SOME MEASUREMENTS ON THE VAPOR VISCOSITIES
OF THE TWO COMMON PENTANES, TWO PENTENES,
AND CARBON TETRACHLORIDE.

Thesis by

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SUMMARY

The present work is a continuation of the investigations begun by Dr. R. K. Day on the behavior of vapors by means of accurate viscosity measurements. The instrument, designed and built by him, has been improved, and his results on normal and iso-pentane have been verified. In addition measurements on two pentenes, similar in structure to the pentanes, have been made at room temperature, and the viscosity-pressure curves for all four hydrocarbons and also for CCl_4 have been obtained at 100° C. A linear relation, with a negative slope, persists in all these curves, the slope for the hydrocarbons being considerably less at the higher temperature, while the curve for CCl_4 is comparable to those for the hydrocarbons at room temperature. Following are the values of the constants in the equation

$$\eta = \eta_0 (1 - \alpha p)$$

the pressure being expressed in atmospheres.

	25° C		100° C	
	$\eta_0 \times 10^6$	100α	$\eta_0 \times 10^6$	100α
normal pentane	67.593	1.15	84.050	0.41
2-pentene	68.927	1.09	85.800	0.24
iso-pentane	69.529	1.04	85.931	0.33
trimethylethylene	70.051	1.30	86.832	0.32
CCl_4			121.75	1.08

INTRODUCTION

The present work of studying the behavior of vapors near saturation by means of viscosity measurements was begun by Dr. R. K. Day under the direction of Dr. R. A. Millikan, and the first results, some measurements on normal and iso-pentane, are discussed by him in his Doctor's thesis of 1930. The negative slopes of the viscosity-pressure curves found by him were entirely new in gas viscosity measurements, the common gases having always a positive slope, but the work represents the first application of a new and elaborate viscometer built by him, and some difficulties were encountered in making the measurements, so that it was not certain that the data were sufficiently accurate to draw definite conclusions.

Accordingly work was begun to improve the instrument, the intention being to repeat measurements on the pentanes at 25°C in order to establish their accuracy. In the meantime, carefully prepared samples of the two pentenes, whose structure is most nearly like the pentanes, were received from the Standard Oil Development Company of Elizabeth, New Jersey, along with samples of normal and iso-pentane which had been obtained from natural sources. Since the pentane samples at hand were synthetic, it was thought worth while to compare viscosity values obtained from the new samples with the old values, as a check upon the purity of the materials. Also measurements were made on the pentenes,

believing that a knowledge of the effect upon viscosity of the removal of two hydrogen atoms from the pentane molecule and the substitution of a double bond would be of value.

Later, when measurements at higher temperatures were made possible, observations were taken on carbon tetrachloride, thus making possible a comparison of a molecule of simple structure with the more complicated hydrocarbons, both being in the vapor state.

Attempts have been made, but without success, to obtain the third isomeric pentane, a molecule of which is symmetrical, according to the chemists' structural formula, about a central carbon atom. It is of special interest to observe the difference in the viscosity of isomers, because this gives directly the effect of molecular structure upon the mean free path.

INSTRUMENTAL CHANGES

The method of measurement used is the rotating cylinder method, chiefly because it is capable of high precision and is also applicable at low pressures. The instrument is described in detail in Dr. Day's thesis and only the more important changes which have been introduced since his work will be given here.

Early difficulties in keeping the instrument casing vacuum tight were thought to be due largely to the lightness of some of the metal parts, the strains set up by frequent evacuation being sufficient to form cracks in

the large solder joints. Accordingly, some of the lower parts were made stronger and all the joints carefully re-soldered. This did not eliminate the difficulties however, and only by carrying out an extended program of locating and stopping the leaks as they formed during the progress of the work has it been possible to attain good working conditions.

The vapors to be examined have a strong solvent action upon nearly all organic materials, so it was advisable to prevent contact of the vapors with any waxes, cements, rubber, or grease. All gaskets are made of lead, the joints are either solder or copper-glass seals, and the stop-cocks are all metal, consisting of a needle valve operated by means of a sylphon. The window is a quarter inch glass plate strongly clamped to the plane brass window face, with a fine lead fuse wire soldered at the ends to form a loop for a gasket.

During the early work it seems that some organic material got deposited within the instrument which gave trouble when the vapors reached pressure near saturation, and repeated efforts to clean the parts separately were un-successful because of their complicated structure, nor could the deposit be pumped out. Finally the entire instrument was filled with liquid carbon tetrachloride, which was warmed and circulated several days, then drained as far as possible and pumped out. This removed the foreign material but rusting of the steel parts set in afterward, probably

started or hastened by impurities in the carbon tetra-
chloride. Finally it became necessary to replace the sus-
pension and one of the ball bearings upon which the outer
cylinder turns. The upper steel parts were copper plated
to prevent further rusting.

The new suspension is somewhat stronger than the
old one, having a cross-section of about 2.2 x 5.8 mils,
so that the period of the inner cylinder is now 150 seconds
instead of 198. The steel ribbon was first heated to about
400° C for several days while supporting a light weight in
order to form a protective layer of oxide to resist the
rust action. It was then carefully annealed while support-
ing a load of 900 gms. by gradual cooling over a period of
two days.

