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VISCOSITY OF GASEOUS ANHYDROUS HYDROGEN FLUORIDE

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ABSTRACT

The viscosity of gaseous hydrogen fluoride was measured by a rotating cylinder viscometer, and was found to be represented over the temperature range from 22 to 56°C. and the pressure range from zero to about one atmosphere pressure by the equation

$$\mu = 113.0 + 0.449t - P^2 \times 10^{-6} \text{ antilog } \left(\frac{10.1}{t - 13.2} + 0.2355\right)$$

where μ is the viscosity in micropoises, t is the temperature in degrees centigrade, and P is the pressure in millimeters of mercury.

The equation is not valid outside the limits covered by the experimental data. The following form of the Sutherland equation based on data at zero association over the temperature range of 22 to 88.6°C. may be extrapolated to higher temperatures provided the pressure is low enough to prevent appreciable association.

$$\mu = \frac{T^{3/2}}{0.057T + 24.476}$$

where T is the temperature in degrees Kelvin.

VISCOSITY OF GASEOUS ANHYDROUS HYDROGEN FLUORIDE

Anhydrous hydrogen fluoride plays a major role in the technology of fluorine and fluorine compounds, and consequently its physical properties are of considerable interest and importance. Reliable data on the density (16,17), viscosity (17), and vapor pressure (9,15) of the anhydrous liquid and the density (3,12,9,18,19) of the anhydrous gas have been obtained, but the viscosity of the anhydrous gas had not previously been investigated. In the course of this study, the viscosity of anhydrous hydrogen fluoride was determined as a function of both temperature and pressure covering the temperature range of 22 to 56°C. and the pressure range of 0 to 1 atmosphere. Above 56°C. the gas was assumed to be unassociated at pressures of 1 atmosphere or less; and hence, measurements were made only at atmospheric pressure between 56 and 88°C. No measurements were made above this temperature because of physical difficulties with the optical units of the apparatus.

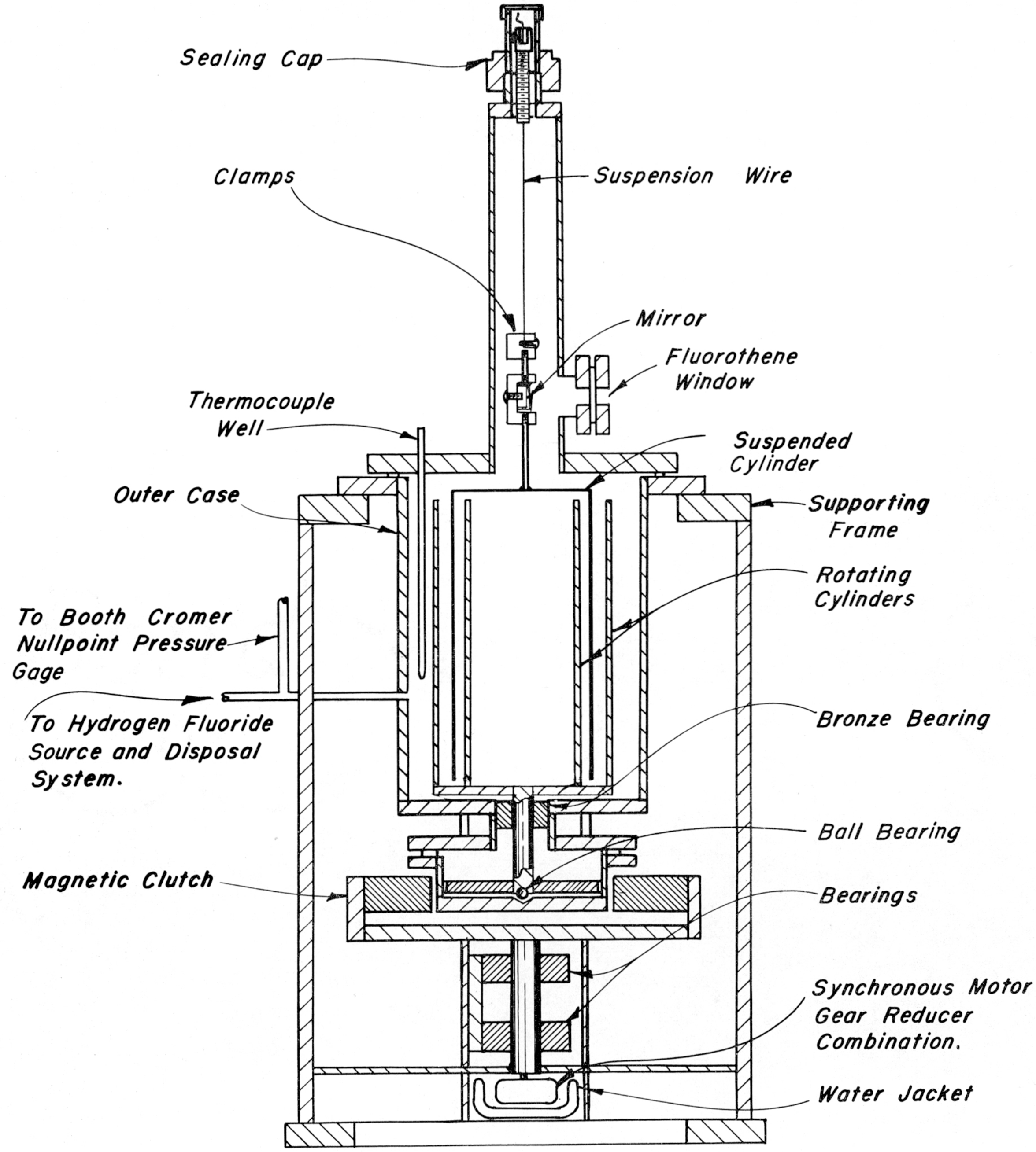
EXPERIMENTAL

The method of measurement of the viscosity, the design of equipment, and the materials of construction were largely determined by the physical and chemical properties of gaseous anhydrous hydrogen fluoride. Since the gas is highly associated and the degree of this association is strongly dependent on the pressure, a rotating cylinder viscometer was used in preference to the capillary type viscometer which is usually employed in gas viscosity work. The viscometer resembled those which have been used for the absolute determination of the viscosity of dry air (1,4,5,7). Although this apparatus was suitable for making absolute measurements, it is also capable of yielding excellent comparative data with considerably less expenditure of effort than would be required for the absolute measurements. For this reason all the determinations made were on a comparative basis. The instrument was calibrated with dry air at each temperature at which measurements were made.

Apparatus

The viscometer in its final form is shown in figure 1. The rotating cylinders cause a torque to be exerted on the suspended cylinder through the viscous drag of the gas. As a result of this torque, the suspended cylinder turns until this torque is balanced by that of the suspension wire acting as a spring. The degree of turning was measured by a beam of light reflected from a small mirror connected by a short shaft to the suspended cylinder. During operation the viscometer was completely sealed, the rotary motion being transmitted from the outside by a magnetic clutch. The details of construction are given below.

Suspended Cylinder. The suspended cylinder, which was 12 inches in length, was made of standard 5 inch copper tubing machined to a wall thickness of 1/16 inch. The tqp of the cylinder was closed by a 1/16 inch copper plate which contained several large uniformly spaced holes to facilitate evacuation. The brass rod connecting the cylinder to the mirror and the suspension wire clamp was attached to the center of this plate. Both the plate



VISCOMETER

FIGURE 1

and rod were silver soldered in place. An attempt to use a nickel suspended cylinder failed because of magnetic interaction between the rotating and suspended cylinders.

Suspension Wire. The effective length of the suspension wire was 12 inches. In the determination of the data in table I a stainless steel suspension wire 0.004 inch in diameter was used. In the determination of the data in tables II and III a beryllium-copper wire 0.005 inch in diameter was used.

Clamps. The clamps which held the ends of the suspension wire are shown in figure 2. The top clamp was supported on a hollow tube whose outside was threaded into the top of the viscometer case. This construction allowed fine adjustment of both the height of the cylinder and the angle of the mirror relative to the window.

