PHYSICAL PROPERTIES AND ASSOCIATION OF THE LIQUID HALOGEN FLUORIDES

By

Emerson E. Garver

A THESIS

Submitted to the School for Advanced Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1957

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Max T. Rogers, without whom this manuscript could not have been written. Throughout the course of this investigation he has offered encouragement, helpfulness and much-needed advice.

He also wishes to make known his debt to J. L. Speirs for aid in instrumentation, to H. B. Thompson for his cogent observations, and to E. Forest Hood for some excellent glass blowing.

The Atomic Energy Commission has made this work possible through a research grant.

****

VITA

Emerson E. Garver was born May 1, 1929 at Akron, Ohio. After attending Western Reserve Academy located at Hudson, Ohio, he spent one year at Swarthmore College and received the Bachelor of Science degree from Kent State University in 1951.

He attended graduate school at the Ohio State University for a year and the following year enrolled at Michigan State University. He was a teaching assistant in chemistry 1952-3 and a research assistant from 1954 to 1956.

Sigma Pi Sigma and Sigma Xi have honored him, and he is a member of the American Chemical Society. He will complete his work for the Doctor of Philosophy degree in the spring of 1957 with a major in physical chemistry and minors in inorganic chemistry, physics and mathematics.

PHYSICAL PROPERTIES AND ASSOCIATION OF THE LIQUID HALOGEN FLUORIDES

By

Emerson E. Garver

AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of Michigan State University of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

Year 1957

Approved Max T Rogers

ABSTRACT

The viscosities of iodine pentafluoride, bromine pentafluoride, and bromine trifluoride have been determined over a temperature range of 15 to 40 degrees Centigrade by means of a modified Ostwald viscometer made of Pyrex. The results have been fitted to a standard exponential equation which relates viscosity to the temperature, and various parameters such as energy, free energy, and entropy of viscous flow were computed. The results have been interpreted in terms of Eyring's theory of viscous flow, and they indicate that bromine trifluoride, and to a lesser extent iodine pentafluoride, are associated liquids. Computations based on the data published thus far on the viscosity of iodine pentafluoride and chlorine trifluoride were included for the sake of comparison. Chlorine trifluoride and bromine pentafluoride are "normal" liquids.

The surface tensions of iodine pentafluoride, bromine pentafluoride, and bromine trifluoride have been determined over the same temperature range by the capillary-rise method. The results were fitted to a standard, linear, surface tension-temperature relationship. Again the results indicated that bromine trifluoride, and perhaps iodine pentafluoride, are associated, while bromine pentafluoride and chlorine trifluoride are probably not.

Various empirical relationships were employed to obtain estimated values of the critical temperatures of the halogen fluorides.

TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
II.	HISTORICAL REVIEW OF THE HALOGEN FLUORIDES	2
III.	THEORY	8
	Viscosity	8
	Surface Tension	14
IV.	APPARATUS AND METHOD	19
	Review of Methods	19
	Viscosity Measurements	19
	Surface Tension Measurements	22
	Construction Materials	24
	Apparatus	25
	Temperature Measurement and Control	31
	Gas-Handling System	32
	Procedure	34
	Materials	37
	Treatment of Calibration Data	38
	Viscosity Measurements	38
	Surface Tension Measurements	49
V.	RESULTS AND DISCUSSION	53
	Viscosity Measurements	53
	Results	53
	Treatment of Data	53
	Precision and Accuracy	61
	Discussion	65
	Surface Tension Measurements	67
	Results	67
	Precision and Accuracy	71
	Discussion	72
VI.	SUMMARY	76
LITERATURE CITED		77
APPENDICES		83

LIST OF TABLES

TABLE		Page
I.	Melting and Boiling Points of Halogen Fluorides	3
II.	Density-Temperature Relationships of Liquid Halogen Fluorides	4
III.	Dielectric Constants and Magnetic Susceptibilities of Liquid Halogen Fluorides	5
IV.	Molar Refractions and Electric Dipole Moments of Gaseous Halogen Fluorides	5
V.	Viscosity Calibration Data for Apparatus III	42
VI.	Viscosity Calibration Data for Apparatus IV	43
VII.	Data for Calculation of the Constant B	44
VIII.	Values of the Constant B	45
IX.	Data for Calculation of Constant C Benzene in Apparatus III.	46
X.	Data for Calculation of Constant C Water in Apparatus IV	47
XI.	Calibration Data for Capillary Radii	51
XII.	Data to Check the Calibration of Pyrex Capillaries for use in Surface Tension Measurements	52
XIII.	Viscosity Data for Iodine Pentafluoride	54
XIV.	Viscosity Data for Bromine Pentafluoride	55
XV.	Viscosity Data for Bromine Trifluoride	56
XVI.	Viscosities of Iodine Pentafluoride	57
XVII.	Viscosities of Iodine Pentafluoride from Apparatus I	58
XVIII.	Viscosities of Bromine Pentafluoride	59
XIX.	Viscosities of Bromine Trifluoride	60
XX.	Thermodynamic Functions for Viscous Flow	62

LIST OF TABLES - Continued

TABLE Page

XXI. Calculated and Observed Precision of Viscosity Results..... 63

XXII. The Surface Tensions of Iodine Pentafluoride..... 68

XXIII. The Surface Tensions of Bromine Pentafluoride..... 69

XXIV. The Surface Tensions of Bromine Trifluoride..... 70

XXV. Calculated and Observed Precision of Surface Tension Results 71

XXVI. Surface Tension-Temperature Relationships for the Halogen Fluorides..... 73

XXVII. Parachors of the Halogen Fluorides..... 73

XXVIII. Atomic Parachors of the Central Halogen Atom..... 73

XXIX. Work of Cohesion of the Halogen Fluorides..... 74

XXX. Estimated Critical Temperatures of the Halogen Fluorides (Centigrade)..... 74

XXXI. Viscosity and Surface Tension of the Halogen Fluorides at 20°C..... 74a

LIST OF FIGURES

FIGURE Page

1. Ostwald Viscometer..... 20

2. Apparatus I for Measurement of Viscosity..... 26

3. Apparatus III and IV for Measurement of Viscosity and Surface Tension..... 29

4. Apparatus II for Measurement of Surface Tension..... 30

5. Vacuum System for Handling Halogen Fluorides..... 33

6. Graph of C versus 1/T for Apparatus III..... 48

INTRODUCTION

The past ten years have seen considerable activity in the field of fluorine chemistry. The halogen fluorides, which have excellent fluorinating abilities, have been widely used but little information concerning their physical properties has been available. Although the great chemical reactivity that characterizes the halogen fluorides makes measurement of their physical properties difficult, modern techniques and materials now make accurate work possible.

Two properties which it seemed desirable to determine are those of viscosity and surface tension. They give insight into the structure of the liquid phase, especially with regard to possible association.

Accordingly, apparatus was designed and constructed to measure surface tension by the capillary-rise method and viscosity by the Ostwald method. Procedures were developed for measuring these properties with a precision of plus or minus one per cent or better over a temperature range of twenty-five centigrade degrees for those halogen fluorides that are liquids at room temperature.

HISTORICAL REVIEW

The Halogen Fluorides

In 1870 Gore (1) prepared the first halogen fluoride, iodine pentafluoride. Since that time five or six more such fluorides have been prepared. They are iodine heptafluoride, bromine pentafluoride, bromine trifluoride, chlorine trifluoride, chlorine monofluoride, and perhaps an unstable monofluoride of bromine. Ruff and Braida (2) suggested that, in the system bromine-bromine trifluoride, the species BrF existed. Fischer, et al., (3) in a study of the solid-liquid equilibria of the above system failed to find solid bromine monofluoride, but did demonstrate the existence of a different species, presumably bromine monofluoride, in the vapor of the above system (4). Iodine monofluoride has been detected only spectroscopically (5), and Aynsley, Nichols, and Robinson (6) observed a bright blue color which they attributed to an unstable trifluoride of iodine.

Although the existence of such compounds is to be expected because halogen-halogen bonds are found in the elements themselves, the halogen fluorides possess unexpected thermal stability. For example, bromine pentafluoride was found not to dissociate at temperatures as high as 350° C. (7). The great differences in electronegativities that exist among the halogens accounts in part for their stability.

Since 1950 several review articles (8,9,10,11,12), as well as some books (7,13,14,15), concerning the chemistry of the halogen fluorides

have appeared, perhaps the most comprehensive being the two volumes edited by J. H. Simons (7,13). An excellent summary of the work published to 1954 has been given by Thompson (16). Therefore the emphasis in this review will be placed upon those physical properties that have been studied since 1954.

The melting points and boiling points of the halogen fluorides are summarized in Table I. Using highly purified iodine pentafluoride, Rogers, et al., (17) found a freezing point of 9.43° C. and a boiling point calculated from vapor-pressure measurements of 100.5° C.

Table II contains in summarized fashion the constants for empirical equations representing densities of liquid halogen fluorides as a function of temperature. It is unfortunate that more refined density measurements for iodine pentafluoride have not been made.

TABLE I

MELTING AND BOILING POINTS OF HALOGEN FLUORIDES

Compound	IF_7	IF_5	BrF_5	BrF_3	ClF_3	ClF
M.p., ° C.	6	9.43	-60.5	8.75	-83	-154
B.p., ° C.	4.5(subl.)	100.5	40.7	125.75	12.0	-100.8

Other physical properties now known include the dielectric constants, magnetic susceptibilities, molar refractions and electric dipole moments. They are listed in Table III and Table IV.

Chlorine trifluoride was found to have a planar T-structure by Smith (30) from microwave spectroscopy. His results are supported by

TABLE II

DENSITY-TEMPERATURE RELATIONSHIPS OF LIQUID HALOGEN FLUORIDES[1]

Compound	IF_5	BrF_5	BrF_3	ClF_3
Reference	2	18	2	19
A	4.38	3.496	3.623	2.729
B	0.004	0.00346	0.00277	0.00307
Reference		20	21	22
a		2.5509	2.8511	1.8853
b		3.484	2.72	2.9424
c		3.45	0.00	3.79

[1] The liquid density in g./cc. is $A-BT$ where T is the absolute temperature, or in the second row, $a-bx10^{-3}t-cx10^{-6}t^2$ where t is the temperature in degrees centigrade.

X-ray diffraction work (31), infrared and Raman spectroscopic data (32), and electric dipole moment measurements (29). Rogers, et al., (27) confirmed the dipole moment, hence supported the structure. Nuclear magnetic resonance absorption studies (33) at first failed to show the "chemical splitting" which is to be expected for a structure in which one fluorine atom is in a different electronic environment from the others (34), but later work (34a) confirmed the planar structure of symmetry C_{2v}.

The structure of bromine pentafluoride probably approximates an octahedron with one corner occupied by the unshared pair of electrons and all the fluorine atoms on the same side of a plane which passes

TABLE III

DIELECTRIC CONSTANTS AND MAGNETIC SUSCEPTIBILITIES OF LIQUID HALOGEN FLUORIDES[1]

Compound	ϵ		χ_M c.g.s. units x 10^{-6}	
ClF_3	4.754 - 0.018t	(2)	-26.5	(25)
BrF_3			-33.9	(25)
BrF_5	8.20 - 0.0117t	(23)	-45.1	(25)
IF_5	41.09 - 0.198t	(24)	-58.1	(25)

[1] References are given in parentheses after the value.

TABLE IV

MOLAR REFRACTIONS AND ELECTRIC DIPOLE MOMENTS OF GASEOUS HALOGEN FLUORIDES[1]

Compound	MR_D (cc./mole) at t° C.			μ (Debye)	
ClF	7.62	24 ° C.	(26)	0.88	(28)
ClF_3	10.34	26 ° C.	(26)	0.554, 0.65	(29,27)
BrF_3	13.22	25 ° C.	(26)	1.19	(27)
BrF_5	15.41	25 ° C.	(26)	1.51	(23)
IF_5	7.62	24 ° C.	(26)	2.18	(27)

[1] References are given in parentheses after the value.

through the bromine atom and is perpendicular to the fourfold axis of symmetry. Mellish and Linnett (35) draw the above conclusion from their observations on directed valency; they show that in the fluorides some factor is operating which is more important than the mutual repulsion of the fluorine atoms and which causes a decrease in the bond angles. They cited in support of the above structure that infrared and Raman spectra (36) indicate a similar symmetry for bromine pentafluoride and that the known structure of the $SbF_5^=$ ion in the compound K_2SbF_5 is the same as the one mentioned. The nuclear magnetic resonance absorption spectrum indicates that one fluorine atom is bonded differently than the other four (34,34a). Also, dipole moment studies (23) support the distorted octahedral structure.

The electric dipole moment studies (27) are in agreement with a planar structure of C_{2v} symmetry for bromine trifluoride. Infrared studies (37) support this structure.

The most probable configuration for iodine pentafluoride is a distorted octahedron in which the iodine atom is slightly displaced toward the corner occupied by the lone electron pair. The large measured dipole moment, 2.18 D, (27) eliminates any symmetrical configurations. Nuclear magnetic resonance absorption data (34,34a) rule out the pentagonal pyramidal form, because at least one fluorine atom is in a different electronic environment from the rest.

Iodine heptafluoride is the only known molecule of the type AB_7. A pentagonal bipyramidal structure has been inferred from the infrared

and Raman spectra (38), although again the nuclear magnetic resonance spectrum (34) contraindicated this configuration when it failed to show the expected "chemical splitting" due to the two different positions occupied by fluorine atoms.

THEORY

The liquid state lacks a comprehensive theoretical development such as we have for the gaseous and solid states. The simplifying assumptions employed for the latter states do not apply well to liquids (39). Two properties which have helped elucidate the structure of the liquid state and the nature of the intermolecular forces are viscosity and surface tension.

Viscosity may be defined as the resistance which a liquid exhibits to the flow of one layer over another (40). In 1867 Newton (41) postulated that this resistence to the flow of the layers is independent of the pressure, proportional to the area, and proportional to the relative velocity. Most liquids conform to these assumptions and accordingly are known as Newtonian liquids. This discussion will be limited to them.

Poiseuille (42) investigated the flow of water through capillary tubes and found the relationship

$$V = \frac{CPr^4 j}{L} \qquad (1)$$

for the volume V flowing in time j, where C is a constant and P is the pressure difference between the ends of the tube of length L and radius r. For a given tube C was found to depend only on the temperature and upon the liquid used. Equation (1) has since been theoretically deduced by many authors and the coefficient of viscosity η shown to be $\pi/8$ (42). The dimensions of the coefficient of viscosity are mass x length^{-1} x time^{-1}

and the unit, which is dyne-second per centimeter squared in the c.g.s. system, is the poise, after Poiseuille. Sometimes the reciprocal of viscosity, the fluidity, is used. In general it has more convenient values. Kinematic viscosity is the viscosity divided by the density.

Perhaps the most striking characteristic of viscosity is the rapid change observed when the temperature changes. An increase in temperature of 100 degrees Centigrade reduces the viscosity of water to one-tenth of its original value (43), and for some fluorocarbons the change is even greater (44).

Many formulae have been proposed to represent the viscosity-temperature relationship. For example, Partington (41) lists 76 equations, most of which are strictly empirical, containing up to five arbitrary constants and relating viscosity to other physical properties such as density, molecular weight, vapor pressure, and heat of vaporization. One of the more useful empirical equations was proposed by Hovorka, et al., (45) in analogy with Kirchoff's formula for vapor pressure as a function of temperature,[1]

$$\log \phi = A - B/T - C \cdot \log T \qquad (2)$$

where ϕ is the fluidity and T is the absolute temperature.

Some authors have regarded the change of viscosity with temperature as due entirely to volume effects. Macleod (46) proposed the equation

$$\eta = A/(v-b)^C \qquad (3)$$

---

[1] Throughout this thesis A, B, and C represent arbitrary constants. See Appendix A.

where v is the specific volume and b, the volume of the molecules themselves, is analogous to Van der Waal's b. Mukherjee (47) used the equation

$$\log \emptyset = A + B \log p(mm.) - 3/2 \log T \qquad (4)$$

In 1930 Andrade (48) introduced the equation

$$\eta = Ae^{B/T} \qquad (5)$$

He derived it by assuming a quasi-lattice structure for the liquid with flow taking place by smooth slippage between two sheets of molecules. Resistance to flow was assumed to originate from molecular agitation which was introduced statistically by the Boltzmann energy distribution.

