Table II. Continued

Compound	ΔHv°	ΔHf°		$-\Delta Hc^\circ$	
2,3-Dimethyl-3-isopropylpentane	10.99	-61.67	-72.66	1630.34	1619.35
2-Methyl-3,3-diethylpentane	11.42	-59.49	-70.91	1632.52	1621.10
2,2,3-Trimethyl-3-ethylpentane	11.09	-60.37	-71.46	1631.64	1620.55
2,2,4-Trimethyl-3-ethylpentane	10.85	-60.55	-71.40	1631.46	1620.61
2,3,4-Trimethyl-3-ethylpentane	11.24	-60.09	-71.33	1631.92	1620.68
2,2,3,3,4-Pentamethylpentane	10.91	-59.08	-69.99	1632.93	1622.02
2,2,3,4,4-Pentamethylpentane	10.52	-59.04	-69.56	1632.97	1622.45

[a] Of the given compound in the given state, from solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard reference state (*4*).

[b] Of the given compound in the given state, in oxygen, to form gaseous carbon dioxide and liquid water, with each substance in its thermodynamic standard reference state (*4*).

vaporization, all at 25° C., and the boiling point at pressures of 760 and 10 mm. of mercury.

In this investigation, the appropriate foregoing relations have been utilized with auxiliary data to calculate values of the standard (*3*) heat of formation, combustion, and vaporization at 25° C. for each of the 35 nonanes and 75 decanes. The auxiliary values required included the standard heats of formation of water and of carbon dioxide and were taken from the tables of the API Research Project 44 (*4*). The values for the heats of combustion of the five most highly branched nonanes in the liquid state are taken from experimental work (*2*).

Tables I and II present the resulting calculated values of the standard heat of formation, combustion, and vaporization, for the nonanes and decanes, respectively.

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Liquid Viscosity above the Normal Boiling Point

PAUL E. PARISOT[1] and ERNEST F. JOHNSON
Department of Chemical Engineering, Princeton University, Princeton, N. J.

INTEREST IN THE accurate determination of viscosity coefficients of liquids in the region between the boiling point and the critical temperature has been stimulated by a growing need for these data, notably in the design of fuel systems for liquid propellant missiles. Moreover, the present lack of viscosity data in this temperature region precludes the development of a liquid viscosity correlation of complete generality for the whole liquid region. This article describes a capillary viscometer which has been designed specially to obtain viscosity data for liquids above their boiling points, particularly to establish calibration data for other viscometric instruments (*5*).

The capillary viscometer was selected over other types of viscometric devices on the basis of the simplicity of the theory and the inherent potential accuracy of the capillary method. Capillary viscometers are widely used to obtain accurate, absolute viscosity data for the normal liquid region not only because of the relative ease of experimental manipulation, but also because the raw data may be converted into viscosity coefficients without undue emphasis on unknown end effects and allowance for experimental divergence from restrictions imposed by the derived theoretical equations.

To realize these advantages of the capillary viscometer in the region above the boiling point, apparatus modifications are required for maintaining the Reynolds number below 2300 while dealing with fluids of very small kinematic viscosities, for making accurate low pressure drop and flow rate measurements under conditions of moderate environmental pressures and temperatures, and for minimizing the effect of end-effect correction terms on the accuracy of the determinations.

THEORY

The basic equation applicable to a capillary viscometer operated under the condition of a continuously varying flow rate or pressure drop is

$$\eta = \frac{\pi r^4 \Delta P}{8L\, dQ/dt} - \frac{m\rho\, dQ/dt}{8\pi L} \qquad (1)$$

where η is the viscosity coefficient in poises, ρ is the density

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[1] Present address, Monsanto Chemical Co., St. Louis, Mo.

of the test liquid in grams per cubic centimeters, ΔP is the pressure drop across the capillary in dynes per square cm., dQ/dt is the flow rate in cubic centimeters per second, and r and L are the radius and length, respectively, of the capillary in centimeters. The second term of the right side of Equation 1 is a correction for the contribution of kinetic energy losses at the entrance and exit of the capillary. The constant m has a value which is characteristic of the capillary end geometry (*1*).

