

THE VISCOSITIES OF NORMAL AND ISOPENTANE
AS A FUNCTION OF PRESSURE

THESIS BY
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This thesis contains preliminary results obtained in an investigation on the "Accurate Comparison by Viscosity Methods developed by Millikan of the Viscosities and hence of the Mean Free Paths of Ring and Chain Hydrocarbons of the same Molecular Weight and Composition" listed as Project No. 12 of American Petroleum Institute of Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

The problem here at hand involves the measurement of small differences in viscosities as well as their actual value with the greatest precision possible. The only type of apparatus known to be capable of such precision is the rotating cylinder apparatus such as was used by Millikan and his collaborators at the University of Chicago to determine accurately the viscosity of air which was required for the oil drop experiment. The Chicago apparatus was therefore, copied in its essential features with the added feature allowing the apparatus to be heated as a whole to temperatures presumably up to 400° centigrade.

The isomers of pentane were picked for two reasons; first, because three isomers exist and should be obtainable in high purity. These three compounds are identical in chemical formula and molecular weight, differing only in the

way the atoms are connected together in the molecule. The organic chemist assigns structural formulas to them as follows:-

Normal pentane:- $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$

Isopentane:- $\text{CH}_3\text{-CH}_2\text{-CH} \begin{array}{l} / \text{CH}_3 \\ \backslash \text{CH}_3 \end{array}$

Neopentane: $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{-C-CH}_3 \\ | \\ \text{CH}_3 \end{array}$

and it is believed that the actual shapes of the molecules are similar to these structural formulae; i.e. the normal pentane is supposed to be a long narrow molecule and the neopentane, a symmetrical one, the isopentane being something intermediate. Unfortunately a sample of pure Neopentane has not yet been obtained so that the measurements here presented are only on the first two of these isomers.

The second reason for selecting the pentanes is because their boiling points are near room temperature so that viscosities can be measured at pressures right up to their saturated vapor pressures. Measurements were therefore made on each compound at all pressures ranging up to ^{the} saturated vapor pressure at 25° Centigrade at which temperature all measurements were made.

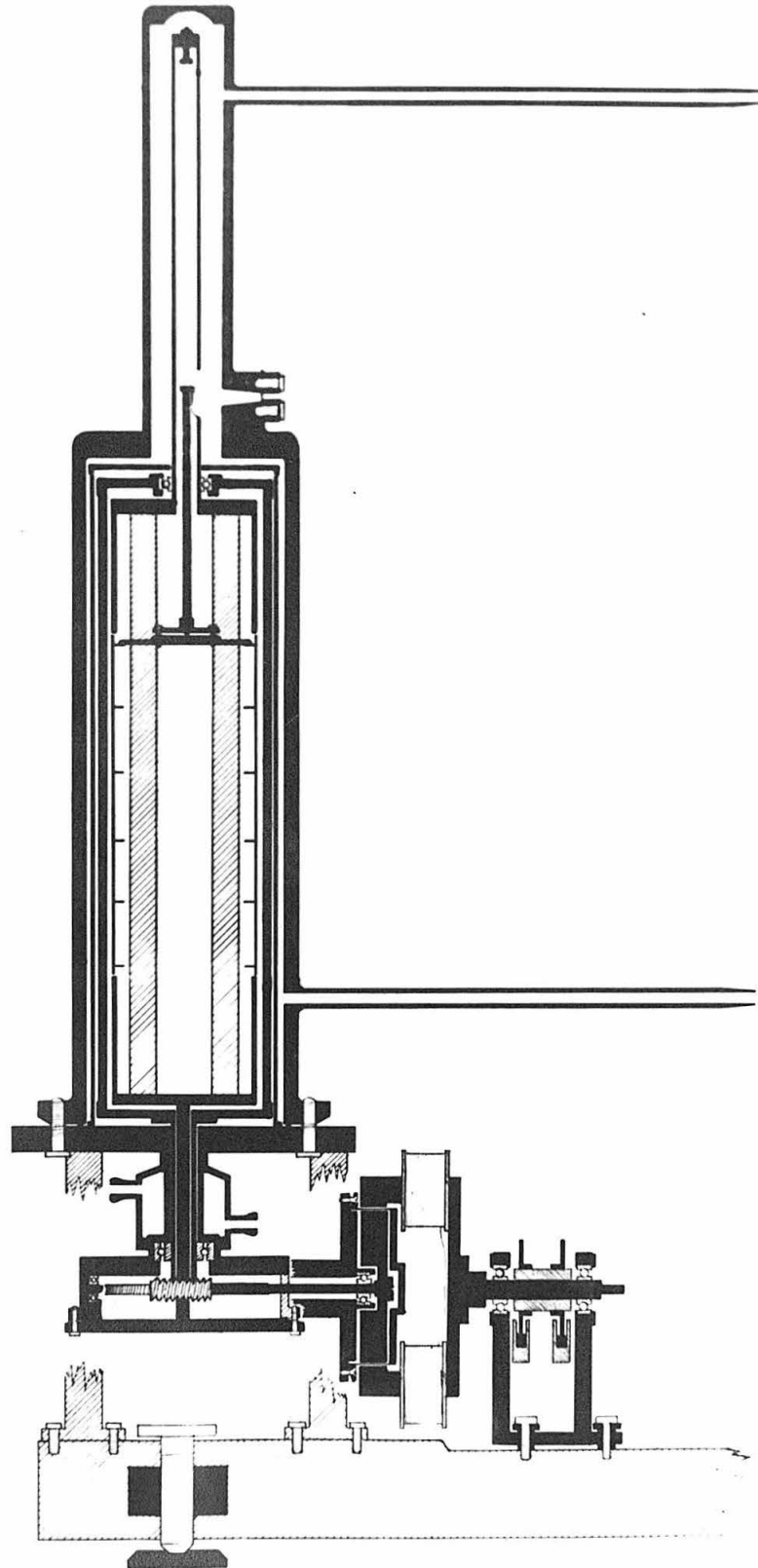


Fig. 1

APPARATUS

The apparatus will be described in detail only where important changes were made from the Chicago rotating cylinder apparatus which has already been described in full by Gilchrist₁, Harrington₂ and others. Considerable care was taken in the design of the apparatus so that it could be made to function also at high temperatures. The description of the apparatus will include these features even though the measurements here presented were all made at 25° centigrade and no attempt has as yet been made to heat the apparatus. Fig. 1 shows a schematic diagram of the apparatus and Fig. 2, the set up as it was.