There have been many modifications of this formula (see 39, 41 and 49). Perhaps the most widely used form is that of Eyring and co-workers (50), who considered viscous flow from the point of view of a chemical reaction that requires an energy of activation before a molecule flows past its neighbors into a vacant space. They deduced, after making certain assumptions about the energy barrier and distances between units of flow, that

$$\eta = \frac{h'N}{V_m} e^{\Delta F^{\ddagger}/RT} \qquad (6)$$

where h' is Planck's constant, N is Avogadro's number, V_m is the molar volume, R is the universal gas constant, T is the absolute temperature, and $\Delta F^{\ddagger}$ is the standard free energy of activation per mole. Since $\Delta F^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger}$, where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the standard

enthalpies and entropies of activation, Equation (6) may be written

$$\eta = \frac{hN}{V_m} e^{-\Delta S^{\ddagger}/R} e^{\Delta H^{\ddagger}/RT} \qquad (7)$$

If then $\Delta S^{\ddagger}$ is assumed constant, since the molar volume does not vary much with temperature, Equation (6) reduces to Equation (5).

After making certain assumptions about the partition function in the liquid state, they showed that

$$\eta = \frac{1.09 \times 10^{-3} M^{\frac{1}{2}} T^{\frac{3}{2}}}{V_m^{2/3} \Delta E_v} e^{E_{vis}/RT} \qquad (8)$$

where M is the molecular weight, E_{vis} is the experimentally observed activation energy per mole for viscous flow, ΔE_v is the energy of evaporation, and the other symbols have their previous meanings. At first glance the pre-exponential factor in Equation (8) is temperature dependent. However, Ewell (51) has showed that this is not the case, and the term is essentially independent of the temperature. Although E_{vis} is a slowly varying function of temperature, generally it varies less than experimental error--except close to the freezing point of the liquid (39). Also, as the exponent increases, the pre-exponential factor decreases (53).

From data on a large number of liquids, Eyring found several empirical relations among the parameters in Equations (6), (7), and (8). The ratio of $\Delta E_v / \Delta F^{\ddagger}$ is 2.45 for most liquids, but it ranges from 1.7 to 4.7, the value for water. He suggested that when the ratio is not close to 2.45 the unit of flow is not the unit of evaporation (52).

For most non-polar molecules of spherical symmetry the ratio of $\Delta E_v/E_{vis} = n$ is in the neighborhood of three, whereas for polar molecules, the ratio is nearer four. Eyring (52) proposed that 1/n signifies the fraction of the size of a unit of flow which must be available as adjacent space in order for viscous flow to take place. Whenever hydrogen bonding is present, n is generally less than three (52,53). However, it is 7.9 for molten cadmium chloride, which Harrap (54) interpreted as indicating that cadmium chloride in the liquid state exists to a certain extent as complex conglomerates that dissociate upon vaporization. Therefore the ratio n, as an indication of association in the liquid state, must be used with caution.

Association of any kind in liquids is evidenced by the fact that E_{vis} shows a marked temperature dependence. Also, although there is no direct relationship known, associated liquids tend to have higher values of E_{vis} than "normal" liquids.

Another method of showing whether association occurs in the liquid state was developed by Grunberg and Nissan (55). They noted that if the work of cohesion, W_c, in kcal./mole, as determined by the relationship,

$$W_c = 4.78 \times 10^{-8} \gamma \, V_m^{2/3} \, N^{1/3} , \qquad (9)$$

where γ is the surface tension in dynes/cm., is divided into E_{vis}, the ratio is approximately one. Since W_c is found from static measurements, it contains no energy terms derived from the breaking of bonds such as may be present in E_{vis}. For associated liquids, then, E_{vis} is noticeably larger than the work of cohesion.

Obviously the viscosity of a liquid is dependent on the size and shape of molecules as well as the intermolecular forces. The first exhaustive attempt to relate the viscosity of a pure liquid to its chemical structure was by Rodger and Thorpe (56,57), who compared viscosities at different temperatures and at different reduced temperatures but found trends only within homologous series.

In analogy with the parachor (See Surface Tension), Friend and Hargreaves (58) proposed a "rheochor" [R]

$$[R] = \frac{M}{d} \eta^{1/8} \qquad (10)$$

[R] was found to be an additive function of atomic rheochors, but the appearance of viscosity to the one-eighth power makes [R] insensitive to small changes in viscosities.

For a wide range of liquids, Souder (54) found that

$$\log(\log \eta) = md-2.9 \qquad (11)$$

where η is viscosity in millipoise , d is density in g./cc., and m is a constant which, when multiplied by the molecular weight, can be resolved into atomic and structural constants.

The above relationships are only approximate. Some authors believe that no simple, true relation between viscosity and chemical structure can be found because of the complexity of the liquid state. Bondi (59) proposed that attempts to relate viscosity data to chemical structure by means of structural constants be limited to geometrically similar compounds. Frenkel (60) postulated that the activation energy E_{vis} is

the fundamental variable which is related to the structure of the liquid, rather than the viscosity coefficient itself.

For the viscosity of an ideal binary solution, Eyring (53) proposed the following relationship:

$$\phi_m = N_1\phi_1 + N_2\phi_2 \qquad (12)$$

where ϕ_m is the fluidity of the mixture and N stands for the mole-fraction of a component. According to Harrap (54), however, the viscosity-composition isotherms generally show negative deviations from linearity, even at low concentrations of one component. Eyring proposed that the activation energy of a mixture is also a linear function of the composition. That is,

$$E_{vis} = N_1 E_{vis1} + N_2 E_{vis2} \qquad (13)$$

For non-ideal solutions Eyring added another term, $N_1N_2 E_{vis12}$, to express the effect of interaction between the components. According to Harrap (54) there is no adequate means of estimating the magnitude of this term.

Surface tension is the second mentioned physical property that has been used in investigating the liquid state and molecular structure. The surface tension of a liquid, γ, is the force per centimeter on the surface of a liquid which opposes the expansion of the surface area (40). This force arises because the molecules at the surface are not attracted equally in every direction as those molecules in the body of the liquid are. There is a net attraction for the surface molecules

toward the bulk of the liquid resulting in the liquid assuming a shape with a minimum of surface area (61). Therefore, as can be seen intuitively, surface tension depends on the intermolecular forces of a liquid.

In 1924 Sugden (62) empirically derived a quantity from surface tension which he named the "parachor" [P]. It is obtained from the relation

$$[P] = \frac{M \gamma^{1/4}}{d-d'} \qquad (14)$$

where M is the molecular weight, d is the density of the liquid and d' is vapor density. When the vapor density is negligible in comparison with the liquid density, the parachor relationship reduces to $V_m \gamma^{1/4}$, where V_m is the molar volume. Therefore a comparison of parachors is equivalent to comparing molecular volumes at equal surface tensions (63). The parachor being a form of molecular volume, it is not surprising that Bayliss (64) found one parachor unit to be equivalent to the volume of a sphere 0.210 $\mathring{A}$ in radius.

At first it was considered that the parachor of a compound could be obtained by adding together atomic constants, and this is roughly true. Using only the atomic constants, one can calculate parachors which agree to within one or two per cent with observed values (62). After it became evident that certain constitutive features, such as double bonds and steric effects, had to be taken into account, calculated values agreed to within 0.2 per cent with observed values for most organic liquids (63).

Of necessity, the atomic and structural parachors are averages obtained from many compounds. Sugden (62), Quayle (63), Mumford and Phillips (65), and Vogel (66), all have published values which can be considered reliable for organic liquids.

For inorganic liquids, however, some discrepancies appear. Liquid nitric oxide has a parachor twice the value calculated from the atomic constants determined from organic compounds (67). Nor is it possible to construct the parachor of phosphorus pentachloride from data on liquid phosporus and phosporus trichloride. When atomic parachors are derived from compounds in which the central atom is in different valencies, different values are obtained. Samuel (68) proposed that separate atomic constants be assigned to each of the different valencies of an atom and showed that this procedure restored agreement between calculated and observed molecular parachors for inorganic liquids. However, as a result of these discrepancies and the relative insensitivity of the parachor to structure, it is not considered a reliable criterion for distinguishing between alternative structures.

The parachor is useful in other ways. Herzog (69) has determined empirical relationships between the parachor and the critical constants of temperature, volume and pressure, and Langemann (70) has shown that there is a linear relationship between the parachor and molecular sound velocity, molar refraction, Souder's viscosity constant m, and Van der Waal's b.

Although the parachor is generally insensitive to temperature changes, when it does change with temperature, it is probably as a

result of association in the liquid state. For a typical associated liquid, e.g. ethanol, the parachor increases from 124.2 at -57° C. to 131.0 at 200° C.[1] This behavior is probably due to the fact that the surface tensions vary more rapidly with temperature for associated liquids than for unassociated liquids.

Another equation involving surface tension that has been widely applied is that proposed by Eotvos (71).

$$\gamma(Mv)^{2/3} = k(t_c - t) \qquad (15)$$

where t_c is the critical temperature in °C. and t is the temperature at which the surface tension and the specific volume v are measured. The constant k is 2.1 for most liquids, but it decreases to around unity for highly associated liquids. To fit the experimental data better, Ramsay and Shields (72) altered equation (15) to

$$\gamma(Mv)^{2/3} = k(t_c - t - 6) \qquad (16)$$

It was once thought that an association factor x could be obtained by the process of setting k equal to 2.1 for all liquids, solving for the molecular weight, and then calculating x from the ratio M(observed)/ M(simplest formula). However, as Partington (41) stated, "Although low values of k mean association, it is fairly well agreed that calculation of association factors from the Ramsay-Shields k is unjustified."

---

[1] Again inorganic liquids furnish unusual exceptions. The parachor of palladium in compounds of the type $(R_2S)_2\ PdX_2$ (R means alkyl, X halogen) changes rapidly with temperature (73).

The variation of surface tension with temperature has no sound theoretical basis at the present. While experimental evidence indicates that many compounds have surface tensions that vary linearly with the temperature, there are many compounds for which the relationship is not linear over a large temperature range. Equations (17-20) are but a few of the empirical relationships proposed.

	reference	
$\gamma = A-BT$	(74)	(17)
$\gamma = A(1-T/T_c)^B$	(75)	(18)
$\gamma^{5/6} = A-BT$	(76)	(19)
$\log \gamma = A+B/T-C\log T$	(77)	(20)

Even though the surface tension disappears at or near the critical temperature, then, extrapolation of data to zero surface tension can yield but estimates of the critical temperature.

APPARATUS AND METHODS

Review of Methods

Viscosity Measurements

Many methods have been developed for measuring viscosity. The shear of a liquid by rotating cylinders, oscillating bodies, falling bodies, and capillary tubes have been used. However, only a few methods can be treated with sufficient mathematical precision to warrant absolute measurements.

The Ostwald type viscometer (Figure 1) is the simplest and most precise method. A known amount of liquid is drawn into the upper reservoir, and the time required for the meniscus to flow between two reference points is noted. Poiseuille's law, Equation (1), is then used to calculate the viscosity. Because the liquid head is the driving force, and it constantly changes, some sort of average head times the density is taken for the constant pressure. Meissner's formula (78),

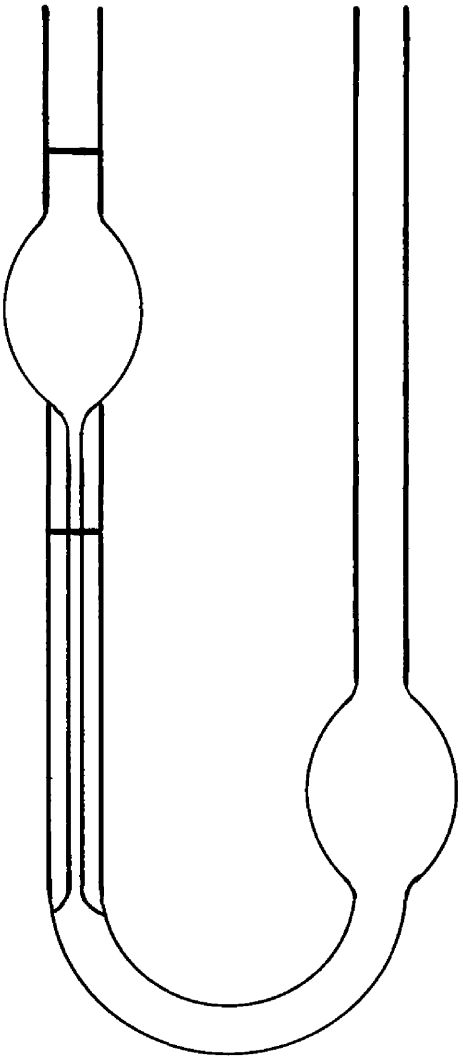
$$P = d\bar{h} = \frac{d(h_1-h_2)}{\ln(h_1/h_2)} \qquad (21)$$

where h_1 and h_2 are the hydrostatic heads at the beginning and the end of the flow, has been most often applied.

Because of Poiseuille's equation it was assumed that there is no acceleration of the liquid as it flows through and that the liquid emerges from the capillary with zero velocity, two corrections are necessary for calculating absolute viscosities. Couette (41) studied

FIGURE 1

OSTWALD VISCOMETER



the consequences of the acceleration of the fluid entering the capillary from the reservoir, and he concluded that the length of the capillary should be increased by a factor 1.64r, where r is the radius. Also Hagenbach (79) derived a correction for the kinetic energy of the emerging liquid. Poiseuille's equation then becomes

$$\eta = \frac{\pi r^4 gdj}{8V(1+1.64r)L} \times \frac{h_1-h_2}{\ln h_1/h_2} - \frac{Vd}{8\pi(1+1.64r)Lj} \qquad (22)$$

Because the factors mentioned above tend to cancel when two liquids are compared in the same apparatus, good relative measurements of viscosity are possible. If the same volume of sample is used, then Equation (1) becomes

$$\eta = Adj \qquad (23)$$

where A is a calibration constant of the instrument. A two-constant equation given by Barr (80) permits more accurate correction for the kinetic energy effect:

$$\eta = Cdj - Bd/j \qquad (24)$$

Two calibrating liquids are necessary to determine the constants B and C.

Another method capable of yielding absolute results is the measurement of the torque required to rotate a cylinder immersed in a liquid. Barr (80) and Fischer (81) have derived the equations which relate the viscosity to torque; they found

$$\eta = \frac{60}{8\pi^2} \times \frac{1}{r^2L} \times \frac{T'}{(r.p.m.)} \qquad (25)$$

where r is the radius and L the length of the cylinder, and T is the

torque which produces a constant rate of rotation measured in revolutions per minute (r.p.m.). In Equation (25), surface tension and end effects were neglected, but they can be minimized by proper design and manufacture of the apparatus. This method has been applied most successfully to systems of highly viscous liquids (81).

Measurement of the rate of fall of a body through a fluid is another means of determining viscosities. Heiks and Orban (82) used a solid cylinder falling through a close-fitting tube to determine the viscosity of benzene up to the critical temperature. For measuring relative viscosities, they used the following equation:

$$\frac{\eta_1}{\eta_0} = \frac{(\sigma_1 - d_1)}{(\sigma_0 - d_2)} \frac{j_1}{j_0} \qquad (26)$$

where σ represents the density of the solid cylinder, d the density of the liquid, j the time, and the subscript zero refers to a standard calibrating liquid. This method is suitable for high pressure and temperature investigations (82).

