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Applicability of a Viscosity Formula of Liquid Mixtures to Gaseous Mixtures

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Synopsis. Since 1929, the writer has carried out an elaborate calculation on the viscosity of binary liquid mixtures,[1] using for an ideal mixture the formula

$$\eta = \frac{\eta_1}{1+\frac{k_2a_2}{k_1a_1}\frac{z_m}{1-z_m}} + \frac{\eta_2}{1+\frac{k_1a_1}{k_2a_2}\frac{1-z_m}{z_m}}$$

or that in hyperbolic form

$$\frac{(\eta-\eta_1)(1-z_m)}{(\eta_2-\eta)\cdot z_m} = \frac{k_2a_2}{k_1a_1} = K \text{ (a constant)}$$

where a is the degree of association, k the molecular field constant and z_m the formal mol fraction of component 2. However, if there occurs a maximum in $(\eta-z_m)$ diagram, we can not evaluate K from the formula, since negative values result in the neighborhood of the maximum. In this case the formula $K=\eta_1M_2a_2/\eta_2M_1a_1$ may be preferable provided that the equality $K=k_2/k_1=\eta_1M_2/\eta_2M_1$ holds for gaseous mixtures where $a_1=a_2=1$. The applicability of the formulas is discussed.

The writer tried to compare his formula for the ideal case[2] with that of Thiesen for gaseous mixtures:[3]

$$\eta = \frac{\eta_1}{1+A\frac{z_m}{1-z_m}} + \frac{\eta_2}{1+B\frac{1-z_m}{z_m}}, \quad A=\frac{a_{12}}{a_{11}}, \quad B=\frac{a_{21}}{a_{22}}$$

where a is an empirical constant defined as "Diffusions konstante".

Among the five mixtures, only the one He–H_2 satisfied conditions for the product A×B to be nearly unity: 0.991, 1.021, and 1.022 at 0, 15, and 100 °C, respectively. indicates that the writer's formula is available for gaseous ideal mixtures as well as liquid ideal mixtures.

The writer proposed another form of $K=\eta_1M_2a_2/\eta_2M_1a_1$ deduced from five liquid mixtures having equivalent association degrees or $a_1=a_2$ in his fundamental formula: C_2Cl_3H (0.99—1.02)-C_2Cl_5H (1.02—1.05), CCl_4 (1.09—1.00)-C_2Cl_4 (0.92—1.01), $C_2H_5COOC_2H_5$ (1.13—1.20)-$CH_3COOC_3H_7$ (1.16—1.21), $C_6H_5CH_3$ (1.16—1.14)-C_6H_5Br (1.19—1.05), m-$CH_3C_6H_4OH$ (1.81—1.60)-p-$CH_3C_6H_4OH$ (1.82—1.62), numbers in parentheses denoting association degrees.[4,5]

Precise measurements were carried out for ideal gaseous mixtures in a few cases: He–H_2 by Gille[6] and Kr–Ar by Kestin *et al.*[7]

Table 1. He–H_2, $\eta(\mu P)$

z_m–H_2	η_{obsd}			K(I)		
	0 °C	15 °C	100 °C	0 °C	15 °C	100 °C
0.00000	189.25	196.11	234.08			
0.03906	185.00	191.33	228.07	1.036	1.135	1.197
0.10431	175.96	183.19	220.32	1.242	1.143	1.020
0.13600	173.27	178.46	215.55	1.138	1.236	1.060
0.24913	160.32	165.28	198.60	1.144	1.199	1.136
0.40284	143.06	147.69	178.47	1.161	1.198	1.114
0.60143	122.67	126.52	151.74	1.144	1.190	1.155
0.81193	101.65	105.48	126.46	1.156	1.185	1.135
1.00000	84.10	87.76	104.50	1.146	1.187	1.117
			K(II)	1.133	1.125	1.128