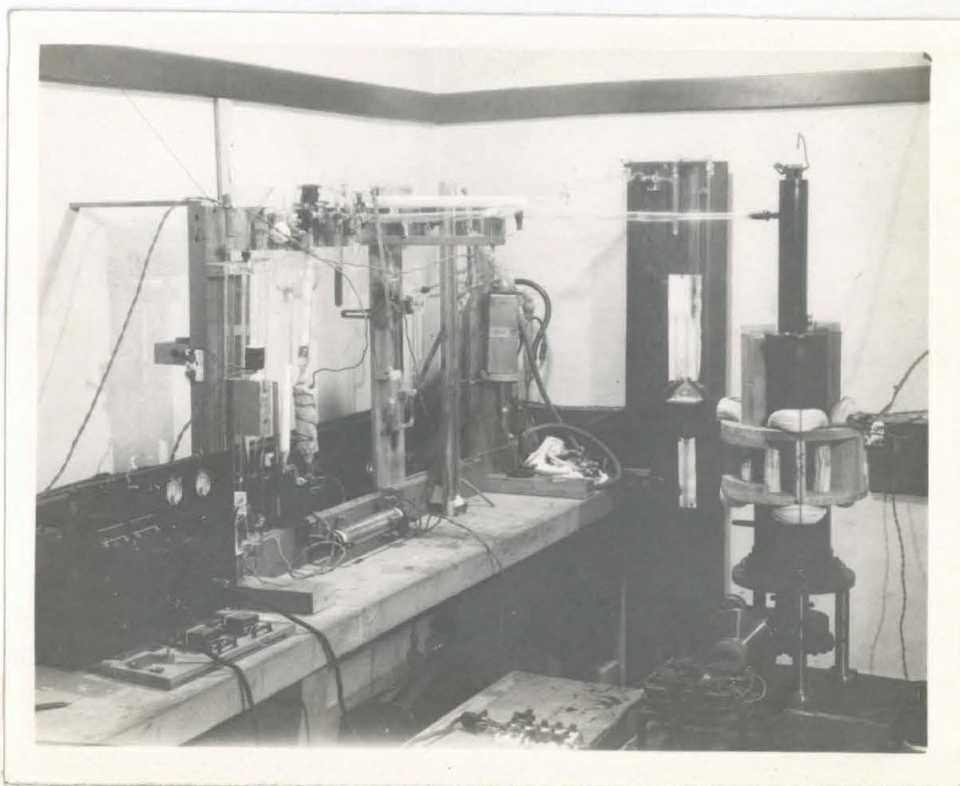


Fig. 2

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1. Phys. Rev. 1, 124(1913)
 2. Phys. Rev. 8, 738(1916)

directly in its final state. Before the final cut was taken on the lathe, its surface was equally accurate with the above. The final cut was taken on the inside of the cylinder and as follows:- After a good cut was taken on the outside of the cylinder giving it the final uniform machined surface, an iron cylinder was fastened rigidly in the lathe and an inside cut taken on it of exactly the same diameter as the outside diameter of the bronze cylinder. Without removing the iron cylinder from the lathe, both cylinders were cooled with carbon dioxide snow and the bronze one slipped inside the iron one, which was easy when cold because bronze has a higher expansion coefficient than iron. The final cut was now taken on the inside of the bronze cylinder while a flame was played on the iron cylinder to insure a tight fit. To remove the bronze cylinder, carbon dioxide snow was used again. In this way there was no chance of changing or hurting the uniformity of the suspended cylinder's outer surface and a uniform wall thickness is also assured.

The guard cylinders were accurately turned to the same diameter as the suspended cylinder and the gap separating them from the suspended cylinder above and below is about $1/2$ mm. The rotating cylinder is accurately centered with respect to the guard cylinders because the top and bottom ball bearings holding the former are centered on the support rods holding the guard cylinders. All moving parts are pivoted on dry ball bearings. Oil had to be avoided because of the temperature and also because of its solubility in hydrocarbon vapors.

To enable the instrument to be adjusted in the cold and then heated up without losing its adjustment, all parts were carefully compensated for thermal expansion, metals are matched throughout so that everything will expand together on heating.

The Suspension:- The suspension used is the same as Harrington and others found best; namely, an uncoiled watch hair-spring of which the Elgin Watch Co. kindly supplied us a variety of samples. The size selected for this work is 1.8 x 5.8 mils in cross section and is used at a factor of safety from the breaking weight of not much over two. When first strung up there was a rapid drift of zero due to readjustment of the suspension to its new conditions. This drift had died down to a very small rate in a month's time, but is perceptible even now six months since it was installed.

Due to the small size of the suspension, the natural period of oscillation of the suspended cylinder about its vertical axis is very large - namely $198\frac{1}{3}$ sec. on this suspension. We have the elementary formula relating this period (P), the moment of inertia (I) and the sensitivity (S) (angular deflection per unit of viscosity torque) which holds for any kind of a suspension that gives simple harmonic motion:-

$$\frac{P^2}{4\pi^2 I} = S$$

It is obvious that to get a high sensitivity, a long period must be tolerated. The moment of inertia has already been cut to a minimum by making the inner cylinder as light as

possible. The magnetic damping device to be described later makes the taking of readings even with this long oscillation period quite easy.

The Constant Speed Motor:- Harrington's apparatus was equipped with a chronograph drive which gave an actual record of the speed all of the time that it ran. For relative measurements, a reproducible constant speed is desirable while its easy measurement is not so important and also for reasons of its convenience and probably greater accuracy a Benioff constant speed motor was adopted. This motor was designed by H. Benioff for use in driving the chronograph drums on the Seismographs in use at the Carnegie Seismograph Station in Pasadena. Many thanks are due him and them for lending their design and helping in its construction.

The speed controlling mechanism (Fig. 3) is a steel reed which is attached to a heavy base, and vibrates with a small permanent straight bar magnet fastened rigidly to the end of the reed and perpendicular to it. This small magnet acts as a plunger in and out of a coil of wire on each side of it. The alternating current which is set up in the one coil is amplified by means of a vacuum tube and fed back to the other coil to drive the reed. This alternating current of exactly the frequency of the reed is now further amplified with vacuum tubes and relays and fed to the motor poles. The reed is in a thermostated box so that its frequency is constant and the motor cannot but be in step with the reed. The error due to inconstancy of the motor speed is smaller than 1 part in 10,000 as estimated by Mr. Benioff.