If the per cent variation of the flow rate during a run is small, and the kinetic energy correction term is an order of magnitude smaller than the first term of Equation 1, the following equation results.

$$\left[\eta + m\rho \frac{(dQ/dt)}{8\pi L} \text{ mean}\right] \frac{dQ}{dt} = \frac{\pi r^4 \Delta P}{8L} \tag{2}$$

Substituting $C = m/8\pi L$, $H = \pi r^4/8L$, and $\Delta P = f(Q)$ into Equation 2 gives

$$\left[\eta + C\rho\,(dQ/dt) \text{ mean}\right] \frac{dQ}{f(Q)} = H dt \tag{3}$$

If the function $f(Q)$ is known, Equation 3 may be integrated between the limits of zero and Q, where Q is the total volumetric flow through the capillary at time t. For convenience the definite integral $\int_0^Q dQ/f(Q)$ is defined as $Q/\Delta P_e$, where ΔP_e is an effective pressure drop. Thus

$$\eta = \frac{H\Delta P_e t}{Q} - \frac{C\rho Q}{\pi t} \tag{4}$$

Equation 4 is a standard equation used for many viscometers of the Cannon-Fenske type. If Q and ΔP_e are made constant by design of the apparatus and its operation, a simple relationship between viscosity and efflux time is obtained. The viscometer has been designed and operated with this objective in mind.

APPARATUS

The viscometer developed in the present work is a multiple-range instrument shown schematically in Figure 1. It offers four possible routes of flow: through capillary tube *A* (0.03 cm. i.d.), tube *B* (0.02 cm. i.d.), a series *C* (0.02 cm. i.d.), and an alternate route through a bypass tube. The capillaries are stainless steel, manufactured by J.D. Bishop Co. All tubes are 68.64 cm. long and 0.145 cm. o. d.

The tubes join on either end to aluminum headers *D* and *E*. Header *D* contains the mechanism of a switching device, a spring-loaded port valve, which allows the selection of any of the three capillary tube routes or the bypass. The top of the internal leg, *F*, of a mercury manometer is connected to header *D*. Mercury displaces the test liquid in this leg, forcing the liquid through the capillaries. The internal leg is 4 inches long and 0.904 inch i.d. A mercury line connects the internal leg to the external manometer leg and mercury reservoir. As shown in Figure 2, header *E* collects the flow from the capillaries and the bypass and directs it through the liquid line to the external liquid reservoir.

The external leg of the manometer, consisting of four efflux bulbs connected in series to the mercury line, is housed in a Jerguson gage capable of withstanding 3000 p.s.i. internal pressure. The bulbs were blown out of the 0.2-cm. borosilicate glass tubing that connects them. Their respective volumetric capacities are: 1.475, 1.670, 1.817, and 1.783 cc. The top bulb applies a head of mercury of approximately 19 cm. Hg.

Two stainless steel reservoirs 9 inches long and 0.922 inch i.d. made from heavy-walled pipe provide storage external to the constant temperature bath for the test liquid and the mercury. The adjustability of the level of the mercury reservoir together with the three valves and the circuitry of the mercury lines allow mercury to be withdrawn from the viscometer flow circuit and the mercury level in either manometer leg to be adjusted independently before runs. A needle valve located directly under the liquid reservoir on the liquid line from the viscometer is the control valve for on-off flow of the test liquid through the viscometer.

The viscometer is enclosed in an American Instrument Co. pressure vessel made of manganese steel and designed for operation up to 5000 p.s.i. at 500° F. This vessel is 40 inches long and 4-3/8 inches in diameter with internal dimensions 32 inches length and 3-5/16 inches in diameter. It has a standard compression closure at the bottom with provision for electrical leads and two fluids lines. The viscometer is mounted on the inner pressure head of the compression closure. The stem of the viscometer flow selector has a T-shaped handle which engages an inverted U end of the shaft passing through the top of the pressure vessel (see Figures 3 and 4).

