

GAS PROPERTIES AT HIGH TEMPERATURES ON THE EXPONENTIAL MODEL

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(Received March 15, 1961)

ABSTRACT. High temperature viscosity data have been utilised to obtain the potential parameters for the exponential model for He, A, N₂, O₂ and CO₂. These parameters can reproduce the experimental viscosity data at high temperatures more satisfactorily than the parameters determined from scattering experiments. The combination rules proposed for the exponential model have been tested in relation to the high temperature inter-diffusion coefficient and the results so obtained are discussed.

I N T R O D U C T I O N

The knowledge of the gas properties at high temperatures is of great importance particularly in connection with high speed gas dynamics, combustion, detonation etc. In the experimental determination of the required gas properties at very high temperatures, many difficulties are to be surmounted and even then the results are liable to large errors. Further, the graphical extrapolation of the low temperature data is likely to give unsatisfactory results at high temperatures. More satisfactory values for the transport coefficients can, however, be obtained by calculating the intermolecular potential from high temperature properties and utilising the equations of the kinetic theory to calculate the required transport property.

At high temperatures small intermolecular separations are predominant (Hirschfelder *et al.*, 1954). Above the Boyle point the attractive part of the intermolecular potential becomes less important than the repulsive part. Hence in the consideration of the high temperature gas properties we may neglect the attractive part of the potential and assume only the repulsive part (Cottrell, 1956). At low and intermediate temperatures the intermolecular potential is believed to be represented reasonably well by the various molecular models (e.g. Lennard-Jones 12 : 6, exp-6, etc.), but their applicability to gases at high temperatures is open to question (1958a, 1958b).

Amdur and his co-workers (1954-57) have tried to fit their molecular scattering data to a potential of the form

$$\phi(r) = \frac{A}{r^8} \quad \dots (1)$$

where A and s are constants and r is the intermolecular separation. Subsequently Amdur and Mason (1958a) have calculated a large number of gas properties at high temperatures from the low and intermediate temperature data and have suggested that a potential of the form

$$\phi(r) = A e^{-\frac{r}{\rho}} \quad \dots (2)$$

may be able to reproduce the experimental data over a wide range of temperatures than the inverse power model. They have obtained the constants A and ρ for several substances from the scattering experiments, but could not test the accuracy of the values by comparison with experimental transport property data, as the collision integrals on the exp-model were not available. Quite recently Monchick (1959) has evaluated the various collision integrals on the exp-model; therefore evaluation of the potential parameters from transport data is also possible. Walker and Westenberg (1960) have utilised these collision integrals to determine the unlike potential parameters from their experimental diffusion data for the gas pairs $\text{CO}_2\text{--O}_2$, $\text{CH}_4\text{--O}_2$, $\text{H}_2\text{O--O}_2$ and CO--O_2 and obtained some interesting results. In the present paper we have determined the potential parameters for the exponential model from the data on high temperature viscosity of pure components. These have been compared with the values available from other sources.

CALCULATION OF POTENTIAL PARAMETERS FROM HIGH TEMPERATURE VISCOSITY

Large amount of experimental data in the temperature range where Eq. (2) is applicable exists for viscosity (1930, 1945, 1958, 1959). It was, however, found that the constants A and ρ given by Amdur and Mason (1958) fail to reproduce these data satisfactorily. Hence it was felt desirable to obtain the constants A and ρ on the exponential model directly from the viscosity data at high temperatures. These constants are likely to reproduce the transport properties better than those determined from the scattering data. The viscosity data for He, A, N_2 , O_2 and CO_2 in the temperature range 800°K–1500°K were utilised for this purpose.

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

$$[\eta]_1 \times 10^7 = 266.93 \sqrt{T} \times M / \sigma^2 \Omega^{(2,2)*} g / \text{cm-sec.} \quad \dots (3)$$

where T is the absolute temperature, M the molecular weight of the substance $\Omega^{(2,2)*}$ are the collision integrals, σ is some arbitrary length parameter which is defined by $\phi(r)$ and is given by (Monchick, 1959).

$$\sigma^2 \Omega^{(l,s)*} = 8x^2 \rho^2 I_{(l,s)}(\alpha) / (s+1)! [1 - \frac{1}{2} \{1 + (-1)^s\} / (1+l)] \quad \dots (4)$$

where l, s are integral numbers, $I(\alpha)_{(l,s)}$ are in the form of integrals depending upon α , and α is related to A in Eq. (2) by (Monchick, 1959).

