CALCULATION OF VISCOSITY OF GAS MIXTURES AT ATMOSPHERIC PRESSURE

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A method is presented for calculating the viscosity of a multicomponent mixture, based on the use of potential functions with variable parameters $\sigma(T)$ and $\varepsilon(T)$. It is shown that the agreement of theory with experiment is good.

Since the available experimental data on viscosity of gas mixtures is limited, theoretical methods which would allow the viscosity η_m to be determined from data on the pure constituents are very important, especially at high temperatures. On the basis of the strict kinetic theory of multicomponent gas mixtures the viscosity of a ν-component mixture is given by the expression [1]

$$[\eta_m]_1 = -\frac{\begin{vmatrix} H_{11} & H_{12} & \cdots & H_{1\nu} & x_1 \\ H_{12} & H_{22} & \cdots & H_{2\nu} & x_2 \\ \vdots & \vdots & & \vdots & \vdots \\ H_{1\nu} & H_{2\nu} & \cdots & H_{\nu\nu} & x_\nu \\ x_1 & x_2 & \cdots & x_\nu & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} & H_{12} & \cdots & H_{1\nu} \\ H_{12} & H_{22} & \cdots & H_{2\nu} \\ \vdots & \vdots & & \vdots \\ H_{1\nu} & H_{2\nu} & \cdots & H_{\nu\nu} \end{vmatrix}}, \tag{1}$$

where

$$H_{ii} = \frac{x_i^2}{\eta_i} + \sum_{\substack{k=1 \\ k \neq i}}^{\nu} \frac{2x_i x_k}{\eta_{ik}} \frac{M_i M_k}{(M_i + M_k)^2} \left[\frac{5}{3A_{ik}^*} + \frac{M_k}{M_i}\right],$$

$$H_{ij} = -\frac{2x_i x_j}{\eta_{ij}} \frac{M_i M_j}{(M_i + M_j)^2} \left[\frac{5}{3A_{ij}^*} - 1\right], \quad i \neq j.$$

The viscosities of pure substances η_i and the quantities η_{ij} are given by the expressions

$$\eta_i \cdot 10^7 = 266.93 \frac{\sqrt{TM_i}}{\sigma_i^2 \Omega_i^{(2,2)*}(T_i^*)} f_\eta^{(3)}, \tag{2}$$

$$\eta_{ij} \cdot 10^7 = 266.93 \frac{\sqrt{2M_i M_j T / M_i + M_j}}{\sigma_{ij}^2 \Omega_{ij}^{(2,2)*}(T_{ij}^*)} f_\eta^{(3)}. \tag{3}$$

In these formulas, x_i and M_i are the mole fraction and molecular weight of the i-th component; T is the absolute temperature; $T^* = kT/\varepsilon$ is the reduced temperature; σ and ε are the parameters of the intermolecular interaction function; $A^* = \Omega^{(2,2)*}/\Omega^{(1,1)*}$ is the ratio of relative collision integrals.

In spite of a certain awkwardness, formula (1) has the undoubted advantage of being based on theory. It may therefore be used for any temperature region (including also high temperatures), and for any mixture, regardless of the number of components. It should be noted that (1) gives a first approximation for the viscosity of a mixture. However, as has been shown in [2], the difference from the second approximation is usually a quantity on the order of 1%. It may therefore be neglected without detriment to the accuracy of the calculations.

The use of (1)–(3) is nevertheless restricted because, for mixtures with components widely different in molecular structure, there is no single potential which would permit correct computation of the interaction between the dissimilar molecules of the components. In addition, in many cases, with complex substances, it is not possible to choose one or the other of the known interaction potentials and thence calculate the viscosity η_i.

The object of the present paper is to show that these difficulties may be overcome by using a method developed by one of the authors [3], which allows a uniform description of all the thermophysical properties of a substance. This method is based on the possibility of representing the intermolecular interaction of any complex molecules by some mean potential function with temperature-dependent potential parameters:

$$u = 4\varepsilon(T)\{[\sigma(T)/r]^{12} - [\sigma(T)/r]^6\}. \tag{4}$$

In the first place this procedure successfully describes the properties of the individual substances (components) at moderate and high temperatures with an accuracy sufficient for practical purposes. The method has shown that the single potential parameters $\sigma(T)$ and $\varepsilon(T)$ give a reliable description not only of the equilibrium properties, but also of the transport coefficients of the gases over a wide range of parameters, including the high-temperature region. This has been verified for a large number of different substances (about 30), composed of both simple and complex molecules, including the polar gases H_2O, NH_3, HF, HCl, and others. Thus, in calculating the viscosity of a mixture consisting of components of different complexity, it is possible to obtain reliable data on the viscosity η_i over a wide enough temperature range.