When mounted, the new suspension showed a remark-
ably constant zero position and a much smaller drift while
in the deflected position, this drift being of the order of
.005% per minute as compared to .04% for the old one. As
will be seen the drift becomes considerably larger however,
at higher temperatures.

In order to compensate for the loss in sensitivity
caused by the larger torque constant, the scale has been moved
back to a distance of 478 cm. from the mirror, and the tele-
scope mounted near the window, thus doubling the sensiti-
vity of the optical system without affecting the magnification
or resolving power. A possible error in the early measure-
ments may be due to pendular oscillations of the inner

cylinder, and the long mirror-to-scale distance has the added advantage of making these oscillations more easily observed. With this system deflection can be read with an accuracy of about .02%.

During the progress of the work it has been necessary to completely dismantle the instrument several times, and in reassembling the method of aligning the cylinders is of course important. The beam supporting the inner cylinder is first adjusted so that the outer surface of the cylinder is strictly vertical. This can be done by means of plumb bobs and a cathetometer within .05 mm. The cylinder is then hung in the instrument and the guard cylinders brought in line with the suspended cylinder by adjustment of the suspension head and the base supports. The two main cylinders will then be coaxial if the machining of the bearings and supports is accurate.

In the past, a slight settling of the base supports on one end of the pier has been observed, which will throw the cylinders slightly out of line, but since the speed of rotation is so adjusted that the deflections are all of the same order of magnitude, the mean distance between the cylinders across which the viscous action takes place will not change between successive runs. This is especially true if the inner cylinder rotates upon its own axis, a condition which depends only upon the initial adjustment, so that in relative measurements no error is expected from this quarter.

The Bourdon spiral pressure gauge of pyrex
tubing has been improved to obtain greater sensitivity and
to make it applicable for measurements at higher temperatures.
A stellite mirror is soldered to a needle, the ends of which
are ground to fine points, and mounted in small glass sockets.
A short copper wire, also soldered to the back of the mirror,
makes possible the adjustment of the system so that it is
very nearly balanced. The mirror is thus held in contact
with the extended arm of the spiral only by gravity and,
there being no elastic properties involved except those of
the spiral itself, the deformation of which is exceedingly
small, neither the zero position nor the calibration
constant is appreciably affected by a change of temperature.
The sensitivity obtained is about 16 m.m. deflection for
a change of pressure of 1 m.m. of mercury. The chief in-
accuracy is in the reproducibility of the zero reading due
to the considerable play which the needle points have in the
glass sockets. Except at low pressures, the gauge is used
only as a null instrument, the pressure being read on a
manometer which is connected to the opposite side of the
spiral from the instrument.

In order to prevent any stresses being set up
between the evacuating system and the top of the instrument
which may throw the cylinders out of alignment, the inlet
tube is a long copper tube with a deep "gooseneck" near
the instrument.

Neither the constant speed motor described by Day nor the rotating field device used for controlling the oscillations of the inner cylinder has required modification.

MEASUREMENTS AT ROOM TEMPERATURE

It, of course, is essential in all measurements that no tendency toward turbulent flow be present. The threshold of turbulence is expected to depend upon the ratio

$$\frac{\rho \, v \, l}{\eta}$$

where ρ is the density, v the velocity of the outer cylinder, l the distance between cylinders, and η the viscosity. A test was carried out under the most extreme conditions of this ratio available, namely iso-pentane at saturation pressure with the speed of the cylinder at two revolutions per minute, but no tendency toward turbulence could be observed.

This is sufficient justification for the procedure of adjusting the speed of the cylinder so that the deflections in all measurements are about the same. Thus for air a gear ratio at the motor of 9:14 is used, while for the hydrocarbons a ratio of 14:9 is applied. Such a procedure tends to minimize errors which may occur from several sources, such as poor alignment of the cylinders, suspension drift, the conversion of straight scale readings to angles, and inaccuracies in the scale itself.

The motor being reversible no zero reading is used, the sum of the deflections taken each way from the zero being all that is desired. The telescope is adjusted

so that the zero reading falls very near to the center of
the scale, which is the foot of a perpendicular drawn from
the mirror to the scale, so that the two deflections are
always very nearly equal. Because of the slight suspension
drift, a definite time schedule is followed in taking read-
ings, the mean value obtained five minutes after the cylinder
crosses its zero position being used in all cases so that no
correction for drift is necessary. This gives sufficient
time for any transient effects arising during the reversal
of the motor to die out, and also permits sufficient read-
ings on the turning points to obtain a good average.

It is well known that at low pressures slippage
occurs between the gas and the walls which is important only
when the mean free path is not a negligible fraction of the
distance between the walls. Assuming no specular reflection
of the molecules at the walls, Millikan finds for the slip [3]
factor

$$1 + 0.7 \, k \, \lambda$$

where λ is the mean free path and the instrument constant,
k is given by

$$k = \frac{2\left(a^3 + b^3\right)}{ab^3 - a^3 b}$$

a and b being the radii of the cylinders. The correction
is inversely proportional to the pressure and amounts to
the following values at 1 m.m. pressure.

substance	at 25° C	at 100° C
air	1.65%	2.19%
pentane	0.38%	0.55%
$C Cl_4$		0.52%

Measurements taken on air at low pressures were found to be in complete agreement with the above equation. The correction has therefore been applied to all measurements where the correction is appreciable in order to obtain the true viscosity.