$$\alpha = \ln(A/kT) \quad \dots \quad (5)$$

Values of the integrals $I(\alpha)_{(l,s)}$ are tabulated (Monchick, 1959) as function of α . Comparing Eq. (3) and (4) we get ($l = s = 2$, for η)

$$]_1 \times 10^7 = 133.46\sqrt{T.M/\alpha^2\rho^2 I(\alpha)_{(2,2)}} \quad (6)$$

In Eq. (6) ρ is temperature independent and $\alpha^2 I(\alpha)_{(2,2)}$ is temperature dependent. Let η_1 and η_2 be the viscosities at temperatures T_1 and T_2 respectively. Then

$$[\eta_2/\eta_1] = (T_2/T_1)^2(\alpha_1/\alpha_2)^2[I(\alpha)_{(2,2)}]_2/[I(\alpha)_{(2,2)}]_1 \quad (7)$$

where $[I(\alpha)_{(2,2)}]_1$ and $[I(\alpha)_{(2,2)}]_2$ represent the collision integrals corresponding to α_1 and α_2 respectively. Hence by knowing the quantities η_1 and η_2 experimentally, values of A can be so adjusted that the right hand side of Eq. (7) becomes equal to $[\eta_2/\eta_1]_{\text{expt}}$. For a particular substance different experimental values of the ratio $[\eta_2/\eta_1]$ were taken and A values were found in each case. The geometric mean of the A values so obtained was taken as the true values of the constants for the substance. Once A is obtained the value of ρ can be found from Eq. (6). The arithmetic mean of all ρ values thus obtained was taken as the true value for the substance. The values of the constants thus obtained are given in Table I. For the sake of comparison the values of the constants obtained by Amdur and Mason (1958) from scattering experiments are also given in the Table I.

TABLE I
Values of the constants A and ρ on the exp-model

Substance	From Viscosity			From Scattering		
	$A \times 10^8$ ergs.	ρ in Å	Range of rigid sphere diameter r_0 in Å	$A \times 10^8$ ergs.	ρ in Å	Range of rigid sphere diameter r_0 in Å
H ₀	0.0615	0.225	1.946-1.984	0.0618	0.220	1.3-2.3
A	5.125	0.244	3.106-3.214	5.174	0.224	2.2-3.4
N ₂	1.053	0.295	3.292-3.383	2.163	2.063	2.4-3.6
O ₂	1.086	0.275	3.082-3.222	--	--	
CO ₂	1.149	0.328	3.654-3.843	--	--	

The potential parameters determined from viscosity and scattering data are not quite consistent.

TABLE II

Substance	T°K	$\eta \times 10^7$ g cm. sec. expt.	$\eta \times 10^7$ g/cm. sec. calculated with force constants from	
			Viscosity	Scattering
He	800	3840 ^T	3873	4042
	850	4000 ^a	4049	4226
	900	4154 ^a	4222	4407
	950	4304 ^a	4394	4584
	1000	4455 ^T	4587	4764
A	800	4621 ^v	4677	5412
	900	4960 ^a	4961	5870
	1000	5302 ^v	5282	6263
	1100	5636 ^a	5626	6649
	1200	5947 ^v	5948	7044
	1300	6256 ^a	6272	7437
	1400	6532 ^a	6601	7802
	1500	6778 ^v	6900	8196
N ₂	800	3493 ^v	3379	3764
	972.5	3916 ^v	3856	4287
	1000	4011 ^v	3929	4367
	1020.7	4017 ^v	3986	4430
	1068.8	4119 ^v	4108	4563
	1120.2	4216 ^v	4240	4710
	1166	4374 ^v	4359	4838
	1220.5	4461 ^v	4499	4984
	1273.2	4582 ^v	4629	5134
	1500	5050 ^v	5174	5728
O ₂	800	4115 ^a	4131	
	1000	4720 ^a	4806	
	1130	5230 ^v	5240	
	1166	5382 ^v	5342	
	1203	5480 ^v	5459	
	1278	5677 ^v	5685	
	1292	5715 ^v	5728	
CO ₂	800	3391 ^v	3375	
	900	3676 ^a	3657	
	1000	3935 ^v	3925	
	1100	4200 ^a	4188	
	1200	4453 ^v	4442	
	1300	4688 ^a	4736	
	1400	4912 ^a	4933	
	1500	5139 ^v	5169	

^T Trautz, M. and Zink, R. (1930).

^v Vasilescu, V. (1945).

^e Raw, C. J. G. and Ellis, C. P. (1958).

^e Raw, C. J. G. and Ellis, C. P., (1959).

^a Values obtained from the interpolation of available high temperature viscosity data.