Surface Tension Measurements

The most accurate method for determining the surface tension of a liquid consists in measuring the height to which it rises in a capillary tube (40). If the contact angle is less than 90°, the liquid rises until the force due to surface tension tending to pull up the liquid is balanced by the force of gravity. If θ is the angle of contact between the wall and the liquid, the force upward is $2\pi r \gamma \cos \theta$, where r is the radius of the capillary, and $2\pi r$ is the perimeter. The force downward,

is the weight of the liquid above the bottom of the meniscus is neglected, is πr^2hdg, where h is the rise, πr^2h is the volume of the suspended liquid, d is the density of the liquid, and g is the acceleration of gravity. At equilibrium the forces are equal, and

$$2\pi r \gamma \cos\theta = \pi r^2hdg,$$

or

$$\gamma = \frac{g}{2} \frac{rdh}{\cos \theta} \qquad (27)$$

For very accurate work, certain corrections are made (See 77). A meniscus correction may be made by adding a term r/3 to the measured height. The effect of vapors over the meniscus is accounted for by subtraction of the vapor density from the liquid density. When a capillary of radius r_1 is contained in another tube of radius r_2, the effective radius becomes the reciprocal of $1/r_1 - 1/r_2$ (83). The method is capable of high precision only when the angle of contact is small or zero. This is a consequence of the fact, as Harkins (84) claims, that contact angles can only be measured to within 25 per cent. With the above factors taken into account, Equation (27) becomes

$$\gamma = \frac{g}{2} \frac{(d-d')\ (h+r/3)}{1/r_1 - 1/r_2} \qquad (28)$$

Another method, often used because of its convenience, is called the maximum bubble-pressure method. A capillary tube, which has one end ground flat, is mounted vertically with that end immersed in the liquid, and an inert gas is forced through it. The pressure at which the bubbles break away from the tip has been related to the surface tension by many

authors. In theory, this method should yield the greatest accuracy, because of the constant forming of a new surface in the body of the liquid. However, no exact expression has been developed. Two recent modifications of this method in which the pressure does not have to be measured are given by Shah and Pathak (85) and Cuny and Wolf (86). An obvious disadvantage of the maximum bubble-pressure method is that it cannot be applied in a sealed system.

The drop-weight method of measuring surface tension consists of weighing a known number of drops falling slowly from the tip of a capillary. The weight has been related to the surface tension by factors described by Harkins (84), whose detailed studies have made this an accurate method.

Many other methods have been used to measure surface tension (See 84), but they are of doubtful accuracy.

Construction Materials

The study of the physical properties of halogen fluorides, as it has been mentioned earlier, is hampered by their chemical reactivity. Materials for construction of equipment must be chosen to prevent corrosion and consequent contamination of the samples. Nickel and Monel metal are suitable for containing halogen fluorides in the liquid form, but once corroded, require mechanical action to clean the surface. Copper and brass are useful when the only contact is with the vapors. When visibility is required, fluorothene (polychlorotrifluoroethylene), a plastic

that machines readily and is transparent when thin, is a possible construction material.

It was once thought that the halogen fluorides attacked glass. However, iodine pentafluoride was prepared and stored in Pyrex[1] (87). Bankes and Maddock (20) found that chlorine trifluoride and bromine pentafluoride did not attack glass if all moisture was excluded. Also, Johnston, et al., (83) used Pyrex in their determination of the surface tension of fluorine at low temperatures. Bromine trifluoride was found to react slowly with Pyrex, but not with Vycor.[2] Therefore, glass or Vycor can be considered possible materials for constructing apparatus.

Apparatus

The first attempt to measure the viscosities was by the rotating cylinder method. The apparatus, which was designed and built by J. L. Speirs, is shown in Figure 2. It features good temperature control and direct reading of viscosities.

The upper part A was a Brookfield viscometer,[3] which is powered by a small, self-starting, synchronous motor that drives the nickel-plated spindle B at four different speeds. Between the spindle and the motor is a beryllium-copper spring. As the motor turns the spindle, the spring moves a pointer in proportion to the drag exerted on the

---

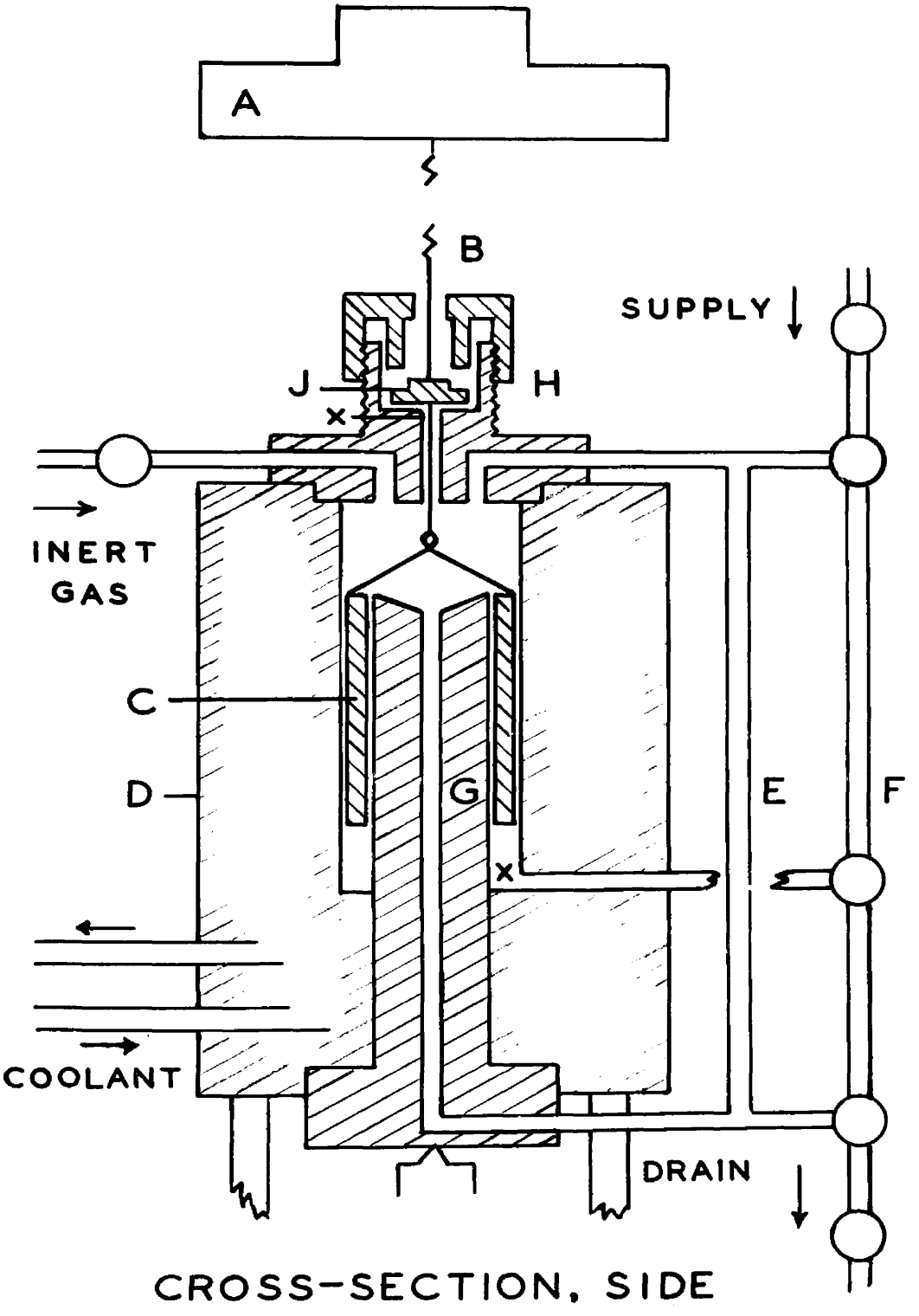
[1] Trademark of Corning Glass Works, Corning, N. Y.

[2] Ibid.

[3] Model LVF made by Brookfield Engineering Laboratories, Inc., Stoughton, Mass.

FIGURE 2

APPARATUS I, VISCOSITY



CROSS-SECTION, SIDE

annular cylinder C. The cylinder, made of Monel, is 2.28 inches long, 1.480 inches in diameter, 0.065 inches thick, and rotates with a clearance of 0.030 inches. It was machined to a tolerance of ± 0.001 inches. The length of the cylinder was adjusted until direct readings were obtained on the scale with water as a standard.

The cooling jacket and housing D and all the lower part except the fluorothene level indicators E and F were constructed of Monel metal. In order to reproduce a constant level of immersion for the cylinder, an overflow drain G was incorporated. The total volume of sample required for operation is 25 cc.

The entire apparatus is suspended within a large tripod, and the lower part supported on three adjustable legs by means of which the upper and lower parts can be aligned and leveled.

For prefluorinating the apparatus, a seal around the spindle is necessary and is accomplished by screwing cap H down on washer J, forcing it against a Teflon gasket. A spring arrangement allows for the necessary extension in the spindle. When the viscometer is operating, cap H is raised, and the washer turns with the spindle. To provide an inert atmosphere, helium is blown over the liquid.

A vacuum-tight seal was never attained, and corrosion products accumulated at points x. Although carbon tetrachloride was used to rinse out the viscometer, it could never be adequately cleaned, and corrosion became severe. For these reasons the method outlined below was employed.

The apparatus by which both the surface tension and the viscosity were measured is shown in Figure 3. It was patterned after the one used by Doescher and Elvrum (78) when they determined these properties for liquid fluorine. To measure the surface tension, the rise in the capillary is observed, and to measure the viscosity, the time of flow through the capillary is obtained.

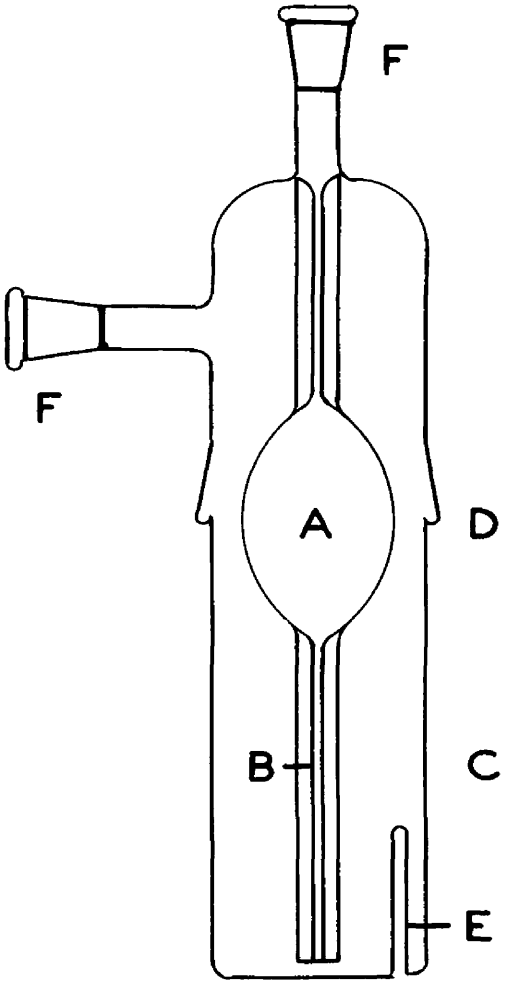
In Apparatus III, used for measurements on iodine pentafluoride and bromine pentafluoride, the reservoir A holds 3cc. of liquid. The precision-bore Pyrex capillary B is 3/4 mm. in diameter. The outer shell or container C was readily constructed from a large, standard-taper glass joint D, which greatly facilitated cleaning. Through the bottom of C was inserted a thermocouple-well made of thin-wall tubing. The standard-taper joints F allow the apparatus to be attached to the gas-handling system described in a later section.

In Apparatus IV, used for measurements on bromine trifluoride, the reservoir holds 8 cc. of liquid. Two capillaries were used. One was a precision-bore Pyrex capillary, again 3/4 mm. in diameter. The other one, used for viscosity measurements, was made of Vycor and was 1.16 mm. in diameter. The container C is also made of Vycor. In other respects, Apparatus IV is like Apparatus III.

For surface tension measurements the first apparatus, Apparatus II (Figure 4), was made from a block of fluorothene. The capillary was formed by a 1/32 inch drill extended by silver-soldering a length of steel wire to it. To provide thin walls for transparancy excess plastic was removed by milling. All joints were sealed with fluorothene wax to

FIGURE 3.

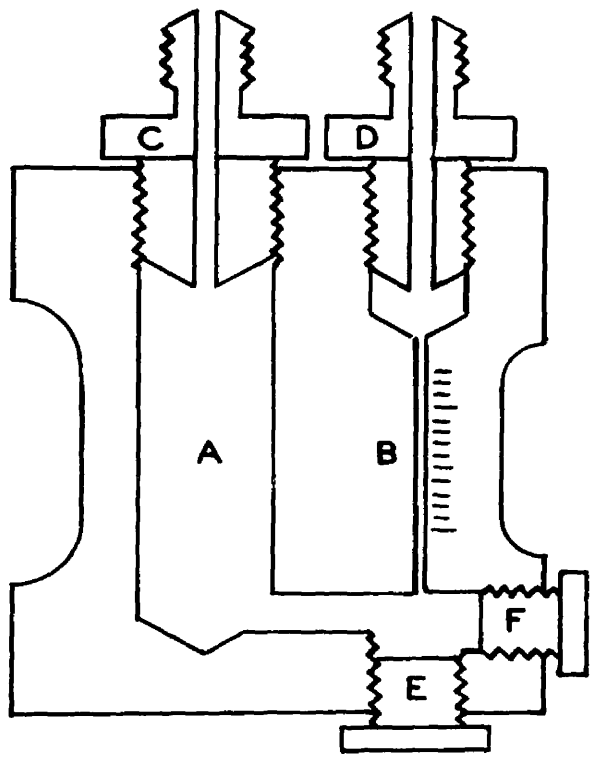
APPARATUS III AND IV
VISCOSITY AND SURFACE TENSION



A, RESERVOIR - 3 cc. in III, 8 cc. in IV.
B, CAPILLARY - 4.3 cm. in III, 7.7 cm. in IV.
D, $\overline{\$}$ 29/42 in III, $\overline{\$}$ 34/49 in IV.
E, THERMOCOUPLE-WELL
F, $\overline{\$}$ 10/30 in III and IV.

FIGURE 4

APPARATUS II, SURFACE TENSION



MADE OF FLUOROTHENE

A, RESERVOIR B, 1/32" CAPILLARY

C, 3/8 X 5/8" PLUG D, 3/8 X 3/8" PLUG

E, F, 3/8 AND 1/4" PLUGS

make vacuum-tight seals. When it became evident that bromine pentafluoride dissolved some of the wax and bromine trifluoride did not wet the plastic, this apparatus was rejected.

Temperature Measurement and Control

Temperature measurements were made with a copper-constantan thermocouple which was made by fusing together the ends of number 22 wire.[1] The output was measured on a precision potentiometer[2] circuit. The ice-point reference was prepared by rinsing crushed ice with distilled water, then mixing the ice with de-ionized water in a clean Dewar flask. The potentials were converted to Centigrade degrees by interpolation on an expanded plot constructed from tables (88). The thermocouple was compared with a mercury thermometer previously calibrated by a platinum resistance thermometer[3] and was found to be accurate to $\pm$ 0.1° C.

Temperature control was maintained by means of two baths. The bath apparatus in which the viscosity-surface tension apparatus was immersed consisted of a clear Dewar flask that was detachable. In the bottom half of the flask was placed an aluminum coil through which water was circulated by a small, impeller-blade pump submerged in a five-gallon reservoir.

---

[1] The wires were purchased from the Wheelco Instrument Company, Chicago, Ill.

[2] A type K-2 potentiometer with a type E galvanometer made by the Leeds and Northrup Company, Philadelphia, Pa.

[3] Appendix B contains the data for the calibration of the thermometer.

In addition to the pump, the second bath contained two knife-edge heaters serving as the heating elements. An auxiliary heater of 500-watts capacity, operated from an auto-transformer, served to heat the baths rapidly and to aid maintainance of temperatures from 30° C. to 45° C. A single 250-watt heater was controlled by the thermoregulating system and served to maintain the thermostat between 13 to 30° C. For temperatures less than room temperature and above 13° C., a copper coil which circulated tap water was added.