SAMPLE OF DATA

Normal Pentane   Gear ratio = 14:9   Pressure = 2.0 cms

Direction of motor	Time	Turning points	Equilibrium position	Deflection
East	11:37:00 a.m.			
24.98° C	38:30	25.44 cm.		
	39:45	24.96	25.195 cm.	
	41:00	25.42	.190	
	42:15	24.96		
West	11:43:30			
	44:30	74.86		
	45:45	75.49	75.185	
	47:00	74.89	.188	
	48:15	75.48	.190	75.190 cm.
	49:30	74.91		25.188
				50.002
East	11:50:45			slip .010
				50.012
	52:00	25.15		temp. .001
				50.013

	53:15	25.24	25.195
	54:30	25.15	.192
25.00° C	55:45	25.23	.188
	57:00	25.14	

Stopped.   Zero position = 50.189 cm.

The time given when the motor is reversed is the time at which the cylinder crosses its zero position.

The values obtained in the last column under "Deflection" are plotted against the pressure to obtain the curves shown. The values obtained at the ends of the curves are then converted to arc lengths, which changes them very little, to the zero pressure intercept is added a very small term to account for the refractivity of the air outside the window, and the result compared with the deflection obtained for air, also reduced to arc lengths, to obtain the true limiting value of the viscosity η_0.

To obtain the pressure variation, that is, the value of "α" in the equation

$$\eta = \eta_0 \left(1 - \alpha p \right)$$

the negative slope of the curve expressed in per cent per atmosphere is added to the refractivity of the vapor expressed in the same units. This last correction is important and constitutes almost the only difference between the present values of "α" and those of Day, who neglected to consider the refractivity. The values used are obtained by plotting the apparent zero position of the cylinder

NORMAL PENTANE 25°C.

ISO-PENTANE 25°C.

2-PENTENE 25°C.

TRIMETHYLETHYLENE 25°C.
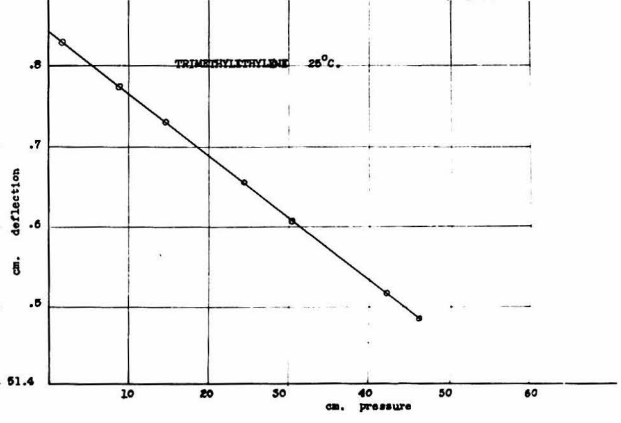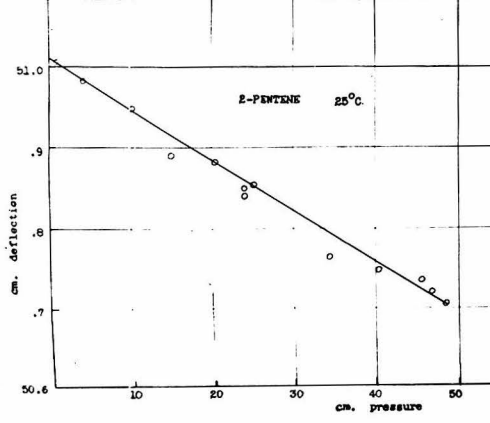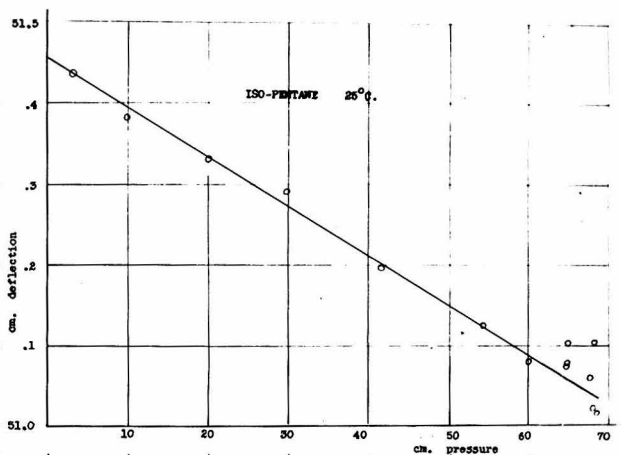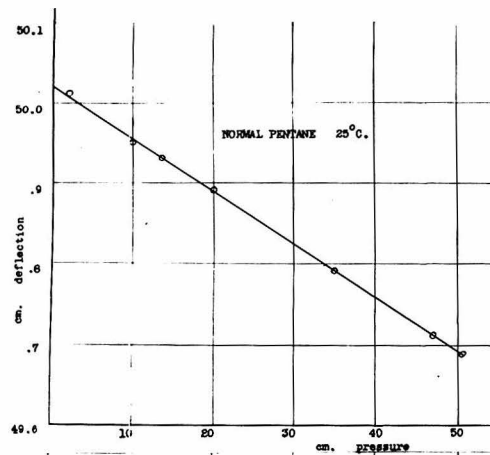
against the pressure. The zero position is obtained by averaging the values given in the column headed by "Equilibrium position" instead of taking their differences, as was done to get the deflection. Since the telescope is mounted a little to one side, making an angle of about 13.5° with the normal to the window, the variation of the apparent zero position with pressure is appreciable, being about 2 m.m., and from the slope of this curve and a knowledge of the angles involved the refractivity may easily be computed with an accuracy sufficient for our purpose. The values obtained agree satisfactorily with the one rather doubtful value given in the International Critical Tables for pentane.