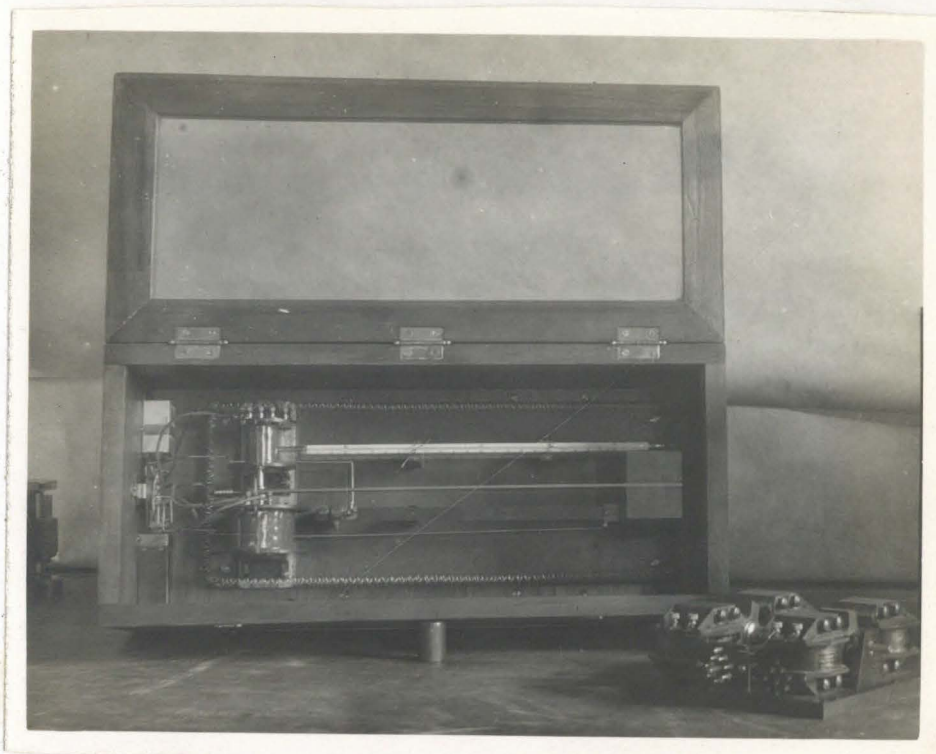


Fig. 3.

The motor has therefore one definite normal speed as determined by the frequency of the reed. This normal speed is about 2 revolutions per second and is reversible. By means of gears, the motor can be made to transmit speeds which are exact multiples of the normal speed by the gear ratio.

The Magnetic Coupling and Worm Gear Drive:- Harrington's method of connecting his motor drive outside the gas chamber with the rotating cylinder inside the chamber was by using a train of gears and shafts going right through a barometric column. Mercury has been considered intolerable in my apparatus because of high temperatures giving high mercury vapor pressures and because a liquid air trap cannot be used when condensable vapors are to be measured. To solve the

same difficulty in my apparatus, therefore, a magnetic coupling through the walls of the gas chamber was used and proved quite satisfactory. The device is shown in Fig. 4. The inside bar of soft iron which follows the electromagnets around is blocked out in brass partly to give inertia to the inside system and also to stop any possible hunting between the systems. Hunting would produce eddy currents in the brass which would tend to damp it. In starting the motor some care was necessary to keep from giving the magnetic coupling too great or too sudden an acceleration at which times the inside rotor would be lost and it was necessary to start over again. Once going, the coupling was never lost.

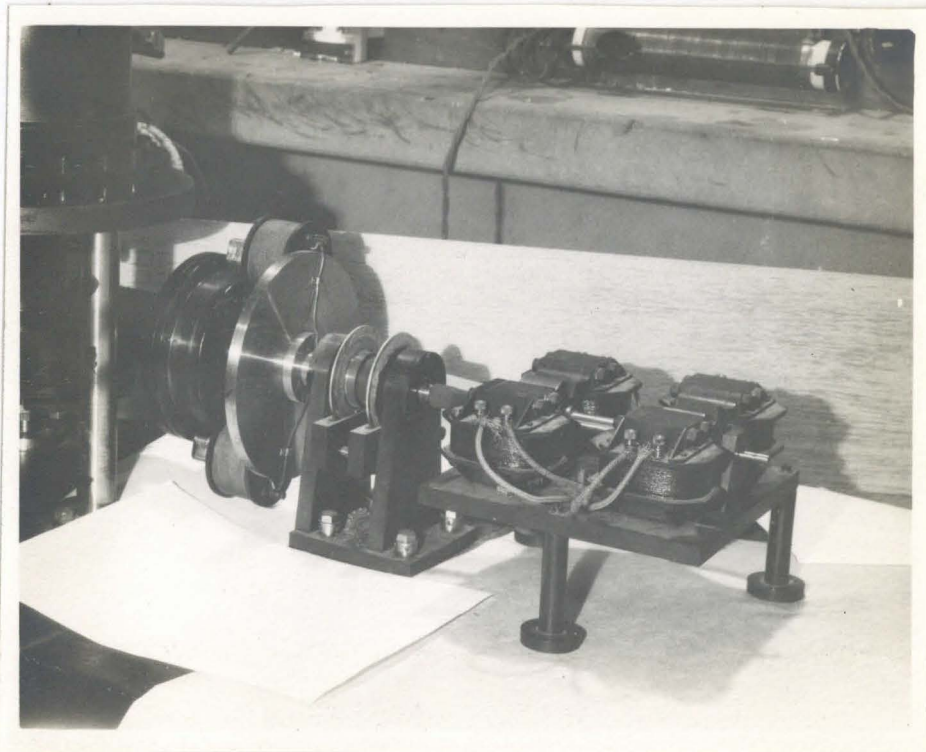


Fig. 4.

Since the motor runs normally at about 2 revolutions per second and it is desirable to have the outer cylinder rotate at about 1 rev. per minute, a worm gear drive of ratio 120:1 was used and was put inside the vacuum chamber. The worm gear and rotating cylinder are the only parts going at slow speed so that any jerkiness due to the motor or the magnetic coupling, is ironed out by the high angular momentum of those systems and the outer cylinder gets a very uniform rotation. The worm gear drive as everything else inside the chamber, must run without oil, so the worm gear was made of cast iron and the worm itself was ground out from a piece of Agate. A little graphite sprinkled over the worm is its only lubrication. This lower section of the apparatus containing the magnetic coupling, worm gear drive and three ball bearings is separated from the main apparatus by a water jacket and kept cool. The upper main central ball bearing is the only bearing which must run hot.