The thermoregulator was identical to the one described by Pruett (89). The temperature-sensitive element was a thermistor in a Wheatstone-bridge circuit, and the heater current was controlled by a saturable reactor. The circuit was an adaptation of that published by Burwell et al. (90). Regulation of the temperature was possible to ± 0.05° C. in the large reservoir and in the Dewar flask.

The Gas-Handling System

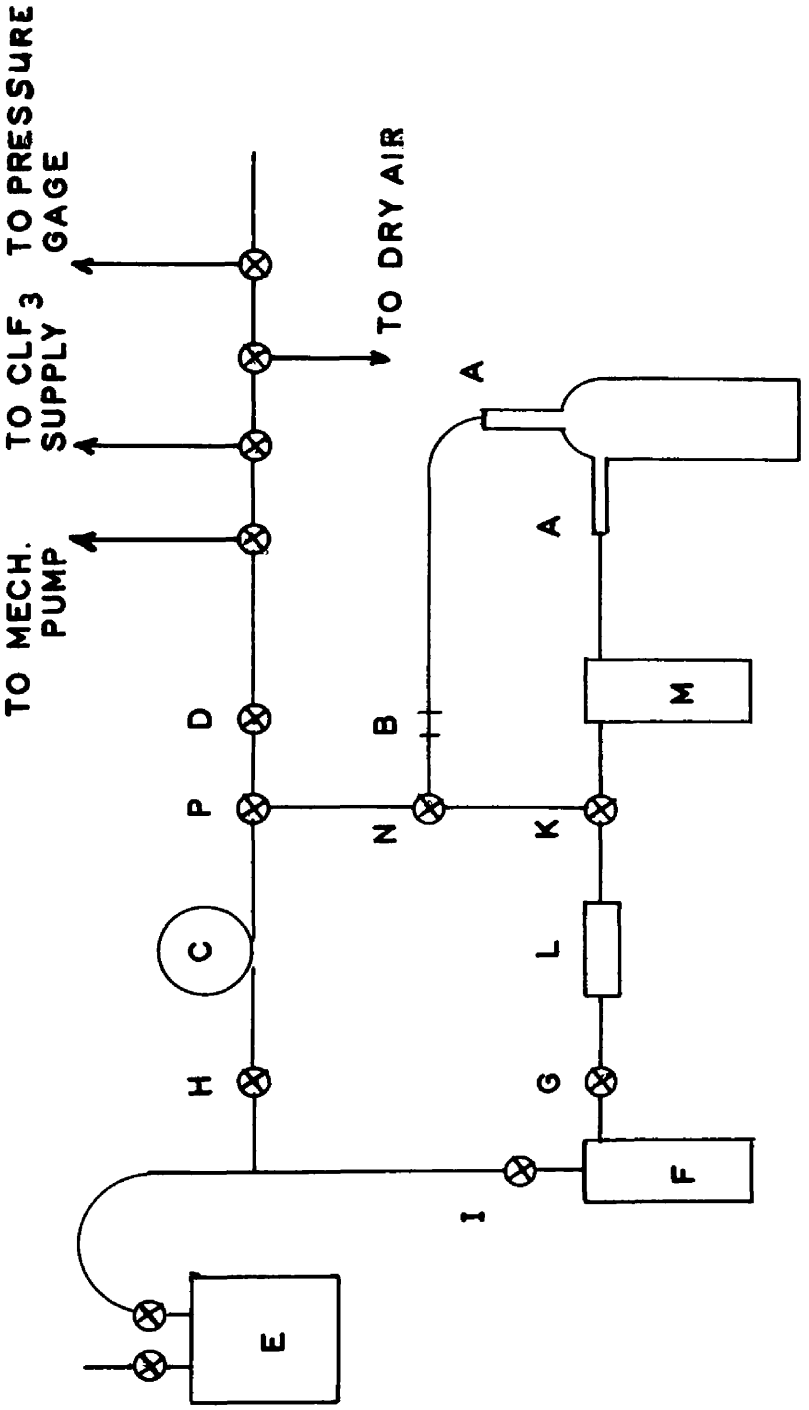
The vacuum system designed for the handling and final purification of the halogen fluorides is shown schematically in Figure 5. The viscosity-surface tension apparatus was attached at points A by means of 10/30 standard-taper joints, the male part being machined from Monel. At point B was a Monel Swagelok[1] union which allowed the apparatus to be tightened into place free of residual torque.

Except for a copper expansion loop C, all tubing (1/4 inch in

[1] Manufactured by the Crawford Fitting Company, Cleveland, Ohio.

FIGURE 5

VACUUM SYSTEM FOR HANDLING HALOGEN FLUORIDES



diameter) was made of Monel, as were the valves (Hoke[1] model M1132).

Valve E opened to the gas handling system described by Thompson (16). The only change from his description was the addition of a protective cold-trap placed before the vacuum pump. Although this trap was of Pyrex, no sign of etching occurred at any time. Not more than two cc. of liquid was allowed to accumulate. The remainder of the system is described in the following section.

Procedure

The entire system was first pre-fluorinated by the introduction of chlorine trifluoride to a pressure of 500 mm.[2] The gases were then pumped off, valves G and H closed and about 6 cc. of liquid drawn from the fluorothene storage container D into the Monel trap F. Valves J and K were closed, and, when valve G was opened, the liquid slowly vaporized into the rest of the system. The tube L contained sodium fluoride pellets[3] which removed any hydrogen fluoride present in the vapors. After an estimated 0.5 cc. of liquid had been pumped away, a Dry-ice-acetone mixture in a Dewar flask was raised around the cell, and solid distillation products allowed to collect on the glass walls. A fluorothene trap E was added to provide one additional stage of purification in the case of bromine trifluoride.

---

[1] Manufactured by Hoke, Inc., Englewood, N. J.

[2] Pressure was measured by a Helicoid gage made by American Chain and Cable Company, Chicago, Ill.

[3] The 1/8 inch pellets were purchased from the Harshaw Chemical Company, Cleveland, Ohio.

When enough material had collected in the cell (as solid) the distillation was halted by closing valve G, dry air was admitted, and the solid allowed to melt. If insufficient sample had collected the liquid was distilled back into trap F, because an open capillary was necessary to maintain a pressure at which a reasonable rate of distillation occurred.

Next the thermocouple was attached and the thermostat raised into position. Thermal equilibrium was considered to be attained when successive measurements of the temperature at ten minute intervals showed no change.

Capillary rise was measured by means of a cathetometer that was capable of measuring length to plus or minus 0.002 cm. Before each measurement it was leveled, the cross-hairs aligned with a plumb-bob line, and the plumb of the capillary checked. At each temperature both levels of the liquid were determined from three to five times, depending upon how reproducible the readings appeared to be. Before each measurement the valves N and K were opened to equalize the pressure in both tubes of the apparatus and the meniscus was agitated to cause it to seek its own level.

For viscosity measurements the reservoir was filled in two different ways. Either valve N was closed and dry air admitted through valve K to force the liquid up, or valve K was closed and the liquid was drawn up slowly by evacuating the reservoir through valve N. The methods were alternated to maintain a pressure as near to that of the atmosphere as possible. Great care was exercised to insure that the

level of the liquid never rose high enough to touch the Monel standard-taper joint. Valve P was then closed, and the pressure was equalized in both sides of the viscometer by opening valve N or K (whichever was closed).

The time of flow between the two marks made above and below the reservoir was measured with a stopwatch,[1] the accuracy of which was checked by time signals from station WWV. Measurements were repeated until three times were obtained which differed by no more than 0.1 seconds. Immediately after flow ceased, the temperatures were recorded, then the level of the capillary tip and level of liquid were determined by use of the cathetometer.

A procedure for handling the halogen fluorides in glass was developed in this laboratory. All glass components were first cleaned, rinsed well with distilled water, and dried at 150° C. They were then assembled in position in the vacuum system, all ground joints being sealed with fluorothene wax. The system was evacuated to a pressure of 0.5 mm. or less and gently flamed, care being taken not to melt the wax. Next chlorine trifluoride was introduced to a pressure of 500 mm., and was condensed as a liquid wherever possible. New metal parts created a white fog which settled on the glass when the chlorine trifluoride was first introduced. However, the glass was not etched, if the process was done slowly, and the powder was easily removed by disassembling the apparatus and washing with water. New apparatus required from two to

---

[1] Type 200B, made by A. R. and J. E. Meylan Stopwatch Co., New York, N. Y.

three repetitions of the above process before no white powder appeared.

To dispose of a sample of halogen fluoride, dry air was admitted to the cell, which was then removed from the system and the liquid poured into a fluorothene beaker and allowed to evaporate. The cell was immediately sealed back into position and evacuated to remove last traces of liquid. At this point the cell was ready to be cleaned.

Materials

All halogen fluorides were purchased from the Harshaw Chemical Company. They were purified by distillation in a Monel still described by Thompson (16) and then were stored in fluorothene beakers.

Previous samples of halogen fluorides had been distilled in the same Monel still. According to Malik (91), iodine pentafluoride was 0.0025 molal in impurities, bromine pentafluoride 0.02 molal, and bromine trifluoride around 1-2 molal. Although the samples used here were a different lot, they were believed to have essentially the same concentration of impurities, except for bromine trifluoride, which probably was less than one molal in impurities. The additional step of distillation into the viscosity cell helped to eliminate previous impurities, but occasionally some dirt or water vapor in the cell would contaminate the liquid. Direct measurement of the impurity content of the material in the apparatus was not possible since it was not designed for precision melting point measurements.

A useful qualitative criterion of purity was the color of the sample. If the apparatus was not prefluorinated, highly colored reaction products

of the halogen fluorides appeared. When iodine pentafluoride was pure it was colorless, and when it was contaminated it assumed a yellowish to light blue tinge. Colorless bromine pentafluoride took on a faint yellow tinge which became orange upon further contamination, and bromine trifluoride, straw-yellow when pure, turned first a bright orange, then a cherry-red as the concentration of impurities increased. For iodine pentafluoride and bromine pentafluoride no observable increase in the flow time was noted with the appearance of a slight color. For bromine trifluoride, however, bubbles appeared, smooth operation of the viscometer was impeded, and no further readings were recorded on that sample.

Another part of the procedure in checking for impurities was noting any residue left in the apparatus in those cases where the sample was not immediately disposed of but distilled into some container. Only for bromine trifluoride did a visible residue ever appear in the apparatus.

Treatment of Calibration Data

Viscosity Measurements

The calibration of the cell for viscosity measurements involved few changes in the procedure and apparatus from that already described for handling the halogen fluorides. The gas-handling system was altered by removal of the sodium fluoride and by the substitution of a different vacuum pump. Instead of the calibration liquids being distilled into the cell, they were poured in after several rinsings were made. Also, to reduce chance of contamination, no wax was used to seal the joints.

Because the volume of halogen fluoride distilled into the cell differed for each sample, it was necessary to know precisely the effect of the level of the liquid upon the time of flow. Therefore, the apparatus was calibrated with different amounts of liquid, the height of the surface above the tip of the capillary tube being measured by the cathetometer. At each level the times of flow were determined as a function of temperature over a 20 degree range.

Apparatus III (Figure 3) was calibrated with benzene and carbon tetrachloride. Although water was tried, its surface tension prevented complete drainage of the reservoir. However, in Apparatus IV, (Figure 3) the Vycor capillary was sufficiently long to allow the use of water, and benzene was used for the second calibrating fluid.

The water samples were from the laboratory distilled water supply, further purified by passage through an ion-exchange column.[1] Its conductivity indicated less than one part per million impurities. The benzene, Baker's A. R. Grade, was partially crystallized then distilled from calcium hydride in an efficient packed-column.[2] At 25° C. the density was found to be 0.87355 g./cc., about the mean of the values listed by Egloff (92). The carbon tetrachloride, Baker's A. R. Grade, was distilled over calcium chloride in the previously mentioned packed-column, its boiling-point range being 76.0-76.4° C. at 723.8 mm. pressure. All liquids were used shortly after purification.

---

[1] Deeminizer, product of Crystal Research Laboratories, Inc., Hartford, Conn.

[2] The benzene was supplied by Dr. T. L. Brown.

A check on the purity of these calibration liquids was made on each sample in the apparatus by means of the surface tension measurements. If the value differed by more than 0.3 dyne/cm. from the accepted value, the sample was discarded and the apparatus cleaned.

The data obtained are listed in Tables V and VI.

In order to find the constants B and C in Equation (24), first log dj was plotted versus the reciprocal of the absolute temperature. A family of straight, parallel lines resulted, one line for each level of liquid used. When the vertical distances between lines for a single liquid were compared, it became obvious that the intercepts were directly proportional to the level of liquid in the apparatus. Therefore all time-density data for one liquid were condensed into one empirical equation of the form

$$\log dj = \frac{a}{T} - b + c(m-f) \qquad (29)$$

where a is the slope, m is the liquid level or mark, and b, c, f are constants. The constant f is actually the lowest mark measured for the calibrating liquids, and the constant b is the intercept calculated for that level. Calculations of the slopes and intercepts were done by a least squares method described by Wilson (93).

For Apparatus III,

$$\log dj = 400/T-0.0264 + 0.114(m-1.00) \qquad (30)$$

For Apparatus IV,

$$\log dj = 496/T-0.3490 + 0.046(m-1.75) \qquad (31)$$

By means of Equation (30) or (31) the flow-times of one calibrating liquid were calculated for those liquid levels at which flow-times were measured for the second liquid. Then the constant B was calculated from the equation given by Barr (80)

$$B = \frac{j_1 j_2}{j_2^2 - j_1^2} \left[\frac{\eta_2 j_1}{d_2} - \frac{\eta_1 j_2}{d_1} \right] \qquad (32)$$

where the subscripts refer to the different calibration liquids and the other symbols have their previous meanings. Pertinent data for these calculations are listed in Tables VII and VIII. The values of density and viscosity were obtained by interpolation from graphs of literature data versus the temperature. For benzene and carbon tetrachloride values from Timmermans (94) were used, and for water values from the Handbook of Chemistry and Physics (95) were used.

Next the constant C was calculated at each temperature and level of liquid used experimentally, by means of the following equation:

$$C = \frac{\eta + Bd/j}{dj} \qquad (33)$$

Data from which C was calculated are listed in Tables IX and X. Unlike the constant B, which was a constant of the apparatus under all conditions, the constant C was a function of temperature and of the level of liquid. When C was plotted versus the reciprocal of the absolute temperature a family of lines was obtained as shown in Figure 6. Values of C were read directly from such a graph.