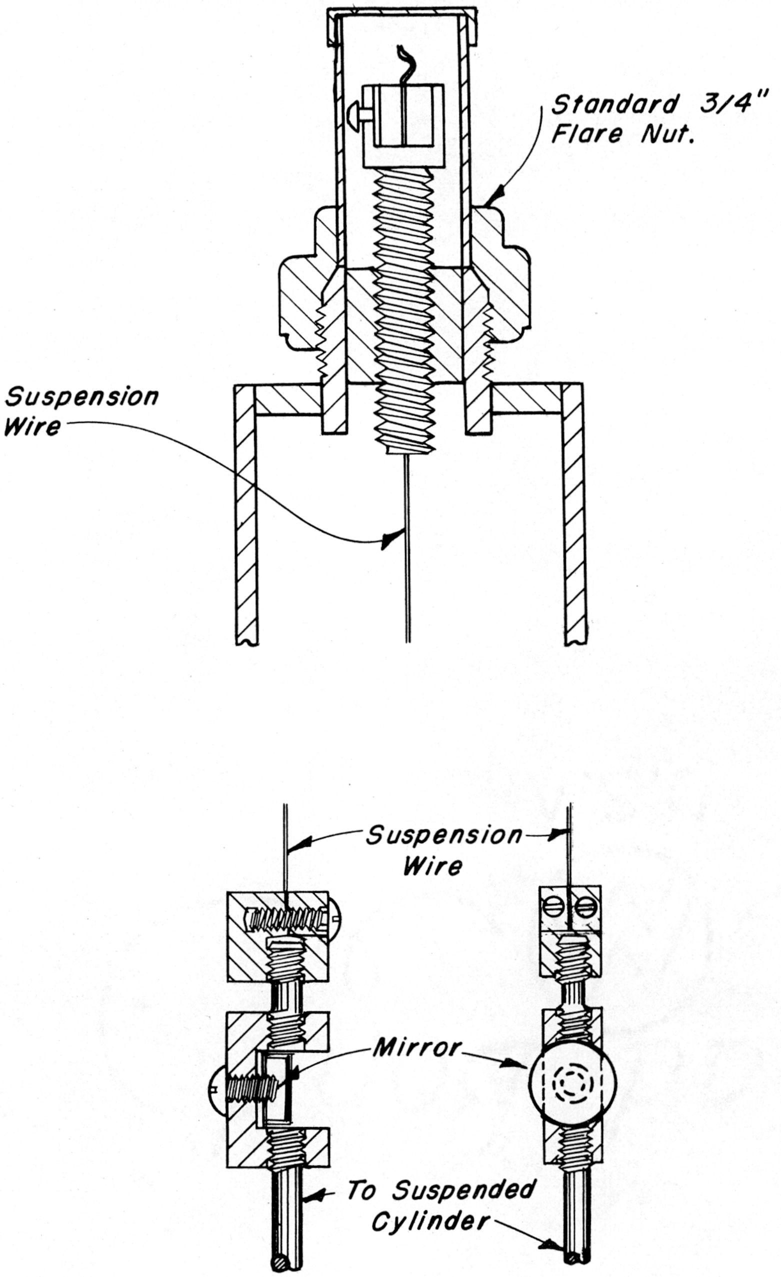
Mirror. The mirror, which was 1/2 inch in diameter and 1/4 inch thick, was made of highly polished monel.

Window. The window was made of 1/16 inch Fluorothene sheet selected for transparency and freedom from optical distortion and was sealed between two flange plates, the Fluorothene also serving as a gasket. Horizontal slits 2 inches by 1/2 inch in both flange plates formed the opening for light.

Rotating Cylinder. The double rotating cylinder, shown in figure 3, was used in the determination of the data in table III. The cylinder used for the data in tables I and II differed in that it consisted of a single nickel cylinder with a 6 inch inside diameter. The cylinders in both cases were mounted on a nickel plate which was supported on a 5/8 inch monel shaft. The bottom end of the shaft contained a conical hole which rested on a single steel ball bearing which in turn rested in a similar conical hole in the bottom of the viscometer case. Lateral stability was furnished by a bronze sleeve bearing near the top of the shaft. (See figure 1.) Both bearings were lubricated by a fluorocarbon grease.

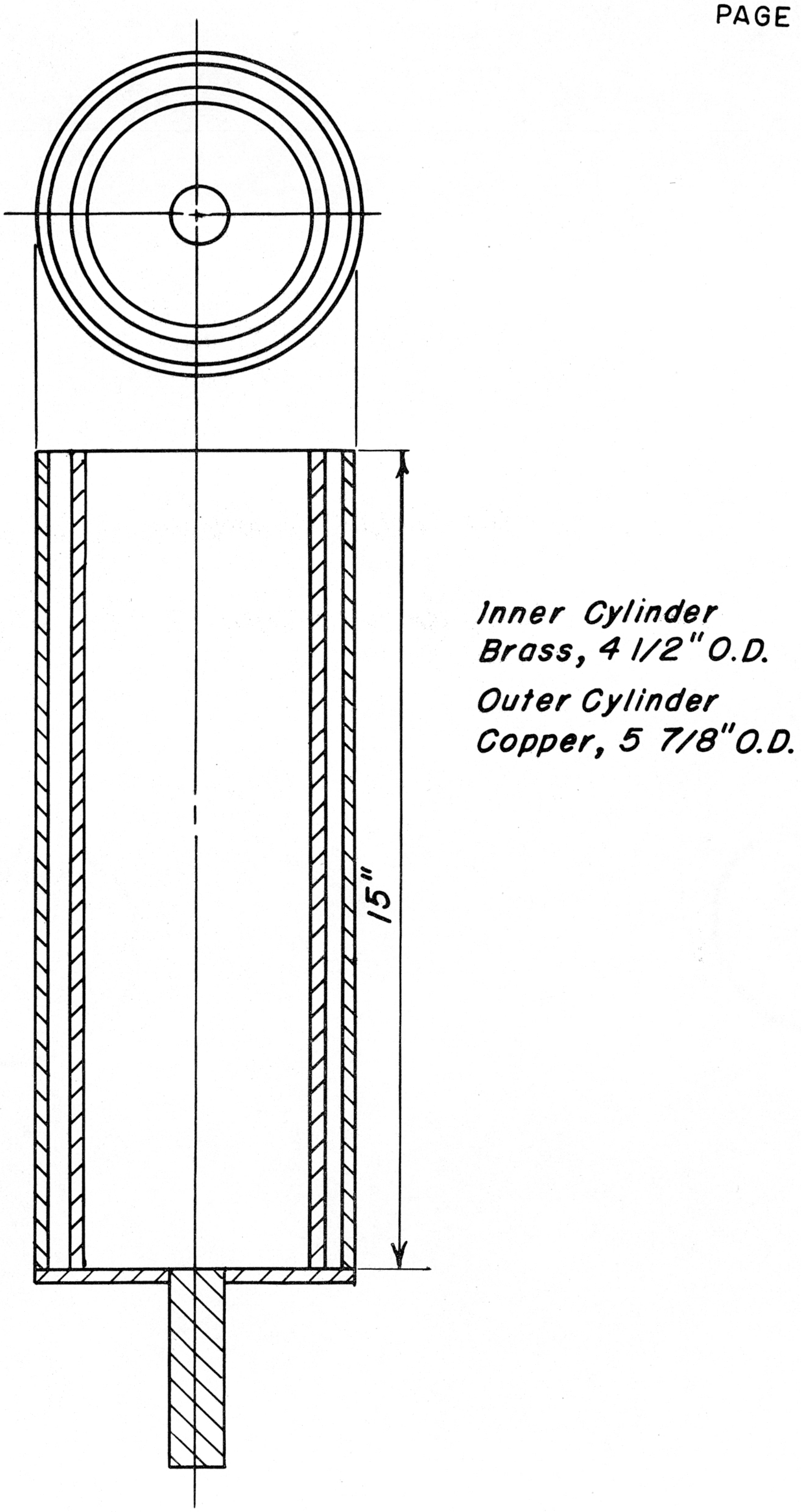
Magnetic Clutch. Rotary motion was transmitted into the sealed viscometer by the magnetic clutch shown in figure 4. Four alnico magnets acting through the case of the clutch held the ends of the nickel plated cross-shaped mild steel magnet in a constant position relative to the outer wheel of the clutch. In this way motion was transmitted without slippage.