To meet the requirement that the environmental pressure

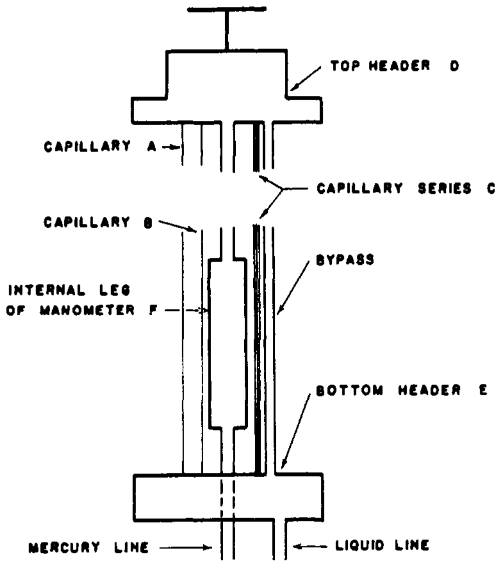

Figure 1. Schematic diagram of the multi-range viscometer

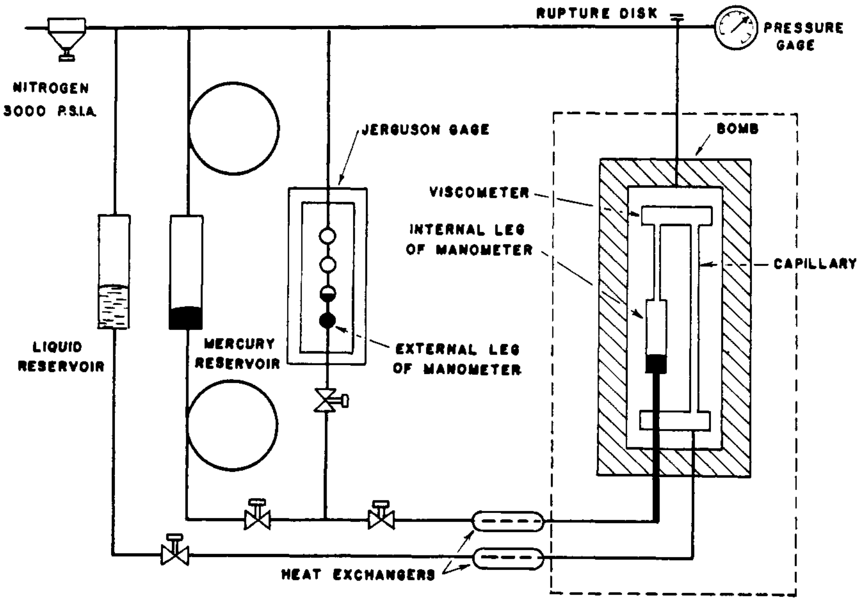

Figure 2. Flow diagram

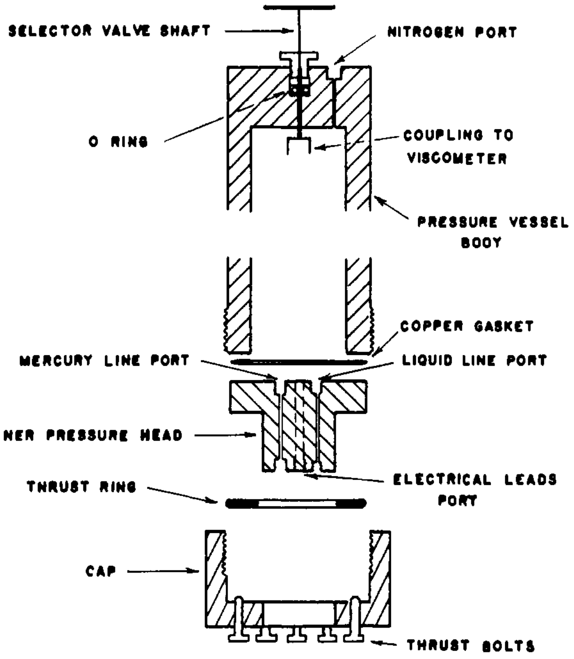

Figure 3. Pressure vessel

exceeds the vapor pressure of the test liquids a nitrogen pressurization system is provided. The high pressure nitrogen is in direct contact with the test liquid only in the liquid reservoir and with the mercury in the mercury reservoir and the external manometer leg. The bomb itself is pressurized, in order that a very small differential pressure exists across the walls of the viscometer whose walls and Teflon seals are designed to withstand only moderate pressure differentials. Pressure regulation of the bomb is achieved by a standard pressure regulator, and the pressure is measured by a Bourdon gage.