TABLE V

VISCOSITY CALIBRATION DATA FOR APPARATUS III

Sample	Level Mark (cm.)	Millivolts	Time (sec.)
Benzene I	1.0	1.101	23.7
		1.000	23.7
		1.002	23.6
		0.780	24.9
		0.780	24.8
		0.777	24.7
		1.350	21.8
		1.350	21.7
		1.350	21.7
		1.587	21.0
		1.618	20.9
		1.608	20.7
		1.630	20.7
Benzene II	1.5	0.990	26.8
		0.719	28.6
		0.720	28.5
		0.764	28.1
		1.047	26.4
		1.047	26.3
		1.290	25.2
		1.286	25.1
		1.517	24.3
		1.525	24.2
		1.546	24.0
		1.556	23.9
Benzene III	1.4	1.060	25.6
		1.046	25.7
		1.058	25.6
		0.807	27.0
		0.810	27.1
		0.582	29.4
		0.582	29.2
		0.580	29.4
		1.467	24.0
		1.490	23.9
		1.130	24.4
		1.310	24.5
		1.310	24.4

TABLE VI

VISCOSITY CALIBRATION DATA FOR APPARATUS IV

Sample	Level Mark (cm.)	Millivolts	Time (sec.)
Water I	1.75	0.526	24.5
		0.550	24.3
		0.575	24.1
		0.790	21.9
		0.795	21.9
		0.795	21.9
		1.035	20.4
		1.037	20.4
		1.040	20.3
		1.334	18.7
		1.334	18.7
		1.334	18.6
		1.539	17.7
Water II	2.49	1.126	21.3
		1.126	21.4
		0.734	24.4
		0.734	24.3
		1.502	19.2
		1.502	19.3
		1.502	19.3
Water III	2.20	0.630	24.5
	2.20	0.630	24.4
	2.21	0.892	22.5
		0.898	22.4
		0.898	22.4
		1.105	21.5
	2.22	1.320	19.5
		1.322	19.6
		1.322	19.5
Benzene I	2.32	0.990	18.6
		0.992	18.6
		0.989	18.7
		0.665	19.7
		0.667	19.6
		0.669	19.6
Benzene II	2.41	0.690	19.7
		1.118	18.8

TABLE VII

DATA FOR CALCULATING CONSTANT B

Liquid	Level Mark (cm.)	Temp. °C.	Density g./cc.	Time (sec.)	η, cp.
		Apparatus III			
Benzene	1.30	19.7	0.879	25.3	0.652
	1.30	26.3	0.872	26.9	0.591
	1.30	26.8	0.872	25.2	0.587
	1.30	33.5	0.865	23.7	0.532
	1.10	19.3	0.880	25.6	0.656
Carbon Tetra-chloride	1.30	19.7	1.595	23.1	0.977
	1.30	26.3	1.582	21.9	0.891
	1.30	26.8	1.581	21.8	0.887
	1.30	33.5	1.568	20.8	0.811
	1.10	19.3	1.596	22.1	0.986
		Apparatus IV			
Benzene	2.32	24.8	0.874	22.0	0.603
	2.32	17.0	0.884	19.6	0.682
	2.41	25.7	0.873	18.8	0.596
	2.41	17.6	0.882	19.7	0.675
Water	2.32	24.8	0.997	22.0	0.898
	2.32	17.0	0.999	24.7	1.083
	2.41	25.7	0.997	22.0	0.880
	2.41	17.6	0.999	24.4	1.066

TABLE VIII

VALUES OF THE CONSTANT B

Apparatus III			Apparatus IV		
Level Mark, cm.	Temp., °C.	B	Level Mark, cm.	Temp., °C.	B
1.30	19.7	2.08	2.32	25	5.09
1.30	26.3	2.03	2.32	17	5.59
1.30	26.8	1.87	2.41	25	5.41
1.30	33.5	2.04	2.41	17	5.10
1.10	19.3	2.25			
	Average	2.1		Average	5.3

TABLE IX

DATA FOR CALCULATION OF THE CONSTANT C
BENZENE IN APPARATUS III

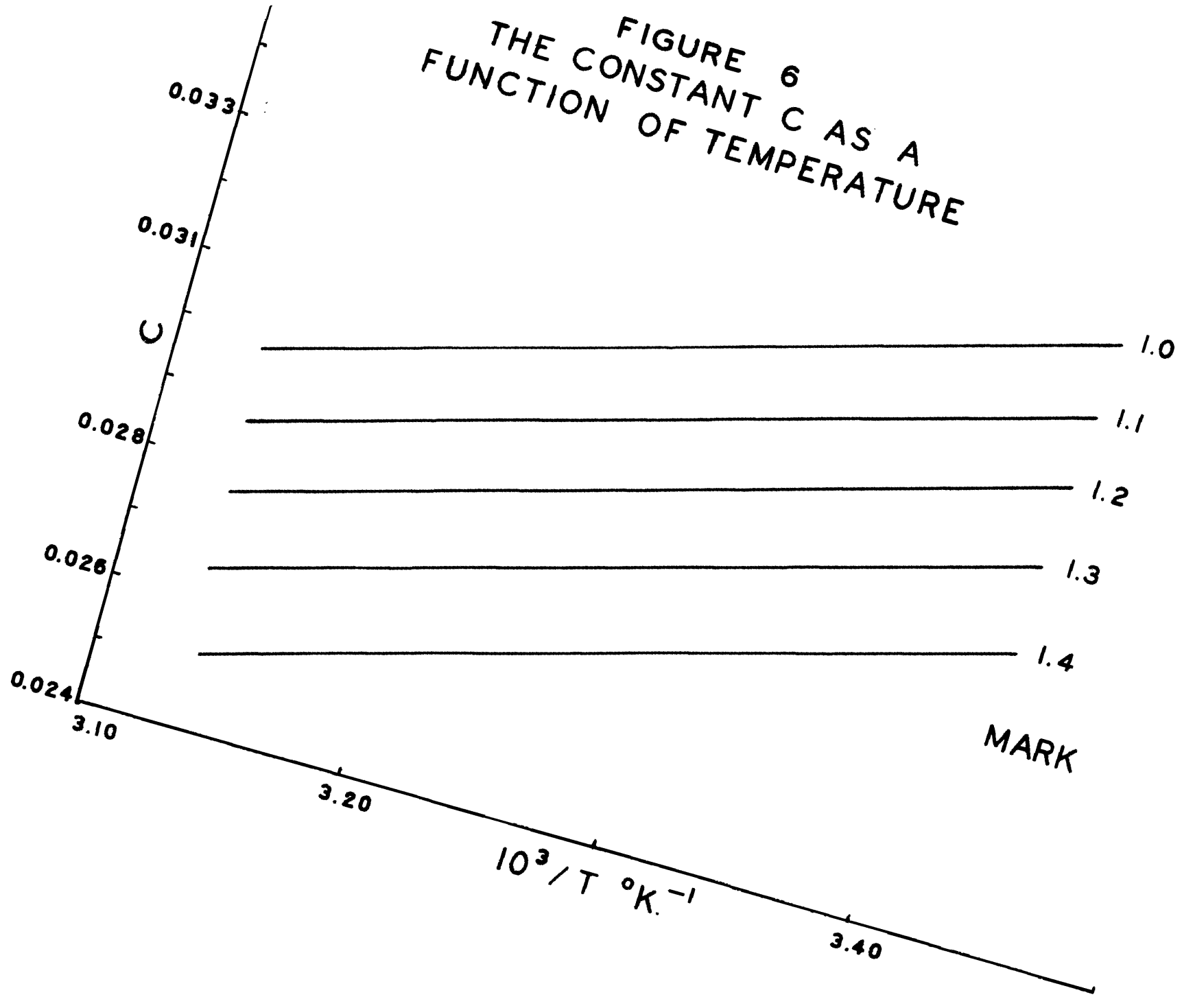
Level Mark (cm.)	$\frac{10^3}{T}$ $^{\circ}K.^{-1}$	η cp.	Density g./cc.	dj g.-sec./cc.	C
1.00	3.348	0.598	0.873	20.55	0.0328
	3.350	0.600	0.873	20.59	0.0329
	3.350	0.600	0.873	20.59	0.0329
	3.413	0.651	0.879	21.82	0.0332
	3.414	0.652	0.879	21.84	0.0332
	3.415	0.653	0.880	21.86	0.0333
	3.257	0.530	0.864	18.90	0.0324
	3.257	0.530	0.864	18.90	0.0325
	3.257	0.530	0.864	18.90	0.0325
	3.199	0.486	0.858	17.91	0.0319
	3.191	0.481	0.858	17.78	0.0320
	3.194	0.483	0.858	17.83	0.0319
	3.187	0.479	0.857	17.72	0.0319
1.50	3.353	0.602	0.874	20.78	0.0322
	3.431	0.667	0.881	25.29	0.0289
	3.431	0.667	0.881	25.29	0.0289
	3.417	0.655	0.880	24.97	0.0288
	3.338	0.590	0.872	23.22	0.0284
	3.338	0.590	0.872	23.22	0.0283
	3.273	0.542	0.866	21.87	0.0281
	3.274	0.543	0.866	21.89	0.0281
	3.216	0.499	0.860	20.75	0.0276
	3.214	0.498	0.860	20.71	0.0271
	3.209	0.494	0.860	20.62	0.0276
	3.208	0.493	0.859	20.60	0.0276
1.40	3.334	0.588	0.872	22.53	0.0293
	3.338	0.590	0.872	22.61	0.0292
	3.334	0.588	0.872	22.53	0.0293
	3.405	0.643	0.879	23.51	0.0302
	3.405	0.643	0.879	23.51	0.0302
	3.404	0.642	0.878	23.49	0.0302
	3.471	0.709	0.885	25.56	0.0302
	3.471	0.709	0.885	25.56	0.0302
	3.472	0.710	0.885	25.59	0.0302
	3.228	0.508	0.861	20.44	0.0285
	3.223	0.504	0.861	20.34	0.0285
	3.224	0.505	0.861	20.36	0.0285
	3.268	0.538	0.865	21.20	0.0289
	3.268	0.538	0.865	21.20	0.0289

TABLE X

DATA FOR THE CALCULATION OF THE CONSTANT C
WATER IN APPARATUS IV

Level Mark (cm.)	$\frac{10^3}{T}$ $^{o}K.^{-1}$	η cp.	Density g./cc.	dj g.-sec./cc.	C
1.75	3.488	1.187	0.999	24.05	0.0583
	3.481	1.168	0.999	23.86	0.0581
	3.473	1.149	0.999	23.64	0.0579
	3.409	1.002	0.998	21.97	0.0566
	3.408	1.000	0.998	21.95	0.0566
	3.408	1.000	0.998	21.95	0.0566
	3.341	0.871	0.997	20.33	0.0556
	3.341	0.871	0.997	20.33	0.0556
	3.340	0.870	0.997	20.30	0.0557
	3.262	0.746	0.995	18.58	0.0553
	3.262	0.746	0.995	18.58	0.0553
	3.262	0.746	0.995	18.58	0.0554
	3.210	0.677	0.993	17.51	0.0556
2.49	3.317	0.831	0.996	21.39	0.0504
	3.317	0.831	0.996	21.39	0.0504
	3.426	1.037	0.999	24.23	0.0518
	3.423	1.033	0.999	24.15	0.0518
	3.220	0.689	0.993	19.15	0.0503
	3.220	0.689	0.993	19.15	0.0502
	3.220	0.689	0.993	19.23	0.0501
2.21	3.458	1.327	0.999	24.40	0.0544
	3.451	1.310	0.999	24.21	0.0541
	3.381	1.180	0.998	22.37	0.0527
	3.379	1.176	0.998	22.32	0.0527
	3.379	1.176	0.998	22.32	0.0527
	3.347	1.127	0.997	21.51	0.0524
	3.265	1.020	0.995	19.61	0.0520
	3.265	1.019	0.995	19.61	0.0520
	3.265	1.020	0.995	19.61	0.0520

FIGURE 6
THE CONSTANT C AS A
FUNCTION OF TEMPERATURE



The precision of the calibrations was checked by calculating the viscosities of the calibrating liquids from experimental data and comparing them with values given in the literature. The root-mean-square deviation[1] was 0.005 cp. for Apparatus III and 0.011 cp. for Apparatus IV.

Surface Tension Measurements

The radii of all capillaries were measured using the method of Young which is summarized by Harkins (84). By means of a glass pipette which had a fine, curved tip, a column of mercury[2] about 5 cm. in length was placed in the clean capillary. A travelling microscope was used to measure the length of the column to within 0.01 mm. Then the mercury was weighed and its volume determined from the known density of mercury at room temperature. If it were not for the volume of the menisci, the volume of the column divided by its length would give the mean cross section of the capillary. Instead of that calculation being made, a slug of mercury approximately 2.5 cm. in length was introduced into one-half of the section formerly occupied by the column. This length was measured, the slug weighed, and the mean radius of the initial section not then occupied was given by the formula

$$r = \left[\frac{w_1 - w_2}{\pi d(l_1 - l_2)}\right]^{1/2} \qquad (34)$$

---

[1] The root-mean-square deviation σ is calculated from the expression $\sigma = \sqrt{\frac{\Sigma \Delta^2}{n'}}$, where Δ is the difference of a single observation from the average, n' the number of observations.

[2] Triply distilled mercury was purchased from the Chicago Apparatus Co., Chicago, Ill.

where w_1 and w_2 are respectively the weights of the column and the slug of mercury, l_1 and l_2 the respective lengths, and d is the density of mercury at room temperature.

Finally a bead of mercury 1.2 cm. in length was introduced into a section of known radius. The length as it was measured in that section was assumed to be correct, and the percentage deviation from that length as the bead was moved stepwise down the capillary, was calculated. The radius was assumed to vary by the same percentage.

Because the precision-bore Pyrex capillary tubing was found to be more uniform in radius than required considering the precision of the cathetometer readings, the mean radius was used directly. Although the Vycor tubing was never used for surface tension measurements, a two-foot length was calibrated in order to locate a 9 cm. length with the smallest radius. The data for this are listed in Table XI.

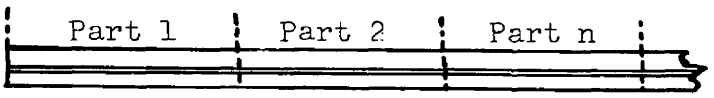
For checking the values of the radii, the surface tension of the benzene was determined at room temperature. Data for this calibration is summarized in Table XII. The close agreement between the calculated values and those interpolated from Sugden's (62) data is probably fortuitous. The formula used was the same as that used by Johnston, et al. (83),

$$\gamma = \frac{g\, d\, h}{2(1/r_1 - 1/r_2)} \qquad (35)$$

where r_1 is the radius of the capillary and r_2 is the radius of the larger tube.

TABLE XI

CALIBRATION DATA FOR CAPILLARY RADII



	Pyrex III	Vycor IV	Pyrex IV
Room Temperature, °C.	24.0	23.5	22.1
Density of Mercury, g./cc.	13.536	13.538	13.541
Length of Column, mm.	65.161	43.681	58.25
Weight of Column, g.	0.3818	0.6374	0.3692
Length of Slug in Part 1.	32.397	23.638	25.90
Length of Slug in Part 2.	32.349	23.707	25.50
Weight of Slug, g.	0.1885	0.3433	0.1682
Radius in Part 1., cm.	0.0372	0.05874	0.0380
Radius in Part 2., cm.	0.0373	0.05882	0.0382
Radius in Part 3., cm.	------	a	

[a] The list is continued in Appendix C.

TABLE XII

DATA TO CHECK THE CALIBRATION OF PYREX CAPILLARIES FOR USE IN SURFACE TENSION MEASUREMENTS

	Apparatus III	Apparatus IV[1]
Radius of Capillary, cm.	0.0372	0.0382
Radius of Large Tube, cm.	1.02	1.28
$1/r_1-1/r_2$	25.91	25.47
Temperature, $^{o}C.$	25.8	20.4
Density, g./cc.	0.8729	0.8786
Average Rise, cm.	1.706	1.707
Calculated Surface Tension, dynes/cm.	28.17	28.88
Surface Tension from Sugden (62), dynes/cm.	28.19	28.83

[1]These data were obtained after the rise for bromine trifluoride had been determined.

RESULTS AND DISCUSSION

Viscosity Measurements

Results

The data obtained for viscosity measurements are listed in Tables XIII, XIV, and XV for iodine pentafluoride, bromine pentafluoride, and bromine trifluoride respectively. Tables XVI, XVIII, and XIX contain various derived quantities and the calculated viscosities for each compound. The viscosities were calculated from the data by means of the calibration for the instrument obtained from Barr's equation--Equation (24).

Some data for the viscosities of iodine pentafluoride were obtained on the rotating cylinder apparatus, Apparatus I. They are listed in Table XVII together with values calculated for the same temperatures from results with the Pyrex viscometer for the sake of comparison. When the first observation was made, some mechanical friction was noted and the cap of the viscometer removed. The friction disappeared, but the sample was then exposed to the moist atmosphere and turned a deep blue. Also the calibration was no longer applicable. Thus the data obtained on Apparatus I were not considered reliable.