Drive. The original drive which was used in obtaining data in table I consisted of a motor and gear reducer combination mounted on the outer frame of the viscometer on the same level as the magnetic clutch. Motion was transmitted from a smooth wheel, mounted on the output of the gear reducer, to the iron band which formed the outer circumference of the magnetic clutch by a small rubber wheel which was held between the two under mild compression. This drive turned the viscometer at 2 rpm. Some slip occurred and the friction drive was replaced with a chain drive which was used in obtaining the data in table II. One sprocket was mounted on the end of the shaft to the magnetic clutch. The other was on the output shaft of a gear reducer which was mounted on the floor near the viscometer. This drive had a speed of 3 rpm. Since occasional binding occurred due to the horizontal position of the sprockets and vibration was transmitted from the motor to the viscometer, the chain drive was replaced by a small 1 rpm.



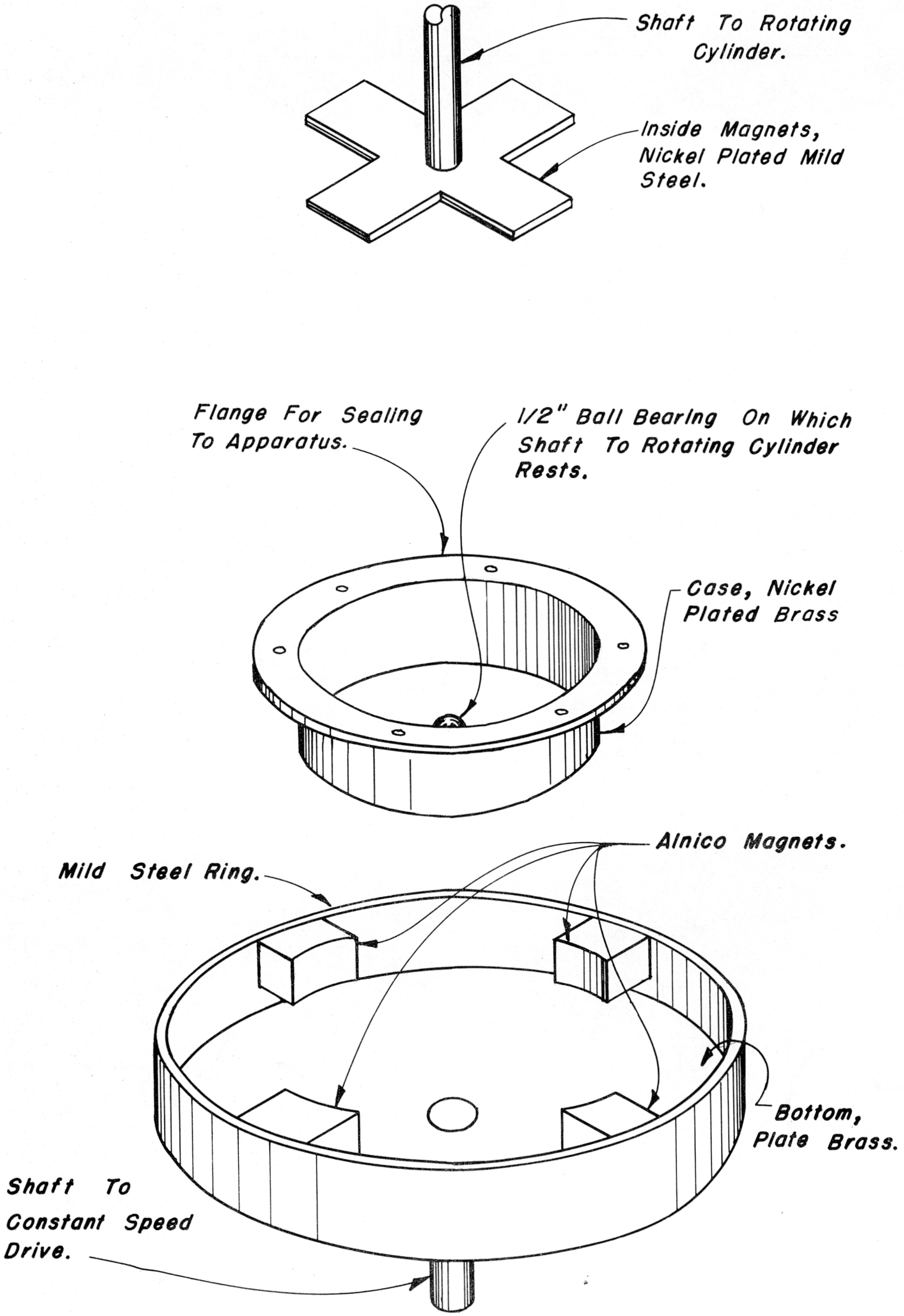
CLAMPS FOR SUSPENSION WIRE

FIGURE 2



ROTATING CYLINDERS

FIGURE 3



MAGNETIC CLUTCH

FIGURE 4

synchronous motor gear reducer coupled directly to the end of the shaft of the magnetic clutch. A piece of heavy gum rubber tubing was used as a flexible coupling. The motor was enclosed in a water jacket to avoid overheating when the viscometer was used at elevated temperature. This drive was used in obtaining the data in table III.

Case. The case of the viscometer was made of nickel and nickel plated steel with the exception of the copper cap over the top suspension wire clamp and the case of the magnetic clutch which was made of brass to avoid shorting the magnetic circuits. The viscometer was made in three major pieces sealed together by flanges with Teflon gaskets and could be disassembled and all working parts removed. The total volume of the viscometer was 13.4 liters.

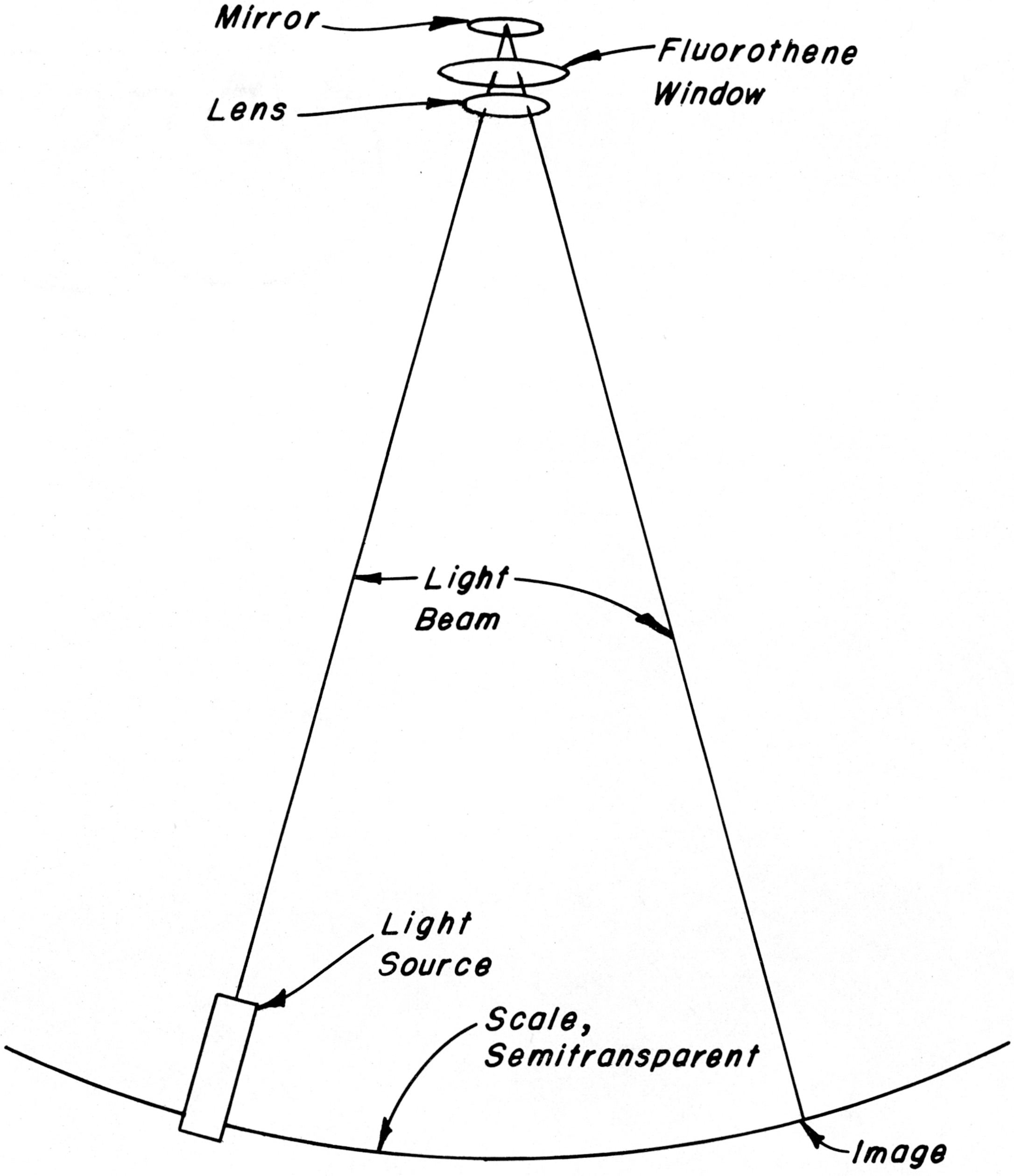
Constant Temperature Box. During the determination of the data in tables II and III the entire viscometer was enclosed in a constant temperature box. The walls of the box consisted of 1/4 inch of transite and 3/4 inch of asbestos cell board. The box was heated by two 750 watt heaters which were controlled by both Fenwal thermostats and variacs. The air in the box was circulated by two blowers.