The values used for 25° C are:

normal pentane	0.157% per atmosphere
iso-pentane	0.157
2-pentene	0.155
trimethylethylene	0.155
carbon tetrachloride	0.130 (at 100°)
air	0.027

At other temperatures the values may easily be computed since they are inversely proportional to the absolute temperature.

The calibration constant of the instrument is simply obtained by using the known value[1] of the viscosity of air at 25° C, namely 183.25×10^{-6}.

The deflections obtained for air are very consistent provided due precaution is taken to remove traces of the vapors which may adhere to the walls of the instrument for some time. For example, the values obtained before and after the four runs at room temperature here given differed by only .006%. A very slow decrease in these values with time has been observed, amounting to about 0.1% in five months and is believed to be due to actual stiffening of the suspension caused by the considerable tension on it, an effect which has been observed by other investigators in similar suspensions.

An estimate of the probable errors in the values of "$\underline{\alpha}$" can best be obtained from an examination of the curves given, but an estimate of the accuracy of the absolute values of the viscosity is much more difficult to make as will be seen from the following discussion.

The first measurements on a vapor at low pressures are almost invariably too high, sometimes as much as one per cent higher than the final values. After repeated flushing out of the instrument at a few centimeters pressure, the points are found to lie fairly close to the final curve, but it is only after higher pressures have once been reached that really consistent results are obtained. These initial discrepancies are almost certainly due to impurities, principally air, and various methods of treating the vapors before admitting them to the instrument have been tried,

but without seeming to have much effect. It is believed that the heavy vapors displace the light gases from the walls and the gases, after being thoroughly mixed with the vapors at the higher pressures, represent only a small percentage impurity and the composition of the vapors will thereafter remain unchanged during the course of the observations.

The initial points are not plotted on the curves, but after consistency has once been established, no observations are discarded and the pressure range is always covered several times. The fact that no difference is observed between points obtained while going up the pressure range from those obtained during the reverse process is strong evidence in support of the above view.

Runs have been taken on both the synthetic and the natural samples of iso-pentane and satisfactory agreement was obtained. The present data on both pentanes were taken from the original synthetic samples upon which Day made his measurements but these values for η_p are about 0.2% lower than his. This difference may be due to less efficient methods of removing the air from the vapors in the earlier work, since P_2O_5 was used for a drying agent, from which it is very difficult to remove the air.

The two high points on the iso-pentane curve near saturation are believed to be due to condensation of liquid on the cylinders caused by an attempt to force the

pressure too high. The discrepancy disappeared after standing for some time at a pressure slightly below saturation.