The temperature measurements within the pressure vessel and viscometer defining the run temperatures were obtained from resistance measurements on Victory Engineering Type 51, bead-in-glass-probe thermistors. A standard type of bridge circuit using a K-2 Leeds and Northrup potentiometer was employed for the resistance measurements. The thermistors were calibrated against a National Bureau of Standards calibrated thermometer.

A liquid bath was used for the constant temperature environment of the viscometer. The bath liquid, Monsanto Arochlor 1248, was circulated through the bath by a $\frac{1}{3}$-hp. centrifugal pump. Three electric Chromalox heating elements, maximum output 900 watts, and a water-cooling coil were employed for coarse heat balance control. More exact regulation of the bath temperature was accomplished by on-off control of a fourth Chromalox heater using a Thermocap relay to sense and control the position of the mercury in the bath thermometer.

PROCEDURE

The apparatus is charged initially with the mercury filling all the mercury lines and partially filling both manometer legs and the mercury reservoir. A sufficient amount of test liquid is then charged to the viscometer to fill the remainder of the internal leg, the capillaries, the headers, and half of the test liquid reservoir. This procedure is required only once for the study of a given test liquid over the whole temperature range. To avoid dissolution of blanket nitrogen into the test liquid a given charge should not be used longer than 10 days.

Determining Viscosity Coefficients. The test liquid line valve is opened and the mercury manometer is allowed to come to a static balance with the bypass circuit opened to speed up the static balancing. The static balancing is regulated by the withdrawal, or addition, of mercury from the mercury reservoir to the manometer so that the mercury meniscus in the external leg is always at a constant level with respect to the position of the efflux bulbs. The test liquid line valve and the bypass are then closed.

Mercury is withdrawn from the reservoir into the external leg in sufficient amount to raise the mercury meniscus to the benchmark above a preselected efflux bulb. This procedure establishes the effective pressure drop for the subsequent determination of efflux time.

The liquid line valve is opened to start the run. The efflux time is defined as the time required for the mercury meniscus to pass from the benchmark above the bulb to the benchmark below as measured by a stopwatch. The movement of the meniscus is observed through a cathetometer. It is normal practice to determine the efflux time for the succeeding bulb as well before resetting. Reset is accomplished by repeating the static balance procedure.

Choice of three different flow resistances, as well as the selection of four levels of effective pressure, afford control of the Reynolds number for the determinations conducted (Figure 5). For the viscosity coefficients reported here, the Reynolds number was kept below 1000.