The lower cold section is in a soldered brass housing involving two set-in rubber gaskets and a flat paper gasket. Duco was applied afterwards to make a sure seal.

The Magnetic Damping Device:- Much effort was spent in trying to damp the oscillations of the suspended cylinder by means of a strong stationary magnetic field through the walls of the suspended cylinder. This was abandoned because the high fields necessary are cumbersome and involve many other difficulties. The bronze suspended cylinder itself was found to be quite magnetic, for one thing.

Finally, a rotating three phase field has been adopted as an eddy current twisting device and has proved itself to be a perfect and very convenient method of damping and is also free from any theoretical objections which may be raised with respect to a stationary field. There is no chance of permanently magnetizing any iron or steel parts of the instrument with alternating current and when turned off there is no question of any residual magnetism. The device is shown in Fig. 5.

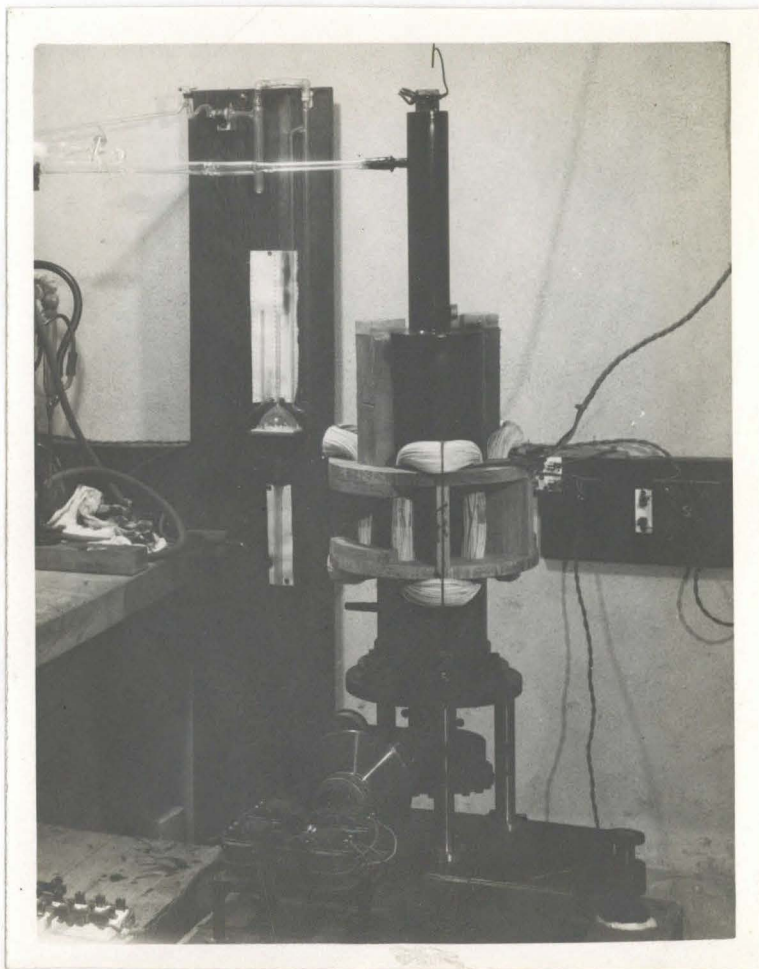


Fig. 5.

Three coils of 500 turns each of #20 insulated copper wire are placed symmetrically 120° apart around the outside apparatus housing, connected in a closed delta and through three resistances of 300 ohms each to the 110 volt-3-phase line. This permits a current of about 0.2 amps. to flow. A reversing switch permits reversing or cutting off the field at any time. The device is really, as before mentioned, a twisting device and it can be used to bring the cylinder to rest in any position desired. There is no kick of any kind when the field is thrown on or off. There is no measureable heating due to the energy dissipated in the apparatus walls. This improvement over Harrington's apparatus makes the taking of readings very much simpler and easier so that successive readings can be taken at ten minute intervals. This means that the time during which the gas is in the apparatus, previously evacuated is a minimum and therefore the impurities introduced due to adsorbed gases in the apparatus and small leaks is also a minimum.

A new apparatus housing of brass was constructed to replace the welded steel one for this first work at room temperature which permits the rotating field to penetrate through the casing to the inner cylinder. I firmly believe that working at high temperatures will not eliminate the possibility of using this rotating field device although this has not yet been worked out.

DEFLECTION MEASUREMENTS

The deflections were measured by the usual telescope and scale method. The scale is a meter stick of maple wood with millimeter scale divisions. Tenths of a millimeter were estimated. The mirror to scale distance is about 214 cm. The scale is perpendicular to the line from the mirror to the exact center of the scale.

Summary of Apparatus Dimensions and Constants

Length of rotating cylinder	- $18\frac{1}{4}$ in.
Inside diameter of rotating cylinder	- 4.690 in.
Length of each guard cylinder	- $3\text{-}7/8$ in.
Length of suspended cylinder	- $10\text{-}1/16$ in.
Outside diameter of suspended cylinder	- 4.218 in.
Weight of suspended cylinder	- 478.5 gms.
Length of suspension	- $9\text{-}3/8$ in.
Period of oscillation of inner cylinder	- $198\text{-}1/3$ sec.

TEMPERATURE CONTROL

This work was done in a sub-basement room which was thermostated at 25° centigrade. The variation of temperature was never greater than 0.2 degrees and during these measurements, temperature control was mostly much better than this. The values of Sutherland's constant (C) for air and isopentane as given in the International Critical Tables are:-

air:- C = 120

isopentane :- C = 500

It is presumed that the value of "C" for normal pentane is similar to that of isopentane. Sutherland's equation may be written as follows to compare small differences in temperature:-

$$\frac{\eta}{\eta'} = \frac{T'+C}{T+C} \left(\frac{T}{T'} \right)^{3/2}$$

Putting $T = 298^{\circ}\text{K}$, we find that 0.2° centigrade changes the viscosity of air 1 part in 1800 and of pentane 1 part in 1300. The temperature control therefore may account for small deviations from the correct value but the accuracy in its worst case is about equal to the accuracy of reading.

PRESSURE MEASUREMENTS

As before mentioned, mercury could not be used in connection with the apparatus. A pressure gauge without mercury was therefore necessary and the pressure measurements should be independent of the nature of the gas or vapor, A Bourdon spiral gauge fulfills these requirements. Such a spiral as is shown in Fig. 6 was blown from PYREX and set up to twist a small galvanometer mirror with a scale about a meter away. 1.3 millimeters deflection on this scale represents a pressure difference of one mm.

