The Quantum Mechanical Treatment of Viscosity by Use of the Rigid Elastic Sphere Model. II. The Sutherland Constant.

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Introduction. In part one of the present study in which the viscosity η was treated theoretically from the standpoint of quantum mechanics, it was shown that its temperature variation was reproduced more correctly over the wide ranges than from the classical standpoint, and especially so if the term originated by Sutherland was introduced, when the elastic rigid sphere model was used. These consequences led us to consider that the Sutherland constant C, determined empirically by the classical formula of viscosity:

$$\eta \propto \frac{\sqrt{T^3}}{Q_{\eta 0}(1+C/T)}, \qquad (1)$$

where Q_{η_0} denoted the viscosity close-section, included not only the generally accepted meaning of the degree of the molecular attraction,(2) but also the quantum mechanical effect. From such reasons it becomes evident that some of the stoichiometrical studies dealing with the constant would be worthy of reinspection by use of the new constant C_0 which correlates to the degree of the intermolecular potential only. It is the object of the present study to carry it out, and to examine the above conclusion.

Determination of C_0. The constant C_0 can be obtained, as in the case of neon, by such procedure that the temperature variation of η fits well with the theoretical formula in the previous paper.(1) However, as it is too laborous to carry out the procedure for many substances, the following simplified method was adopted conventionally.

It was assumed that the quantal viscosity cross-section did not depend upon the velocity of molecules but depend only on the temperature. Thus the Sutherland constant C_0 having quantal meaning was given also by (1), on the condition that Q_{η_0} and C must be replaced by Q_η and C_0, respectively, in the formula. So the C_0 can be determined by the relation:

$$T = H\frac{\sqrt{T^3}}{\eta_a} - C_0 \tag{2}$$

graphically, where H denotes the proportional constant.

Sutherland Constant and Boiling-point. It is known that the Sutherland constant of various substances has a close relation with their boiling-points, and consequently also with their critical points. These relations are expressed by the following simple rules:

Rankine's rule . . . . . $C = T_k/1.12$,

and Vogel's rule . . . . . . $C = 1.47 \times T_S$,

where T_K and T_S denote the critical and the boiling points expressed in absolute temperature, respectively.

As shown in table 1, these rules reproduce the experimental values fairly well in most of the substances. The theoretical derivation of them has not been succeeded, though they are presumed plausible from the qualitative point of view, showing the correlations of the intermolecular force between the concerned two quantities. To the exceptions belong such gases as acetylene, hydrogen, helium, hydrogen chloride and water.(5) However, if we examine the table carefully, a tendency of systematic deviation is recognized; i.e., some substances which have smaller molecular weight give too low values as expected from the rules. Now, the discrepancy found in the low molecular gases may be removed, if we substitute the constant C for the new one C_0 calculated as above, considering the

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(1) See the previous paper.

(2) Kennard, "Kinetic Theory of Gases", New York (1938) 154.

(3) Rankine, *Proc. Roy. Soc.*, A**84**(1910), 181.

(4) Vogel, *Ann. der Physik*, **43**(1914), 1235.

(5) Most of the figures are indebted to the table given by H. Adzumi ("Kwagaku-Jikkengaku", **2**(1942), 40).

meaning of the rules. The idea was tested as shown in the third column of table 1.

Table 1. Test of the Rankine's and Vogel's Rules.

	Sutherland Constand Calculated by		$\frac{T_K}{1.12}$	$1.47\times T_S$
	Classical Method	Quantal Method		
He	80 (Schultz) 70 (Vogel)	32 (20–100°C)	4.6	6.2
Ne	61 (Trautz-Binkele) 56 (Rankine)	42 (15–100°C)	40	40
A	142 (Rankine) 147 (Trautz-Binkele)	136 (20– 80°C)	135	124
Kr	188 (Rankine)	——	187	178
H_2	83 (Schmidt) 83 (Trautz-Stauf) 79 (Adzumi)	31 (20–100°C)	30	30
D_2	79*	32 (-50– 23°C)	—	24
N_2	103 (Trautz-Baumann) 118 (Smith)	——	112	114
O_2	138 (Vogel) 125 (Trautz-Melster)	——	137	132
CH_4	170 (Adzumi) 198 (Rankine)	147 (40–100°C) 175 (0–100°C)	170	160
C_2H_6	280 (Adzumi) 287 (Titani)	267 (20–100°C) 260 (20–100°C)	275	272
C_2H_4	259 (Titani)	247 (20–120°C)	253	249
C_3H_8	318 (Titani)	——	330	335
HCl	317 (Harle) 360 (Trautz-Narath)	——	289	279
H_2O	961 (Braune-Linke) 650 (Schuhgajew)	——	576	548
C_2H_2	196 (Titani) 220 (Adzumi)	——	276	278
CO	118 (Smith) 111 (Trautz-Bauman)	——	120	122
CO_2	274 (Smith)	——	271	286

