[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Viscosity and Heat Conductivity of Steam

BY FREDERICK G. KEYES*

The molecular theory of the transport properties, viscosity, heat conduction and diffusion, is based upon the general equations of Maxwell and Boltzmann, and the solution of these equations through the efforts of Chapman and Enskog[1] beginning over thirty years ago. The theoretical expressions obtained depend upon the particular molecular constructs assumed and are of course simplest for the classical potential-free elastic sphere model. The predicted transport properties for the van der Waals model, an elastic sphere with spherically symmetrical negative potential, are of particular interest in view of the information available regarding the correspondence between the predicted behavior of a gas in the uniform state composed of van der Waals constructs, and the observed properties.

Attempts have also been made to deduce transport properties for a more general model than the van der Waals, but the computational difficulties are increased considerably. Recently J. O. Hirschfelder, R. B. Bird and E. L. Spotz[2] carried through the arduous labor of evaluating the "collision integrals" required in the calculations of transport properties for a special potential form. The integrals are tabulated for 84 temperature levels using the following function, where γ_1 and γ_2 are constants

$$E(r) = \gamma_1 r^{-12} - \gamma_2 r^{-6} \qquad (1)$$

Application of the integrals to the calculation of the viscosity of a large number of pure gases and mixtures has recently been published.[3] The accord of the predicted values with the observed data in the case of most non-polar molecular species at low pressures is all that could be expected. The authors cite the non-applicability of equation (1) to polar molecules and state the difficulties to be surmounted before the viscosity for this class of substances can be computed.

The prediction of heat conductivity is fairly good in the case of helium. In the case of methane, nitrous oxide, carbon dioxide, oxygen and air, however, the accord with the observations is less satisfactory.

The present paper contains the results of some measurements on the heat conductivity of steam over a range of pressure and temperature, along with a review of the available data on the viscosity of steam.

Reliable data for the viscosity, heat conductivity and heat capacity are of importance in the case of steam for dealing with heat transfer problems in power generation. Mainly because of this practical need a considerable concentration of effort has been brought to bear on the measurement of all three of the aforementioned properties.

Observations on the viscosity of water vapor at low pressures using the capillary method were published in 1924 by C. J. Smith[4] for the temperature range 100 to 263°. During the following years a series of papers have appeared (refs. 5–13 incl.) for temperatures extending to 550° and pressures to 250 kg./sq. cm. for the Russian work of Timroth and Vargaftig[10] using the capillary-tube method. The earlier work of Hawkins, Solberg and Potter[8, 11] was carried out with a falling cylinder viscosimeter and to pressures of over 200 atm. A later investigation by the same authors but using a thick-walled nickel capillary device 262 cm. long led to results over the temperature range 188.5 to 550°, and the pressure range 4.93 to 123 atm. The method of obtaining the pressure drop in the capillary was by radiographs which together with other refinements leads to confidence in the results obtained. The smoothed results from the latter measurements given by Leib[14] are recommended by Hawkins, Sibbitt and Solberg.[13]

The Russian data were also obtained with the capillary viscosimeter using, however, a short capillary and a "ring" balance for the determination of the pressure differences which varied from 4.62 to 6.28 mm. The pressure effect found by Timroth and Vargaftig is much smaller than that obtained by Hawkins, Solberg and Potter in 1940. Also, the low pressure values of the former exhibit a tendency to higher values at the upper range of temperature than is shown by the results of Smith and Hawkins, Solberg and Potter (Fig. 1).

The published heat conductivity data are due to S. W. Milverton[15] (below 100°) and to Timroth

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* Editorial Board 1940–1946.

(1) Sidney Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge University Press, 1939.

(2) J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *J. Chem. Phys.*, **16**, 968 (1948).

(3) J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *Trans. A. S. M. E.*, **71**, 921 (1948).

(4) C. J. Smith, *Proc. Roy. Soc.* (*London*), **106**, 83 (1924).

(5) H. Speyerer, *Forschungsarbeiten auf dem Gebiete des Ingenieurswesens*, No. 373 (1925).