Secondly, the fact that any intermolecular interaction, independently of the structure of the colliding

Table 1

Comparison of Calculated Values of Viscosity of H_2—CO_2 Mixtures with Experimental Values [4]

x_{H_2}, %	$\eta \cdot 10^7$, g/cm · sec					
	T=400 °K		T=500 °K		T=550° K	
	experiment	calculation	experiment	calculation	experiment	calculation
0	1944	1897	2353	2312	2556	2515
11.79	1951	1899	2360	2308	2554	2508
19.93	1945	1897	2358	2302	2542	2500
41.29	1933	1878	2321	2265	2506	2452
59.46	1878	1824	2239	2184	2471	2356
78.50	1713	1669	2026	1976	2173	2122
88.88	1526	1483	1783	1740	1904	1861
100.00	1081	1090	1256	1264	1341	1346
mean error, %		2.44		2.09		2.10

molecules, is described by the single potential function (4), gives a basis for the use of the function to describe the interaction of nonhomogeneous molecules. This makes it possible to calculate coefficients in accordance with (3), in which the collision integrals $\Omega^{(2,2)*}$, tabulated in [1] for the potential (4), may be used. For this purpose it is necessary to know the potential parameters σ_{ij} and ε_{ij}. When components i and j are composed of spherical molecules, σ_{ij} and ε_{ij}, as is known, may be reliably determined according to the following empirical relations:

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j), \; \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \qquad (5)$$

Since the model corresponding to potential (4) with variable parameters $\sigma(T)$ and $\varepsilon(T)$ is a generalized model of a pseudo-spherical gas (with centrally-symmetric forces), for a mixture with any components the most probable rules for combining the potential parameters must be the rules (5).

In the present work we calculated the viscosity of mixtures according to (1)–(3), using the intermolecular interaction potential functions (4) and the combination rules (5). For this purpose it was necessary to know only the potential parameters, $\sigma(T)$ and $\varepsilon(T)$, of the pure components. There parameters are given in Tables 3 and 4 for some gases. Viscosities were calculated for 20 binary mixtures and for a number of multicomponent mixtures for which experimental data appear in the literature, and a comparison with experiment was made. The mixtures comprised gases of different complexities, H_2, O_2, N_2, CO_2, CH_4, C_2H_4, NH_3, H_2O, etc.

It should be noted that for all the mixtures checked, both binary and multicomponent (Fig. 4), good agreement (3% or better) with experiment was found. It is important to stress here that good results were also obtained for systems which had a far from linear dependence of viscosity on composition (H_2—CO_2, Table 1).

There is naturally very great interest in the results of comparison with mixtures whose components correspond to various molecular models and cannot be described by the classical Lennard-Jones potentials with constants ε and σ.

In this respect mixtures containing a polar component are typical. For all such complex systems on which there are experimental data (NH_3—H_2, NH_3—O_2, NH_3—N_2, NH_3—C_2H_4, etc.), good agreement with experiment (1–3%) is observed. As an illustrative example we shall make a comparison with the experimental data of [4] for the mixture NH_3—C_2H_4 in Table 2 and NH_3—N_2 in Fig. 1.

An exception is the unique mixture of 50% H_2O and 50% N_2 shown in Fig. 2, for which considerable discrepancies (on the order of 15–20%) with the experimental data [5] were observed. As regards the data of [5], it should be noted that they fall outside the general relation observed for the viscosity of binary mixtures. In the first place, the fact should be borne in mind that these data practically coincide with the viscosity of pure water vapor. Secondly, if, using the data of [5], we try to construct the dependence of mixture viscosity on composition, as in Fig. 3, the curve $\eta_m = f(x)$ is seen to be anomalous (there is a steep

Table 2

Comparison of Calculated Values of Viscosity of NH_3—C_2H_4 Mixtures with Experimental Data [4]