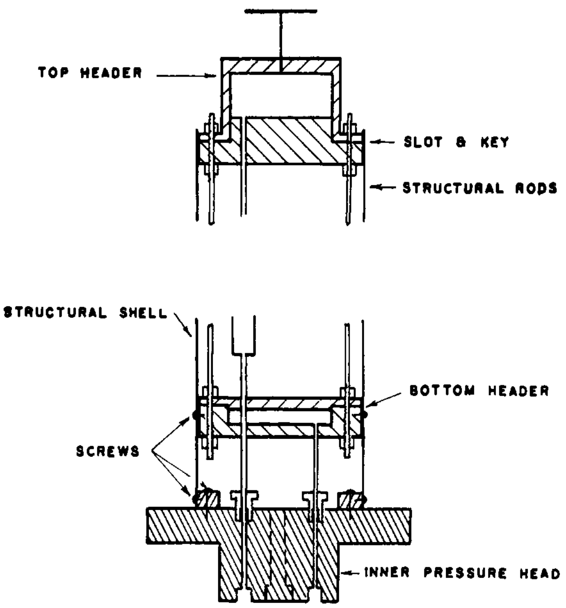

Figure 4. Viscometer mounting

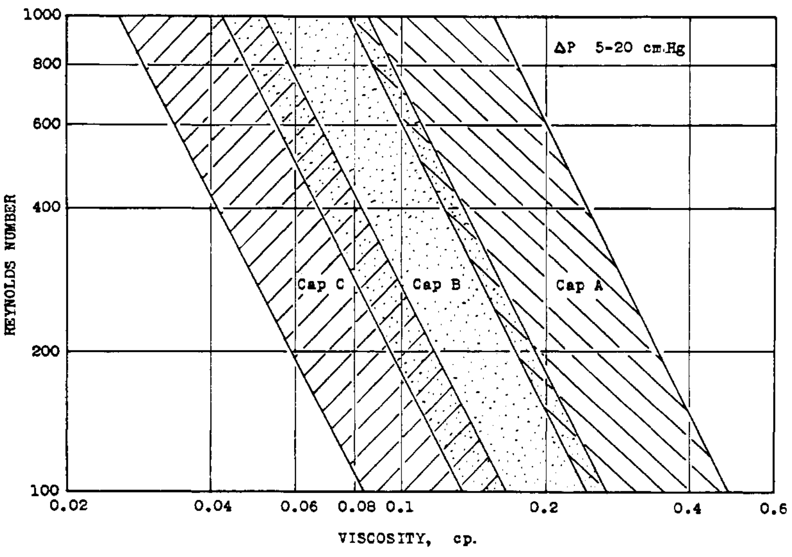

Figure 5. Approximate Reyonolds number for multi-range viscometer runs

RESULTS

The effective pressure drops used in this viscometer are a function only of the initial pressure drops chosen by fixing both the position of the static balance with the efflux bulbs and the variation of the mercury head with the flow from the bulbs. Since the cross-sectional areas of the internal leg and the test liquid reservoir are very nearly the same, variation of the test liquid heads contributes negligibly to variation of the pressure drop. Run types are listed consecutively as follows:

Efflux Vol., Cc.	Effective Pressure Drop, Cm. Hg	Efflux Vol., Cc.	Effective Pressure Drop, Cm. Hg
1.475	19.15	1.817	10.49
1.670	15.13	1.783	6.68
1.670	14.78	1.783	6.24
1.817	10.90		

The two different effective pressure drops listed for each efflux bulb other than the first bulb are the result of the practice of successively draining two bulbs in series before resetting. Efflux from the first bulb of such a series alters the mercury level in the internal leg from the static balance level. Thus, a correction in the initial pressure drop gives a different effective pressure.

The major variation of the pressure drop, $f(Q)$, with total flow is caused by the variation of the mercury head in the external leg. This variation was measured in a separate experiment for each of the bulbs and plotted in Figure 6. The contribution to the variation of the pressure drop by the changing level in the internal leg was calculated from the dimensions of the leg and the efflux volumes.

The constant $H = \pi r^4/8L$ in Equation 4 was determined by calibration, since the radius of the capillaries over their full length could not be accurately measured. Twelve runs were made at 26.6° C. for the calibration of capillary B using the test liquid n-hexane as the calibrating liquid. The value for the viscosity coefficient of n-hexane at 26.6° C., as obtained from the data of Thorpe and Rodgers (*10*) is 0.2996 cp. (Only the determinations involving this capillary are reported here.) A least squares fit of the data from these runs using Equation 4 gives a value for H of 6.41×10^{-11} cc. $\pm 0.4\%$ at the 95% confidence level. The calibration runs are included in the summary of all the runs given in Table I.

Since the correction term was small at the calibration temperature, an accurate value for C could not be obtained without considering the data for the other temperature conditions for which the correction term was larger. The value for C is 1.05×10^{-2} poise, seconds per gram $\pm 10\%$. Density data for n-hexane with reported accuracy of 1% (*2*) were used in the correction term.