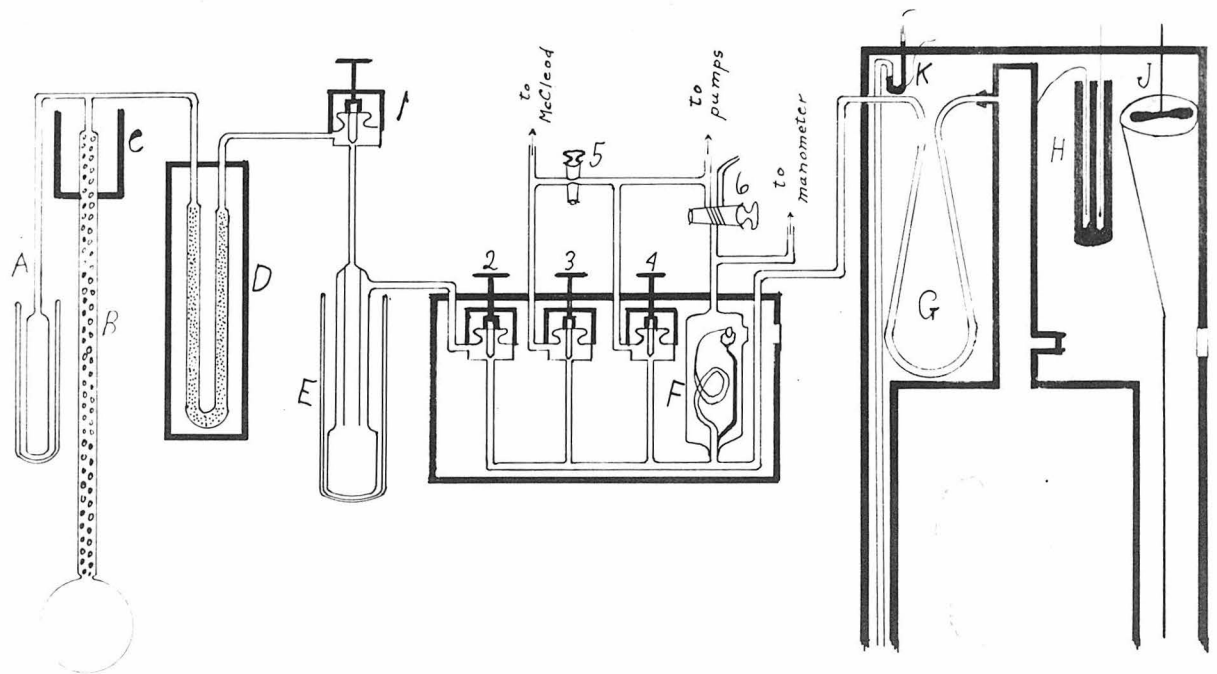## THE TEMPERATURE CONTROL SYSTEM

The importance of the temperature control system in these experiments can not be over-emphasized. This will be realized more clearly when one remembers that the normal speed of the rotating cylinder is about 6 m.m. per second so that a convection current in the neighborhood of the inner cylinder having a speed of only a half a millimeter per minute may cause an appreciable disturbance, and since the vapors are adsorbed to a very large extent on the walls, a slight local change in temperature may cause large convection currents.

During the measurements at room temperature, the temperature of the entire room was controlled so that the temperature of the instrument seldom varied by more than a tenth degree from the desired value of 25° C. For work at higher temperatures, the instrument is enclosed in felt one inch thick, with only the magnetic clutch and the three legs protruding. The loss of heat from these parts is compensated by heating coils wound directly on them. This compensation need not be accurate because the parts are not directly connected to the cylinder chamber.

Other coils are wound at different heights about

the cylinder casing with from one to two inches clearance
between the casing and the bare wires. A tube extending
nearly the full length of the enclosure and made of thin
felt, provides a path for the circulating air, which is
drawn up through the tube by means of the fan marked "J" in
the drawing, and driven down past the heating coils. The
fan is driven by a motor from the outside.

A massive copper block "H" contains two holes
bored nearly to the bottom, in one of which is placed a
Beckman thermometer which can be read from the outside.
In the other are mounted the junctions of several copper-
constantan thermocouples, their opposites being mounted in
small copper tubes soldered to various parts of the instru-
ment. There are two near the top of the cylinder casing,
two near the bottom, one on the base plate which is supported
directly by the legs, one on one of the legs, and one on the
magnetic clutch housing. The thermocouples may be connected
by means of switches to a galvanometer on the outside, which
has a sensitivity of about 10 cm. per 0.1^o difference in the
temperature of the junctions. The copper block has a tendency
to remain slightly below the mean temperature of the instru-
ment, so that a small current in a heating coil wound on it
is sufficient to keep these temperatures very nearly the
same. The currents are adjusted in the main heating coils
until there is no appreciable temperature gradient along the
cylinder casing as shown by galvanometer deflections. These

to
McLeod

to
pumps

to
manometer

A

B

C

D

E

F

G

H

I

J

K

1

2

3

4

5

6

four thermocouples are then connected in series to give, together with the thermometer readings, the temperature of the main part of the instrument.

When this adjustment has been made, the expansion tubes "K" provide an automatic control. These are filled with xylol in contact with mercury at the top which closes a relay circuit by making contact with a needle adjusted at the proper height in the small upper tube. The relays increase or decrease the current in the heating coils by only a small amount. This arrangement does not permit the temperature to vary by more than 0.1^o during a run provided the outer magnets on the magnetic clutch are kept going, while this variation can be measured to 0.01^o.

A double mica window permits observations on the inner mirror through the felt wall.

THE VAPOR PURIFICATION SYSTEM

The vapor to be studied is first frozen down and sealed on at "A" and the entire system evacuated. Cock no. 1 is then closed and the material distilled over into the fractionating column "B" where it is fractionated using ice in the reflux chamber "C", the first components being drawn off occasionally through the cock and removed by the pumps. The principal purpose of the column is to separate the air but it, of course, will also help to separate any other impurities including water. It is a recent addition and has

been used only in the case of carbon tetrachloride.

The trap "E" is then immersed in liquid air and a slow stream of vapor permitted to pass through the drying tubes and freeze out in "E" at very low pressures. The drying tubes are filled with $Mg(ClO_4)_2 \cdot 3H_2O$ which is supposed to be nearly as efficient as P_2O_5 and has the advantage of never losing its crystalline form since it takes up the water to form the hexahydrate. It can be renewed simply by heating in vacuum by means of the furnace "D".