(6) W. Schougayew, *J. Exp. Theoret. Phys., U. S. S. R.*, **3**, 247 (1933).

(7) W. Schiller, *Forschungsarbeiten auf dem Gebiete des Ingenieurswesens*, **5**, 71 (1934).

(8) G. A. Hawkins, H. L. Solberg and A. A. Potter, *Trans. A. S. M. E.*, **57**, 395 (1935).

(9) K. Sigwart, *Forschungsarbeiten auf dem Gebiete des Ingenieurswesens*, **7**, 125 (1936).

(10) D. L. Timroth and N. Vargaftig, *J. Tech. Phys. U. S. S. R.*, **2**, 461 (1939).

(11) G. A. Hawkins, H. L. Solberg and A. A. Potter, *Trans. A. S. M. E.*, **62**, 677 (1940).

(12) D. L. Timroth, *J. Phys. U. S. S. R.*, **2**, 419 (1940).

(13) G. A. Hawkins, W. L. Sibbitt and H. L. Solberg, *Trans. A. S. M. E.*, **70**, 19 (1948).

(14) E. F. Leib, *Combustion*, **12**, 45 (1940).

(15) S. W. Milverton, *Proc. Roy. Soc.* (*London*), **A150**, 287 (1935).

and Vargaftig,[16] the data of the latter authors extending to 500° and to 250 atm. During the past two years however additional measurements have been completed by the writer and D. J. Sandell, Jr.,[17] for steam and nitrogen to 400° and 150 atm. A considerable difference exists between the Russian results and the new measurements for steam, Tables I and II.

TABLE I

HEAT CONDUCTIVITY OF STEAM

($10^5\ \lambda$ in IT[d] calories per sec. per cm. per °C.)

, °C.	$10^5\lambda$ (T. V.) calcd.[a]	$10^5\lambda$ (T. V.) obsd.[b]	$10^5\lambda$ (K. S.)[c]
		20 kg. per cm.^{2}	
250	10.58	10.97 (+3.5)	9.33 (+13.4)
300	11.14	11.33 (+1.7)	10.04 (+11.0)
350	12.18	12.11 (−0.5)	10.87 (+12.0)
400	13.65	13.61 (−0.3)	11.78 (+15.9)
500	18.20	18.55 (+2.0)	13.70 (+32.8)
		100 kg. per cm.^{2}	
350	17.09	15.83 (−7.3)	13.78 (+24.0)
400	16.59	16.28 (−1.9)	13.46 (+25.3)
500	19.54	20.22 (+3.5)	14.43 (+35.4)
		150 kg. per cm.^{2}	
350	23.53	21.67 (−7.9)	18.11 (+30.0)
400	19.77	18.61 (−5.9)	15.45 (+27.3)
500	20.69	20.83 (+0.7)	15.09 (+38.1)

[a] Correlation values computed from the following equations based on Timroth and Vargaftig's values reported in 1940: $10^5\lambda_0 = 0.3191\ \sqrt{T}\ 10^{0.6616 \times 10^9 T^3}$: $10^5\lambda = 10^5\lambda_0 + 2.486(10^{0.77 \cdot 10^9 \tau^4 p} - 1)$ pressures in kg. per cm.^{2}. [b] Timroth and Vargaftig's reported values. The bracketed number is the quantity $[(\lambda_{\text{obsd.}} - \lambda_{\text{calcd.}})/\lambda_{\text{obsd.}}] \times 100$. [c] Values computed from the following equations based on the new observations of the heat conductivity. The bracketed adjacent numbers are the deviations in per cent. relative to the T. V. computed value. $10^5\lambda_0 = 1.5456\ \sqrt{T}/(1 + 1737.3\tau/10^{12\tau})$; $10^5\lambda = 10^5\lambda^0 + 1.096\ (10^{0.934 \cdot 10^9 \tau^4 p} - 1)$ pressures in atm. [d] International Steam Tables Calorie, London, 1929 (4.186 i. j.).