Put as follows for the viscosity of an ideal gaseous mixture:

$$\frac{(\eta-\eta_1)(1-z_m)}{(\eta_2-\eta)\cdot z_m} = K \qquad \text{(I)}$$

Applying the relation to the mixtures He–H_2 and Kr–Ar, we obtain the results given in Tables 1 and 2, and Figs. 1 and 2. K(I) denotes the values calculated by means of (I), and K(II) the values obtained from the relation

$$K = \eta_1M_2/\eta_2M_1 \qquad \text{(II)}$$

We see in Tables 1 and 2 that the values of K(I) and K(II) coincide with each other, though all the values of

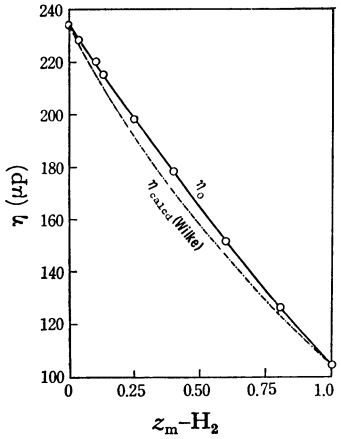

Fig. 1. He–H_2 (100 °C)

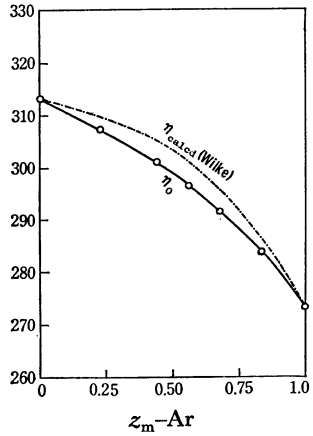

Fig. 2. Kr–Ar (100 °C)

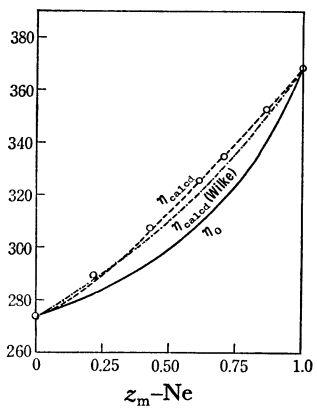

Fig. 3. Ar–Ne (100 °C)

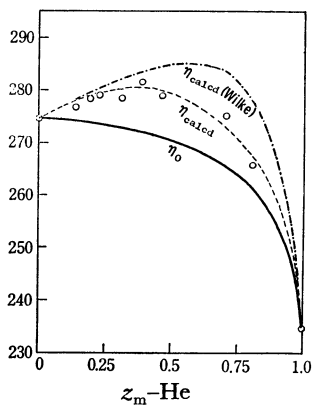

Fig. 4. Ar–He (99 °C)

TABLE 2. Kr–Ar, $\eta(\mu P)$

z_m–Ar	η_{obsd}							
	25 °C	100 °C	190 °C	300 °C	380 °C	510 °C	600 °C	700 °C
0.0000	254.79	312.97	375.58	442.57	490.08	557.75	602.68	652.61
0.2306	250.97	307.26	367.92	432.59	478.34	543.50	587.30	635.90
0.3915	247.46	302.42	361.23	423.95	468.29	531.62	574.27	622.35
0.5613	243.25	296.47	352.95	413.32	455.99	517.29	558.44	606.06
0.6793	239.59	291.49	346.22	404.89	—	—	—	—
0.8355	233.80	283.57	335.91	392.30	431.76	489.05	527.38	572.66
1.0000	226.29	273.25	323.08	377.22	414.34	468.48	505.05	547.76