When sufficient material has collected, cocks 1, 2, 3, and 4 are closed and the trap allowed to warm up. The vapor is then admitted or withdrawn from the instrument at will through cock no. 2. Cock no. 3, leading to the McCleod gauge, is not essential but provides a parallel path to the pumps through cock no. 5 which speeds up the pumping considerably since the metal cocks have only a small opening.

Since pressures in the instrument are sometimes required above the saturation pressure at room temperature, provision must be made to heat the system extending from cock no. 1 to the instrument. The connecting tubing has been wound with resistance wire, the trap can be put in hot water, and the other cocks and the spiral pressure gauge "F" are enclosed in a felt box which can be heated to any desired temperature. The pressure of air on the outside of the spiral is made nearly equal to the pressure in the instrument

by means of cock no. 6.

     The loop of copper tubing "G", aside from its purpose of preventing lateral forces on the top of the instrument, also prevents any cool vapor from entering the instrument directly, which may cause internal temperature gradients. The fan, copper block, and felt housing are supported from the ceiling so that no excess weight will be acting on the pier.

MEASUREMENTS AT 100° C

     The standard formula for the rotating cylinder apparatus[3] is:

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

where Θ is the angle of deflection; I, the moment of inertia of the suspended system; b and a, the radii of the outer and inner cylinders; P, the natural period of the suspended system; ℓ, the length of the inner cylinder; and Ω, the angular velocity of the rotating cylinder. For a given gas, we may, therefore, write for any temperature t :

$$\eta_t = \eta_{25} \frac{\Theta_t P_{25}^2 (1 + a \cdot 25)}{\Theta_{25} P_t^2 (1 + a t)}$$

where a is the linear coefficient of expansion of the cylinders, and the angular velocity is the same at the two temperatures.

     The periods are measured in vacuum in order that the moment of inertia will not be affected by gas moving with the cylinder and to reduce the damping coefficient.

The period is found to be independent of the amplitude within the accuracy of measurement, which indicates that the rate of drift is truly proportional to the deflection so that it will have no first order effect upon the period but only increases the damping coefficient. The effect of the damping coefficient upon the period is about .002%. Since the drift rates are not the same at the two temperatures, the deflections must be reduced to zero time interval by means of the known drift rates before applying this formula.

We obtain in the case of air, the following values.

$$L\ \Theta_{25} = 55.933 \text{ cm.} \qquad P_{25} = 150.574 \text{ sec.}$$
$$L\ \Theta_{100} = 67.991 \qquad P_{100} = 152.487$$
$$a = 2.0 \times 10^{-5} \text{ per degree for bronze.} \qquad \underline{L} \text{ is}$$

the mirror-to-scale distance.

This gives for air

$$\eta_{100} = 216.88 \times 10^{-6} \text{ poises}$$
$$S = 111.7$$

where the Sutherland constant $\underline{S}$ is obtained from the Sutherland formula:

$$\eta = \frac{AT^{3/2}}{S + T}$$

The above results are in good agreement with those obtained by capillary tube methods.

Using this value of η_{100}, the vapor viscosities can be obtained in the same way as before by comparing the deflections with those for air after the same time interval.

The interval used in these measurements is six minutes.

SAMPLE OF DATA

Normal Pentane   Gear Ratio - 14:9   Pressure - 73.0 cm.

Direction of motor	Time	Turning points	Equilibrium position	Position on 6th min.
West	11:17:30 a.m.			
100.03° C	19:45	81.47 cm.		
	21:00	82.44	81.988 cm.	
	22:15	81.60	82.010	
	23:30	82.40	82.038	82.04 cm.
100.02° C	24:45	81.75		
East	11:26:00			
	29:00	18.34		
	30:15	17.93	18.122	
	31:30	18.29	.108	18.105
100.05° C	32:45	17.92	.102	
	34:00	18.28		
West	11:35:15			
	37:45	81.80		
	39:00	82.10	81.965	
	40:15	81.86	82.000	
100.04° C	41:30	82.18	82.032	82.03
	42:45	81.91		
East	11:43:45			
	46:45	18.40		
100.05° C	48:00	17.89	18.118	

	49:15	18.29	.082	18.07
	50:30	17.86	.060	
Stopped	51:45	18.23		

Deflection

$$
\begin{array}{r}
82.035 \\
\underline{18.085} \\
63.95 \\
\text{temp.} \quad \underline{.01} \\
63.94
\end{array}
$$