Temperature Measurement. The temperature of the viscometer was measured by a Chromel-Alumel thermopile located between the rotating cylinder and the outer shell of the viscometer. (See figure 1.) A double range potentiometer and an ice-water cold junction were used with the thermopile. The temperature could be read to 0.1°C.

Pressure Measurement. The pressure was measured by an automatic null point indicator of the Booth-Cromer type (2). The inert gas side of the indicator was connected to an absolute mercury manometer which could be read easily to 1 mm. However, when the viscometer contained highly associated hydrogen fluoride, the pressure sometimes drifted as much as 5 mm. due to slight temperature changes or to solution of the gas in the fluorocarbon grease.

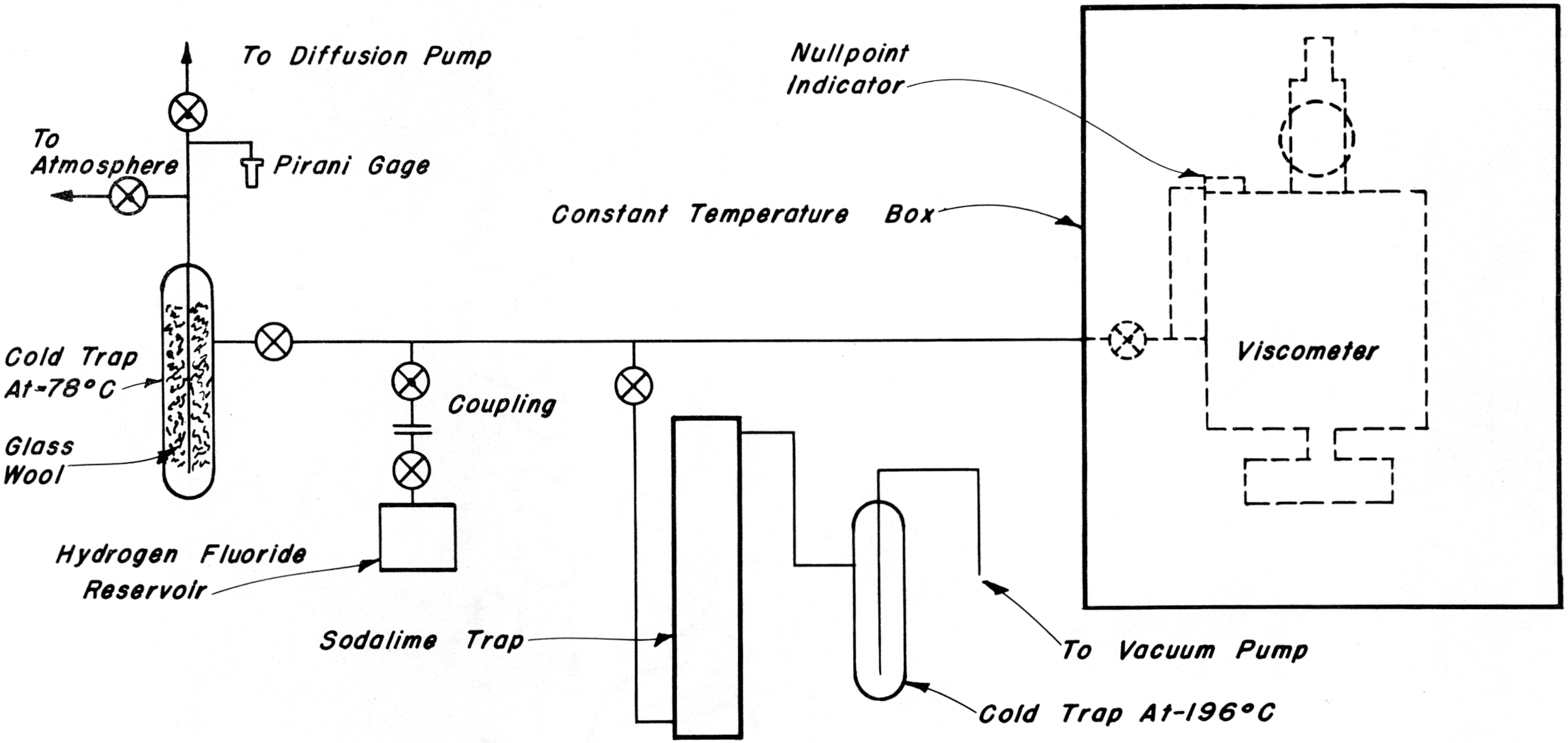
Optical System. The general arrangement of the optical system is shown in figure 5. The light beam from a 10 volt spot light was reflected from the mirror onto the translucent plastic scale. The scale was arc shaped and was placed so that the mirror was at the center of curvature or about 45 inches from the scale. A small focusing lens of 1 meter focal length was mounted on the outside of the viscometer window. The scale was marked in 1,200 divisions of slightly less than 1 mm. each. The position of the light image could be read to about 0.5 division. One division equaled about 1.5, 1.0, and 0.8 micropoises in the experimental arrangements used to obtain the data in tables I, II, and III respectively.

Charging and Disposal Manifold. The charging and disposal manifold are shown in figure 6. Rough evacuation was accomplished by pumping through the soda lime trap. A high vacuum could be obtained with the diffusion pump. To protect the diffusion pump from the action of hydrogen fluoride, the viscometer was evacuated with a mechanical pump and purged at least three times with dry air containing less than 10^{-5} mole per cent water vapor before using the diffusion pump.



OPTICAL SYSTEM

FIGURE 5



MANIFOLD FOR ADDING AND REMOVING HYDROGEN FLUORIDE

FIGURE 6

Materials

Purification of Hydrogen Fluoride. The hydrogen fluoride was purified by a method developed by Wendolkowski and Barber (9). Commercial anhydrous hydrogen fluoride was allowed to flow into a copper tank where it reacted with sodium fluoride to form the bifluoride. The tank was then evacuated thoroughly at room temperature to remove volatile impurities. After this the bifluoride was decomposed thermally, the evolved hydrogen fluoride passing into a second tank containing cobalt trifluoride. After several hours with occasional agitation, any water present was assumed to have reacted, and the hydrogen fluoride was volatilized into the storage tank of the viscometer. The purity as determined by freezing point measurements was 99.97%.

