	800	0.998 ^d	0.837
	900	1.215 ^d	1.085
1000	1.468 ^d	1.299	

TABLE IV (cont'd.)

Systems	T °K	D_{12} cm ² /sec expt	D_{12} cm ² /sec calculated using the combination rules proposed
	300	0 160 ^a	0 156
	400	0 270 ^a	0 203
	500	0 400 ^a	0 391
	600	0 565 ^a	0 538
CO ₂ -O ₂	700	0 740 ^a	0.705
	800	0 928 ^a	0.887
	900	1.142 ^a	1 086
	1000	1 386 ^a	1 302

^a = Srivastava, K. P (1959).

^b = Walker, R. E. and Westenberg, A. A., (1959).

^c = Paul, R., and Srivastava, I. B., (1961).

^d = Walker, R. E. and Westenberg, A. A., (1958).

^e = Walker, R. E. and Westenberg, A. A., (1960).

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