The data at $100°$ are not quite so consistent as those taken at room temperature, partly because the drift rate is much larger and partly because the temperature variations are more rapid. The three high points on the CCl_4 curve were taken in succession at the end of the run and are not believed to be as reliable as the others because a slight leak was found in one of the stop-cocks later.
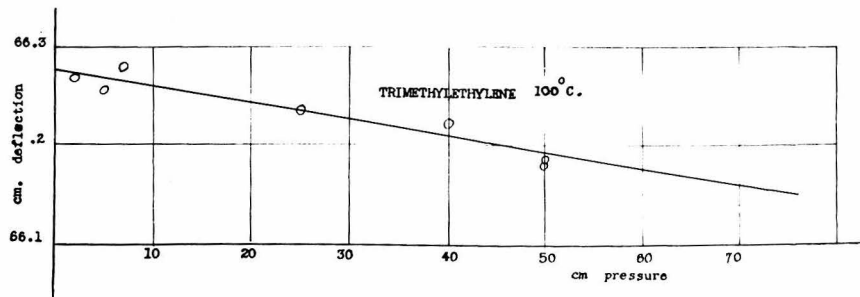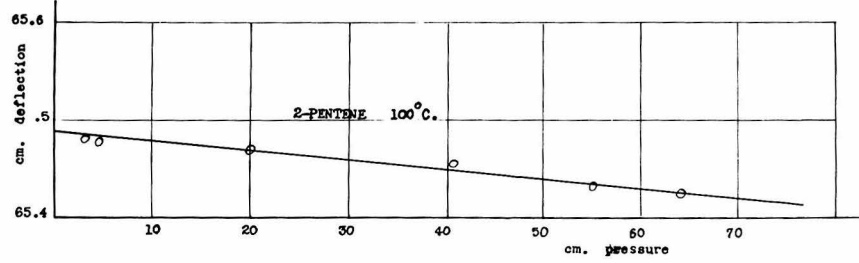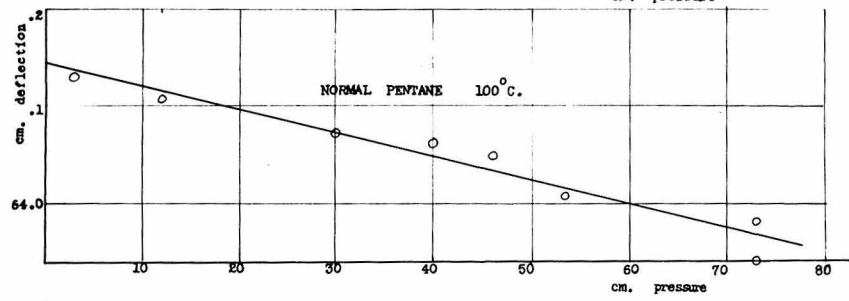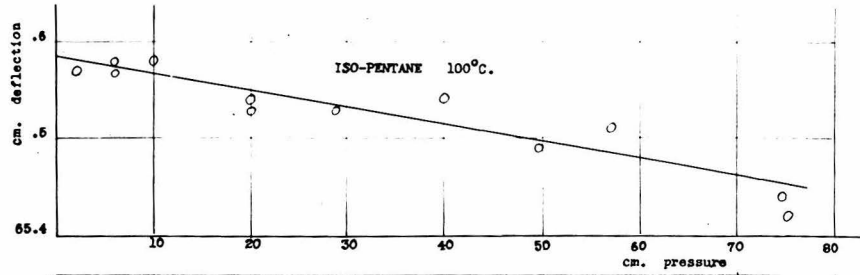
The curves do not represent viscosity until after the correction for the refractivity of the vapor has been applied and this in some cases nearly doubles the magnitude of the slope.
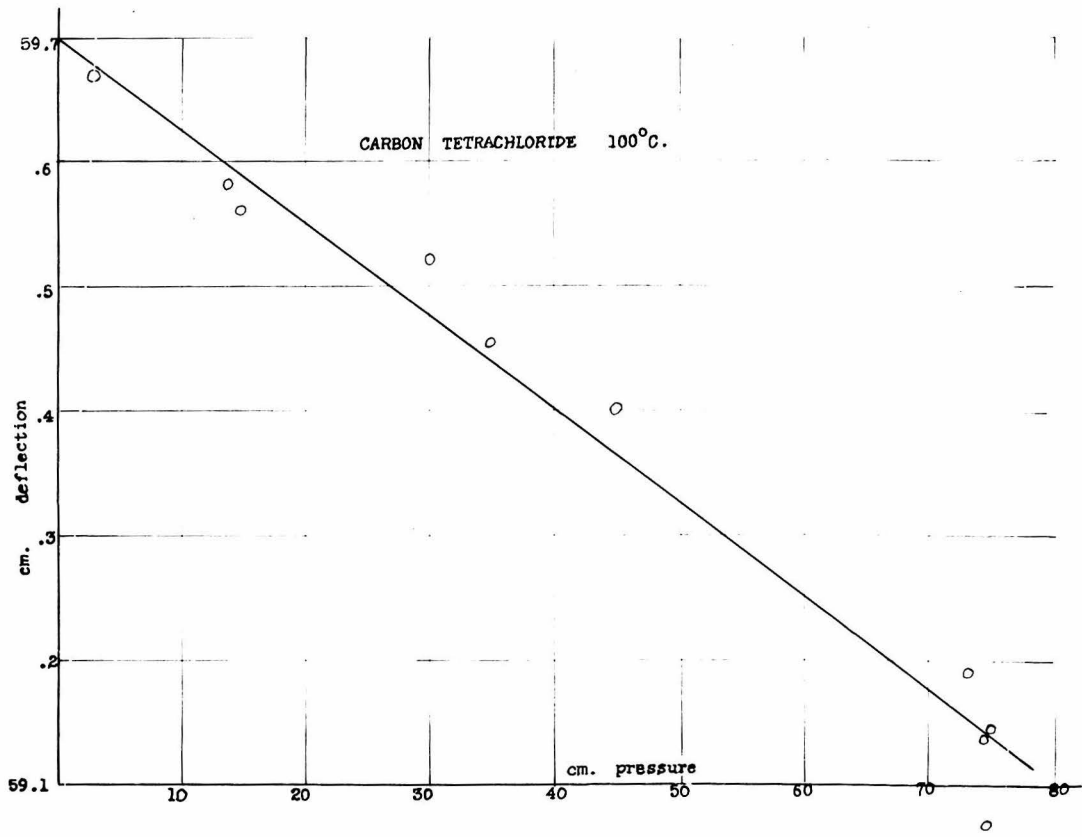
NUMERICAL RESULTS