Procedure

Calibration. During the determination of the data in table I the viscometer was calibrated three times with dry air and twice with hydrogen. During all subsequent work, for each temperature at which viscosity measurements were made the viscometer was calibrated with dry air before and after making the measurements with hydrogen fluoride. Tests of the effect of pressure on the viscometer deflection were made with dry air, hydrogen, uranium hexafluoride, and hexafluorobutene. These results are summarized in tables IV and V.

The viscosity of dry air used in the calculations was 183.0 micropoises at 23°C. with a Sutherland constant of 117. These values were obtained by Hopper and Lady (6) by averaging together a number of the most careful absolute viscosity measurements. The viscosity of hydrogen was obtained by correcting to a constant temperature and averaging the values given by three investigators (8,10,20). The value was 88.13 micropoises at 20°C. The viscosity of uranium hexafluoride which was used was that determined by Meyerson and Eicher (13), 179.7 micropoises at 42°C.

Reading of the Viscometer. When given an impetus, as from starting the rotating cylinder, the suspended cylinder started a rotational oscillation. The period of the oscillation varied among suspension wires, being 208 seconds for the 0.004 inch stainless steel wire and averaging 177 seconds for a number of 0.005 inch beryllium-copper wires. The amplitude of this oscillation could be reduced by starting and stopping the rotating cylinder at the appropriate points in the cycle, but the oscillation could not be entirely stopped. For this reason the rest points were determined in a manner entirely analogous to that used in reading an undamped analytical balance. The first and final readings of each sequence were always at the same end of the cycle so as to avoid bias due to damping of the oscillation by the viscous drag of the gas. The difference between the rest points determined with the rotating cylinder in motion and stationary constituted the viscometer deflection.

RESULTS

The results of all viscosity measurements made are given in tables I, II, and III. The data in tables I and II were determined using the single

6 inch i.d. rotating cylinder and were corrected for turbulent effect as will be explained later. The data in table III were determined using the double rotating cylinder, figure 2, and are believed to be free from systematic error.

The data in table IV show the effect of pressure with unassociated gases upon the deflection of the viscometer at different molecular weights and rates of rotation of the single 6 inch i.d. cylinder. The data in table V show that this effect was eliminated by the use of the double rotating cylinder and a slower rate of rotation.

DISCUSSION AND CALCULATIONS

When true viscous conditions exist in the space between the rotating and suspended cylinders, a rotating cylinder viscometer behaves according to equation 1.

$$\phi = \frac{\mu \tau^2 \omega l a^2 b^2}{\pi I \, (a^2 - b^2)} \qquad (1)$$

where μ is the viscosity of the gas,
ϕ is the angular deflection of the suspended cylinder,
I is the moment of inertia of the suspended cylinder,
τ is the period of oscillation of the suspended cylinder,
l is the effective heights of the cylinders,
ω is the rate of rotation of the rotating cylinder,
b is the inside diameter of the rotating cylinder,
and, a is the outside diameter of the suspended cylinder.

In the case of the double rotating cylinder, of course, the equation for the calculation of the angular deflection consists of the sum of two terms, the first term being identical to equation 1 and the second term being the same as equation 1 except that b becomes the inside diameter of the suspended cylinder and a becomes the outside diameter of the inner rotating cylinder. The strength of the suspension wire acting as a spring is expressed in this equation in terms of the moment of inertia, I, and the period of oscillation, τ, because it is usually calculated from these values. From equation 1 it is apparent that if the viscometer is calibrated with a gas of known viscosity, then the ratio of the unknown to the known viscosity is directly proportional to the ratio of the deflection produced by the gas of unknown viscosity to the deflection produced by the gas of known viscosity. (See equation 5.) However, when the original single rotating cylinder was used, small deviations from this relationship were observed. The changes in viscometer reading with pressure shown in table IV are greater in magnitude and different in sign from the small viscosity changes which occur with unassociated gases in the pressure range of this work (14).

Numerous efforts were made to explain this change in apparent viscosity as due to vibration, but changes in the drive mechanism and damping of floor vibration were not effective in reducing the error. Further, the effect of the slip factor was calculated and found to be negligible. However, the

TABLE I

THE VISCOSITY OF HYDROGEN FLUORIDE

Temp., °C.	Pressure, mm. of Hg	Viscosity, Uncorrected, micropoises	Viscosity Corrected, micropoises	Deviation from Equation 14, micropoises
21.8	46	120.8	121.5	-1.2
22.1	46	120.7	121.4	-1.5
22.3	103	119.9	120.5	-2.3
22.1	104	120.1	121.4	-1.2
22.6	239	122.0	122.5	+0.6
22.6	239	122.0	122.5	+0.6
22.7	337	121.1	121.5	+0.5
21.9	365	120.3	120.7	+1.2
22.2	368	120.9	121.3	+1.2
22.2	369	119.7	120.1	+0.2
22.9	438	118.0	118.3	-2.4
21.6	596	113.9	114.0	+1.0
22.1	606	114.3	114.4	+0.1
21.0	651	111.1	111.2	+3.2
21.5	677	113.0	113.1	+3.4
22.9	686	116.2	116.3	+6.2
21.2	729	112.0	112.0	+9.7
21.2	741	114.9	114.9	+5.6
21.4	742	112.0	112.0	+4.5
22.8	760	116.5	116.5	+3.1
23.3	55	122.8	123.5	+0.1
23.9	70	124.2	124.9	+1.3
23.9	70	123.5	124.2	+0.5
23.3	153	122.9	123.5	0.0
23.9	184	122.5	123.1	-0.1
23.8	184	122.3	122.9	-0.3
23.7	184	122.3	122.9	-0.2
23.1	263	121.4	121.9	-0.3
23.7	288	122.5	123.0	+0.7
23.5	286	121.8	122.3	0.0
23.3	285	121.7	122.2	+0.1
23.0	338	121.7	122.1	-0.1
23.3	378	121.5	121.9	+0.9
23.1	438	118.8	119.1	+0.8
23.1	442	118.9	119.2	+0.7
23.1	443	119.3	119.6	-0.3
23.2	545	115.7	115.9	-2.3
23.4	547	115.1	115.3	-2.3
23.1	605	115.5	115.6	-1.2
23.3	611	114.5	114.6	-2.5
23.8	622	115.1	115.2	-2.5
23.5	657	112.4	112.5	-4.0
23.5	657	113.9	114.0	-2.5
23.4	741	114.4	114.4	+0.1

TABLE I (Contined)

Temp., °C.	Pressure, mm. of Hg	Viscosity, Uncorrected, micropoises	Viscosity Corrected, micropoises	Deviation from Equation 14, micropoises
24.2	71	123.7	124.4	+0.6
24.5	255	123.3	123.8	+0.7
24.5	255	123.6	124.1	+1.0
24.4	384	120.7	121.1	-0.9
24.0	490	118.2	118.4	-2.8
24.2	492	119.2	119.5	-1.0
25.1	690	117.6	117.7	-0.8
25.3	695	116.7	116.7	-2.0
25.4	695	116.8	116.8	-2.0
24.7	743	116.2	116.2	-0.7
24.0	746	115.5	115.5	0.0
24.4	746	115.0	115.0	-1.4
24.0	758	116.9	116.9	+1.6
24.1	764	117.3	117.3	+2.0
24.6	767	117.2	117.2	+1.0
25.0	774	117.1	117.1	+0.5