COMPARISON WITH EXPERIMENT

(a) *Viscosity*

An obvious test of the success of any molecular model is its ability to reproduce various experimental data with the same set of constants. In Table II, the experimental and the calculated values of the viscosity coefficients of He, A, O₂, N₂ and CO₂ at high temperatures are given. The calculated values on the exp-model from the force-constants obtained by Amdur and Mason (1958) from scattering data are also given. It can be seen from Table II that the experimental viscosity data are reproduced much better on the exponential model with the force constants determined in the present work than with those determined from scattering data. This is due to the fact that the rigid sphere diameter range of validity of the two sets of parameters are different. Parameters from scattering data are expected to be more appropriate at still higher temperatures.

(b) *Inter-diffusion coefficient*

The binary diffusion coefficient may be written to the first approximation as (Hirschfelder *et al.*, 1954)

$$[D_{12}]_1 = 0.002628 \sqrt{T^3(M_1 + M_2)/2M_1M_2/p\sigma_{12}^2\Omega_{12}^{(1,1)}} \quad (8)$$

where p is the pressure in atmospheres, M_1 and M_2 are the molecular weights of the species 1 and 2 respectively. Using the values of $\sigma_{12}^2\Omega_{12}^{(1,1)*}$ as determined with the help of Eq. (4), the expression (8) for the diffusion coefficient on the exp-model becomes,

$$[D_{12}]_1 = 0.002628 \sqrt{T^3(M_1 + M_2)/2M_1M_2/4p\alpha_{12}^2\rho_{12}^2I_{(1,1)}(\alpha_{12})} \quad (9)$$

The constants A_{12} and ρ_{12} for the pair 1-2 may be approximated by the use of the combination rules given by Amdur and Mason (1958)

$$1/\rho_{12} = 1/2(1/\rho_1 + 1/\rho_2) \quad (10)$$

$$A_{12} = (A_1 \times A_2)^{1/2} \quad (11)$$

and α_{12} is defined as before

$$\alpha_{12} = \ln(A_{12}/kT) \quad (12)$$

The values of the integrals $I_{(1,1)}(\alpha_{12})$ as functions of α_{12} have been tabulated by Monchick (1959).

Recently Walker and Westenberg (1958, 1959 and 1960) have measured the inter-diffusion coefficients at high temperatures for a number of gas pairs by the "point source technique." By using the combination rules, Eqs. (10) and (11), the inter-diffusion coefficients for the systems He-A, He-N₂, CO₂-N₂ and CO₂-O₂ have been calculated by us with the force constants determined from viscosity.

The results of these calculations together with the experimental values are given in Table III. Examination of the results in Table III shows that the agreement between the calculated and the experimental values of the diffusion coefficients is very poor for systems involving CO_2 . This discrepancy in the case of CO_2 can be attributed to the fact that the CO_2 molecule is a much poorer approximation to spherical elastic particle than the other simple molecules and the simple combining rules valid for central force fields are not as appropriate. This has also been observed by Walker and Westenberg. Further, Mason *et al.* (1960) have pointed out that the effect of excitation or charge exchange will be important in case of high temperature diffusion and thermal diffusion in particular. Besides, multiplicity of the different interaction energy curves governing collisions should also be taken into account.

TABLE III

Calculated and experimental values of binary diffusion coefficients for system He-A, He- N_2 , CO_2 - N_2 and CO_2 - O_2

System	T°K	D_{12} cm ² /sec. expt.	D_{12} cm ² /sec. cal- culated with force constants from viscosity
He-A	700	3.500	3.062
	800	4.355	3.852
	900	5.338	4.692
	1000	6.1905	6.067
	1100	7.207	7.131
He- N_2	700	3.000	3.074
	800	3.828	3.864
	900	4.686	4.747
	1000	5.614	5.676
	1100	6.572	6.674
CO_2 - N_2	700	0.8095	0.6232
	800	1.022	0.7794
	900	1.251	0.9506
	1000	1.486	1.134
	1100	1.724	1.345
	1200	1.937	1.544
CO_2 - O_2	700	0.7696	0.6469
	800	0.9759	0.8102
	900	1.197	0.9872
	1000	1.440	1.180
	1100	1.679	1.387

The small amount of discrepancy observed in the calculated and the experimental values of the diffusion coefficients for He-A at the lower temperature can be explained by assuming that the diffusion corresponds to more penetrating collisions than other transport properties at the same temperature (Hirschfelder and Eliason, 1957) and therefore the parameters from scattering data are expected to give better agreement.

ACKNOWLEDGMENTS

The author wishes to express his thanks to Prof. B. N. Srivastava, D.Sc., F.N.I., for his valuable guidance. Thanks are also due to Dr. A. K. Barua for suggesting the problem and valuable discussions throughout the progress of the work.

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