TABLE II

HEAT CONDUCTIVITIES OF STEAM FOR PRESSURES APPROACHING ZERO

, °C.	$10^5\lambda_1$ (T. V.)[a]	$10^5\lambda_0$ (T. V.)[b]	$10^5\lambda_0$ (K. S.)[c]	Dev.[d]
250	9.08	9.05	8.52	6.1
300	10.18	10.16	9.52	6.7
350	11.52	11.50	10.52	9.3
400	13.18	13.17	11.53	14.2
500	17.94	17.93	13.57	32.2

[a] Computed from the equation $10^5\lambda_1 = 0.3191/T\ 10^{0.6616 \cdot 10^9 T^3}$. [b] The values in column three are the λ_1 values (1 kg. per cm.^{2}) of Timroth and Vargaftig corrected by the relation *c* Table I. [c] These values are computed from the $10^5\lambda_0$ equation based on the new observations. [d] $[(\lambda_0\ \text{T.V.} - \lambda_0 \text{K.S.})/\lambda_0\ \text{K.S.}] \times 100$.

TABLE III

COMPARISON OF VISCOSITIES RECORDED BY TIMROTH (1940) WITH COMPUTED VALUES

p	250°C.	300°C.	350°C.	400°C.	450°C.
1[a]	1.78	1.97	2.16	2.35	2.56
[b]	1.77	1.96	2.15	2.36	2.57
40	1.80	1.99	2.18	2.37	2.58
	1.80	1.98	2.18	2.39	2.60
100			2.30	2.49	2.69
			2.32	2.51	2.72
150			2.46	2.59	2.78
			2.49	2.60	2.80
200				2.74	2.88
				2.75	2.89

[a] The observed viscosities are taken from data published by D. L. Timroth.[12] The units are poises × 10^4. [b] The computed values are from the following formulas: $10^4(\eta_p \text{ poises}) = 10^4[\eta_0 + 0.00137p + 0.0186\ (10^{0.91\tau^8 p^2 \cdot 10^{18}} - 1)]$. $10^4(\eta_0 \text{ poises}) = 1.460\sqrt{T}/(16171\ \tau/10^{100\tau} - 1)$. *p* is in kg. per cm.^{2}; $\tau = T^{-1} = (273.16 + t°\text{C.})^{-1}$.

TABLE IV

COMPARISON OF VISCOSITIES RECORDED BY E. F. LEIB FROM THE DATA OF HAWKINS, SOLBERG AND POTTER WITH COMPUTED VALUES

p p. s. i. a.	kg./cm.^{2}	°F. °C.	550 247.8	600 315.6	650 343.3	750 398.9	850 454.4
14.7	1.03	[a]	1.99	2.08	2.17	2.35	2.51
		[b]	1.99	2.08	2.17	2.35	2.52
600	42.18		2.47	2.53	2.59	2.74	2.89
			2.47	2.53	2.60	2.74	2.88
1400	98.43			3.39	3.33	3.33	3.39
				3.29	3.28	3.32	3.39
2200	154.68				4.32	3.99	3.94
					4.06	3.94	3.92
2800	196.86					4.52	4.34
						4.45	4.34

[a] The observed viscosity values are based on Hawkins, Solberg and Potter[11] original data as published by Leib.[14] The units are poise × 10^4. [b] The computed values are from the following formulas: $10^4(\eta_p,\ \text{poises}) = 10^4[\eta_0 + \tau p\ (6.364 - 2.307 \cdot 10^{-3} \times 10^{1340\tau}) + (3.89 \cdot 10^{-2} \times p^2\ 10^{-5.476 \cdot 10^{-3} T})]$. $10^4(\eta_0,\ \text{poises}) = 0.1501\sqrt{T}/(1 + 444.7\ \tau)$ (H. S. and P.). *p* is in kg. per cm.^{2}; $\tau = T^{-1} = (273.16 + t°\text{C.})^{-1}$.