Table I. Calculated Viscosity Coefficients

Temp., ° C.[b]	Press. P.S.I.A.	ΔP_e, Cm. Hg	Time, Sec.	$H\Delta P_e t/Q$, Cp.	$C\rho Q/t$, Cp.	Viscosity Cp.	Viscosity Av.,[a] cp.
26.6[b]	15	19.15	274.5	0.3041	0.0056	0.2985	
		15.13	394.7	0.3049	0.0044	0.3005	
		14.78	400.7	0.3024	0.0048	0.2981	
		10.90	594.2	0.3040	0.0032	0.3008	
		10.49	615.3	0.3031	0.0030	0.3001	
		6.24	1014.0	0.3016	0.0019	0.2997	0.2997
41.1	15	19.15	239.2	0.2644	0.0064	0.2580	
		14.78	348.4	0.2624	0.0049	0.2575	0.2578
60.9	43	19.15	202.4	0.2231	0.0073	0.2158	
		14.78	294.3	0.2210	0.0057	0.2153	0.2156
80.6	67	19.15	174.7	0.1916	0.0083	0.1833	
		15.13	248.3	0.1902	0.0066	0.1836	
		14.78	254.1	0.1901	0.0064	0.1837	
		10.49	385.9	0.1884	0.0046	0.1838	0.1836
101.4	96	19.15	151.1	0.1652	0.0092	0.1560	
		14.78	218.4	0.1627	0.0072	0.1555	0.1562
122.2	100	19.15	130.3	0.1419	0.0103	0.1316	
		15.13	183.6	0.1395	0.0082	0.1313	
		14.78	187.5	0.1392	0.0081	0.1311	
		10.49	283.9	0.1376	0.0058	0.1318	0.1319
122.3	170	19.15	131.0	0.1427	0.0103	0.1325	
		15.13	184.2	0.1400	0.0082	0.1318	
		14.78	188.7	0.1400	0.0080	0.1320	
		10.49	283.7	0.1370	0.0058	0.1316	0.1324
142.0	186	19.15	114.6	0.1243	0.0112	0.1131	
		15.13	160.9	0.1218	0.0090	0.1128	
		14.78	164.6	0.1217	0.0088	0.1129	
		10.49	246.2	0.1187	0.0064	0.1123	0.1132
165.1	183	19.15	98.9	0.1069	0.0124	0.0945	
		15.13	138.4	0.1044	0.0100	0.0944	
		14.78	141.0	0.1039	0.0098	0.0941	
		10.90	203.9	0.1019	0.0074	0.0945	
		10.49	210.7	0.1014	0.0072	0.0942	
		6.24	335.7	0.0979	0.0044	0.0935	0.0946
165.4	315	19.15	100.7	0.1089	0.0122	0.0967	
		15.13	141.3	0.1066	0.0098	0.0968	
		14.78	143.9	0.1060	0.0097	0.0963	
		10.49	215.1	0.1034	0.0070	0.0964	0.0970
181.6	321	19.15	86.0	0.0927	0.0131	0.0796	
		15.13	119.8	0.0901	0.0106	0.0795	
		14.78	122.2	0.0897	0.0104	0.0793	
		10.49	182.3	0.0874	0.0076	0.0798	0.0800

[a] Corrected for temperature effect on capillary. [b] Calibration runs for determining viscometer constant H. Viscosity coefficient (*10*).