TABLE II

THE VISCOSITY OF HYDROGEN FLUORIDE

Temp., °C.	Pressure, mm. of Hg	Viscosity, Uncorrected, micropoises	Viscosity Corrected, micropoises	Deviation from Equation 14, micropoises
29.2	68	124.2	125.7	-0.4
29.3	148	124.3	125.6	-0.4
29.2	229	124.3	125.4	-0.3
29.2	340	124.1	125.0	-0.2
29.3	460	123.7	124.3	-0.3
29.6	555	122.7	122.9	-1.1
29.8	670	121.8	122.0	-1.3
28.9	743	119.1	119.1	-2.7
28.5	768	119.2	119.2	-2.0
29.0	802	117.7	117.6	-3.6
36.1	125	128.0	129.3	+0.2
36.2	229	127.8	128.9	-0.3
36.4	318	128.0	128.9	+0.1
36.6	448	127.4	128.1	-0.4
36.6	609	126.8	127.1	-0.6
36.2	814	125.1	125.0	-1.2
36.5	870	125.9	125.7	-0.2
36.4	757	126.9	126.9	-1.1
36.6	762	125.5	125.5	+0.2
45.1	131	131.6	132.9	+0.2
44.9	231	131.3	132.4	-0.5
45.1	318	131.4	132.3	-0.5
45.2	491	131.5	132.1	-0.3
45.5	647	131.5	131.7	-0.2
45.0	751	130.7	130.6	-0.6
45.1	852	130.6	130.5	-0.1
54.0	71	136.0	137.5	+0.3
53.9	150	135.7	137.0	-0.1
53.9	236	135.7	136.8	-0.1
53.7	338	135.0	135.9	-0.9
53.7	428	135.4	136.1	-0.4
54.1	538	135.5	136.0	-0.4
53.8	640	135.4	135.7	-0.3
54.3	754	135.3	135.3	-0.4
54.4	800	135.1	135.0	-0.5
54.4	872	135.1	134.9	-0.2
54.5	922	134.8	134.5	-0.4
54.0	982	135.2	134.7	+0.4
68.4	750	142.4	No correction needed	
77.8	750	148.2		
88.6	750	153.5		

TABLE III

THE VISCOSITY OF HYDROGEN FLUORIDE

Temperature, °C.	Pressure, mm. of Hg	Viscosity, micropoises	Deviation from Equation 14
27.3	58	125.2	-0.1
27.2	104	125.9	+1.2
27.1	237	125.0	-0.2
25.1	447	124.3	+2.4
25.5	622	120.3	+0.3
25.5	698	119.8	+1.0
32.4	111	127.5	+0.1
32.2	222	127.4	+0.2
32.2	526	126.7	-0.2
32.0	622	126.1	+1.0
31.9	709	125.3	+1.0
33.6	111	127.4	-0.4
33.6	207	127.3	-0.6
33.4	416	126.2	-0.9
33.4	608	125.6	-0.4
33.4	702	124.6	-0.7
34.2	95	127.4	-1.0
33.8	202	127.6	-0.4
33.7	370	127.1	-0.3
33.5	579	127.1	+0.9
33.6	724	125.5	+0.2
38.4	108	129.8	+0.4
38.3	200	130.0	0.0
38.0	380	129.1	+0.3
38.3	414	129.9	+0.4
38.2	600	128.7	+0.7
38.3	714	127.0	+1.0
45.7	115	133.0	-0.5
45.6	197	133.4	0.0
45.6	398	132.5	-0.4
45.6	615	131.7	-0.5
45.6	728	130.3	-1.3
55.7	10	137.3	-0.7
55.7	21	137.8	-0.1
55.4	399	137.2	-0.2
55.4	604	136.3	-0.5
55.4	727	136.1	-0.2

TABLE IV

EFFECT OF PRESSURE ON VISCOMETER READING WITH SINGLE 6 INCH ROTATING CYLINDER

Gas	Temp., °C.	Change in Viscometer Reading, Micropoises per mm. Hg	Number of Points	Rate of Rotation, rpm.
Air	25	3.1×10^{-3}	40	3
UF_6	42	64×10^{-3}	14	3
H_2	25	-2×10^{-4}	6	3
Air	25	1.46×10^{-3}	6	2

TABLE V

EFFECT OF PRESSURE ON VISCOMETER DEFLECTION WITH DOUBLE ROTATING CYLINDER AT 1 RPM.

Gas	Molecular Weight	Pressure, mm. of Hg	Temperature, °C.	Viscometer Deflection
Air	29	747	24.1	220.33
Air	29	70	24.2	220.75
Hexafluoro-cyclobutene	162	555	23.5	136.5*
Hexafluoro-cyclobutene	162	38	23.8	136.9*

*From these data the viscosity of hexafluorocyclobutene vapor can be calculated as 113.6 micropoise at 23.5°C. and 113.9 micropoise at 23.8°C.

change in viscosity reading was proportional, within the precision with which this second order effect could be measured, to the density of the gas and to the square of the rate of rotation. Since this is similar to the case of turbulent flow through pipes where the pressure drop is approximately proportional to the density of the fluid and to the square of the linear velocity, the force acting on the suspended cylinder probably has a small turbulent component in addition to the major viscous component. Turbulence had not been anticipated because the Reynold's numbers* involved are only 27 at 3 rpm. and 18 at 2 rpm. for air at one atmosphere. These values are far below 2,500, the value below which turbulent flow usually is considered not to occur in round pipes. However, similar small deviations from viscous behavior have been observed by others (13).

The elimination of this systematic error in the determination of the viscosity was accomplished in two ways. First, in order to obtain correct future data, a double rotating cylinder (figure 2) was constructed which produced an adequate deflection at one rpm. The Reynold's number for the largest of the spaces between this cylinder and the suspended cylinder was calculated to be 7. The effect of gas pressure on the deflection produced by this cylinder was tested with both air and the high molecular weight gas, hexafluorocyclobutene, and was found to be nil. (See table V.) This double cylinder was used in obtaining the data in table III, which data are believed to be free of bias.

Second, the data in tables I and II were corrected by taking into consideration the contribution of a small turbulent component to the force acting upon the suspended cylinder. The change of the viscometer reading due to the presence of a small turbulent component may be expressed by equation 2.

$$\phi - \phi^{o} = K\omega^{2}\rho \qquad (2)$$

where ϕ is the observed viscometer deflection,

ϕ^{o} is the viscometer deflection at a pressure low enough that no turbulence exists,

K is a constant,

ω is the rate of rotation,

and ρ is the density of the gas.

At a constant rate of rotation and at a constant temperature equation 2 becomes

$$\phi - \phi^{o} = K' \, PM \qquad (3)$$

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*Reynold's numbers were calculated assuming a condition analogous to flow between two parallel plates. The velocity of the surface was considered to be the maximum velocity and the average velocity to be equal to 2/3 the maximum velocity.

where ϕ and ϕ° have the same meaning as before
K' is a constant
P is the pressure
and, M is the molecular weight,

For unassociated hydrogen fluoride and air, the ratios of the molecular weights to the viscosities were observed to be nearly equal, or

$$\left(\frac{M}{\mu}\right) \text{air} \cong \left(\frac{M}{\mu}\right) \text{hydrogen fluoride} \tag{4}$$

Also since ϕ° represents the viscometer deflection produced by purely viscous forces, equation 5 holds.

$$(\mu/\phi^\circ)_{\text{air}} = (\mu/\phi^\circ)_{\text{hydrogen fluoride}} \tag{5}$$

From equations 3, 4, and 5 at constant pressure and temperature, one obtains the relationships given by equations 6, 7, and 8 for unassociated hydrogen fluoride and air.

$$\left(\frac{\phi - \phi^\circ}{\phi^\circ}\right) \text{air} \cong \left(\frac{\phi - \phi^\circ}{\phi^\circ}\right) \text{hydrogen fluoride} \tag{6}$$

or

$$\left(\frac{\phi - \phi^\circ}{\phi^\circ} + 1\right)_{\text{air}} = \left(\frac{\phi}{\phi^\circ}\right) \text{air} \cong \left(\frac{\phi}{\phi^\circ}\right) \text{hydrogen fluoride} \tag{7}$$

or

$$\left(\frac{\mu}{\phi}\right) \text{air} \cong \left(\frac{\mu}{\phi}\right) \text{hydrogen fluoride} \tag{8}$$

Equation 8 shows that unassociated hydrogen fluoride and air may be compared directly providing the measurements are made at the same pressure. Since all of the calibrations used directly in the calculation of viscosities were made with air at one atmosphere, the viscosities of hydrogen fluoride measured at one atmosphere and at sufficiently high temperatures to reduce association to a low level needed no correction. The viscosities measured at lower temperatures and at pressures other than one atmosphere were corrected by calculating the deflections which would have been produced by air at the same pressure and temperature as the particular measurement in question and then using equation 8. These adjusted air deflections were calculated from calibration data for air at one atmosphere obtained before and after each set of hydrogen fluoride runs and the data of table IV. This correction was adequate for the data at low pressures and correspondingly low association. The agreement of viscosities extrapolated to zero pressure from the data of tables I and II and those from table III may be cited as support of the validity of the correction. At high pressures a greater correction would be justified because of the increase in the average molecular weight of hydrogen fluoride due to association. However, because of the poor precision of the data in this range, further correction was not made.