TABLE V

VALUES OF THE VISCOSITY OF STEAM AT "ZERO" PRESSURE 10^4 (η_0 POISES)

°C.	100	250	300	350	400	450	500	600
Hawkins, Solberg and Potter	1.32	1.85	2.02	2.18	2.34	2.50	2.65	2.93
Smith	1.27	1.84	2.03	2.21	2.39	2.57	2.74	3.07
Timroth Eq. A	1.26	1.77	1.96	2.15	2.36	2.57	2.79	3.26
Eq. C	1.20	1.80	2.00	2.20	2.39	2.59	2.78	3.17

Hawkins, Solberg and Potter (E. F. Leib) $10^4\ (\eta_0 \text{ poises}) = \dfrac{0.1501\sqrt{T\ °\text{K.}}}{1 + 446.8\ \tau}$

C. J. Smith $10^4\ (\eta_0 \text{ poises}) = \dfrac{0.1851\sqrt{T\ °\text{K.}}}{1 + 680\ \tau}$

D. L. Timroth (Eq. A) $10^4\ (\eta_0 \text{ poises}) = \dfrac{1.460\sqrt{T\ °\text{K.}}}{16171\ \tau/10^{100\tau} - 1}$

D. L. Timroth (Eq. C) $10^4\ (\eta_0 \text{ poises}) = \dfrac{0.2347\sqrt{T\ °\text{K.}}}{1 + 1039.6\ \tau}$

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(16) D. L. Timroth and N. Vargaftig, *J. Phys. U. S. S. R.*, **2**, 101 (1940).

(17) Thesis, Massachusetts Institute of Technology, August, 1949, presented by Dewey J. Sandell, Jr., in partial fulfillment of the requirements for the Ph.D. degree; also, Office of Naval Research Summary Report, Task Order XI, Contract No. N5ori-78, Project Designation No. NR-058-037, October, 1949.

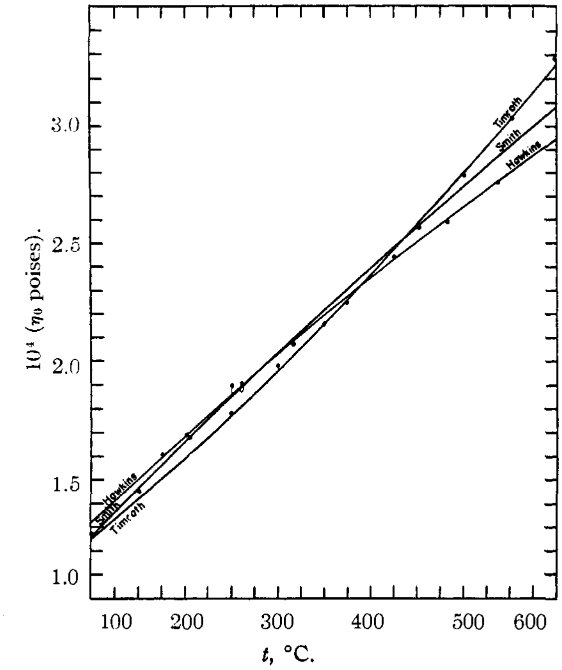

Fig. 1.—Comparison of η_0 values from J. C. Smith, Hawkins, Solberg and Potter (Leib) and D. L. Timroth.

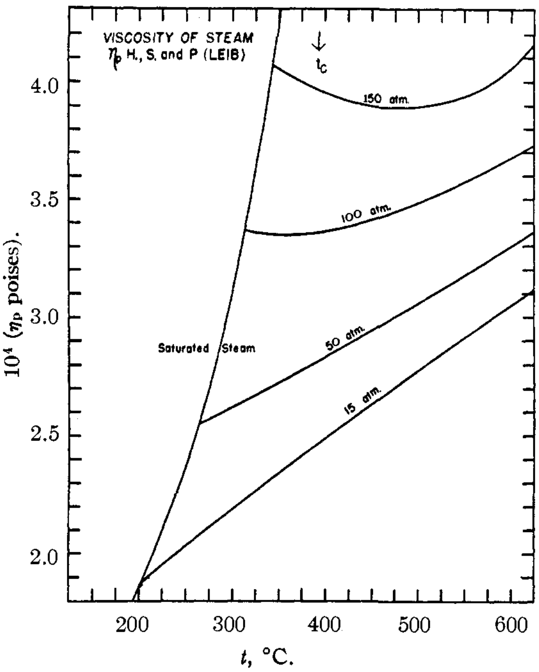

Fig. 2.—Viscosity of steam, η_p, H., S. and P. (Leib).