Representing the viscosity by means of the equation

$$\eta = \eta_0 \left(1 - \alpha p \right)$$

where p is the pressure in atmospheres, and obtaining the values of these constants from the curves in the manner previously described, the following results are obtained.

ISO-PENTANE 100°C.

NORMAL PENTANE 100°C.

2-PENTENE 100°C.

TRIMETHYLETHYLENE 100°C.

CARBON TETRACHLORIDE 100°C.

25° C.

	$\eta_0 \times 10^6$	100α		
normal pentane	67.593	1.15	$CH_3-CH_2-CH_2-CH_2-CH_3$	
2-pentene	68.927	1.09	$CH_3-CH = CH-CH_2-CH_3$	
iso-pentane	69.529	1.04	$CH_3-CH_2-CH<^{CH_3}_{CH_3}$	
trimethylethylene	70.051	1.30	$CH_3-CH=C<^{C H_3}_{C H_3}$	
air	183.25	-0.13		

100° C.

normal pentane	84.050	0.41	297.5	36 C
2-pentene	85.800	0.24	303.0	36.5
iso-pentane	85.931	0.33	266.3	27
trimethylethylene	86.832	0.32	281.5	38.4
carbon tetrachloride	121.75	1.08		76.7
air	216.88		111.7	

It will perhaps be more instructive to refer the slope of the curves to molecular density instead of to the pressure, so that the values at different temperatures will be on a more comparative basis. If we write

$$\eta = \eta_0 (1 - \alpha'\rho)$$

where ρ is the density referred to the density at 0° C. and one atmosphere pressure, α' may be obtained from the above values by means of the relation

$$\alpha' = \frac{T}{273}\alpha$$

The deviations from ideal gas laws will affect the last
figures by not more than three units, and are here neglected.

Values of 100 α'

	25°C	100°C
normal pentane	1.26	0.56
2-pentene	1.19	0.32
iso-pentane	1.14	0.45
trimethylethylene	1.42	0.43
carbon tetrachloride		1.48
air	-0.14	

It will be seen that, for both temperatures, the
values of η_0 are in the order in which we might have predicted
them, those hydrocarbons for which we should expect, from
the structural formula, the least cross-section, having the
largest viscosity.

The values of Sutherland's constant $\underline{S}$ given in the
second table are computed from the equation $\eta_0 = \dfrac{A T^{3/2}}{S+T}$
but this equation is not expected to hold at these low temp-
eratures except in the case of air. This is born out by the
unusually low values given, $\underline{S}$ being for most substances
slightly higher than the critical temperature, and the critic-
al temperatures for normal and iso-pentane are 470° and 461° K
respectively. In fact, Rappenecker, from measurements on iso-
pentane at 100° C and 212° C by the capillary tube method,
finds the value

$$S = 500$$

However, his value for η, 88.51×10^{-6} at 100°C, and atmospheric pressure, is 4% higher than mine. The difference seems to be too large to attribute to experimental error and may possibly be due to incomplete separation of air in his case. No other values are listed for these materials.

The most important contribution, however, of the present investigation is the establishment of the negative slopes of the viscosity pressure curves, a condition which persists at temperatures much higher than the boiling point, whereas, all previous measurements, save those of Day, have been made on gases and show a positive slope. The present measurements suggest that probably all vapors act in the same way at sufficiently low temperatures, and one can not help but remark upon the parallel behavior of the second virial coefficient as related to pressure. The hypothesis has been advanced that $(-\alpha)$ is very closely connected with, [5],[6] perhaps equal to, Van der Waal's coefficient b, but it seems to behave more like the virial coefficient of which b is only a part. The two must however, be explained on different grounds. It is desirable that the present viscosity theory be analyzed more carefully and extended to obtain the first order pressure effect. It is suggested that triple collisions may play an important role, and that molecular association may be present at these low temperatures, undetected by compressibility measurements alone. Such investigations may throw more light upon the process of condensation. In

this connection it is of interest to note that no departure from linearity is observed near saturation in any of the curves.

One would like to extend these observations to obtain the temperature dependence of α more closely and over a wider range, as well as of η_p, and perhaps to go to higher pressures but with the instrument in its present condition, it is not considered safe to go much above atmospheric pressure, and the upper limit of temperature is probably about 150°C where the accuracy will be much reduced because of the increased suspension drift. Some knowledge of the effect of temperature on α may be obtained however, by examining other materials representing different stages of the transition from a gas to a vapor, and such observations would of course, also have many other values.

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