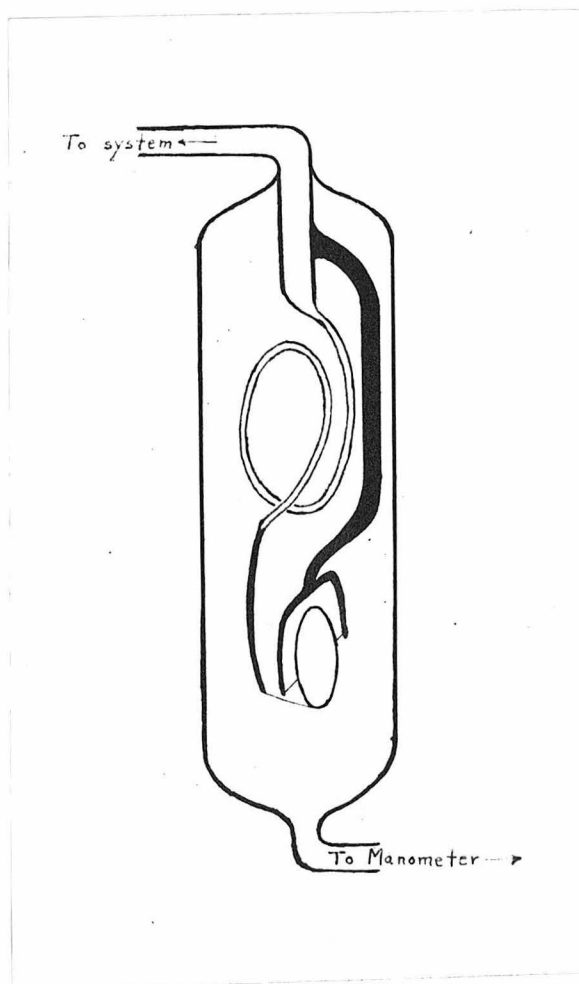


Fig. 6

of mercury between the inside and outside of the spiral. The inside of the spiral is connected to the apparatus system and the spiral itself is enclosed in a chamber connected to a separate system in which the air pressure is regulated at will and measured by means of a closed tube mercury manometer. The spiral is thus used as a zero instrument capable of reading small deviations and pressure readings are taken directly on the mercury manometer. The final measurements are accurate to about 1 mm of mercury.

THE ORGANIC COMPOUNDS

The two isomers of pentane which occur in natural gasoline were obtained in a very pure state. Normal pentane was obtained directly from the Eastman Research Laboratory. Isopentane was found unavailable in a sufficiently pure state, so that our Chemistry Department undertook to synthesize it for this work.

To test the purity of these compounds, the freezing points and the range of temperature over which freezing takes place were measured. This physical property was chosen, first because it is the property which organic chemistry uses in general as a criterion of purity and further because the difference in the freezing points of the two isomers is 28°C, whereas the difference in boiling point, for instance, is only 8°C. Therefore, a reasonable check of freezing points and a small range of freezing should indicate high purity. A single junction copper-constantan thermocouple was used and calibrated roughly with liquid oxygen and solid CO₂. Since

both freezing points are equally far in error from the measured values, it is suspected that the calibration may be that far wrong. The chief interest was in the range of freezing so that no further efforts were taken to check the calibration.

The hydrocarbon was put into a small Dewar flask evacuated to the extent that complete freezing took place in about 20 minutes when the flask with the liquid hydrocarbon, thermocouple and stirring rod inside, was immersed in liquid air. A time temperature curve was then plotted. The results follow:-

	<u>Freezing</u>	<u>Point</u>	<u>Difference</u>	<u>Range of</u>
	<u>Meas.</u>	<u>Int. Crit.</u>		<u>Freezing</u>
		<u>Tables</u>		
N. Pentane	- 132.8°C	- 131.5°C	1.3°C	1.0°C
Isopentane	- 161.1°C	- 159.7°C	1.4°C	0.3°C

The introduction of the hydrocarbon into the apparatus involved some difficulties at first because of its solvent action on stopcock grease and waxes. Red sealing wax which is apparently insoluble, still underwent some decomposition when it was used as a stopcock lubricant, especially when it was heated to turn at which time a yellow vapor was given off discoloring the P₂O₅ tube. Phosphoric acid as a stopcock lubricant worked fine for a while, but would not last out the number of turns required for a set of measurements. The phosphoric acid does not have the rubber-like quality necessary for standing pressure without slowly being pushed away until a break develops in the film around the cock and it leaks.

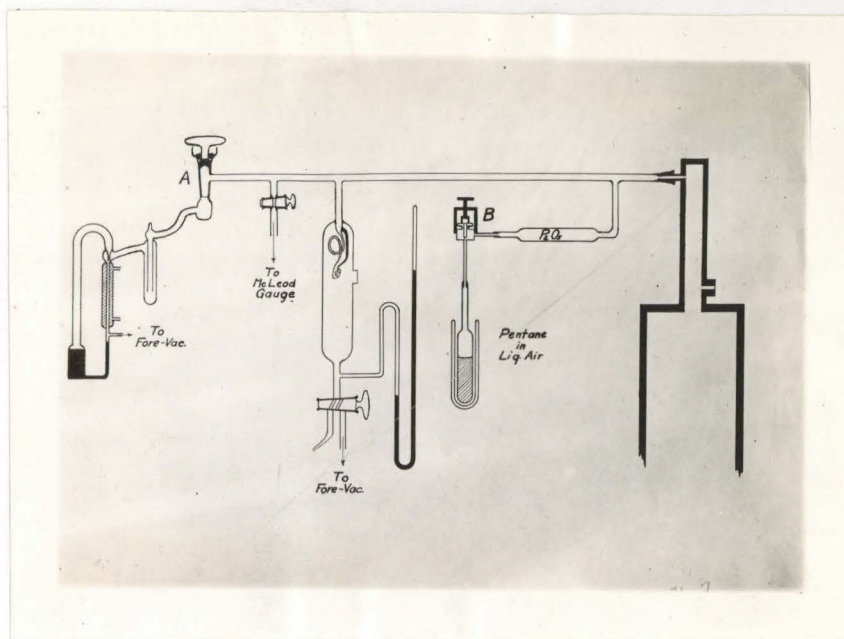


Fig. 7.

The arrangement shows in Fig. 7 was finally adopted. An all metal-stopcock (B) using a single Sylphon-bellow and closing with a large angle tapered needle on a silver seat was finally introduced and found very satisfactory. This cock is used between the flask with the hydrocarbon and the apparatus system, and is connected to the glassware on each side with a copper-PYREX seal.