The viscosity data of Timroth and Vargaftig[17a] and Hawkins, Solberg and Potter (Leib) have been empirically expressed as a function of pressure and temperature. The respective equations are given at the foot of Tables III and IV. A comparison of the η_0 values appears in Table V, and a graphical representation in Fig. 1 showing the relation of the observations to the analytical representations. The Figs. 2 and 3 give the course of values for viscosity and heat conductivity of steam along the saturation line and in the superheat. The general course of the constant pressure lines resembles the appearance of the isopiestics for specific heat.

A relationship of special interest arises in the kinetic theory of gases, namely, the equation

$$\lambda_0 = f\eta_0 C_v^0 \qquad (2)$$

where the low pressure heat conduction, λ_0, is related to the viscosity η_0 and specific heat at constant volume C_v^0. The value of f from the theory for smooth spherically symmetrical constructs is 2.5, and the same value results for the same construct reflecting inversely as the fifth power of the distance between centers. The experimental data for monatomic gases, as is well known, is in accord with the theoretical deduction. There is however an exception in the case of helium, for at −192° Eucken found 2.23 for f, and Weber at −252° the number 2.02.

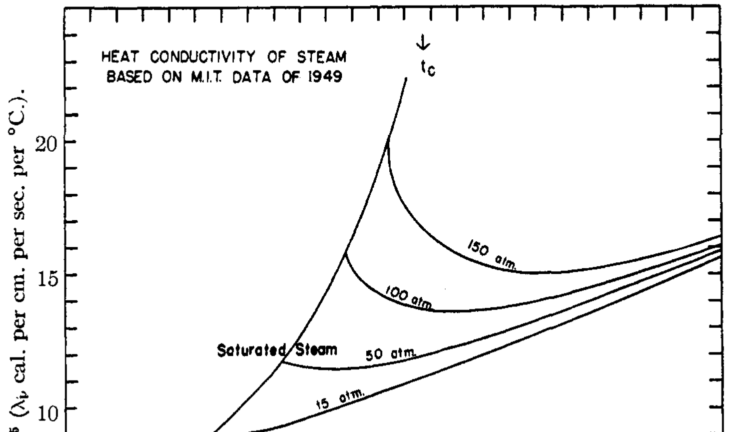

Fig. 3.—Heat conductivity of steam based on M. I. T. data of 1949.

For diatomic gases, f, on the basis of the observed facts, is of the order of 1.9 and for molecules possessing an increasing number of atoms f becomes progressively smaller.

(17a) The Russian viscosity data were originally formulated for the Keenan and Keyes Steam Tables in 1943. However, in Table III a new formulation of the η_0 values is given which reproduces a trend in the Russian data which is not found in the low pressure data of Hawkins, Solberg and Potter, or indeed for any other substance. The trend if continued would lead to extraordinarily large viscosity values at higher temperatures.

Accurate values of the quantities in equation 2 for polar molecules have not been generally available. However in the case of steam highly accurate values of C_V^0 and of C_V[18] under pressure are available, and now also η and λ values from the correlation of the available viscosity data and the new heat conductivity data given in Table I. The value of f is given in Table VI for steam at "zero" pressure and at saturation for 300° and 84.78 atm.

TABLE VI

VALUES OF THE RATIO $\lambda/\eta C_V$ FOR STEAM

t, °C.	C_{p0} i. j.	$10^5\lambda$ i. j.	$10^5\lambda$	C_V^0 i. j.	$\lambda_0/\eta_0 C_V^0$	Prandl number $(\eta_0 C_p^0)/\lambda_0$
100	1.891	22.10	12.67	1.457	1.20	1.08
300	2.002	38.42	20.27	1.540	1.20	1.06
600	2.206	63.95	30.75	1.744	1.19	1.06

For t = 300 °C. and p_{sat}; 84.78 atm. we have $C_V = 2.89$ i.j.; $\eta_p = 3.34 \cdot 10^{-4}$(H.S.P.); $\lambda_p = 6.00 \cdot 10^{-4}$ i.j. (K.S.), and $\lambda_p/\eta_p C_V = 0.622 = f$.