Treatment of Data

The viscosities calculated from the data and the calibration constants were fitted by a least-squares method to Equation (5), which shows that a graph of the logarithm of viscosity versus the reciprocal of

TABLE XIII

VISCOSITY DATA FOR IODINE PENTAFLUORIDE

Sample	Level Mark, cm.	Millivolts	Time, sec.
I	1.30	1.002	25.5
		1.010	25.4
		1.014	25.4
		0.737	27.8
		0.737	27.8
		0.737	27.8
		1.160	24.3
		1.161	24.2
		1.162	24.3
		1.126	24.5
		1.505	22.0
		1.504	22.1
		1.504	22.1
II	1.10	1.042	24.0
		1.041	24.1
		1.040	24.0
		0.738	26.6
		0.735	26.7
		0.735	26.7
		1.445	21.4
		1.445	21.3
		1.445	21.3
		1.515	20.9
		1.515	20.6
		1.515	20.9
III	1.30	0.737	27.7
		0.743	27.8
		0.745	27.8
		0.987	25.7
		0.983	25.7
		1.257	23.2
		1.257	23.3
		1.257	23.3
		1.605	21.1
		1.605	21.0
		1.605	21.0
IV	1.30	1.615	21.7
		1.612	21.7
		1.032	25.4
		1.032	25.4
		1.032	25.3
		0.720	28.4
		0.717	28.4
		0.715	28.5

TABLE XIV

VISCOSITY DATA FOR BROMINE PENTAFLUORIDE

Sample	Level Mark, cm.	Millivolts	Time, sec.
I	1.45	1.067	13.5
	1.40	1.010	13.5
		1.000	13.6
	1.35	0.774	13.7
		0.770	13.7
	1.30	0.700	13.8
	1.20	1.316	12.2
II	1.25	0.224	14.7
		0.206	14.6
		0.211	14.6
	1.20	0.775	13.5
		0.775	13.4
		0.768	13.4
		0.900	13.4
		0.904	13.4
	1.15	1.500	12.8
		1.500	12.7
III	1.52	0.135	15.9
		0.147	15.5
		0.141	15.4
	1.45	0.757	14.4
		0.770	14.0
		0.775	14.0
	1.40	0.962	13.7
		0.957	13.7
IV[1]	1.50	0.575	15.3
V	1.50	0.480	14.3
		0.480	14.3
		0.480	14.4
	1.45	0.600	14.1
		0.600	14.1
	1.30	1.128	13.1
		1.140	13.0
	1.20	0.079	14.4
		0.072	14.6
		0.090	14.4

[1] Impure sample.

TABLE XV

VISCOSITY DATA FOR BROMINE TRIFLUORIDE

Sample	Level Mark, cm.	Millivolts	Time, sec.
I	1.80	0.887	20.3
		0.890	20.3
		1.215	18.6
		1.202	18.7
		1.207	18.7
II	2.00	0.798	21.2
		0.805	21.1
		0.805	21.2
		1.051	19.8
		1.060	19.6
		1.065	19.7
		1.412	18.4
		1.396	18.2
		1.403	18.3
III	2.47	0.517	24.1
		0.515	24.0
		0.515	23.9
		0.991	20.7
		0.991	20.7
		0.991	20.7
		0.667	23.1
		0.665	23.1
		1.598	18.5
		1.595	18.6
		1.595	18.5

TABLE XVI

VISCOSITIES OF IODINE PENTAFLUORIDE

Mark, cm.	Temp. °C.	Liquid Density	Time, sec.	C[1]	Viscosity, cp.
			Sample I		
1.30	25.3	3.187	25.5	0.0302	2.191
	25.5	3.186	25.4	0.0302	2.191
	25.6	3.186	25.4	0.0302	2.181
	18.9	3.212	27.8	0.0306	2.489
	18.9	3.212	27.8	0.0306	2.489
	18.9	3.212	27.8	0.0306	2.489
	29.0	3.172	24.3	0.0300	2.038
	29.0	3.172	24.2	0.0300	2.029
	29.0	3.172	24.3	0.0300	2.038
	28.3	3.175	24.5	0.0300	2.062
	37.4	3.138	22.0	0.0295	1.739
	37.4	3.138	22.1	0.0295	1.748
	37.4	3.138	22.1	0.0295	1.748
			Sample II		
1.10	26.3	3.183	24.0	0.0319	2.159
	26.3	3.183	24.1	0.0319	2.169
	26.3	3.183	24.0	0.0319	2.159
	18.7	3.213	26.6	0.0324	2.526
	18.7	3.213	26.7	0.0324	2.526
	18.7	3.213	26.7	0.0324	2.526
	32.9	3.156	21.4	0.0315	1.817
	32.9	3.156	21.3	0.0315	1.807
	32.9	3.156	21.3	0.0315	1.807
	37.7	3.137	20.9	0.0312	1.726
	37.7	3.137	20.6	0.0312	1.696
	37.7	3.137	20.9	0.0312	1.726
			Sample III		
1.30	18.7	3.213	27.7	0.0306	2.480
	18.9	3.213	27.8	0.0306	2.490
	18.9	3.213	27.8	0.0306	2.490
	24.9	3.188	25.7	0.0302	2.214
	24.8	3.188	25.7	0.0302	2.222
	31.5	3.162	23.2	0.0298	1.901
	31.5	3.162	23.3	0.0298	1.911
	31.5	3.162	23.3	0.0298	1.911
	39.9	3.128	21.1	0.0293	1.621
	39.9	3.128	21.0	0.0293	1.621
	39.9	3.128	21.0	0.0293	1.621

[1] B is 2.1.

TABLE XVI

VISCOSITIES OF IODINE PENTAFLUORIDE
(continued)

Mark, cm.	Temp. °C.	Liquid Density	Time, sec.	C [1]	Viscosity, cp.
			Sample V		
1.30	40.0	3.128	21.7	0.0293	1.686
	40.0	3.128	21.7	0.0293	1.686
	26.1	3.184	25.4	0.0301	2.171
	26.1	3.184	25.4	0.0301	2.171
	26.1	3.184	25.3	0.0301	2.162
	18.3	3.215	28.4	0.0307	2.565
	18.2	3.215	28.4	0.0307	2.565
	18.2	3.215	28.5	0.0307	2.575

[1] B is 2.1.

TABLE XVII

VISCOSITIES OF IODINE PENTAFLUORIDE
FROM APPARATUS I

Temperature, Corrected	Scale	Reading, cp.	Correction, cp.	Viscosity, cp.	Viscosity, cp.[1]
36.1	0-.5	1.84	-0.02	1.82	1.82
36.1	direct	2.00	-0.12	1.88	1.82
25.0	direct	2.32	-0.12	2.20	2.22
15.6	direct	2.96	-0.12	2.84	2.64

[1] Values calculated from results with Apparatus III.

TABLE XVIII

VISCOSITIES OF BROMINE PENTAFLUORIDE

Mark, cm.	Temp. °C.	Liquid Density	Time, sec.	C[1]	Viscosity, cp.
			Sample I		
1.45	26.9	2.458	14.4	0.0288	0.574
1.40	25.5	2.463	13.5	0.0293	0.591
1.40	25.3	2.464	13.5	0.0293	0.601
1.35	19.7	2.483	13.6	0.0301	0.643
1.35	19.6	2.483	13.7	0.0301	0.643
1.30	17.8	2.489	13.8	0.0307	0.675
1.20	2.3	2.543	14.4	0.0327	0.824
			Sample II		
1.25	5.8	2.531	14.7	0.0320	0.829
1.25	5.3	2.532	14.6	0.0320	0.819
1.25	5.4	2.532	14.6	0.0320	0.819
1.20	19.7	2.483	13.5	0.0315	0.670
1.20	19.7	2.483	13.4	0.0315	0.659
1.20	19.5	2.483	13.4	0.0315	0.659
1.20	22.8	2.472	13.4	0.0313	0.648
1.20	22.9	2.472	13.4	0.0313	0.648
1.15	28.9	2.451	12.8	0.0313	0.580
1.15	28.9	2.451	12.7	0.0313	0.602
			Sample III		
1.50	3.8	2.537	15.5	0.0299	0.832
1.50	3.7	2.538	15.4	0.0299	0.823
1.45	19.6	2.483	14.0	0.0293	0.647
1.45	19.7	2.483	14.0	0.0293	0.647
1.40	24.3	2.467	13.7	0.0294	0.621
1.40	24.2	2.467	13.7	0.0294	0.619
			Sample V		
1.50	12.3	2.508	14.3	0.0293	0.683
1.50	12.3	2.508	14.3	0.0293	0.683
1.50	12.3	2.508	14.4	0.0293	0.692
1.45	15.3	2.498	14.1	0.0296	0.669
1.30	28.4	2.453	13.1	0.0300	0.571
1.30	28.4	2.452	13.0	0.0300	0.560
1.20	2.0	2.544	14.4	0.0327	0.827
1.20	1.8	2.545	14.6	0.0327	0.849

[1] B is 2.1.

TABLE XIX

VISCOSITIES OF BROMINE TRIFLUORIDE

Mark, cm.	Temp. °C.	Liquid Density	Time, sec.	C[1]	Viscosity, cp.
			Sample I		
1.80	22.5	2.805	20.3	0.0558	2.445
	22.6	2.805	20.3	0.0558	2.445
	30.5	2.783	18.6	0.0550	2.054
	30.2	2.784	18.7	0.0550	2.073
	30.3	2.783	18.7	0.0550	2.073
			Sample II		
2.00	20.3	2.811	21.2	0.0548	2.563
	20.5	2.810	21.1	0.0548	2.543
	20.5	2.810	21.2	0.0548	2.563
	26.5	2.794	19.8	0.0539	2.234
	26.7	2.793	19.6	0.0539	2.196
	26.8	2.793	19.7	0.0539	2.214
	35.2	2.769	18.4	0.0535	1.935
	34.9	2.768	18.2	0.0536	1.902
	35.0	2.768	18.3	0.0535	1.915
			Sample III		
2.47	13.2	2.830	24.1	0.0539	3.054
	13.2	2.830	24.0	0.0539	3.036
	13.2	2.830	23.9	0.0530	3.018
	25.0	2.798	20.7	0.0507	2.219
	25.0	2.798	20.7	0.0507	2.219
	17.0	2.820	23.1	0.0523	2.760
	16.9	2.820	23.1	0.0523	2.760
	39.6	2.757	18.5	0.0502	1.770
	39.6	2.757	18.6	0.0502	1.789
	39.6	2.757	18.5	0.0502	1.770

[1] B is 5.3.

absolute temperature is a straight line. It was assumed that the temperatures were accurate and any deviations from the straight line were due to errors in the viscosity values only. Values for the constants A and B, are assembled in Table XX, together with the energies of viscous flow and similar derived constants.

Precision and Accuracy of Results

The precision of the results may be said to depend upon the precision of the calibration. For Apparatus III the root-mean-square deviation was 0.005 cp., and for Apparatus IV it was 0.011 cp., both values being around one per cent of the viscosity of the calibrating liquid used. These results conformed to expectations when compared with results obtained by Elvrum and Doescher (78) with this type of apparatus.

The expected precision of a particular viscosity measurement was calculated by the perfect differential method (93); that is, the error in the viscosity is given by the expression

$$\Delta \eta = \left[\sum_i \left(\frac{\partial f(\eta)}{\partial x_i} \Delta x_j \right)^2 \right]^{1/2} \qquad (36)$$

where $\Delta\eta$ is the error and $\partial f(\eta)/\partial x_i$ is the partial derivative of the analytical expression for the viscosity, $f(\eta)$, with respect to each of the parameters, x_i, affecting the viscosity. The following is a sample calculation for Equation (36) with iodine pentafluoride as the liquid.

$$(\Delta\eta)^2 = [(Cd + Bd/j^2)^2 \Delta j^2 + (dj \Delta C)^2 + (d/j \cdot \Delta B)^2 + (\Delta d)^2 (Cj - B/j)^2] \qquad (37)$$

TABLE XX

THERMODYNAMIC FUNCTIONS FOR VISCOUS FLOW

Compound	ClF_3[a]	BrF_3	BrF_5	IF_5
Slope[b]	428.5	844.1	519.1	796.3
B	986.8	1944.	1195.	1834.
A $x10^{+4}$ (poise)	1.48	0.341	1.11	0.47
E_{vis}(kcal./mole)	1.970	3.860	2.374	3.644
ΔH_v(kcal./mole)	6.58[d]	10.3[e]	7.31[f]	9.88[g]
ΔE_v[c](kcal./mole)	6.01	9.67	6.69	9.28
$\Delta F^{\ddagger}$(kcal./mole)	2.32	3.35	2.76	3.51
$\Delta S^{\ddagger}$(e.u.)	-1.22	1.73	-1.31	0.39
$\Delta E_v/E_{vis}$(n)	3.07	2.5	2.8	2.5
$\Delta E_v/\Delta F^{\ddagger}$	2.59	2.88	2.43	2.64

[a] Data reported by Bankes, et al. (96).
[b] The slope was calculated for a graph of log η vs. 1/T.
[c] The constants apply to Equation (5).
ΔE_v was calculated from the relation $\Delta E_v = \Delta H_v - RT$.
The temperature was chosen to represent the range for which the vapor pressure, from which ΔH_v was calculated, is valid.
[d] Reference (13).
[e] Reference (97).
[f] Reference (98).
[g] Reference (17).

TABLE XX (Cont.)

THERMODYNAMIC FUNCTIONS FOR VISCOUS FLOW

Compound	SbF_5[a]	H_2O[c]
Slope[d]	1030.	908.
B	2374.	2090.
A x 10^4 (poise)	14.3	0.0805
E_{vis}(kcal./mole)	4.72	4.15
ΔH_V(kcal./mole)	10.37	10.54
ΔE_V(kcal./mole)	9.80	9.95
$\Delta F^{\ddagger}$(kcal./mole)	6.57	0.88
$\Delta S^{\ddagger}$(e.u.)	-6.43	11.14
$\Delta E_V/E_{vis}$(n)	2.08	2.40
$\Delta E_V/\Delta F^{\ddagger}$	1.46	4.7

[a]Calculated from data reported by references (105) and (106) for 16°C.
[b]Calculated from data in reference (7) for 0.0°C.
[c]Calculated from data in reference (95) and (55) for 20°C.
[d]The slope was calculated from a graph of log η vs. 1/T.

B = 2.10 ± 0.11, C = 0.03 ± 0.0001, j = 25 ± 0.1 seconds, and d = 3.0 ± 0.001 g./cc. When these values are substituted into Equation (37),

$$(\Delta \eta)^2 = [\, 0.56 \times 10^{-4} + 1.74 \times 10^{-4} + 1.0 \times 10^{-4} + 0 \,]$$

$$= 0.018 \text{ cp.}$$

For Apparatus IV the estimated error in constant C was 0.0001 and the constant B, 0.20. Table XXI compares the calculated and observed precisions.

TABLE XXI

CALCULATED AND OBSERVED PRECISION OF VISCOSITY RESULTS

Compound	Calculated Precision, cp.	Per[a] Cent	Observed Precision, cp.	Per[a] Cent
IF_5	0.018	0.9	0.028	1.3
BrF_5	0.023	3.4	0.024	3.5
BrF_3	0.036	1.6	0.042	1.9

[a] Based upon the mean viscosity.

Thus for Equation (24) the calculated and observed estimates roughly agree. According to Wilson (93), agreement is a good check on the accuracy of error estimates. The reason for the poor precision lies in the small times of flow. Although a longer capillary would have increased the times of flow, it would have caused the apparatus to be unwieldy for distillation. A larger reservoir would have required too large a sample. While a decrease in the radius of the capillary was

the most potent means of increasing times of flow, such a decrease would have hindered the use of the capillary as a surface tensiometer.

In addition to Equation (24), the one-constant equation was employed in calculation of the viscosities of halogen fluorides. The constants obtained from the calibration data were plotted as a function of temperature, and interpolated values were read from the graph in the viscosity calculations. While precision of the calibration increased, and the deviation for bromine pentafluoride and trifluoride decreased to one per cent or less, it was thought that the two-constant equation yielded sufficiently more accuracy to warrant its use. Comparison of the energies of viscous flow obtained by the different methods showed that the two constant equations yielded higher results by about 8.2 per cent for iodine pentafluoride and 7.3 bromine pentafluoride. For bromine trifluoride there were no calculations based upon the one-constant equation. In terms of absolute viscosities, the two calibrations yielded essentially the same results for iodine pentafluoride and bromine trifluoride, but the bromine pentafluoride results were much higher for the one-constant equation, as one would expect if the kinematic viscosities were much lower than those of the calibrating liquids. Thus the use of the two-constant equation apparently improved the accuracy of the measured viscosities at the expense of the precision.