* Calculated from the data of Van Cleave and O. Masse (*J. Can. Res.*, 12 (1935), 57).

According to the above procedure, C'_0s were calculated for several gases, the molecular weights of which were comparatively small. As shown in table 1, the coincidence of the values with the experimental ones became better in most cases,⁽⁶⁾ except such gases as acetylene and water, these exception being probably on account of the same reason as occurred in Trouton's rule. However, the improvement is slight for helium; C_0 is still too large. Such circumstances may be due to the insufficiency of the correction term of Sutherland type, because, if we use the values at

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(6) The formula is given by equation (1) times $1/(1+C_0/T)$.

low temperatures, the discrepancy can be improved; i.e., $C_0=4$ from 273–89°K, and C_0 tends to zero from 89° downwards.(7)

Generally speaking, the coincidences seem better if the constants 1.12 and 1.47 were selected slightly larger and smaller, respectively, because these were determined in connection with C, and not with C_0.

The Sutherland Constant and Electric Moment. As the Sutherland constant is a measure of potential energy between molecules, it can be derived theoretically for simple gases. For nonpolar gases, Debye(8) has obtained the following formula:

$$\text{The Sutherland constant} = \frac{217}{205}\cdot\frac{7}{20\pi}\cdot\frac{P_0\tau^2}{Rr_0^8}\,, \qquad (3)$$

where P_0 is the molecular polarisation, τ the mean electric moment and R the gas constant. For some quadrapole molecules the equation was tested by himself, comparing the observed τ with those calculated from other values. As shown in table 2, it was found that there lies some disagreement in lighter gases such as in hydrogen and helium. However, as the Sutherland constant which was used for the calculation was C and not C_0 if the notation of this paper was used, considerable disagreement has been observed for the lighter gases, because C has the meaning as pointed above by the author. This idea may be ascertained if the calculation is carried out, using C_0 instead, and the other constants being reserved unvaried. As shown in table 2, the calculated electric moment for He, H_2 and Kr (the fourth column) coincides with the experimental values (the second column), thus the result as expected being obtained.

It becomes thus evident that the Sutherland constant which is determined by the quantum-mechanical formula can be regarded as a reasonable measure of the intermolecular force. This conclusion becomes, in turn, a support to the argument in the introduction of the previous paper; i.e., the necessity of the application of the quantum mechanics in the transport phenomena.

Table 2. Electric Moment and Sutherland Constant.

Gase	τ from the critical data	τ from eq. (1) and from	
		C obtained classically	C_0 obtained quantally
He	2.84	4.33 (75)**	2.83 (32)*
Kr	11.2	11.4 (162)	10.5 (136)
Xe	18.9	20.6 (252)	——
H_2	3.20	5.60 (182)	3.4 (31)
N_2	13.3	13.4 (113)	——
O_2	11.2	11.7 (137)	——

* Considering the temperature range used for comparison, 32 was adopted.

** Numbers in parenthese are the Sutherland constants used.

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(7) As it may be expected, the determination of C became easier in this method, because the experimental values lie on a straight line over wider temperature ranges.

(8) P. Debye, *Physik. Zeit.*, **21** (1921), 179.

Summary.

1) According to the conclusion of the previous paper, the "Sutherland constant" in the viscosity coefficient for various substances has been calculated quantum-mechanically by a simple procedure.

2) The Sutherland constant C_0 thus calculated has been found to obey Rankin's and Vogel's rules even in the substances of low molecular weight.

3) The disagreement in the Debye's formula between electric moment and Sutherland constant has been shown to disappear if C_0 was used instead of the classically determined Sutherland constant.

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