To isolate the apparatus system, a large glass cock (A) is used with the usual grease, but this need only be turned at the beginning of the run after which it simply presents a grease surface to the system. The hydrocarbon will be absorbed easily and probably in considerable quantity in this grease yet since the grease has no appreciable vapor pressure

by itself, it is not conceivable how the organic vapor can be in anyway contaminated by being absorbed and evaporated any number of times by the stopcock grease. Before going from one compound to another, this cock, connecting the pumps and another smaller one connecting the McLeod gauge to the apparatus were carefully cleaned and lubricated with fresh grease. In addition to these two grease stopcocks, other parts which could absorb hydrocarbons by solution were several rubber gaskets and a little soft wax used to plug up leaks. The same argument as to contamination holds here and it is held that the compounds introduced were not in anyway contaminated by the apparatus itself.

Contamination of the vapors is still possible in a variety of ways. Air leaks in the apparatus have been the greatest source of trouble. The apparatus, all told, has a tremendous surface area inside, so that adsorption on these walls of any kind of gas is easily possible. Stacy* speaks of a "Hydrogen Effect" in his measurements on air at low pressures, this being presumably due to adsorbed Hydrogen in the apparatus. Troubles of this nature will be described later in discussing the measurements.

EXPERIMENTAL PROCEDURE

The equation used which gives the viscosity co-efficient in terms of instrument constants and the deflection angle of the inner cylinder assumes a motion of the gas between

*Stacy - Phys. Rev. (1923) 21, p 245.

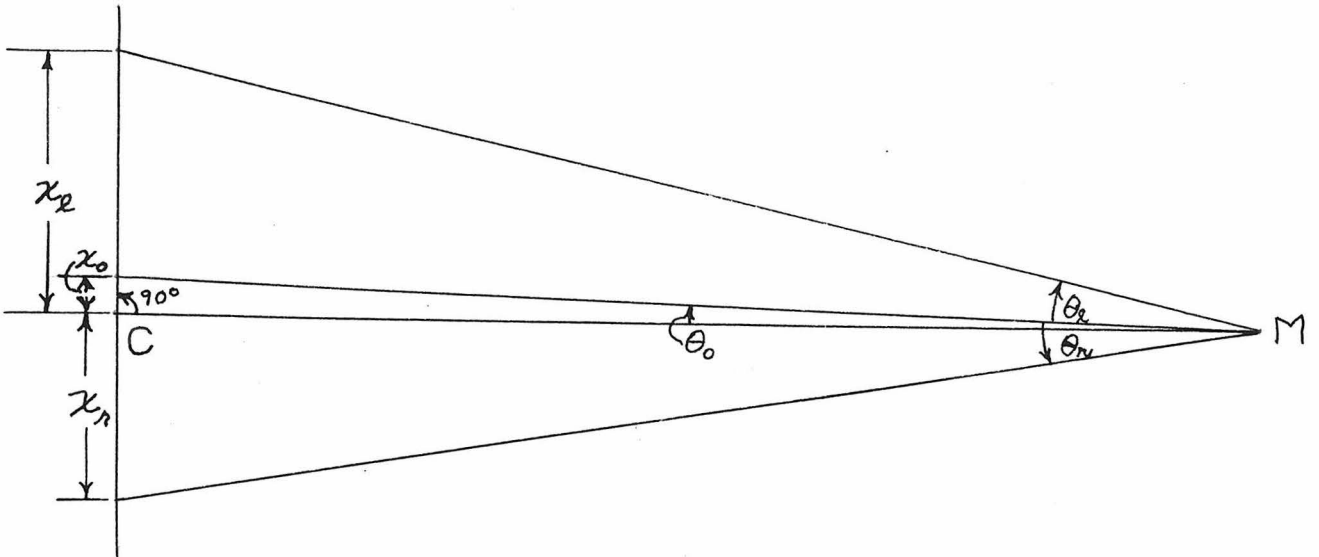
the walls of the cylinders due only to the motion of the rotating cylinder. At times when this condition of a "static" gas was not satisfied such as when there was a large leak or if some condensed hydrocarbon was evaporating inside due to a recent fast reduction in pressure from a saturated vapor, the deflected position of the inner cylinder was irregular and a reading quite impossible. The experimental procedure was therefore as follows: The pentane in its flask is frozen by immersing this in liquid air. The flask with the frozen pentane is easily sealed on as shown in the diagram and the whole system evacuated with metal stopcock (B) open and the liquid air still on the pentane. When a good vacuum is obtained, stopcock (B) is closed and the liquid air removed allowing the pentane to warm up to room temperature. The apparatus is now isolated from the pumps by closing stopcock (A) and a small portion of pentane let in by opening stopcock (B), and again closing it. The pressure is read and the motor driving the outer cylinder is started. The swing of the inner cylinder is arrested within a few millimeters of its deflected position using the rotating field damping device. Maxima and Minima are observed until exactly ten minutes after the motor was started, at which time, its direction is reversed and readings taken in the other direction. The deflected reading taken is the mean of the last three readings corrected by interpolation such that the middle one comes 7-1/2 minutes after the motor was started. If the right and left readings agree by a rough calculation and apparatus conditions

are all perfect, more pentane is let in and the procedure repeated. In most cases, one deflection in each direction was sufficient and the mean of these was taken to represent the viscosity at this pressure and this value plotted as a point on the curve. A run consists of a series of measurements at increasing pressures after which liquid air was put on the pentane flask and measurements taken at decreasing pressures until it was all frozen out again. By going back and forth on the pressure in each run, it is possible to check up on any differences between "early" and "later" readings taken at the same pressure which would be caused by leaks in the apparatus or other sources of contamination which would vary with the time. In general, it will be noticed that "later" viscosities tend to be lower than earlier ones.

The procedure regardless of the pressure range or the number of readings taken at a pressure was always to deflect in alternate directions for ten minutes each. This procedure was also followed on calibration runs on air and on hydrogen. The reason for this as well as computing the deflection mean for the 7-1/2 minutes after the motor was started, is to cancel out the effect of the "nachwirkung" of the suspension. After the inner cylinder is deflected and damped, there is a small drift of the deflected mean position to increasing deflections with time due to slow adjustment of the suspension to its new conditions in the deflected position. By following the above procedure on readings and calibration both, the error due to this drift is a minimum.