A requisite for accuracy was the maintenance of viscous flow. That the conditions were fulfilled is proved by the fact that the Reynold's numbers (99) were less than 1000 for each apparatus. For Apparatus III the number was 350, and for Apparatus IV it was 370.

Discussion

It can be seen from Table XX that the four halogen fluorides under discussion fall into two groups on the basis of the thermodynamic properties for viscous flow. For chlorine trifluoride and bromine pentafluoride the energies of viscous flow are around two kilocalories per mole, and for bromine trifluoride and iodine pentafluoride the values are nearly four. A typical non-associated liquid like benzene has a E_{vis} of approximately 2.5 kilocalories per mole whereas water, a typical associated liquid, has a E_{vis} at room temperature of 4.0 kilocalories per mole. Comparison indicates that chlorine trifluoride and bromine pentafluoride are similar to benzene in flow properties, and the bromine pentafluoride and chlorine trifluoride are more like water.

Inspection of the data shows that $\Delta S^{\ddagger}$ is negative for the first pair and positive for the second. This fact further supports the thesis that chlorine trifluoride and bromine pentafluoride are similar in flow properties and different from bromine trifluoride and iodine pentafluoride. Large positive values of $\Delta S^{\ddagger}$ are usually observed for associated liquids whereas $\Delta S^{\ddagger}$ is negative for non-associated liquids.

According to theory, the ratio of $\Delta E_v/E_{vis}$ should be in the neighborhood of three for symmetrical, non-polar molecules, and should be lower for associated liquids (53). The ratio is near three for the chlorine trifluoride pair, but for the other pair the ratio is 2.5, which is close to the value 2.3 found for water at room temperature (53). If iodine pentafluoride and bromine trifluoride are associated liquids these values are reasonable.

The ratio $\Delta E_v / \Delta F^{\ddagger}$ is near 2.45 for most of the liquids discussed by Eyring (51) and the halogen fluorides have values of this ratio close to 2.45 also. Although bromine trifluoride has a value of 2.88, the value of 4.7 for water is considered by Eyring to be valid for the rule (53).

The graph of log η versus 1/T for bromine trifluoride seems to have a slight curvature convex to the temperature axis just as observed in the case of water (95). However, the precision of the data does not warrant attributing this curvature to association.

Since this research was completed, Robinson and Hetherington (100) have reported values for the viscosity of iodine pentafluoride. They used a differently modified Ostwald viscometer, obtained data over a temperature interval of 15 to 70° C., but used only two different samples. At 45° C. the results are identical to those reported here, but at 15° C., they reported a viscosity of 2.67 cp. In this paper the value reported is 2.73 cp., a 2.2 per cent difference that is within experimental error for both determinations only if the maximum allowed errors are added. Thus they report a smaller value for the slope of the curve log η versus 1/T than is reported in this paper. The value reported here for the slope should be more accurate since more samples were utilized in obtaining the data and a correction for the kinetic energy term, which tends to yield a larger slope, was made. Favoring the smaller slope are the facts that errors in viscometric determinations tend to yield high values and Robinson et al. used a larger temperature range.

Listed in Table XX for purposes of comparison are the thermodynamic functions for antimony pentafluoride and water. Water is typical of liquids that have hydrogen bonding, and because the same factors which influence the association of the liquid halogen fluorides presumably are operating in antimony pentafluoride, this liquid is included. It should be emphasized that the functions for antimony pentafluoride may be in error, because the available data is sparse and probably not accurate. Nevertheless the conclusion can be drawn that the derived functions E_{vis} and n do fit an associated liquid.

It can be seen from Table XX that the values of E_{vis} and n of bromine trifluoride and iodine pentafluoride tend toward those of associated liquids, whereas those values of chlorine trifluoride and bromine pentafluoride do not.

Muetterties and Phillips (34a), who have studied the nuclear magnetic resonance spectra of the halogen fluorides as a function of temperature, concluded that dimerization is the mechanism by which fluorine exchange occurs. If their assumptions are correct, they show that the order of dimer stability is $BrF_3 > ClF_3 > IF_5 > BrF_5$. One might conclude then that viscosity results should show the same order. However, the rates of exchange do not depend only upon the concentration of species involved. Fewer dimers taking part in a faster reaction could account for the same observed rate of exchange. A concentration of dimers from 10^{-6} to 10^{-8} molar can account for the observed rates (107). Thus the relative degree of association of the halogen fluorides on a bulk scale as determined by viscosity measurements in this work is not contradicted.

Surface Tension Measurements

Results

The data obtained for surface tension measurements are listed in Tables XXII, XXIII, and XXIV for iodine pentafluoride, bromine pentafluoride, and bromine trifluoride respectively. The equation chosen for representation of the data was the linear form, Equation (17). This equation represents the data within experimental error and is the simplest to apply. The constants for Equation (17) are listed in Table XXV.

Because the samples on which the surface tension measurements were made were from the same source as those for viscosity measurements and received the same treatment, the purity estimates utilized for viscosity measurements are assumed to be applicable.

For bromine trifluoride, the surface tension measurements were made in a Vycor apparatus with a Pyrex capillary (Apparatus IV). The liquid did not wet the Vycor surface properly, and a Pyrex capillary had to be used. Since bromine trifluoride attacked the Pyrex slowly with the formation of bubbles, each sample was discarded immediately as soon as the formation of bubbles signaled contamination. Measurements were obtained on only two samples before contamination took place. It was found that exposure of cold bromine trifluoride to a partial vacuum for twelve hours previous to the distillation produced a light yellow liquid that did not form bubbles for three or four hours after contact with the Pyrex. Measurements of the capillary radius at the points where the menisci fell were made after exposure. No measurable corrosion occurred.

TABLE XXII

THE SURFACE TENSIONS OF IODINE PENTAFLUORIDE

Sample	Weight[a]	Milli-volts	Temp. °C.	h,[b] cm.	Density, g./cc.	Surface Tension, dynes/cm.
I	5	1.002	25.2	0.493	3.187	29.7
	3	0.725	18.4	0.507	3.214	30.8
	5	1.161	29.2	0.489	3.171	29.2
II	This sample was impure					
III	5	1.032	26.1	0.488	3.184	29.4
	5	1.175	26.4	0.490	3.182	29.5
	5	1.535	38.2	0.476	3.135	28.2
	5	1.025	25.9	0.490	3.185	29.5
	5	0.759	19.2	0.508	3.211	30.8
IV	3	1.613	40.1	0.465	3.127	27.5
	3	1.032	26.0	0.483	3.184	29.2
	3	0.717	18.2	0.497	3.215	30.2

[a] The weight represents the number of observations at that temperature and is used in obtaining the average.

[b] The symbol h represents the capillary rise.

TABLE XXIII

THE SURFACE TENSIONS OF BROMINE PENTAFLUORIDE

Sample	Weight[a]	Milli-volts	Temp. °C.	h,[c] cm.	Density, g./cc	Surface Tension, dynes/cm.
I	3	0.844	21.4	0.488	2.477	22.9
	1	1.078	27.2	0.485	2.457	22.5
	5	1.069	27.0	0.481	2.458	22.4
b	3	1.337	33.5	0.452	2.435	20.8
	3	0.776	19.7	0.492	2.483	23.1
II	5	0.821	20.8	0.490	2.479	23.0
	1	0.360	9.2	0.510	2.521	24.3
	1	0.375	9.6	0.505	2.519	24.1
	1	0.390	10.0	0.510	2.517	24.3
	1	0.560	14.3	0.500	2.501	23.6
	1	0.568	14.5	0.495	2.501	23.4
	1	0.573	14.7	0.500	2.500	23.5
	1	0.576	14.7	0.500	2.500	23.5
III	5	1.057	26.7	0.486	2.459	22.6
	5	1.300	32.6	0.468	2.442	21.6
	5	0.963	24.3	0.491	2.467	22.9
	2	0.630	16.1	0.495	2.484	23.5

[a] The weight represents the number of observations at that temperature, the data being averaged.

[b] This point was discarded on a statistical basis.

[c] The symbol h represents the capillary rise.

TABLE XXIV

THE SURFACE TENSIONS OF BROMINE TRIFLUORIDE

Sample	Temperature °C., corr.[a]	h,[b] cm.	Density, g./cc.	Surface Tension dynes/cm.
I	Bubbles developed			
II	12.0	0.715	2.833	37.1
	18.9	0.690	2.816	36.4
	27.1	0.680	2.789	35.6
	45.0	0.670	2.741	33.8
III	26.1	0.690	2.797	35.1
	36.6	0.680	2.767	34.6
	14.2	0.710	2.827	36.8

[a] A calibrated thermometer was used to measure bath temperatures for the surface tensions of bromine trifluoride in Apparatus IV.

[b] The symbol h represents the capillary rise.

Precision and Accuracy

When the perfect differential equation for estimating errors, Equation (36), was applied to the formula for surface tension, $\gamma = rgdh/2$, and maximum values for r, d, and h were properly substituted, the estimated r.m.s. error in the surface tension values was found to be as shown in Table XXV. The table also contains the observed r.m.s. deviations for each compound.

Only in the case of bromine pentafluoride are the calculated and observed deviations much different. According to Wilson (93) agreement is a check on the accuracy of the error estimations.

TABLE XXV

CALCULATED AND OBSERVED PRECISION OF SURFACE TENSION RESULTS

Compound	Calculated Precision, dynes/cm.	Per Cent	Observed Precision, dynes/cm.	Per Cent
IF_5	0.33	1.1	0.29	1.0
BrF_5	0.28	1.2	0.16	0.7
BrF_3	0.32	0.9	0.30	0.8

Thus a deviation of ± 0.3 dynes/cm. may be assigned to the surface tensions of iodine pentafluoride and bromine trifluoride and of ± 0.2 dynes/cm. to bromine pentafluoride and chlorine trifluoride (96).

Discussion

The surface tensions of the halogen fluorides are presented as functions of temperature in Table XXVI. They are intermediate between water at 70 dynes per centimeter and fluorocarbons at 10 dynes per centimeter at room temperature. A linear relationship between γ and T represents the data within experimental error.

Table XXVII shows the parachors of the halogen fluorides. The values are averages of those calculated at 10, 20 and 30 degrees Centigrade. Little variation with temperature was noted.

From the values of the parachors, the atomic parachors of the central atom with different valencies can be calculated assuming a constant value for the atomic parachor of fluorine. Samuel (68) first applied this technique, Bankes, et al., (96) extended it to the chlorine fluorides, and they showed how the values obtained fit fairly well into a series of phosphorus and sulfur atomic parachors. From Table XXVIII it can be seen that the halogens form a series with obvious trends themselves. The atomic parachors shown for tervalent iodine and pentavalent chlorine have been estimated.

According to Grunberg and Nissan (55) the ratio of E_{vis} to the work of cohesion, W_c, as computed from surface tension data, is approximately one. For water and ethanol the ratio is 2.3 and 1.5 respectively. Table XXIX lists the work of cohesion and the ratio of E_{vis} to it for the four liquids under discussion here. It should be noted that bromine trifluoride has the highest value (1.9), iodine pentafluoride next (1.8), and the last two have the same value (1.5). Here is another indication

TABLES XXVI

SURFACE TENSION-TEMPERATURE RELATIONSHIPS FOR THE HALOGEN FLUORIDES[a]

	ClF_3	BrF_3	BrF_5	IF_5
A	26.7	38.3	25.4	33.0
B	0.16	0.100	0.113	0.130
r.m.s. dev.	±0.2	±0.3	±0.2	±0.3

[a] For the equation $\gamma = A - Bt$ dynes/cm.

TABLE XXVII

PARACHORS OF THE HALOGEN FLUORIDES

	ClF_3	BrF_3	BrF_5	IF_5
[P]	111.5	120.6	154.4	162.5

TABLE XXVIII

ATOMIC PARACHORS OF THE CENTRAL HALOGEN ATOMS

Valence	Cl	Br	I
1	54.3	68.0	90.0
3	36.5	45.6	(60)
5	(19)	29.5	37.5

TABLE XXIX

WORK OF COHESION OF HALOGEN FLUORIDES

	ClF_3	BrF_3	BrF_5	IF_5
W_c(kcal/mole)	1.26	2.01	1.59	2.03
$\Delta E^{\ddagger}/W_c$	1.5	1.9	1.5	1.8

TABLE XXX

ESTIMATED CRITICAL TEMPERATURES OF THE HALOGEN FLUORIDES (CENTIGRADE)

ClF_3	BrF_3	BrF_5	IF_5	Reference
167	383	225	252	a.
154	327	197	240	(101) b.
208	397	237	327	(102)
174	330	244	267	(103)
170	368	217	315	(104)
170	360	220	280	best value

[a] Linear extrapolation of surface tension data.

[b] 3/2 T_B, where T_B is the boiling point in ^{o}K.

TABLE XXXI

VISCOSITY AND SURFACE TENSION OF THE HALOGEN FLUORIDES AT 20°C.

Compound	ClF_3	BrF_3	BrF_5	IF_5
Viscosity (c.p.)	0.429	2.57	0.530	2.43
Surface Tension (dynes/cm.)	23.5	37.8	23.1	30.4

that the former pair of liquids is associated compared to the latter, although the high value of the ratio for the latter pair casts some doubt on the certainty of the conclusion.

There is no reliable method for estimating critical temperatures of inorganic compounds. In most cases the methods apply only to organic compounds or non-associated compounds. From the many empirical approaches, five of the best have been chosen to estimate the critical temperatures for the halogen fluorides. No direct measurements have been reported for these quantities. The results are assembled in Table XXX. The "best value" was obtained by choosing a value between the extremes, emphasizing the method that seemed to apply best. Linear extrapolation of the surface tension data was ignored for bromine trifluoride and iodine pentafluoride because of possible association effects. As a qualitative check, the "best values" were used in the Eotvos equation, Equation (15), to calculate the constant k. The values were 2.15, 1.90, 2.02, and 1.97 for chlorine trifluoride, bromine trifluoride, bromine pantafluoride, and iodine pentafluoride in order. The average value for several hundred compounds is 2.12 (41). If the halogen fluorides are not much associated, the estimated critical temperatures are nearly correct.

SUMMARY

The viscosities of iodine pentafluoride, bromine pentafluoride, and bromine trifluoride have been determined over a temperature range of 15 to 40 degrees Centigrade by means of a modified Ostwald viscometer made of Pyrex. The results have been fitted to a standard exponential equation which relates viscosity to the temperature, and various parameters such as energy, free energy, and entropy of viscous flow were computed. The results have been interpreted in terms of Eyring's theory of viscous flow, and they indicate that bromine trifluoride, and to a lesser extent iodine pentafluoride, are associated liquids. Computations based on the data published thus far on the viscosity of iodine pentafluoride and chlorine trifluoride were included for the sake of comparison. Chlorine trifluoride and bromine pentafluoride are "normal" liquids.

The surface tensions of iodine pentafluoride, bromine pentafluoride, and bromine trifluoride have been determined over the same temperature range by the capillary-rise method. The results were fitted to a standard, linear, surface tension-temperature relationship. Again the results indicated that bromine trifluoride, and perhaps iodine pentafluoride, are associated, while bromine pentafluoride and chlorine trifluoride are probably not.

Various empirical relationships were employed to obtain estimated values of the critical temperatures of the halogen fluorides.

LITERATURE CITED

(1) G. Gore, Proc. Roy. Soc., 19, 235 (1870).

(2) O. Ruff and A. Braida, Z. anorg. u. allgem. Chem., 214, 91 (1933)

(3) J. Fischer, R. K. Steunenberg and R. C. Vogel, J. Am. Chem. Soc., 76, 1497 (1954).