z_m–Ar	K (I)							
	25 °C	100 °C	190 °C	300 °C	380 °C	510 °C	600 °C	700 °C
0.2306	0.5164	0.5554	0.5700	0.6014	0.6120	0.5893	0.6239	0.6326
0.3915	0.5378	0.5377	0.5846	0.6193	0.6278	0.6432	0.6379	0.6305
0.5613	0.5312	0.5602	0.5921	0.6333	0.6397	0.6479	0.6476	0.6243
0.6793	0.5395	0.5621	0.5990	0.6429	—	—	—	—
0.8355	0.5503	0.5609	0.6088	0.6563	0.6592	0.6576	0.6639	0.6322
1.0000	0.5350	0.5553	0.5909	0.6306	0.6347	0.6345	0.6433	0.6299
K(II)	0.5366	0.5459	0.5541	0.5592	0.5637	0.5674	0.5687	0.5678

K(I) are greater than those of K(II) at 380—700 °C, the divergence in $(\eta_{obs}-\eta_0)/\eta_0$ being at most 0.5%. If we take the relation

$$\eta_0 = \frac{\eta_1}{1+K\frac{z_m}{1-z_m}} + \frac{\eta_2}{1+\frac{1}{K}\frac{1-z_m}{z_m}}, \quad K = \frac{\eta_1 M_2}{\eta_2 M_1}$$

as a basic formula, any gaseous mixture can be analyzed as for liquid mixtures.[1]

As an example of non-ideal gaseous mixtures, two mixtures Ar–Ne (100 °C) and Ar–He (99 °C) are quoted from the measurements of Kestin, Wakeham and Watanabe[7] and Kalelkar and Kestin.[8]

The results are summarized in Tables 3 and 4 and Figs. 3 and 4. The curves denoted by η_{calcd} (Wilke) in Figs. 1—4 are plotted by use of Wilke's semi-theoretical formula for gaseous mixtures:[9]

$$\eta = \frac{\eta_1}{1+\phi_{12}\frac{z_m}{1-z_m}} + \frac{\eta_2}{1+\phi_{21}\frac{1-z_m}{z_m}},$$

$$\phi_{12} = \frac{[1+(\eta_1/\eta_2)^{1/2}\cdot(M_2/M_1)^{1/4}]^2}{2\sqrt{2}\,(1+M_1/M_2)^{1/2}},$$

$$\phi_{21} = \frac{[1+(\eta_2/\eta_1)^{1/2}\cdot(M_1/M_2)^{1/4}]^2}{2\sqrt{2}\,(1+M_2/M_1)^{1/2}}$$

TABLE 3. Ar–Ne, $\eta(\mu P)$, 100 °C

z_m–Ne	η_{obsd}	η_o	δ	$\delta/(1-z_m)z_m^2$
0.0000	273.25			
0.2093	289.14	281.88	7.26	(209.6)
0.4267	307.52	291.11	13.41	128.5
0.6145	325.34	308.93	16.41	112.7
0.7054	334.72	318.51	16.21	110.6
0.8639	352.41	340.67	11.74	115.6
1.0000	369.06			116.1
		K=0.3740		

TABLE 4. Ar–He, $\eta(\mu P)$, 99 °C

z_m–He	η_{obsd}	η_o	δ	$\delta/(1-z_m)z_m$
0.0000	273.07			
0.2270	276.27	271.68	4.59	28.16
0.4390	278.27	268.58	8.69	35.29
0.6308	276.35	266.13	10.22	43.88
0.7596	270.36	261.77	8.59	47.04
0.9048	253.99	251.21	2.78	32.27
1.0000	231.73			36.91
		K=0.1181		

Coincidence is satisfactory between η_0 and observed η_{obsd}(○) (Figs. 1 and 2), η_0 being less than η_{obsd}(Figs. 3 and 4). We can therefore apply any suitable functional form of z_m, generally $(1-z_m)^{\nu_1} z_m^{\nu_2}$ to the difference $\delta=(\eta_{obsd}-\eta_0)$, where ν_1 and ν_2 are the numbers of both component molecules which take part in a reaction to form a molecular compound or an aggregate or "embryo" as called by Lekenby and co-workers.[10]

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