$x_{C_2H_4}$, %	$\eta \cdot 10^7$, g/cm · sec			
	T=473.15° K		T=523.15° K	
	experiment	calculation	experiment	calculation
0	1646	1646	1813	1848
11.33	1647	1631	1809	1821
19.29	1648	1621	1805	1805
30.39	1639	1608	1791	1783
42.28	1622	1590	1764	1750
70.07	1595	1571	1729	1713
89.04	1561	1558	1689	1685
100.00	1541	1550	1666	1670
mean error, %		1.09		0.66

Table 3
Potential Parameters ε/k, °K and σ, Å

T, °K	For H_2O		For NH_3		For CO_2	
	ε/k	σ	ε/k	σ	ε/k	σ
300	—	—	—	—	222.1	3.931
350	—	—	—	—	220.5	3.927
400	632.6	2.971	377.9	3.251	219.0	3.925
450	620.2	2.958	366.9	3.236	217.4	3.920
500	609.0	2.946	356.4	3.221	215.7	3.916
550	599.1	2.936	346.7	3.207	213.8	3.913
600	589.9	2.926	337.3	3.194	211.3	3.910
650	580.6	2.918	327.2	3.182	208.4	3.908
700	572.0	2.911	315.2	3.171	206.4	3.906
750	564.0	2.904	303.2	3.161	206.9	3.904
800	556.3	2.898	294.0	3.152	208.0	3.902
850	548.5	2.892	287.6	3.144	209.4	3.901
900	541.0	2.886	283.6	3.137	210.5	3.899
950	532.7	2.881	282.0	3.131	211.4	3.898
1000	523.5	2.876	282.1	3.125	212.1	3.897
1100	502.5	2.868	283.1	3.115	213.1	3.894
1200	481.1	2.860	285.1	3.106	213.8	3.891
1300	466.1	2.852	287.7	3.097	214.3	3.889
1400	458.0	2.845	290.6	3.090	214.7	3.887
1500	454.1	2.839	293.5	3.083	215.0	3.885
1600	453.5	2.834	296.2	3.076	215.2	3.883
1700	454.4	2.828	298.5	3.070	215.5	3.881
1800	456.0	2.824	300.5	3.065	215.7	3.879
1900	458.1	2.819	302.2	3.060	215.9	3.877
2000	461.0	2.815	303.6	3.055	216.1	3.875
2200	467.4	2.807	306.0	3.045	216.3	3.872
2400	473.2	2.800	307.8	3.037	216.5	3.869
2600	478.2	2.794	309.2	3.029	216.7	3.867
2800	482.2	2.788	310.2	3.022	216.8	3.865
3000	485.5	2.782	311.2	3.016	216.9	3.863

T, °K	For C_2H_4		For N_2		For O_2	
	ε/k	σ	ε/k	σ	ε/k	σ
200	—	—	95.89	3.702	117.8	3.467
250	—	—	95.57	3.702	117.6	3.467
300	213.9	4.235	95.16	3.701	117.3	3.466
350	212.6	4.231	95.01	3.701	116.9	3.466
400	211.4	4.227	95.25	3.700	116.5	3.465
450	210.2	4.223	95.41	3.700	116.7	3.465
500	208.9	4.220	95.51	3.699	116.9	3.464
550	207.4	4.217	95.59	3.699	117.0	3.464
600	205.4	4.214	95.64	3.699	117.1	3.464
650	203.2	4.212	95.68	3.699	117.2	3.464
700	202.6	4.210	95.71	3.699	117.3	3.463
750	202.9	4.209	95.72	3.699	117.3	3.463
800	203.9	4.208	95.75	3.699	117.4	3.463
850	205.0	4.206	95.74	3.698	117.4	3.463
900	205.9	4.205	95.74	3.698	117.4	3.463
950	206.6	4.204	95.75	3.698	117.4	3.462
1000	207.2	4.203	95.75	3.698	117.4	3.462
1100	208.0	4.202	95.75	3.698	117.4	3.462
1200	208.4	4.201	95.76	3.698	117.5	3.462
1300	208.7	4.200	95.76	3.698	117.5	3.462
1400	208.9	4.199	95.76	3.697	117.5	3.462
1500	209.0	4.198	95.76	3.697	117.5	3.462
1600	209.1	4.197	95.76	3.697	117.5	3.461
1700	209.2	4.196	95.76	3.697	117.5	3.461
1800	209.3	4.195	95.76	3.697	117.5	3.461
1900	209.4	4.195	95.76	3.697	117.5	3.461
2000	209.4	4.194	95.76	3.697	117.5	3.461
2200	209.5	4.192	95.76	3.697	117.5	3.461
2400	209.5	4.191	95.76	3.696	117.5	3.461
2600	209.5	4.189	95.76	3.696	117.5	3.460
2800	209.5	4.188	95.76	3.696	117.5	3.460
3000	209.5	4.187	95.76	3.696	117.5	3.460