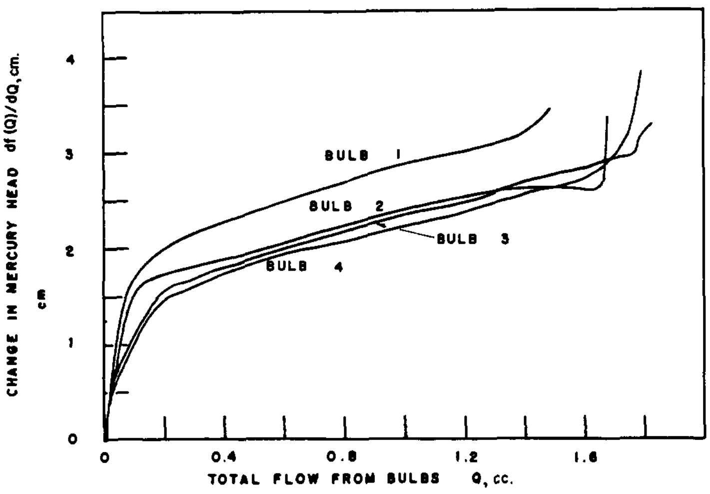

Figure 6. Effect of efflux flow on the mercury head

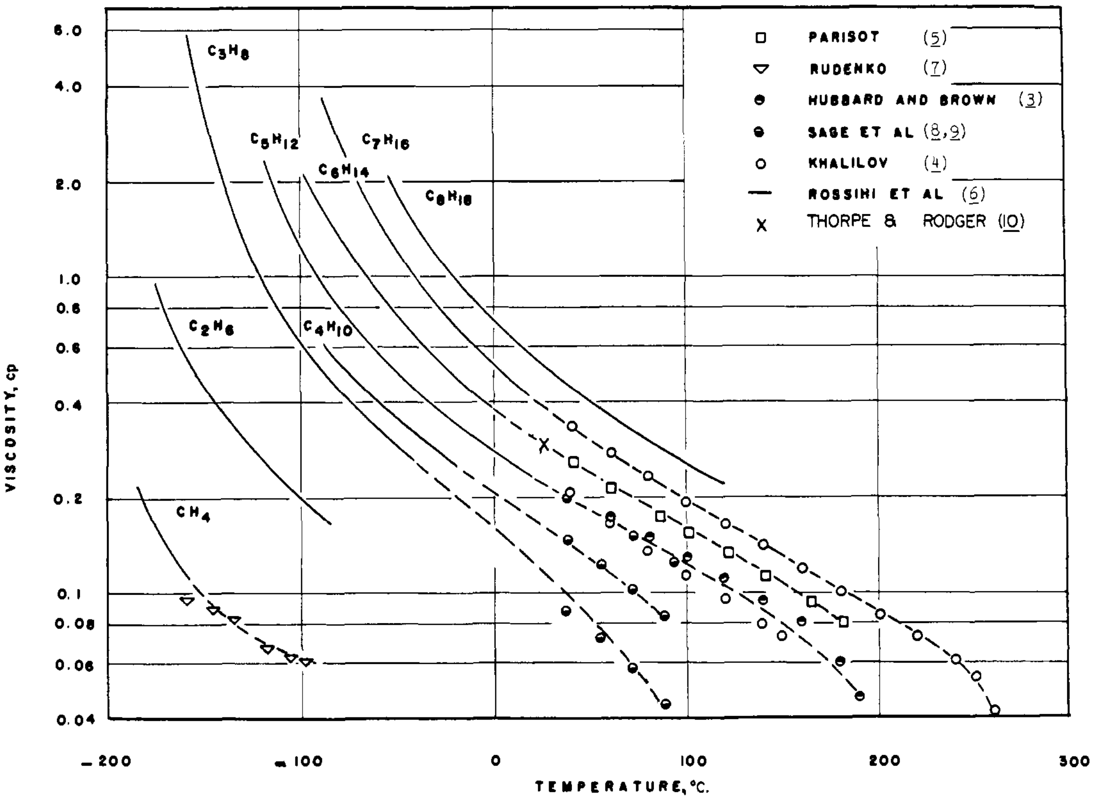

Figure 7. Viscosity of some liquid hydrocarbons ⟶

The summary of results in Table I represents 96 independent determinations. All efflux times are averaged data of at least two determinations at the same run conditions. The calculation of the values for the major term of Equation 4 as listed in column five includes the effect of expansion of the mercury flow on the displaced volume of the test liquid in the internal leg for the conditions where the two legs were at different temperatures. The correction for the effect of change of geometrical dimensions of the capillary tube with temperature was applied in calculating the average value for the viscosity coefficients listed in column eight.

The viscosity data for n-hexane are plotted in Figure 7 together with some other available data on liquid hydrocarbons at or near saturation pressures.

The reproducibility of the efflux times was better than 0.5%, and the largest contribution of the correction term to the calculation of the viscosity coefficients was 15% at 180° C. Since these two factors cause the major errors, the relative accuracy of the viscosity determinations of n-hexane up to 180° C. is better than $\pm 2\%$.

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NOMENCLATURE

C = viscometer correction term constant, poise sec./g.
H = capillary geometry constant, $\pi r^4/8L$, cc.
L = capillary length, cm.
m = kinetic energy correction term constant, dimensionless
ΔP = pressure drop, dynes/sq. cm.
ΔP_e = effective pressure drop, cm. Hg
Q = volumetric flow, cc.
r = capillary radius, cm.
t = efflux time, sec.
ρ = test liquid density, g./cc.
η = viscosity coefficient, poise

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