If this further correction resulting from the effect of association on the turbulent component were made for the datum point representing the conditions of greatest association from table I, the correction would have been 1.5%. For this point the average molecular weight, as calculated by the method of Long, Hildebrand, and Morell (12) was 3.0 times that of the monomer. For the point representing the highest degree of association in table II (with an average molecular weight equal to 2.4 times that of the monomer) the correction would have been 4.5%. The effect on most of the points in these tables would have been much less. In all subsequent correlations, the values used from tables I and II were those corrected for the dependence of the viscosity upon the density of the calibrating gas resulting from a slight turbulence of the gas between the rotating and suspended cylinders.

The slip factor calculations are verified by the data of table V. If the effect of slip had been important, then the deviations should have been even larger with the double rotating cylinder than with the single rotating cylinder because the distances between the moving and stationary surfaces were smaller in the case of the double rotating cylinder. No increase in the viscosity with increase in pressure was observed, indicating, in agreement with the calculations, that the effect of the slip factor is negligible.

Since the degree of association of hydrogen fluoride is affected greatly by the pressure, the viscosity would also be expected to be affected. As can be seen in tables I, II, and III such a pressure dependence was observed, and at constant temperature the viscosity could be expressed as a function of pressure by an equation of the form

$$\mu = \mu_o - mP^2 \tag{9}$$

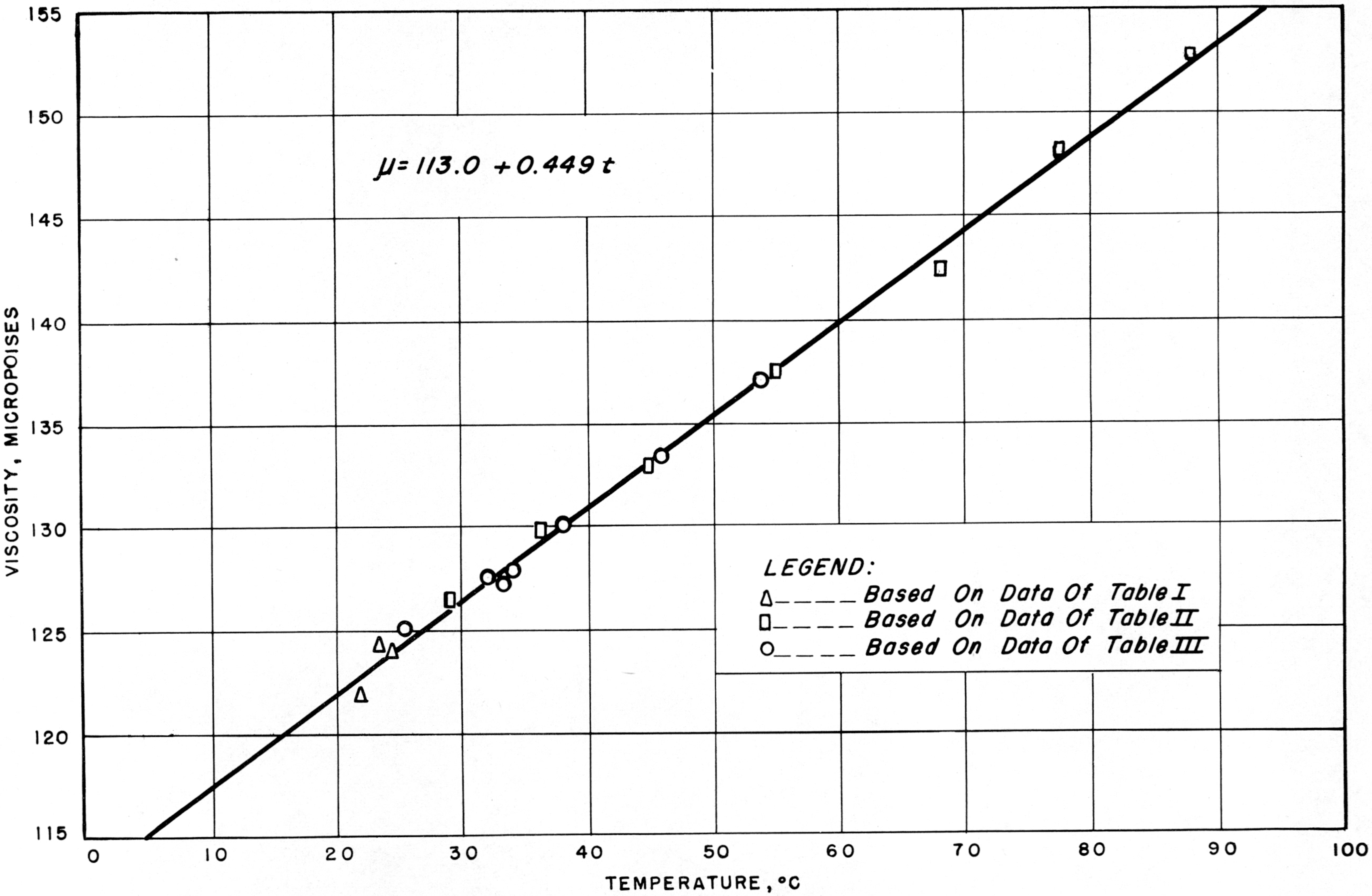
where μ is the viscosity in micropoises,
μ_o is the viscosity extrapolated to zero pressure, i.e. zero association,
m is a constant,
P is the pressure in millimeters of mercury,
and μ_o and m are functions of temperature.

Values of μ_o were found to be correlated with temperature by equation 10 and are shown in figure 7.

$$\mu_o = a + bt \tag{10}$$

where $a = 113.0 \pm 0.3$
$b = 0.449 \pm 0.016$
and t is the temperature in degrees centigrade.

The precisions or limits of error are given at the 95% confidence level. The equation is based not only on the values obtained by extrapolation to zero pressure but also on individual points determined at 1 atm. and 68.4, 77.8, and 88.6°C. At these temperatures it was assumed that association was negligible. The root mean square deviation of points from the line of the equation was 0.6 micropoises. The largest deviation of -1.3 micropoises may be a result of slight association of the hydrogen fluoride under one atmosphere pressure at 68.4°C. As calculated from the equation of Long,



VISCOSITY OF GASEOUS HYDROGEN FLUORIDE AT ZERO ASSOCIATION AS A FUNCTION OF TEMPERATURE

FIGURE 7

Hildebrand, and Morrel (12), the association was only 0.3%; but using the more recent equation of Jarry and Davis (9), the association was calculated to be 1.1%. The latter degree of association would result in a small but measurable deviation from equation 10.

The data at zero association were also correlated using the Sutherland equation:

$$\frac{\mu_1}{\mu_2} = \left(\frac{T_1}{T_2}\right)^{3/2} \left(\frac{T_2 + C}{T_1 + C}\right) \qquad (11)$$

where μ_1 and u_2 are the viscosities at absolute temperatures T_1 and T_2

and C is the Sutherland constant for hydrogen fluoride gas (430 ± 40 at the 95% confidence level).