Table 4
Potential Parameters at the Boyle Temperature

Gas	T_B, °K	$\frac{\varepsilon_B}{k}$, °K	σ_B, Å
H_2O	1550	453.6	2.836
NH_3	963.3	282.0	3.129
CO_2	705.0	206.4	3.905
C_2H_4	692.1	202.6	4.211
N_2	324.4	94.96	3.701
O_2	397.9	116.5	3.465

Table 5
Viscosity of the Pure Components

T, °K	$\eta \cdot 10^7$, g/cm · sec					
	H_2O	NH_3	CO_2	C_2H_4	N_2	O_2
200	—	—	—	—	1260	1424
250	—	—	—	—	1515	1728
300	—	—	1444	1020	1748	2010
350	—	—	1675	1173	1962	2272
400	1277	1352	1897	1321	2160	2513
450	1466	1555	2108	1468	2348	2742
500	1661	1757	2312	1608	2527	2957
550	1858	1959	2515	1740	2698	3163
600	2057	2157	2701	1869	2861	3359
650	2258	2358	2887	1992	3021	3551
700	2458	2559	3061	2110	3175	3736
750	2657	2756	3223	2224	3325	3916
800	2853	2936	3378	2333	3470	4090
850	3048	3126	3526	2436	3612	4260
900	3242	3292	3673	2536	3751	4426
950	3436	3445	3815	2636	3881	4588
1000	3630	3593	3955	2733	4020	4746
1100	4015	3879	4229	2979	4277	5054
1200	4392	4144	4494	3098	4529	5353
1300	4754	4404	4750	3272	4771	5642
1400	5084	4652	4998	3440	5006	5920
1500	5391	4895	5241	3603	5235	6193
1600	5680	5129	5476	3762	5460	6458
1700	5958	5359	5706	3918	5680	6717
1800	6228	5587	5931	4070	5895	6972
1900	6488	5809	6152	4217	6103	7221
2000	6742	6028	6369	4364	6311	7466
2200	7230	6458	6790	4648	6710	7941
2400	7704	6871	7198	4925	7102	8403
2600	8162	7277	7590	5193	7478	8849
2800	8610	7676	7973	5450	7846	9285
3000	9048	8060	8346	5703	8204	9709

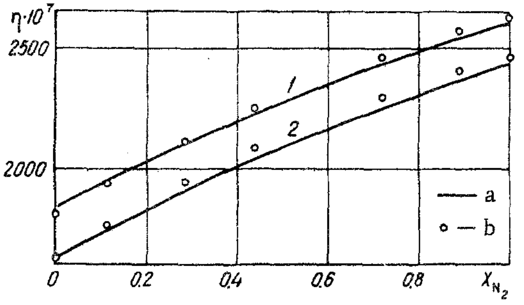

Fig. 1. Dependence of the viscosity of the mixture NH_3—N_2 (g/cm • sec) on composition and temperature: 1) at 523.15° K; 2) 473.15° K; a) data of present paper; b) experimental data of [4].

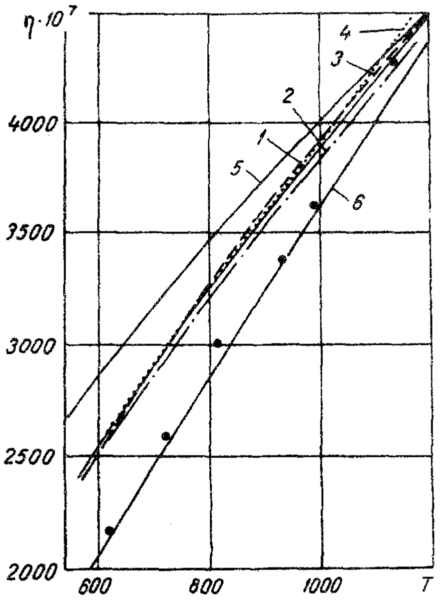

Fig. 2. Dependence on T(°K) of the viscosity η (g/cm• sec) of a mixture of 50% (molar) H_2O and 50% N_2: 1, 2, 3, 4) calculated curves from the data of the present paper, from the Wilke formula [6], and by the methods of [7] and [8], respectively; 5, 6) experimental curves for N_2 and H_2O; the points are experimental of [5].