(4) J. Fischer, J. Bingle and R. C. Vogel, ibid., 78, 902 (1956).

(5) R. A. Durie, Proc. Roy. Soc. (London), 207, 388 (1951).

(6) E. E. Aynsley, R. Nichols and P. L. Robinson, J. Chem. Soc., 623 (1953).

(7) J. H. Simons, Ed., "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York (1950).

(8) H. J. Emeléus, Bull. Soc. Chim. France, 909 (1953).

(9) N. N. Greenwood, Revs. Pure and Appl. Chem. (Australia), 1, 84 (1951).

(10) V. Gutman, Angew. Chem., 62, 312 (1950).

(11) A. G. Sharpe, Quart. Revs., 4, 115 (1950).

(12) H. S. Booth and J. T. Pinkston, Chem. Revs., 41, 421 (1947).

(13) J. H. Simons, Ed., "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York (1954).

(14) E. B. Maxted, "Recent Advances in Inorganic Chemistry," Clarendon Press, Oxford, England (1947).

(15) H. Hazeldine and A. G. Sharpe, "Fluorine and Its Compounds," John Wiley and Sons, Inc., New York (1951).

(16) H. B. Thompson, Ph. D. Thesis, Michigan State University (1953).

(17) M. T. Rogers, J. L. Speirs, H. B. Thompson, and M. B. Panish, J. Am. Chem. Soc., 76, 4843 (1954).

(18) O. Ruff and W. Menzel, Z. anorg. u. allgem. Chem., 202, 49 (1931).

(19) C. F. Swinehart and F. J. Burton, private communication to H. S. Booth and J. J. Pinkston, See Simons, Vol. I.

(20) A. A. Bankes and J. J. Maddock, J. Chem. Soc., 2779 (1955).

(21) L. Stein, R. C. Vogel and W. H. Ludewig, J. Am. Chem. Soc., 76, 428 (1954).

(22) A. A. Bankes and A. J. Rudge, J. Chem. Soc., 191 (1950).

(23) M. T. Rogers, R. D. Pruett, H. B. Thompson and J. L. Speirs, J. Am. Chem. Soc., 78, 44 (1956).

(24) M. T. Rogers, J. L. Speirs, and H. B. Thompson, ibid., 76, 4841 (1954).

(25) M. T. Rogers, M. B. Panish and J. L. Speirs, ibid., 77, 5292 (1955).

(26) M. T. Rogers, J. G. Malik and J. L. Speirs, ibid., 78, 46 (1956).

(27) M. T. Rogers, R. D. Pruett, and J. L. Speirs, ibid., 77, 5280 (1955).

(28) "Table of Electric Dipole Moments of Substances in the Gaseous State," Bureau of Standards Circular 537, Washington, D. C. (1953).

(29) D. W. Magnuson, J. Chem. Phys., 20, 229 (1952).

(30) D. F. Smith, ibid., 21, 609 (1953).

(31) R. D. Burbank and F. N. Bensey, ibid., 21, 602 (1953).

(32) R. L. Potter, ibid., 17, 957 (1949).

(33) H. S. Gutowsky and C. J. Hoffman, ibid., 19, 1259 (1951).

(34) H. S. Gutowsky, D. W. McCall and C. P. Slighter, ibid., 21, 279 (1953).

(34a) E. L. Muetterties and W. D. Phillips, J. Am. Chem. Soc., 79, 322 (1957).

(35) C. E. Mellish and J. W. Linnett, Trans. Faraday Soc., 51, 1311 (1955).

(36) C. V. Stephenson and E. A. Jones, J. Chem. Phys., 20, 1830 (1952)

(37) H. H. Claassen, J. G. Malm, and B. Weinstock, paper presented before the Symposium on Molecular Structure and Spectra, The Ohio State University, Columbus, Ohio, June 11-15 (1956).

(38) R. C. Lord, J. Am. Chem. Soc., 72, 522 (1950).

(39) E. N. Da C. Andrade, Endeavour, 13, 117 (1954).

(40) F. Daniels, "Outlines of Physical Chemistry," John Wiley and Sons, Inc., New York (1948).

(41) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. II Longman Green and Co., New York (1951).

(42) J. L. M. Poiseuille, Mem. Acad. Sci., Paris, 9, 433 (1846).

(43) E. C. Bingham and H. S. Jackson, Nat. Bur. Standards (U.S.) Tech. News Bull., 14, 75 (1918).

(44) L. L. Burger and G. H. Cady, J. Am. Chem. Soc., 73, 4243 (1951).

(45) F. Hovorka, H. P. Lankelma and S. C. Stanford, ibid., 60, 820 (1938).

(46) D. B. Macleod, Trans. Faraday Soc., 19, 6 (1923).

(47) A. K. Mukherjee, J. Indian Chem. Soc., 29, 56 (1930).

(48) E. N. da C. Andrade, Nature (London), 125, 125 (1930).

(49) U. Rost, Kolloid Z., 142, 132 (1955).

(50) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," Chapter 9, McGraw-Hill Book Co., New York (1941).

(51) R. H. Ewell, J. Applied Phys., 9, 252 (1938).

(52) J. F. Kinkaid, H. Eyring and E. A. Stearn, Chem. Revs., 28, 301 (1941).

(53) W. E. Roseveare, R. E. Powell and H. Eyring, J. App. Phys., 12, 669 (1941).

(54) B. S. Harrap and E. Heyman, Chem. Revs., 48, 56 (1951).

(55) L. Grunberg and A. H. Nissan, Trans. Faraday Soc., 45, 125 (1949).

(56) T. E. Thorpe and J. W. Rodger, Phil. Mag., 185A, 397 (1895).

(57) T. E. Thorpe and J. W. Rodger, ibid., 189A, 71 (1897).

(58) J. N. Friend and W. D. Hargreaves, ibid., 37, 120, 201 (1946).

(59) A. Bondi, Ann. N. Y. Acad. Sci. 53, 870 (1951).

(60) J. Frenkel, "Kinetic Theory of Liquids," Oxford University Press, Oxford (1946).

(61) N. K. Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, Oxford (1938).

(62) S. Sugden, "The Parachor and Valency," G. Rutledge and Sons, Ltd., London (1930).

(63) O. R. Quayle, Chem. Revs., 53, 443 (1953).

(64) N. S. Bayliss, J. Am. Chem. Soc., 59, 444 (1937).

(65) S. A. Mumford and J. W. C. Phillips, J. Chem. Soc., 2112 (1929).

(66) A. I. Vogel, ibid., 624 (1948).

(67) G. H. Cheesman, ibid., 889 (1932).

(68) R. Samuel, J. Chem. Phys., 12, 167 (1944).

(69) R. Herzog, Ind. Eng. Chem., 36, 997 (1944).

(70) R. T. Lagemann and W. S. Dunbar, J. Phys. Chem., 49, 428 (1945).

(71) Eötvos, Ann. Phys., 27, 448 (1886).

(72) W. Ramsay and J. Shields, Trans. Roy. Soc. (London, A184, 647 (1893).

(73) F. G. Mann and D. Purdie, J.Chem. Soc., 1549 (1935); 8731 (1936).

(74) R. H. Fowler, Proc. Roy Soc. (London), A159, 229 (1937).

(75) A. Ferguson, Trans. Faraday Soc., 19, 41 (1923).

(76) S. S. Mitra and N. K. Sanyal, J. Chem. Phys., 23, 1737 (1955).

(77) S. S. Mitra and D. N. Chakravarty, Z. physik. Chem., A205, 1 (1955).

(78) R. N. Doescher and G. W. Elvrum, J. Chem. Phys., 20, 1834 (1952).

(79) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York (1941).

(80) G. Barr "A Monograph of Viscometry," Oxford University Press, London (1931).

(81) E. K. Fischer, "Colloidal Dispersions," John Wiley and Sons, New York (1950).

(82) J. R. Heiks and E. Orban, J. Phys. Chem., 60, 1025 (1956).

(83) H. L. Johnston, D. L. White, and J. Heng Hu, J. Am. Chem. Soc., 76, 2584 (1952).

(84) A. Weissberger, "Techniques of Organic Chemistry," Vol. I, Interscience Publishers, New York (1945).

(85) G. M. Shah and P. D. Pathak, Current Sci. (India), 24, 11 (1955).

(86) K. H. Cuny and K. L. Wolf, Ann. Physik, 17, 57 (1956).

(87) R. E. Dodd and P. L. Robinson, "Experimental Inorganic Chemistry," Elsevier Press, Inc., New York (1953).

(88) "Reference Table for Thermocouples," National Bureau of Standards Circular 508.

(89) R. D. Pruett, Thesis, Michigan State University (1955).

(90) R. L. Burwell, Jr., A. H. Peterson and G. B. Rathman, Rev. Sci. Instr. 60, 608 (1948).

(91) Jim G. Malik, Thesis, Michigan State University, Ph. D. (1954).

(92) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York (1939).

(93) E. Bright Wilson, Jr., "An Introduction to Scientific Research," McGraw-Hill Book Co., Inc., New York (1952).

(94) J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, (1950).

(95) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, 31st Edition.

(96) A. A. Bankes, A. Davies, and A. J. Rudge, J. Chem. Soc., 731 (1953).

(97) G. D. Oliver and J. W. Grisard, J. Am. Chem. Soc., 74, 2705 (1952).

(98) M. T. Rogers and J. L. Speirs, J. Phys. Chem., 60, 1462 (1956).

(99) W. L. Badger and W. L. McCabe,"Elements of Chemical Engineering," McGraw-Hill Book Co., New York,

(100) G. Hetherington and P. L. Robinson, J. Chem. Soc., 3681 (1956).

(101) C. M. Guldberg, Z. physik. Chem., 5, 374 (1890).

(102) Herzog, Ind. Eng. Chem., 36, 997 (1944).

(103) W. T. Smith, Jr., S. Greenbaum, G. P. Rutledge, J. Phys. Chem., 58, 443 (1954).

(104) R. F. Marschner and J. B. Beverly, J. Chem. Ed., 33, 604 (1956).

(105) A. A. Woolf and N. N. Greenwood, J. Chem. Soc., 2200 (1950).

(106) R. C. Shair and W. F. Schurig, Ind. and Eng. Chem., 43, 1624 (1951).

(107) M. T. Rogers, private communication (1957).

APPENDICES

APPENDIX A

List of Symbols Used

$\mathring{A}$	Angstrom units
A,B,C,	Empirical constants
a,b,c,	Empirical constants
b	Van der Waal's b
d	Liquid density
D'	Vapor density
ΔE_V	Energy of vaporization
E_{vis}	Energy of activation for viscous flow (experimental)
$\Delta F^{\ddagger}$	Free energy of activation for viscous flow
g	Gravitational constant
ΔH_V	Heat of vaporization
$\Delta H^{\ddagger}$	Heat of activation for viscous flow
h	Capillary rise
h'	Planck's constant
$\bar{h}$	Mean hydrostatic head
h_1, h_2	Hydrostatic head
j	Time in seconds
k	Eotvos constant
L	Length of capillary
l_1, l_2	Lengths of mercury slugs
M	Molecular weight

m'	Souder's viscosity constant
m	Calibration mark
N	Avogadro's number
N_1, N_2	Mole fractions
n	The ratio $\Delta E_v / \Delta E^{\ddagger}$
n'	The number of observations
P	Pressure head
[P]	Sugden's parachor
p	Vapor pressure (mm. Hg.)
r	Capillary radius
R	Universal gas constant
MR_D	Molar refraction for sodium light
[R]	Rheochor
R'	Alkyl group
T	Absolute temperature
T_c	Critical temperature, $^{\circ}K$
T'	Torque
t	Temperature, $^{\circ}C$
t_c	Critical temperature, $^{\circ}C$
V	Volume of flow
V_m	Molar volume
v	Unit volume
W_c	Work of cohesion
w_1, w_2	Weight of mercury slugs
X	Halogen atom

γ	Surface tension in dynes/cm.
ϵ	Dielectric constant
η	Viscosity
μ	Electric dipole moment
σ	Root-mean-square deviation
σ_1, σ_2	Solid density
ϕ	Fluidity
χ_M	Molar magnetic susceptibility
θ	Angle of contact between liquid and solid
log	logarithm to the base 10
ln	logarithm to the base e

APPENDIX B

Mercury Thermometer Calibration

The temperature control used was described on page 32. The mercury thermometer was immersed to the -3.0° C. mark. The platinum resistance thermometer[1] had been calibrated by the National Bureau of Standards and the data fitted to the following equation:

$$R_t = R_o \left[1 + ut + uv \left(1 - \frac{t}{100}\right) \frac{t}{100} \right]$$

where R_t is the resistance of the thermometer at t° C. R_o was found to be 25.5031 ohms (16), and u and v were given as 0.00392604 and 1.4919, respectively. A method of successive approximations was used to find t to the nearest 0.01° C. from the measured resistance.

R_t (ohms)	Temperature of Platinum Resistance Thermometer	Temperature of Mercury Thermometer	t corrected[2]
28.2941	27.58	26.96	27.56
28.2971	27.61	27.00	27.60
28.1225	25.88	25.30	25.90
27.8449	23.12	22.53	23.10
27.6185	20.88	20.28	20.87
27.4625	19.34	18.75	19.34
27.3535	18.26	17.67	18.27
27.0505	15.26	14.70	15.28
26.7975	12.76	12.18	12.76
28.5651	30.27	29.70	30.31
28.8152	32.75	32.10	32.72
28.8181	32.78	32.15	32.77
29.2505	37.08	36.43	37.08
29.5640	40.77	40.1	40.8

[2] "t corrected" is the temperature calculated by applying the stem correction and adding 0.60° C. to the observed reading.

[1] Leeds and Northrup serial number 1016073 platinum resistance thermometer was used with No. 1011417 Mueller bridge, type G-1.

APPENDIX C

Calibration Data for the Vycor Capillary

Inches from Reference Tip	Length of Slug (cm.)	Per Cent Deviation	Corrected (Radius (cm.)
0.0-0.5	15.58	0.00	0.05874
0.5-1.0	15.56	0.13	0.05882
1.0-1.5	15.53	0.32	0.05893
1.5-2.0	15.50	0.51	0.05904
2.0-2.5	15.30	1.80	0.05980
2.5-3.0	15.33	2.25	0.06006
3.0-3.5	-----	----	-------
3.5-4.0	15.04	3.46	0.06077
4.0-4.5	14.99	3.66	0.06089
4.5-5.0	14.99	3.66	0.06189
5.0-5.5	14.96	3.98	0.06108
5.5-6.0	14.96	3.92	0.06104
6.0-6.5	15.03	3.53	0.06081
6.5-7.0	15.08	3.21	0.06063
7.0-7.5	15.14	2.82	0.06040
7.5-8.0	15.25	2.12	0.05999
8.0-8.5	15.40	1.16	0.05942
8.5-9.0	15.44	0.91	0.05927
9.0-9.5	15.54	0.26	0.05889
9.5-10.0	15.65	-0.45	0.05848
10.0-10.5	15.73	-0.96	0.05818
10.5-11.0	15.72	-0.90	0.05821
11.0-11.5	15.80	-1.41	0.05791
11.5-12.0	15.82	-1.54	0.05784
12.0-12.5	15.79	-1.35	0.05795
12.5-13.0	15.71	-0.87	0.05823
13.0-13.5	15.59	-0.06	0.05836
13.5-14.0	15.42	1.03	0.05934
14.0-14.5	15.31	1.73	0.05976
14.5-15.0	15.14	2.82	0.06040
15.0-15.5	14.88	4.50	0.06138
15.5-16.0	14.53	6.74	0.06270
16.0-16.5	14.55	6.61	0.06263
16.5-17.0	14.47	7.12	0.06292
17.0-17.5	14.47	7.12	0.06292
17.5-18.0	14.45	7.25	0.06300
18.0-18.5	14.50	6.93	0.06281
18.5-19.0	14.57	6.48	0.06255