From the least mean squares plot of $T^{3/2}$ versus T, equation 12 was obtained.

$$\mu = \frac{\frac{T^{3/2}}{\mu}}{0.057\ T + 24.476} \qquad (12)$$

where μ is the viscosity at temperature T°K.

Equation 12 is believed to be the best equation available for extrapolation to higher temperatures. Its validity depends on the assumption that the viscosities obtained by extrapolation to zero association may be correlated with viscosities at one atmosphere and temperatures sufficiently high to prevent association in the same manner as viscosities at different temperatures and the same pressure are correlated for an ordinary nonassociated gas.

It was found that m, the proportionality constant in equation 9, could be expressed as the following function of temperature (see figure 8):

$$\log\ (m \times 10^6) = \frac{10.1}{t - 13.2} + 0.2355 \qquad (13)$$

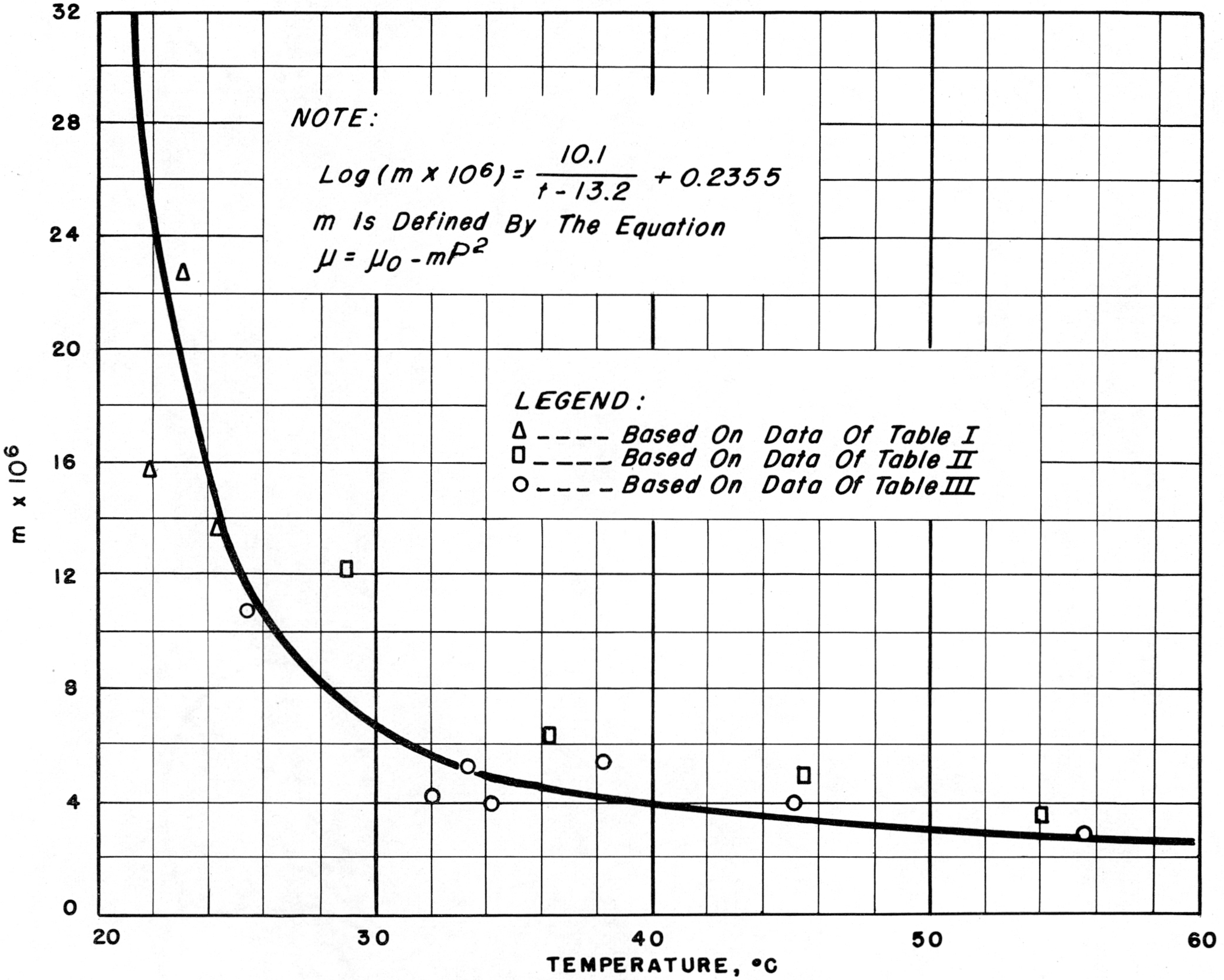
where t is the temperature in degrees centigrade.

The equation is entirely empirical and should not be used outside of the range in which it is known to apply, 22 to 56°C. This is particularly true at the lower temperature where m is increasing very rapidly. (See figure 8.)

Equations 10 and 13 may be combined to form a general equation for the viscosity of gaseous hydrogen fluoride

$$\mu = 113.0 + 0.449t - P^2 \times 10^{-6}\ \text{antilog}\ \left(\frac{10.1}{t-13.2} + 0.2355\right) \qquad (14)$$

The same limitations apply to the use of this equation as apply to equation 13.



EFFECT OF TEMPERATURE ON THE PRESSURE DEPENDENCE OF THE VISCOSITY OF GASEOUS HYDROGEN FLUORIDE

FIGURE 8

The deviations of all experimental points from the equation are given in tables I, II, and III. The root mean square deviation and algebraic average deviation for each table and for the total are given in table VI.

TABLE VI

DEVIATIONS OF EXPERIMENTAL POINTS FROM EQUATION 14

Table No.	Algebraic Average Deviation, micropoises	Root Mean Square Deviation, micropoises	Number of Determinations
I	+0.22	2.3	60
II	-0.54	0.94	38
III	+0.04	0.73	37
Overall	-0.04	1.7	135

The root mean square deviation shows the precision of fit of the equation. The data in table I are poorer than those in tables II and III, due to several factors. First, the magnetic clutch was driven by a friction clutch which had a slight inconstant slip. Second, these were the first data obtained and various fine points of the technique had not been developed. Third, and perhaps most important, these data are in the temperature range in which association was greatest and small shifts in either temperature or pressure had a relatively large effect on the viscosity.

The small algebraic average deviation for all the data, and the equally small algebraic average deviation for the data of table III show that the data of table III have little bias from the mean of all the data. Data in tables I and II show more bias than the data in table III, but in both cases the algebraic average deviation is less than the root mean square deviation.

SUMMARY

The viscosity of gaseous hydrogen fluoride has been measured as a function of both temperature and pressure over the temperature and pressure ranges of 22 to 56°C. and 0 to approximately 1 atmosphere respectively. Measurements also were made at one atmosphere at temperatures up to 88.6°C.

Since the gas movement in the viscometer during some of the early determinations was not completely viscous in nature, it was necessary to apply a small correction to these data. Upon discovery of the non-viscous nature of part of the gas movement, alterations were made in the equipment so as to achieve purely viscous conditions during the determination of the remainder of the data.

The data were correlated by the general equation

$$\mu = 113.0 + 0.449t - P^2 \times 10^{-6} \text{ antilog } \left(\frac{10.1}{t-13.2} + 0.2355\right) \qquad (14)$$

where μ is the viscosity in micropoises,
P is the pressure in millimeters of mercury,
and, t is the temperature in degrees centigrade.

This equation is entirely empirical and should not be used outside of the range of the data. Since no data on the viscosity of unassociated gaseous hydrogen fluoride at higher temperatures is currently available, an equation based on the Sutherland equation and suitable for extrapolation to higher temperatures was derived and is stated below.

$$\mu = \frac{T^{3/2}}{0.057\ T + 24.476} \qquad (12)$$

where μ is the viscosity in micropoises, and T is the temperature in degrees Kelvin.

The Sutherland constant is 430 ± 40 at the 95% level of confidence. This equation is not applicable if the hydrogen fluoride is appreciably associated.

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