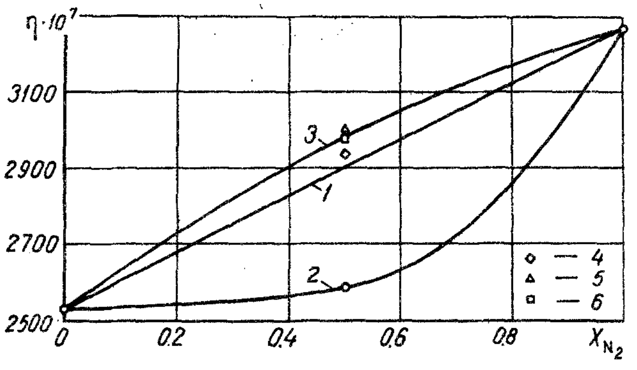

Fig. 3. Dependence of viscosity η (g/cm• sec) of a 50% H_2O—50% N_2 mixture on composition at temperature 718.55 ° K: 1) according to a linear law; 2) according to the experimental data of [5]; 3) according to the data of the present paper; 4) according to the Wilke formula [6]; 5) according to the method of reference [7]; 6) according to the method of [8].

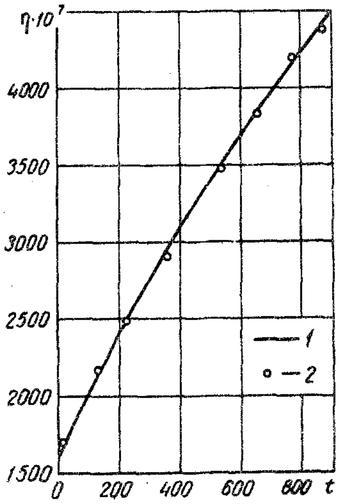

Fig. 4. Dependence of viscosity η (g/cm• sec) of a mixture of 19.82% CO_2—79.54% N_2—0.64% O_2 on temperature t (°C): 1) according to the data of the present paper; 2) according to the experimental data of [9].

negative slope of η_m with viscosity, calculated according to a linear law). For binary mixtures, as a rule, the observed behavior of the curve is the opposite (Fig. 1).

Figure 2 also gives values of viscosity calculated by other independent methods, described in references [6, 7, 8], and our data practically coincide with the results of these calculations, the discrepancies being not more than 2%. This in turn confirms the correctness of our calculations, and is also evidence that the data of [5] should be considered appreciably too low.

Tables 3 and 4 give the potential parameters of several gases used for calculating the viscosities of the mixtures illustrated in Figs. 1–4. These parameters were found by the method described in [3]. It may be seen from the table, that the dependence of the potential parameters on temperature is the stronger, the more complex the gas molecule. For diatomic gases (N_2, O_2) the potential parameters do not change appreciably with change of temperature, since their molecules do not possess appreciable asymmetry. Constant potential parameters of these gases have been given repeatedly in the literature, but they were suitable for calculating either the second virial coefficient alone, or the viscosity alone. Although the σ and ε/k given in the present paper for diatomic gases may be considered practically constant for calculating viscosity, their value rests in the fact that they are unique for calculating both transport and thermodynamic properties. Moreover, it should be kept in mind that the quantity σ enters into the formulas for calculating the second and third virial coefficients at the third and sixth power, respectively. Therefore a small error in σ may lead to large errors in calculating the virial coefficients. Table 5 gives the viscosities of pure gases calculated on the basis of the potential parameters obtained in this paper.

Thus, the following conclusions may be drawn:

1. The use of the potential function (4) with variable potential parameters permits a reliable description of the viscosity not only of pure components, but also of mixtures.

2. The method of calculating the viscosity of a mixture, using the exact formulas of kinetic theory, the proposed potential function with variable parameters, and the combination rules (5), is a universal one, gives high accuracy in practice, and may be used for any multicomponent mixture over a wide temperature range, including the high-temperature region.

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