COMPUTATION OF RESULTS

The following diagram shows the method of measurements:



C is the center of the scale and the foot of the perpendicular from the mirror. It is the origin for all measurements. x_0 , x_l , and x_r are the distances from C of the zero position, the deflection to the left and the deflection to the right respectively. θ_l , θ_r and θ_0 are the angles between MC and the beams of light to the three positions above. The distance MC is called "d" in the computations.

The results are calculated according to the following formulae:-

$$\theta_l + \theta_0 = \tan^{-1} \frac{x_l}{d}$$

$$\theta_r - \theta_0 = \tan^{-1} \frac{x_r}{d}$$

$$\theta_0 = \tan^{-1} \frac{x_0}{d}$$

$$\theta_l + \theta_r = \tan^{-1} \frac{x_l}{d} + \tan^{-1} \frac{x_r}{d} = 2\theta$$

The standard formula for the rotating cylinder apparatus⁽¹⁾ is:-

$$\eta = \frac{\pi \theta I (b^2 - a^2)}{a^2 b^2 P^2 \Omega l}$$

In all of these measurements a comparison is made between the deflection for the gas in question and dry air so that the relative viscosity equation reduces itself to:-

$$\frac{\eta}{\eta_{\text{air}}} = \frac{\theta}{\theta_{\text{air}}}$$

Harrington's value for η_{air} is used in the calculations.

$$\eta_{\text{air}} \text{ (at } 23^\circ\text{C.)} = 1822.6 \times 10^{-7}$$

The formula for the variation of the viscosity of air with Temperature near 23°C is given by Prof. Millikan⁽²⁾:-

$$\eta_T = \eta_{23^\circ\text{C}} + .000000493 (T - 23)$$

$$\text{This gives } \eta_{25} = 1832.5 \times 10^{-7}$$

RESULTS

In the following table "p" is the pressure in mm. of mercury, "t" is the time in minutes between the reading and the time when the apparatus was shut off from the pumps. The calibration deflection on air at 25°C is taken as the mean of a calibration run immediately before and after the readings taken.

1: Harrington:- loc. cit.

2: Millikan:- Ann. der Physik (1913) 41 p.759

Normal Pentane: $\theta_{\text{air}} = 4^{\circ}.5101$

Isopentane: $\theta_{\text{air}} = 4^{\circ}.5081$

NORMAL PENTANE

	No.	p.	t.	x_l	x_r	$\eta \times 10^7$
	7	9	15	17.101	14.964	676.98
	8	17	35	17.108	14.970	677.22
	9	25	55	17.099	14.982	677.30
	10	50	75	17.090	14.976	677.02
Run	11	102	95	17.068	14.965	676.29
#1	12	50	115	17.088	14.967	676.77
	13	25	135	17.086	14.979	676.98
	14	17	155	17.079	14.979	676.81
	15	9	175	17.085	14.971	676.77
	16	0.38	14	17.016	14.908	673.97
	17	1.3	34	17.100	14.994	677.51
	18	4	54	17.118	15.014	678.40
	19	9	74	17.124	15.021	678.64
	20	51	94	17.090	14.976	677.02
Run	21	146	114	17.069	14.954	676.08
#2	22	250	134	17.048	14.935	675.23
	23	200	154	17.058	14.940	675.56
	24	100	174	17.078	14.948	676.16
	25	25	199	17.083	14.958	676.49
	26	8	224	17.089	14.956	676.57
	27	200	28	17.080	14.912	675.43
	28	300	63	17.058	14.882	674.34
	29	402	88	17.046	14.881	674.05
Run	30	479	210	17.041	14.855	673.40
#3	31	484	230	17.038	14.852	673.28
	32	455	300	17.030	14.853	673.12
	33	350	345	17.062	14.856	673.85
	34	250	365	17.080	14.890	674.97

ISOPENTANE

	No.	p.	t.	x_1	x_r	$\eta \times 10^7$
Run #1	1	2.9	30	17.860	15.124	696.60
	2	11.5	55	17.882	15.142	697.45
	3	25	75	17.868	15.141	697.12
	4	50	95	17.858	15.118	696.42
	5	101	115	17.850	15.112	696.13
	6	50	135	17.855	15.111	696.22
	7	24	155	17.857	15.108	696.20
	8	11.5	175	17.855	15.110	696.20
Run #2	9	2.1	15	17.939	15.031	696.30
	10	11.5	35	17.954	15.035	696.70
	11	25	55	17.946	15.030	696.42
	12	50	75	17.942	15.023	696.20
	13	101	95	17.924	15.012	695.59
	14	150	115	17.916	15.008	695.32
	15	201	135	17.906	14.997	694.89
	16	251 $\frac{1}{2}$	155	17.901	14.990	694.63
	17	350	175	17.894	14.983	694.34
	18	250	195	17.905	14.976	694.42
	19	150	215	17.919	14.991	695.05
20	50	235	17.934	14.999	695.53	
Run #3	21	25	15	17.966	15.003	696.28
	22	50	35	17.960	14.995	695.98
	23	100	55	17.951	14.986	695.60
	24	202	75	17.929	14.975	694.91
	25	300	95	17.910	14.956	694.12
	26	350	115	17.908	14.946	693.87
	27	400	135	17.903	14.945	693.74
	28	450	165	17.901	14.932	693.43
	29	497	195	17.871	14.924	692.62
	30	550	235	17.868	14.919	692.46
	31	650	448	17.874	14.911	692.41
	32	658	525	17.867	14.903	692.10
	33	600	570	17.855	14.902	691.84
	34	553	595	17.875	14.906	692.33
	35	400	625	17.892	14.915	692.89
	36	300	645	17.897	14.934	693.40
	37	149	665	17.931	14.957	694.58

DISCUSSION OF THE ACCURACY OF
THE RESULTS

Since the measurements were made with the apparatus in a condition such that small leaks were constantly developing in a cracked soldered joint, some consideration is necessary to justify the experimental results. As mentioned before, the "runs" were all taken by going first up the pressure scale and then down without evacuating between readings. It is a safe presumption that any contamination due to a leak would be a continuous process with time and therefore it should not be possible to go up and down the pressure scale and check the results. In most cases viscosities on the up-scale half of the run are higher than those on the later down scale half although Run #3 on normal pentane for instance shows no regularity in this respect. The explanation of these lower viscosities after the pentane has been in the apparatus for a longer time, is entirely unknown to me although in most cases the results are all within the limit of error so that no anxiety need be felt about it.