It appears from Table VI that the value of f for steam in the perfect gas state is independent of temperature within the accuracy of the elements of the ratio and very much smaller than the values derived from the Eucken relation 1/4 $(9\gamma - 5)$ which is 1.68 for C_p^0/C_V^0 or γ_0, 1.30, 1.30, 1.26, respectively, for the temperatures of the table. The assumption underlying the Eucken relation must accordingly be invalid, a situation which is recognized and discussed in Chapman and Cowling's book.[19] Hirschfelder, Bird and Spotz[3] after noting the discrepancies between theory and observation using the potential equation (1) for non-polar substances, state "This indicates that the Eucken assumption is not valid[20] and hence equation (76) must be modified so as to take into account the difficulty of transferring energy from translation to rotation and vibration." The f value in Table VI for steam indicates a very large deviation in the case of the polar molecule water relative to non-polar gases.

Summary

A series of measurements of the heat conductivity of steam to 350° and 150 atm. have been made during the past two years using a concentric cylinder device especially adapted for measurements under pressure. Comparison with data published by Timroth and Vargaftig obtained through the use of hot wire method shows the new values to be lower by amounts up to 38% (150 atm.). The low pressure (zero) values of Timroth and Vargaftig exhibit a trend to very high values with increasing temperature which is not verified in new measurements.

A correlation of the viscosity values of steam due to Timroth and to Hawkins, Solberg and Potter has been carried out. The values of the latter are believed to be the more reliable. The value of the ratio, heat conductivity, by the product, specific heat and viscosity, is 1.2 and independent of temperature between 100 and 600°. The ratio decreases with pressure increase.

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(18) F. G. Keyes, *J. Chem. Phys.*, **15**, 602 (1947); **17**, 923 (1949).

(19) Ref. 1, pp. 238 and 240 in particular.

(20) That is for non-polar substances having more than two atoms.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, AND THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

The Dipole Moments and the Interconvertibility of Diethyl Disulfide and Trisulfide[1a]

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Polysulfides of an order higher than two have been known for many years.[2] Likewise their interconvertibility was separately recognized by various early investigators. Holmberg[2] observed that diethyl disulfide gave higher order polysulfides in a sealed tube reaction with sulfur and ammonia. Recently, Olin[3] reported that heating disulfides with sulfur and a trace of amine gave polysulfides. The reverse reaction was observed by Twiss[4] to take place when polysulfides were destructively distilled at atmospheric pressure.

The linear structure of disulfides was indicated by the electron diffraction work of Beach and Stevenson.[5] The structure of diethyl trisulfide was investigated chemically by Baroni and Levi,[6] who claimed to isolate a linear trisulfone from the oxidation with nitric acid. We have been unable to repeat this reaction. Baroni, further, made parachor measurements to confirm the linear structure. Bezzi[7] claimed to have proved the linear structure by molecular refraction calculations. While this paper was in preparation, Dawson and Robertson[8] reported the X-ray diffrac-

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(2) Claesson, *J. prakt. Chem.*, **15**, 216 (1877); Holmberg, *Ann.*, **359**, 81 (1908); *Ber.*, **43**, 220 (1910); Thomas and Riding, *J. Chem. Soc.*, 3271 (1923); *ibid.*, 2460 (1925); Chakravarti, *ibid.*, 964 (1923).

(3) Olin, U. S. Patent 2,237,627 (1941).

(4) Twiss, THIS JOURNAL, **49**, 493 (1927).

(5) Beach and Stevenson, *ibid.*, **60**, 2872 (1938).

(6) Levi and Baroni, *Atti Accad. Lincei*, **9**, 772, 903 (1929) Baroni, *ibid.*, **11**, 905 (1930); **14**, 28 (1931).

(7) Bezzi, *Gazz. chim. ital.*, **65**, 693, 704 (1935).

(8) Dawson and Robertson, *J. Chem. Soc.*, 1256 (1948).