It will be noticed that the largest deviations are at the very low and very high pressures. These are the difficult pressures at which to work. The apparatus, as mentioned before, has stopcock grease, rubber gaskets and other materials inside which tend to absorb the pentane. These absorptions produce the most trouble in the very low and very high pressure ranges. At low pressures, small quantities of evaporating or condensing vapors are large percentages of the total vapor present and at pressures near saturation, very

large amounts of pentane, even puddles, may accumulate. The evidence for this is in the large changes in pressure on standing which were noticed at the high pressures. During these changes of pressure, the deflections were always uncertain which is probably due to currents of vapor blowing on the inner cylinder.

The reasons that the initial low pressure readings are often high may be because of the displacement of air or other gases then adsorbed on the walls of the apparatus. Attempts at measuring the effect on the viscosity caused by small air impurities in isopentane gave the result that up to 0.2% air made no detectable difference and larger percentages caused a rise in viscosity although the percentage rise is still much smaller than the percentage of air impurity. Air impurities therefore do not seem to affect the viscosity of the pentanes very much. Still the fact that air leaks increase instead of decrease the viscosity, cannot account for the previously mentioned fact that the viscosities on the return part of a run going to lower pressures tend to be lower than the early measurements.

The errors due to fluctuations in speed of the motor or any imperfections in the apparatus, are believed to be within the accuracy of reading because of the consistency of readings taken on air and hydrogen. The air-hydrogen ratio was also checked to within the accuracy of reading. The accuracy of reading of the deflections is estimated at 0.1 mm on the scale. Since deflections on the pentanes were about 150 mm., this

is 1 part in 1500 or 0.07%. The maximum error due to temperature fluctuations is of the same order. The measurements here presented may be said to be accurate to 0.2%

An impurity might very easily get into the hydrocarbon due to accidental causes or through the medium of the apparatus. There is no reason to believe that there has been impurity introduced and every precaution was taken to prevent it. I mention this only because it would be so easy to absorb an organic impurity and extremely difficult to detect it. For this reason the relative values on each compound are probably more accurate than the absolute values.

PREVIOUS MEASUREMENTS

The only previous work which was found on either of these compounds, is the measurements by Rappenecker (ref.†) on isopentane at 100°C and 212.5°C using the capillary tube method.

His values are:-

$$\eta = 885.1 \times 10^{-7} \text{ at } 100^{\circ}\text{C}$$

$$\eta = 1164 \times 10^{-7} \text{ at } 212.5^{\circ}\text{C}$$

$$\text{Sutherland's constant (C)} = 500$$

Extrapolating his values with the help of his Sutherland constant and Sutherland's equation gives $\eta = 691 \times 10^{-7}$ at 25°C. He used "Kahlbaum" isopentane and worked at a few centimeters of mercury above atmospheric pressure. This extrapolated value agrees with my high pressure value of 691.5×10^{-7} at

ref. Rappenecker - Zeit. Phys. Chem. 72, 695 (1910)

650 mm, which is a nice check though not much weight can be put on this as a check when one considers the different conditions under which the two experiments were performed.

DISCUSSION OF RESULTS

After all the measurements were made, they were plotted and it is quite apparent that a straight line fits best the points of each curve. It will be further noticed that the slopes of the lines on the two isomers are of the same order of magnitude (ratio:85/76). The difference between the absolute values at any pressure is about 2.8% the isopentane having the greater viscosity.

These values are as would be expected. The isopentane being a more compact molecule would be expected to have a smaller collision area and consequently a longer mean free path and larger viscosity. The decrease in viscosity with increase of pressure on each compound seems to indicate an increase in the effective size of the molecule with increase of pressure. This fact and the apparent linear relationship need careful theoretical consideration. Kinetic Theory interpretation of this decrease of viscosity with increase of pressure and of the apparent linear relationship may lead to some interesting and new knowledge of the behavior of gaseous vapors from the molecular viewpoint.

MEAN FREE PATH

The Landolt-Bornstein Tables* use the following

* Vol. I. p.119

formulae to calculate viscosities into mean free path data:-

$$L \text{ (in cm.)} = \frac{\pi}{8} \cdot \frac{1}{0.49} \cdot \frac{1}{1,013,250} \cdot \eta_0 \cdot \Delta\Omega$$

$$\text{where } \Delta\Omega^2 = \frac{8}{\pi} \cdot 273 \cdot \frac{R}{m}$$

L = mean free path; η_0 = viscosity at 0°C ;
 $\Delta\Omega$ = molecular velocity; R = gas constant;
 m = molecular weight. Since the measurements here presented are at 25°C , and Sutherland's constant has not been measured in this range, L will be calculated at 25°C , using η_{25° and $\Delta\Omega$ calculated at 25°C .

$$\Delta\Omega_{25^\circ}^2 = \frac{8}{\pi} \cdot 298 \cdot \frac{R}{72} = 8.7634 \times 10^8$$

$$L_{25^\circ} = 2.3414 \times 10^2 \times \eta_{25^\circ}$$

which gives:-

	normal pentane	$L_{25^\circ\text{C}}$
pressure		
10 mm		1.5853×10^{-6}
500 mm		1.5758×10^{-6}
	isopentane	
10 mm		1.6306×10^{-6}
650 mm		1.6191×10^{-6}

SUMMARY

The vapor viscosities of both normal and isopentane have been accurately measured by the rotating cylinder method at different pressures ranging from a few millimeters pressure to the saturated vapor pressures and at 25° centigrade. Each isomer shows a linear decrease of viscosity with increasing pressure, the total decrease in each case being slightly less than one percent. The difference between the absolute values of the viscosities of the isomers at any pressure is about 2.8%, the isopentane having the higher viscosity, which is consistent with what would be expected from the organic chemists structural picture of these isomers.

The measured values are:-

Normal Pentane	
pressure	viscosity (c.g.s.units)
10 mm	677.1 x10 ⁻⁷
500 mm	673.0 x10 ⁻⁷
Isopentane	
10 mm	696.4 x10 ⁻⁷
650 mm	691.5 x10 ⁻⁷

These results may also be expressed as follows:-

normal pentane: $\eta_{25^{\circ}} \times 10^7 = 677.2 - .0084p$

isopentane: $\eta_{25^{\circ}} \times 10^7 = 696.5 - .0077p$

where p = pressure of the vapor in millimeters of mercury.

The Research was carried out under the personal direction of Prof. R. A. Millikan. Credit is due Mr. Pearson and his shop for help in design and accurate construction of the apparatus and thanks are expressed to Mr. Wm. Bleakney for assistance in the work.

NORMAL PENTANE

